Quantum computational, structural and electrochemical properties of substituted dithizones and photochromic dithizonato phenylmercury complexes

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by

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Acknowledgments

Wherewithal shall a young man cleanse his way? by taking heed thereto according to thy word.

Psalm 119:9 (KJV)

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Mart-Marie Biggs and Charl Jafta for being awesome friends.

The NRF (National Research Foundation) for financial support.

And Jesus came and spake unto them, saying, All power is given unto me in heaven and in earth. Go ye therefore, and teach all nations, baptizing them in the name of the Father, and of the Son, and of the Holy Ghost: Teaching them to observe all things whatsoever I have commanded you: and, lo, I am with you alway, *even* ***unto the end of the world. Amen.***

Matthew 28:18-20 (KJV)

Table of Contents

LIST OF ABBREVIATIONS iii

LIST OF STRUCTURES iv

1. INTRODUCTION **1**

2. LITERATURE SURVEY **3**

2.1. INTRODUCTION 3

2.2. DITHIZONE – THE LIGAND 3

2.2.1. Discovery and Synthesis 3

2.2.2. Structure and Geometry 5

2.2.3. Substitution Derivatives of Dithizone 7

2.2.4. Oxidation Products of Dithizone 9

2.3. DITHIZONATO METAL COMPLEXES 10

2.3.1. Analytical Applications 10

2.3.2. Photochromism 11

2.3.3. Ultra-fast Laser Spectroscopy 14

2.4. CRYSTAL STRUCTURES 16

2.4.1. Dithizone 16

2.4.2. Dehydrodithizone 17

2.4.3. Dithizonatophenylmercury(II) 18

2.5. COMPUTATIONAL CHEMISTRY 19

2.5.1. Introduction 19

2.5.2. Structure and Spectroscopy 22

2.5.3. Photochromism of Dithizonatophenylmercury(II) 26

2.6. ELECTROCHEMISTRY 27

2.6.1. Introduction 27

2.6.2. Redox Properties of Dithizone 29

3. RESULTS AND DISCUSSION **38**

3.1. INTRODUCTION 38

3.2. SYNTHESIS 39

3.2.1. Dithizone Derivatives 39

3.2.2. Metal Dithizonates 46

3.3. X-RAY CRYSTALLOGRAPHY 49

3.3.1. Introduction 49

3.3.2. *Ortho*-Methoxydehydrodithizone 49

3.3.3. *Ortho*-Fluorodithizone-disulphide 55

3.4. COMPUTATIONAL CHEMISTRY 60

3.4.1. Introduction 60

3.4.2. Dithizone Derivatives 61

3.4.3. Mercury Dithizonates 67

3.5. ELECTROCHEMISTRY 74

3.5.1. Introduction 74

3.5.2. Dithizone Derivatives 75

3.5.3. Mercury Dithizonates 81

4. EXPERRIMENTAL 92

4.1. INTRODUCTION 92

4.2. MATERIALS 92

4.3. SPECTROMETRY 92

4.4. ELECTROCHEMISTRY 92

4.5. SYNTHESIS 93

4.5.1. Dithizone Derivatives 93

4.5.2. Mercury Dithizonates 99

5. SUMMARY AND FUTURE PERSPECTIVES 103

6. ABSTRACT 104

7. SAMEVATTING 105

8. APPENDIX I

UV/visible Data I

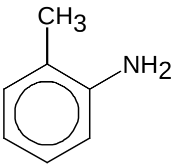
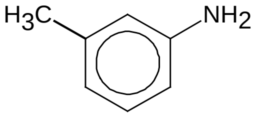
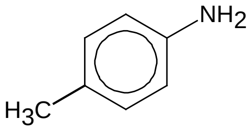
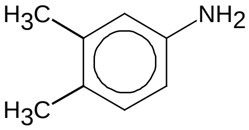
Electrochemistry Data IX

Quantum Computational Data and X-Ray Crystallographic Data CD rom

List of Abbreviations

DMSO	dimethyl sulfoxide
H_2Dz	dithizone
DFT	density functional theory
Dz	dehydrodithizone
$(HDz)_2$	dithizone disulphide
ppb	parts per billion
$Hg(HDz)_2$	dithizonatomercury(II)
DPM, PhHgHDz	dithizonatophenylmercury(II)
DCM	dichloromethane
OD	optical density
fs	femto second
ps	pico second
MO	molecular orbital
LDA	local density approximation
GGA	generalized gradient approximation
STO	Slater-type orbitals
GTO	Gaussian-type orbitals
ADF	Amsterdam density functional
SZ	single-zeta
DZ	double-zeta
DZP	double-zeta polarized
TZP	triple-zeta polarized
TZ2P	triple-zeta doubly polarized
TDDFT	time-dependent density functional theory
LCI	limited configuration interaction
CV	cyclic voltammetry
SCE	saturated calomel electrode
NMR	nuclear magnetic resonance
LUMO	lowest unoccupied molecular orbital
HOMO	highest occupied molecular orbital
B3LYP	B3 Becke 3-parameter exchange and Lee-Yang-Parr correction
PW91	Perdew-Wang (1991) exchange and correlation functional
UV/visible	ultra-violet and visible
ZORA	zero order regular approximation
HB1	hydrogen bridge-1
HB2	hydrogen bridge-2
HB3	hydrogen bridge-3
Ph	C_6H_5
Ar	substituted phenyl ring

List of Structures

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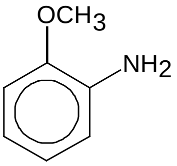
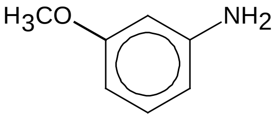
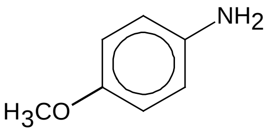

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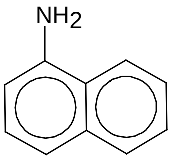

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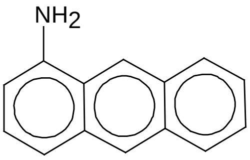

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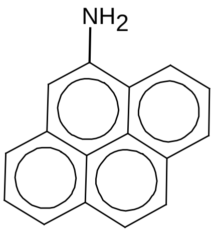

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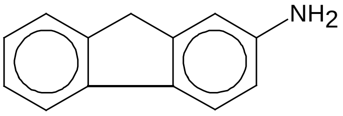

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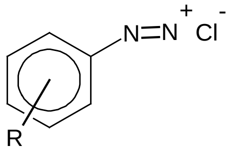

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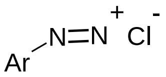
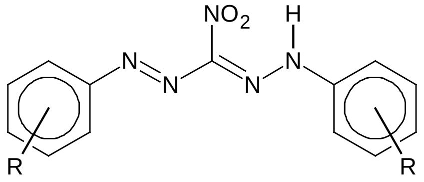


[10h-10k]

a – *o*-CH_3
b – *m*-CH_3
c – *p*-CH_3
d – *o*-OCH_3
e – *m*-OCH_3
f – *p*-OCH_3
g – *3,4*-$(CH_3)_2$
h – α-Napthyl
i – α-Anthracene
j – α-Pyrene
k – β-Fluorene



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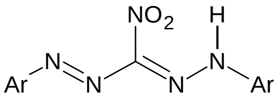

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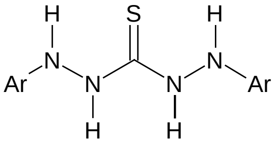

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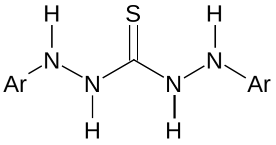

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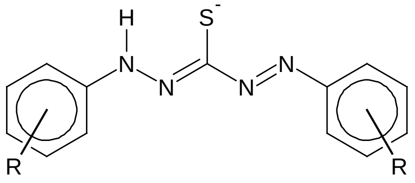

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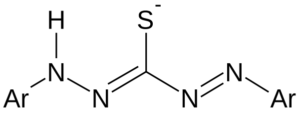

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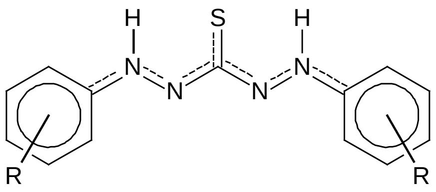

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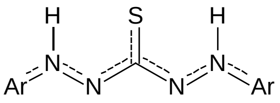

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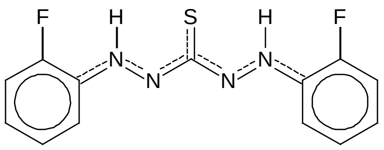
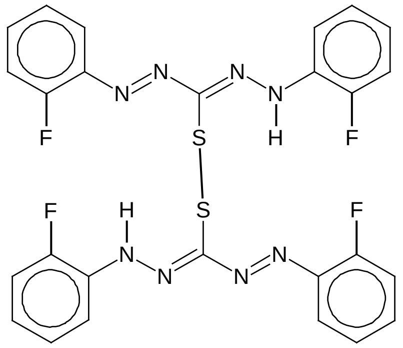
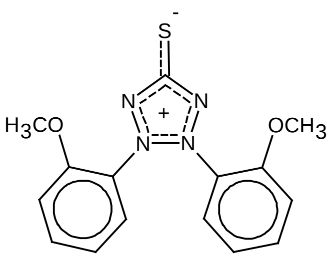


[15] *Ortho*-Fluorodithizone



[16] *Ortho*-Fluorodithizone Disulphide



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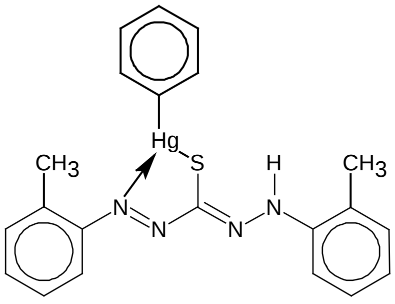

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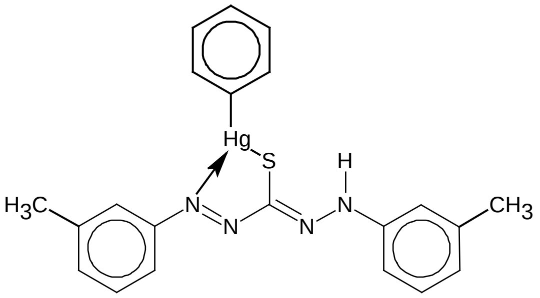

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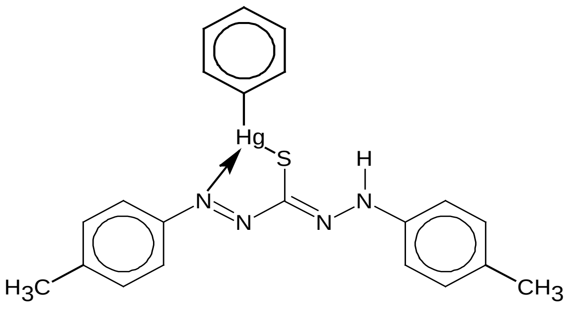
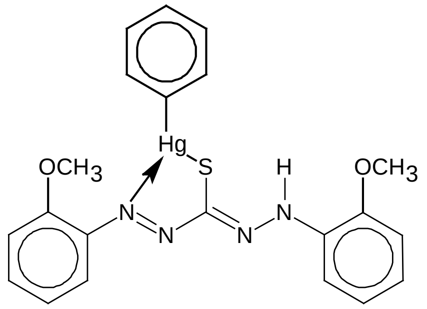
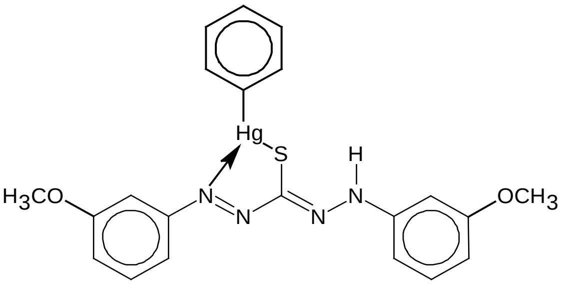


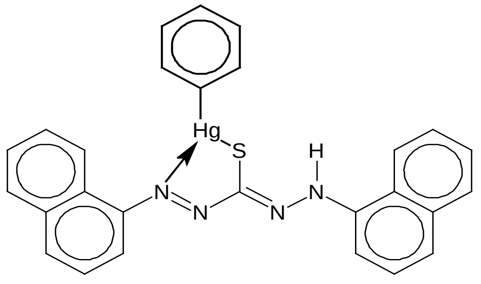
[18c]



[18d]



[18e]



[18h]

1. Introduction

Dithizone (1,5-diphenylthiocarbazone, $(PhNHN)_2CS$, simply abbreviated as H_2Dz) is a well-known intensely colored compound which has extensive applications as the dithizonato metal complex in analytical chemistry, especially in the spectrophotometric analyses of heavy metals like lead and mercury.[1,2,3] Metal complexes of dithizone also have possible applications in the fields of materials science and nanotechnology, wherein the pronounced photochromicity (colour change under the influence of light, especially also sunlight) exhibited by some metal dithizonato complexes might be employed in exotic textiles,[4] graphic display systems, or as a means of data storage.[5]

Up to now essentially only unsubstituted dithizone had been used in analytical applications. The same is true for its mercury complexes, as far as the mentioned possible commercial applications are concerned. Even amongst projects aimed at understanding the basic fundamentals of its chemistry, very few deals with substituted dithizones containing electron donating and/or withdrawing groups, or perhaps even sterically altered derivatives. For this specific reason the current research project was undertaken, namely to start exploring the borders within which both the ligand and corresponding mercury complexes still retain its characteristic UV/visible and photochromic behaviour, by (a) electronically altering the ligand, (b) extending the aromatic ring system in the ligand and (c) to explore the borders of oxidation of both the ligands and complexes using electrochemistry.

The specific goals set forward for this project are:

1. Synthesis.

    To synthesize electron donating ligands which are symmetrically substituted, i.e. on both phenyl rings, including *ortho, meta* and *para*-methoxy, and *ortho, meta* and *para*-methyl, as well as the *3,4*-dimethyl derivatives. Different synthetic procedures are considered, with the aims of economy and convenience in mind.

    To synthesize dithizones with extended phenyl ring systems, i.e. instead of benzene rings introducing naphthalene, anthracene, pyrene and fluorene.

    To complex the successfully derivatized dithizonates to phenylmercury(II), and test it for photochromicity.

---

[1] H. M. N. H. Irving in *Dithizone*, Analytical Sciences Monographs No.5, The Chemical Society, London, 1977

[2] H. M. N. H. Irving, *CRC Crit. Rev. Anal.Chem.*, 1980, **8**, 321

[3] A. T. Hutton, *Polyhedron*, 1987, **6**, 13

[4] Y. Shimano and P. Yap, 70 50 355, *Chem. Abs.*, 97 349h, 1974, **80**

[5] J. A. Davis and M. Thomas (San Diego State University) in *Photochromic Materials Study*, Rome Air Development Centre, Final Technical Report No. DADC-TR-85-177, Sept. 1985

2. X-ray Crystallography.

   To grow crystals suitable for X-ray crystallography, serving as ultimate characterization of compounds here prepared.

3. Computational Chemistry.

   To do comprehensive Amsterdam Density Functional (ADF) quantum computational studies of all the ligand and complex species, as well as their isomers. This includes geometry optimizations and determination of relative energies, molecular orbital representations and Time-Dependant Density Functional Theory calculations of UV/visible spectra (oscillators), and to relate computational data to experimentally observed photochromic behaviour.

4. Electrochemistry.

   Lastly, to do a full electrochemical study, on all substituted dithizones and their mercury complexes, using cyclic voltammetry. Apart from the electron donating derivatives here synthesized electron withdrawing fluorinated derivatives are also included, thus enabling comparison over a wide range of electronically altered ligands. The aim is to investigate the “electronic borders” within which photochromism takes place, and to compare the relative stabilities against oxidation, of a molecule which may otherwise readily be reduced.

2. Literature Survey

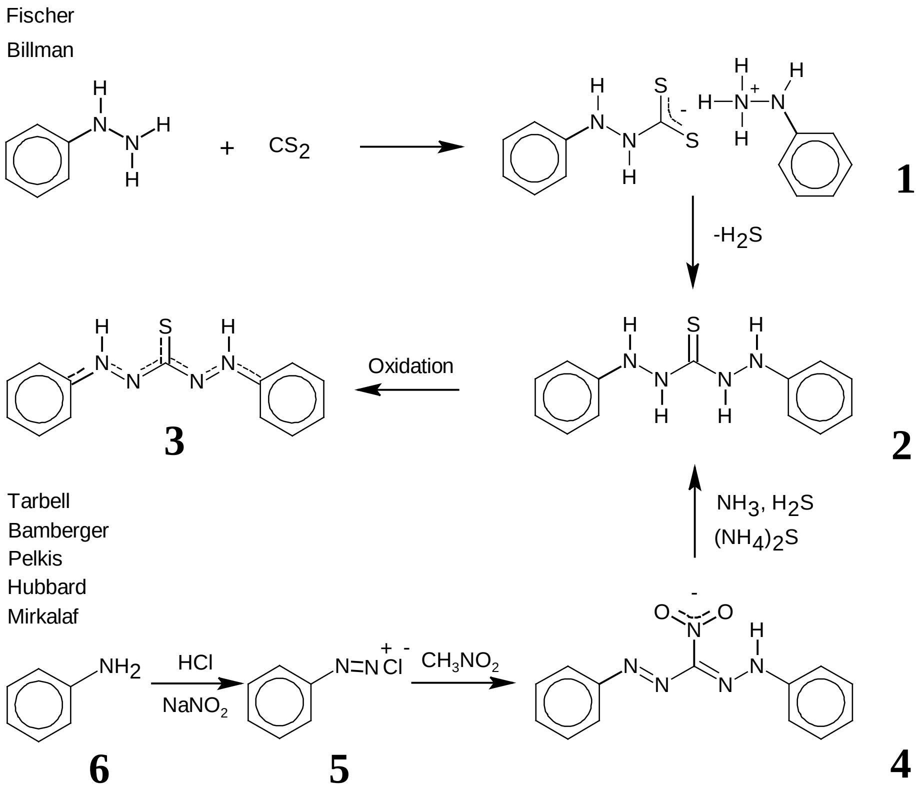
2.1. Introduction

A survey of dithizone, its derivatives and complexes is presented in this chapter. The published methods that were used to synthesize dithizone and its derivatives are reviewed. Related published crystal structures, UV/visible spectroscopy, laser spectroscopy, computational chemistry and electrochemistry are illustrated and discussed.

2.2. Dithizone – The Ligand

2.2.1. Discovery and Synthesis

Emil Fischer, during his extensive research on derivatives of phenylhydrazines in 1878, noticed the formation of an unstable white salt, β-phenyldithiocarbazic acid phenylhydrazine, **1**, when solutions of carbon disulphide and phenylhydrazine were mixed in organic solvents, see Scheme 2.1.[6] The thiocarbazide, **2**, with careful heating, was obtained with loss of hydrogen sulphide.



Scheme 2.1 The synthetic scheme above describes the reaction pathways and conditions followed by the mentioned authors, to synthesize dithizone, **3**, and some derivatives. For the sake of simplicity only the underivitized parent compound is shown here.

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[6] E. Fischer, *Annalen*, 1878, **190**, 67

Addition of dilute alkali and acidifying with dilute acid results in dithizone (H_2Dz) **3**. The almost black oxidation product **3** was investigated in greater detail and its empirical formula confirmed as $C_{13}H_{12}N_4S$.[7]

In 1943 Billman and Cleland[8] introduced an improved method to that of Fischer. Their method involved the preparation of **1** in 97 % yield. Next, hydrogen sulphide was driven off from the phenylhydrazine salt, **1**. Solvent free conditions were thought to be ideal, while the temperature had to be kept between 96 and 98 °C to give 60-75 % yield of thiocarbazide, **2**. Lastly, the thiocarbazide was oxidised by boiling in a methanolic potassium hydroxide solution for 5 minutes, and acidifying with dilute acid yields 75 % of **3**, with an overall yield of about 60 %.

Also in 1943 Hubbard and Scott[9] (products listed in Table 2.2, page 7) published a method similar to an earlier method reported by Bamberger[10], however they did not synthesize the traditional phenyl ring compound, but instead the double-ringed naphthyldithizone derivative. This method (Scheme 2.1) does away with first preparing **1**, but instead starts from naphthalenediazonium chloride, **5**, the latter being prepared by diazotization of β-naphthylamine with sodium nitrite at 0 ˚C in water. The mixture is cooled to -10 ˚C and a sodium acetate solution is added drop wise. To this mixture, kept at -5 ˚C, an alkaline nitromethane solution is slowly added. The deep red nitoformazan, **4**, then precipitates out. Reduction is carried out with ammonium hydrosulfide - obtained from ammonia and hydrogen sulphide gases. Naphthyldithizone is lastly obtained by deprotonating the thiocarbazide, **2**, with alcoholic potassium hydroxide and precipitation with dilute hydrochloric acid. The overall naphthyldithizone yield was 21 %.

Pelkis, Dubenko and Pupko[11] in 1957 used a similar method to that of Bamberger and Tarbell[12], as shown in Scheme 2.1 (previous page). Ring-substituted anilines, **6**, are dissolved in concentrated hydrochloric acid and diazotized with sodium nitrite. The nitroformazan, **4**, is prepared by coupling nitromethane and the substituted benzenediazonium chloride, **5**. Reduction to give **2**, is similar to that described by Hubbard and Scott. Ammonium sulphide (20 % aqueous), as used by Mirkalaf[13] in 1998, does away with the noxious NH_3 and H_2S gases during conversion of **4** to **2,** making the synthesis significantly more convenient. Dithizone, **3**, is obtained by deprotonation with 2 % alcoholic alkali and precipitation with 1 % hydrochloric

---

[7] E. Fischer and E. Besthom, *Annalen*, 1882, **212**, 316

[8] J. H. Billman and E. S. Cleland, *J. Am. Chem. Soc.*, 1943, **65**, 1300

[9] D. M. Hubbard and E. W. Scott, *J. Am. Chem. Soc.*, 1943**, 65**, 2390

[10] E. Bamberger, R. Padova and E. Omerod, *Lieb. Ann.*, 1926, **260**, 307

[11] P. S. Pelkis, R. G. Dubenko and L. S. Pupko, *J. Org. Chem. USSR.*, 1957, **27**, 2190

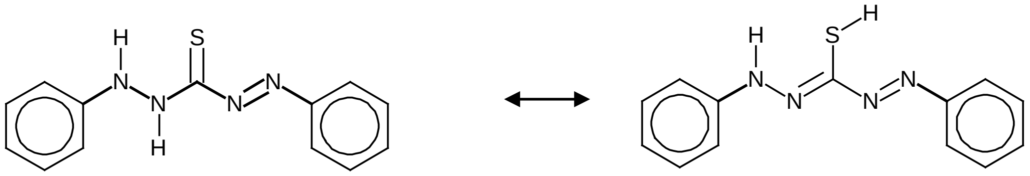
[12] D. S. Tarbell, C. W. Todd, M. C. Paulson, E. G. Lindstrom and V. P. Wystrach, *J. Am. Chem. Soc.*, 1948, **70**, 1381

[13] F. Mirkhalaf, D. Whittaker and D. J. Schiffrin, *J. Electroanal. Chem.*, 1998, **452,** 203

acid. With this method Pelkis *et al.* obtained fairly good to excellent yields which were in the range of 28 – 98 %. They synthesized a number of electron donating and withdrawing derivatives, see Table 2.3 (page 8).

2.2.2. Structure and Geometry

In 1878 Fischer[6] proposed an equilibrium between the keto and enol forms of dithizone in solution, see Figure 2.1. He assumed from UV/visible spectra of dithizone (Figure 2.2) that the long wave band (620 nm) belongs to the keto form while the short wave band (450 nm) belongs to the enol form. Because of Fischer’s assumption, as early as 1940[9] and 1960[14], scientists believed that dithizone has tautomers, i.e. in solution a proton shifts within the molecule without changing the shape of the molecule. The two most common tautomers as proposed by Fischer are the keto and enol forms. Dithizone[15] is insoluble in water but soluble in organic solvents, and gives strongly coloured solutions characterized by two absorption bands. Dithizone in its pure solid form has a violet-black colour with metallic reflex.



Thione (Keto) **Thiol (Enol)**

Figure 2.1 The postulated thione (keto) and thiol (enol) forms of dithizone in organic solutions.

Dilute solutions of the free ligand are solvatochromic, i.e. having different colours in different solvents; in methanol it is orange with λ_{max} = 472 nm while dichloromethane solutions are green, with λ_{max} = 450 and 608 nm.[16]

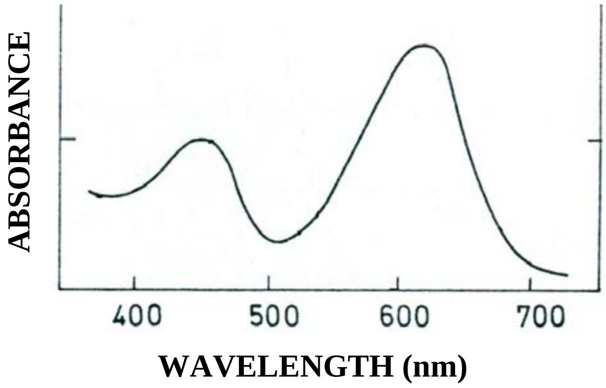


Figure 2.2 Absorption spectrum of dithizone in chloroform as solvent. The figure was stylistically changed.[15]

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[14] K. S. Math, Q. Fernando and H. Freiser, *Anal. Chem.*, 1964, **36**, 1762

[15] H. M. N. H. Irving in *Dithizone*, Analytical Sciences Monographs, Chem. Soc., London, 1977, 6 and 85

[16] K. G. von Eschwege Ph.D Dissertation, 2006, UFS Sasol Library

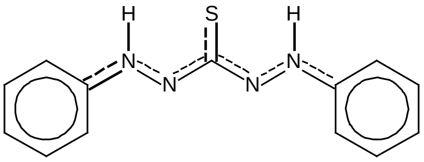
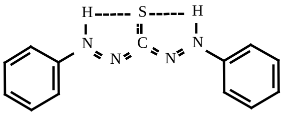
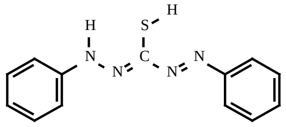
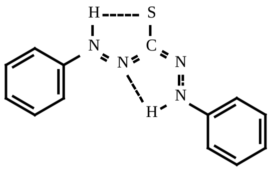
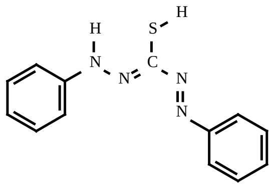


Figure 2.3 The solid symmetric form of dithizone as determined by X-ray crystallography.[17]

While using low temperature (-50 °C) ^{1}H NMR techniques Hutton[3] in 1987 however concluded that the two absorption bands are due to the symmetric form of dithizone in solution, both bands originating from one symmetric structure, see Figure 2.3. He came to this conclusion because of the observation of the N-H signal at δ 12.60 ppm, a doublet with a coupling constant that did not change with temperature lowering. This excludes the possibility of having a rapid tautomeric equilibrium. The symmetric solid state structure was determined by Laing[17] in 1977, using X-ray crystallography.

Table 2.1 ADF gas phase calculated optimization energies of different possible isomers of dithizone, H_2Dz. Hydrogen bonding patterns and optimization energy differences are indicated.[16]

Tautomer/isomer of dithizone	**Relative energy (kcal mol^{-1})**
	0
	7.84
	14.53
	12.45

On the contrary Schönherr *et al.* in 2002,[18] also studied dithizone using ^{1}H NMR spectroscopy at room temperature and they found two signals, at δ 12.60 ppm and δ 1.60 ppm, which corresponds to the N-H and S-H bonds respectively. He concluded that dithizone does indeed have an equilibrium at room temperature, but an equilibrium between the enol and

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[17] M. Laing, *J. Org. Chem., Perkin Trans.*, 1977, **2**, 1248

[18] T. Schonherr, V. Schimd, R. Linder and U. Rosellen, *Inter. J. Quantum Chem.*, 2002, **86**, 90

symmetric forms of dithizone. They argue that there is a relatively small energy barrier of 3 kcal mol^{-1} for the proton transfer between the enol and symmetric forms.

Preliminary (Density Functional Theory) DFT quantum computations by Von Eschwege[16] in 2006 on the symmetric and enol forms as well as the corresponding hydrogen bridge and the twisted form indicated that the symmetric form is the dominant species in solution, see Table **2.1**.

2.2.3. Substitution Derivatives of Dithizone

Since the discovery of dithizone in 1878 a number of dithizone derivatives have been synthesized specifically to investigate the effect of electron donating and withdrawing groups on different positions on the dithizone phenyl rings.[9,11,19] Apart from these, dithizone derivatives with extended ring systems had also been synthesized, see for example Figure 2.4 and Table **2.2**.[9]

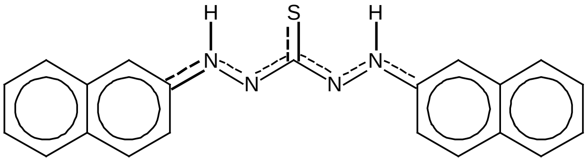

Figure 2.4 The proposed structure of β-naphthyldithizone.

Tarbell *et al.*[12] used different methods to synthesize dithizone derivatives, such as the Fischer and Bamberger methods. This includes successful syntheses of phenyl-substituted dithizones, $(R)H_2Dz$, where R is: o-OC_6H_5, p-OC_6H_5, o-OCH_3, o-C_6H_5, p-C_6H_5, m-C_6H_5, o-(p-CH_3O-C_6H_4O), o-SC_6H_5, o-SCH_3. All dithizones are symmetric, i.e. substituents are on both phenyl rings and in the same positions.

Table 2.2 Selected dithizone derivatives $(R)H_2Dz$ synthesized by Hubbard and Scott.[9] R-groups are phenyl substituents, except in the case of $C_{10}H_7$, where phenyls are replaced by naphthyls.

Dithizone Derivative, R	M.p. ˚C
p-Br	125
o-CH_3	140-142
p-CH_3	145-147
p-C_6H_4	215-217
α-$C_{10}H_7$	-
β-$C_{10}H_7$	135-137

Tarbell *et al.*[12] and Pelkis *et al.*[11,19] improved the nitroformazan method of Bamberger[10] by coupling the substituted benzenediazonium chloride, **5** (Scheme 2.1) with nitromethane in dilute acetic acid mixed with acetate ion.

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[19] P. S. Pelkis, R. G. Dupenko and L. S. Pupko, *J. Org. Chem. USSR.*, 1957, **27**, 1917

Table 2.3 Electron withdrawing and electron donating dithizone derivatives (R)H_2Dz synthesized by Pelkis, Dupenko and Pupko, with corresponding reaction yields and UV/visible absorbance maxima. All UV/visible absorbance spectra were measured in benzene except for *para*-fluorodithizone which was measured in acetone. All solution concentrations were 6.6×10^{-5} M.[11,19]

R, Electron withdrawing	**Yield (%)**	**λ_{max}**	**R, Electron donating**	**Yield (%)**	**λ_{max}**
o-Cl	98	465,645	H_2Dz	-	450, 620
m-Cl	79	460,631	*o*-OCH_3	-	486, 659
p-Cl	76	452,626	*m*-OCH_3	51	465, 634
o-Br	64	475,640	*p*-OCH_3	63	476, 646
m-Br	61	440,640	*o*-CH_3CH_2	-	480, 655
p-Br	-	454,638	*m*-CH_3CH_2	23	470, 635
o-I	87	475,655	*p*-CH_3CH_2	32	465, 646
m-I	74	455,645	*o*-$C_6H_4OCH(CH_3)_2$	74	460, 650
p-I	89	460,660	*o*-$C_6H_4OC_4H_9$	78	490, 655
m-F	65	420,625	*o*-OC_5H_{11}	70	500, 655
p-F	54	445,620	*o*-$C_6H_4OC_6H_5$	-	480, 650
2,4-$(Cl)_2$	29	455,665	*o*-$C_6H_4SCH_3$	-	475, 640
2,4-$(Br)_2$	44	445,645	*p*-$C_6H_4SCH_3$	63	530, 675
2,4-$(I)_2$	30	470,675	*p*-$C_6H_4SCF_3$	44	450, 640
2-CH_3-4-Br	28	460,630			
2,5-$(CH_3)_2$-3,6-$(Br)_2$	32	450,630			

Very good yields were often obtained for the mono-substituted electron withdrawing dithizone derivatives, while yields of less than 50 % were obtained for the di-substituted dithizone derivatives, as may be seen in the last entries in Table 2.3 for the electron withdrawing groups. Compounds in this series are soluble in hydrocarbons and chlorinated hydrocarbons, giving green solutions. Introducing electron withdrawing substituents to the phenyl rings of dithizone in general caused both absorption maxima to be red-shifted relative to that observed for dithizone in benzene; $\lambda_{max1} = 450$ nm and $\lambda_{max2} = 620$ nm.[19] Pelkis *et al.* observed that by introducing electron withdrawing and electron donating groups to the phenyl rings of dithizone, the long-wave maximum extinction coefficient is decreased with a simultaneous increase of the same at the shorter wave maximum. They interpreted it as the keto-enol equilibrium being shifted towards the enol form.[11]

Electron donating substituent groups are also listed in Table 2.3. Whereas the red shift of the *ortho*-halogenated ligands relative to the unsubstituted dithizone were at most 25 nm for the shorter wavelength band in the case of the electron withdrawing derivatives, much larger red shifts are seen for the electron donating ligands, with that of *para*-C_6H_4-SCH_3 most pronounced, shifting as much as 80 nm to 530 nm. Such large shifts are responsible for entirely new colours, which, in case of the latter, correspond to that of a typical purple substance, instead of the traditional blue-green colour of unsubstituted dithizone. Second to *para*-C_6H_4-SCH_3 is the *ortho*-OC_5H_{11} derivative, with λ_{max1} at 500 nm. Most substitutions on the phenyl rings of dithizone therefore lead to red shifts, as may be seen in the afore going table.[19]

2.2.4. Oxidation Products of Dithizone

Thiols[20,21] are normally oxidized to disulfides by using elemental iodine. Iodine's interaction with dithizone was studied: in a dilute chloroform solution, containing water, dithizone was immediately oxidized to a red (λ_{max} = 420 nm) product while HCl appeared in the aqueous phase. A thermal fission reaction results in the formation of dithizone-disulfide, $(HDz)_2$, yielding stoichiometric amounts of dithizone (H_2Dz) and a yellow compound, dehydrodithizone (Dz), which has two protons less than dithizone, see Figure 2.5. The disulphide of dithizone in solution is unstable, at 25 ˚C the half life of the disulfide is 10.5 minutes in acetone and 77 days in *n*-hexane. Dithizone may also be oxidized with potassium hexacyanoferrate(III) or any of a variety of oxidizing agents to dehydrodithizone, Dz.[22] Dehydrodithizone, because of its polar character, has varied electronic spectra in different solvents, e.g. orange in acetone (λ_{max} = 460 nm) and almost colourless in water (λ_{max} = 380 nm).

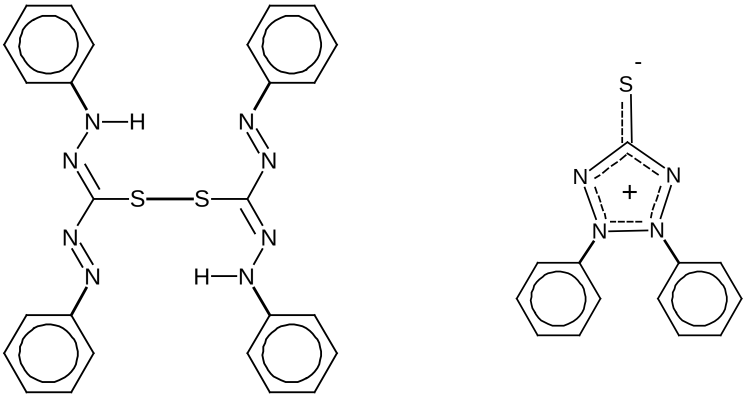

Figure 2.5 Structures of the dithizone disulfide, $(HDz)_2$ (left), and dehydrodithizone, Dz (right).

Dehydrodithizone, Dz, has been used as intermediate for the anchoring of dithizone on cross-linked polyvinylpyridine, which was finally used for the preconcentration of nanogram levels of mercury.[23] Dehydrodithizone can also be reduced with an alkaline solution of dextrose, amongst others.[24]

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[20] A. M. Kiwan and H. M. N. H. Irving, *J. Chem. Soc. B*, 1971, 898

[21] A. M. Kiwan, H. M. N. H. Irving, *J. Chem. Soc. B*, 1971, 901

[22] H. M. N. H. Irving, A.M. Kiwan, D.C. Rupainwar, S.S. Sahota, *Anal. Chim. Acta* 1971, **56,** 205

[23] R. Shah and S. Davi, *React. Funct. Polym.*, 1996, **31**, 1

[24] J. W. Ogilvie and A. H. Corwin, *J. Am. Chem. Soc.*, 1961, **83**, 5023

Jian *et al.* recently proposed two new methods for the preparation of dehydrodithizone, Dz.[25] In the first method dithizone was dissolved in acetone and hydrogen peroxide added while keeping the mixture at 40 – 60 °C. The solution gradually changes colour from green to red. After 3 hours the reaction was complete and recrystallization done from ethanol.

In the second method dithizone is dissolved in acetonitrile. The solution is heated to 50 °C, and an aqueous solution of sodium hydroxide is added dropwise. After 15 minutes the colour changed from green to red, but stirring was continued for a further 12 hours, yielding the red Dz product.

2.3. Dithizonato Metal Complexes

2.3.1. Analytical Applications

Helmuth Fischer[26] in 1925 demonstrated the vast importance of the then newly discovered dithizone ligand as a means to detect and determine heavy metal ions. In the sixties about 100 related articles were published per annum, but the role of dithizone as sensitive reagent for the direct determination of trace metals, by liquid-liquid extraction followed by spectroscopy, gradually became less important. Harry Irving in 1977 did a thorough review of the whole subject, see Figure 2.6.[15,2]

By using dithizone in ethanol as extractant, Van Staden and Taljaard[27] in 2004 formulated methods for the simultaneous sequential injection analysis of South African soil and water samples comprising of many different metal ions. Comitre and Reis,[28] using dithizone as complexing agent, accomplished UV/visible spectrophotometric detection limits of 12 ppb (parts per billion) for the analysis of lead in plant materials. Detection limits compared well with results obtained from inductively coupled plasma optical emission spectroscopy (ICP OES).

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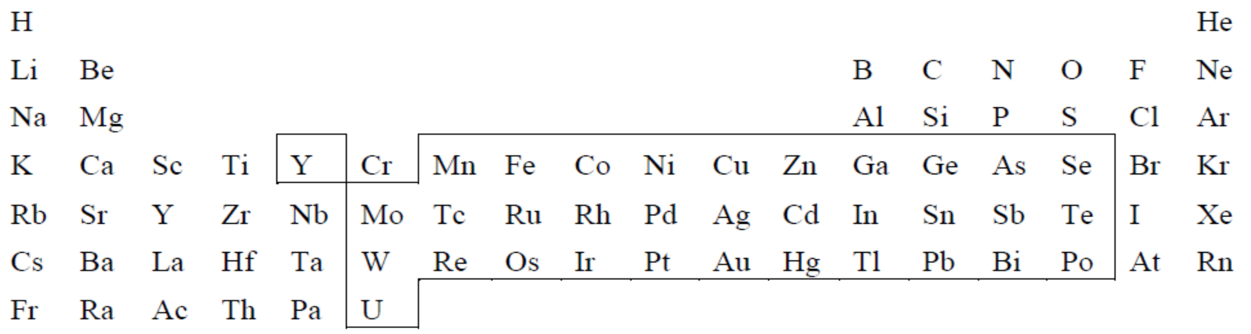
[25] F. Jian, P. Zhao, L Zhang and Y Hou., *J. Org. Chem.* 2005, **70**, 8322

[26] H. Fisher, *Wiss. Versöffentlich. Siemens-Werken*, 1925, **4**, 158

[27] J. F. Van Staden and R. F. Taljaard, *Talanta*, 2004, **64**, 1203

[28] A. L. D. Comitre and B. F. Rice, *Talanta* 2005, **65**, 846



H																	He
Li	Be											B	C	N	O	F	Ne
Na	Mg											Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	Y	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
Fr	Ra	Ac	Th	Pa	U												

Figure 2.6 Metals that can be extracted with dithizone and precipitated as sulfides.[15]

Hubbard and Scott concluded that β-naphthyldithizone was superior to dithizone for quantitatively determining trace metals such as mercury and zinc in biological material.[9] Figure 2.7 shows the efficiency for extracting Zn with dithizone and β-naphthyldithizone.[29] At pH 8.3 both the reagents extract Zn equally well. As the pH increases to above 8.5 there is a drop in efficiency of dithizone extraction compared to that of β-naphthyldithizone, which remains unimpaired to at least pH 10.5.

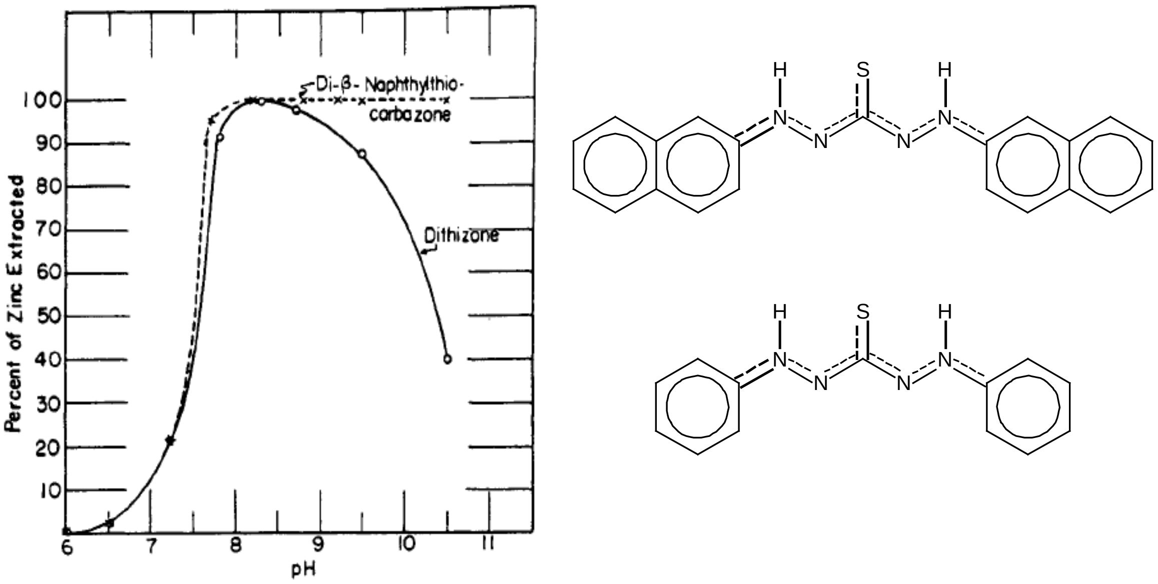


Figure 2.7 The pH dependence of β-naphthyldithizone and dithizone during Zn extractions, and the structures of β-naphthyldithizone (top right) and dithizone (bottom right).[29]

2.3.2. Photochromism

The reversible photo-transformation of a chemical species between two geometrical forms having different absorbance spectra is commonly known as photochromism. The change in the physical properties of molecules, such as fluorescence, refractive index, polarizability and

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[29] J. Cholack, D. M. Hubbard and R. E. Burkey, *Ind. Eng. Chem.*, 1943, **15**, 754

electrical conductivity, are induced by the change in molecular and electronic structure. An interesting example is 11-*cis*-retinal[30] which is responsible for human vision, see Figure 2.8. The salicylideneanilines,[31] Figure 2.9, is also a good example of photochromism.

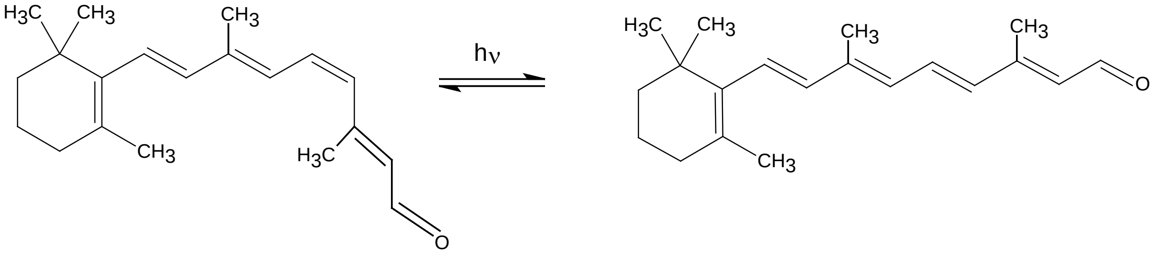

Figure 2.8 The *cis-trans* photochromic reaction of retinal with absorption of light.

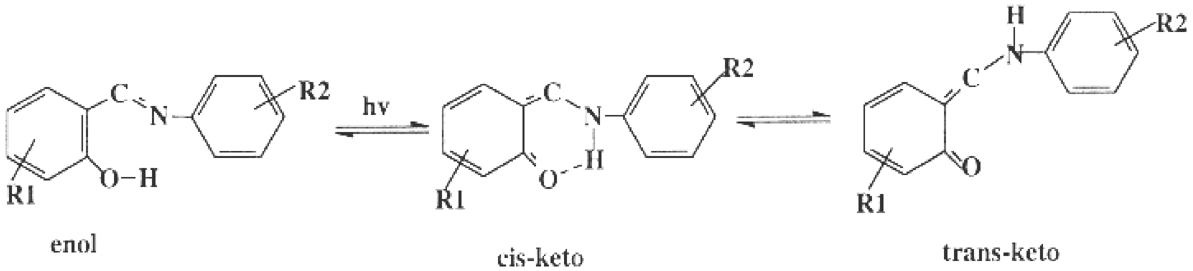

Figure 2.9 Photochromism of salicylideneanilines.[31]

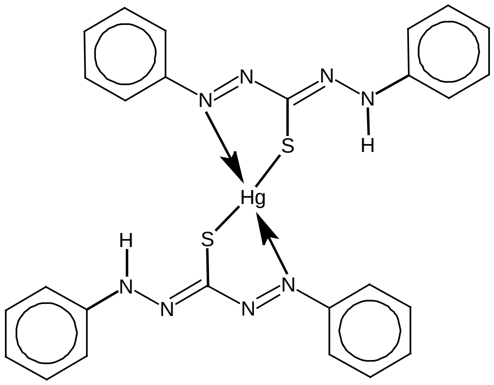

Figure 2.10 The proposed structure of dithizonatomercury(II).[32]

Irving and co-workers,[33] and Webb and co-workers[34] independently showed that dithizonatomercury(II), Hg(HDz)$_2$ complexes are photochromic, see Figure 2.10. Webb and co-workers observed the photochromic reaction when sunlight was shone on a dilute solution of the dithizonatomercury(II) complex dissolved in benzene, they also found that the reaction may be

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[30] D. D. Ebbing and S. D. Gammon, General chemistry 6th ed. Houghton Mifflin company, 1999

[31] X. Tang, D. Jia, K. Liang, X. Zhang, X. Xia, Z. Zhou, *J. Photochem & Photobiol A:, Chemistry* 2000, **134**, 23

[32] L. S. Meriwether, E. C. Breitner and C. L. Sloan, *J. Am. Chem. Soc.*, 1965, **87**, 4441

[33] H. Irving, G. Andrew and E. J. Risdon, *J. Chem. Soc.*, 1949, 541

[34] J. L. A. Webb, I. S. Bhatia, A. H. Corwin and A. G. Sharp, *J. Am. Chem. Soc.*, 1950, **72**, 91

repeated indefinitely. Irving and co-workers also observed the same phenomenon when the chloroform dithizonate solution turned from an orange colour to a blue colour, when irradiated with sunlight. When the photochromic reaction is followed on a UV/visible spectrometer a single isosbestic point is observed for the mercury complexes, indicating the absence of intermediates, see Figure 2.11.

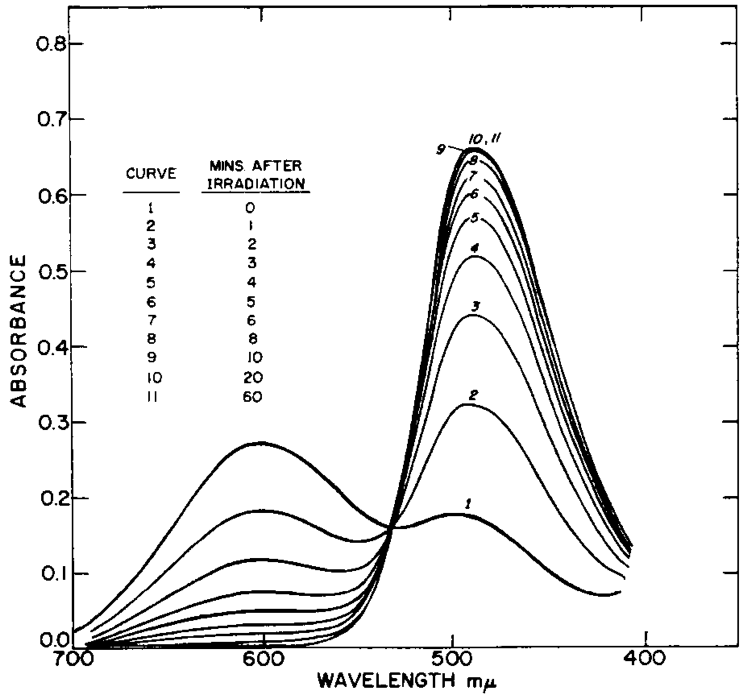

Figure 2.11 The return reaction of dithizonatomercury(II), Hg(HDz)$_2$ (9.4 x 10^{-6} M) after irradiation in benzene and chloroform. The back reaction was followed at different time intervals as indicated by the solid lines. The single isosbestic point indicates the absence of intermediates.[32]

Table 2.4 contains data for a selection of photochromic dithizonate complexes,[32] the solvents ranging from chlorinated to oxygenated solvents. Metal dithizonates has the highest solubility in chloroform, but solvents such as carbon tetrachloride, dichloromethane, toluene, tetrahydrofuran, acetone and ethyl acetate are also suitable for spectrophotometric studies. All dithizonates are insoluble in water, except if it is specifically derivitized in a way to become water-soluble, i.e. carrying sulphonic or carboxylic acid or salt groups on the phenyl rings. The most visible photochromic reactions are observed in dry, non-polar solvents, such as the halogenated solvents, carbon disulphide and toluene. The activated form always has a higher λ_{max} than the ground state. The temperature at which the reactions take place range from -80 to +25 °C, with life times of less than a second to about 60 seconds.

Table 2.4 Photochromic reactions of metal dithizonates.[32] The activated form results from irradiation with light.

Complex	Solvent	Colour and absorbance maxima (nm) Normal form	Colour and absorbance maxima (nm) Activated form	Temp. (°C)	Approx. return time (s)
$Pd(HDz)_2$	Chloroform	Green (450, 640)	Blue (450, 520, 570, 630)	25	5-10
	Benzene	Green	Orange	25	5-10
	Dichloromethane	Green	Orange	-10	1-2
$Pt(HDz)_2$	Benzene & carbon tet.	Yellow (490, 708)	Red	25	1-2
$AgHDz{\cdot}H_2O$	Tetrahydrofuran	Yellow (470)	Violet	25	2-5
				10	40-60
$Zn(HDz)_2$	Dichloromethane	Red (530)	Violet-blue	25	1-2
	Tetrahydrofuran & ethylacetate	Red	Violet-blue	-40	< 1
$Cd(HDz)_2$	Tetrahydrofuran & acetone	Orange (500)	Violet	-80	<1
$Hg(HDz)_2$	Benzene & chloroform	Orange (490)	Blue (605)	25	30-90
$Pb(HDz)_2$	Tetrahydrofuran	Red (520)	Blue	-80	< 1
$Bi(HDz)_3$	Dichloromethane, xylene, ethyl acetate & methanol	Orange (498)	Violet	-30	< 1
	Pyridine	Orange	Violet	-30	10
$BiCl(HDz)_2$	Tetrahydrofuran & dichloromethane	Orange (490)	Blue (605)	-40	2-5

The metal has little effect on the colour of the complex; it does however have an effect on the return rate to the ground state. The order of return reaction rates is as follow:

$$Hg < Pd < Ag < Pt < Zn < Bi < Cd < Pb.$$

2.3.3. Ultra-fast Laser Spectroscopy

In DCM dithizonatophenylmercury(II) (PhHgHDz) exhibit a photochromic reaction with a return time of about 1 minute.[35] However in methanol no visible photochromic reaction is observed. The initial photochromic reaction of PhHgHDz in DCM and methanol solutions was investigated by femtosecond transient absorption spectroscopy by Schwoerer *et al.* at the Laser

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[35] K. G. von Eschwege, J. Conradie and J. Swarts, *J. Phys. Chem. A*, 2008, **112**, 2211

Research Institute in Stellenbosch.[36] Ultrafast excitation within less than 100 fs was found to cause a radiationless photoreaction with a time constant (time it takes to reach 1 - 1/e = 63 % of its final value) of 1.5 ps in methanol (Figure 2.12) which was interpreted as the C=N isomerization pathway through a conical intersection (point where pathway splits into b and c, Figure 2.13). Photochromism of PhHgHDz in a very polar solvent like methanol was for the first time observed, clearly indicating that photochromism is not absent in methanol but that the back reaction is so fast that it cannot be seen with the naked eye.

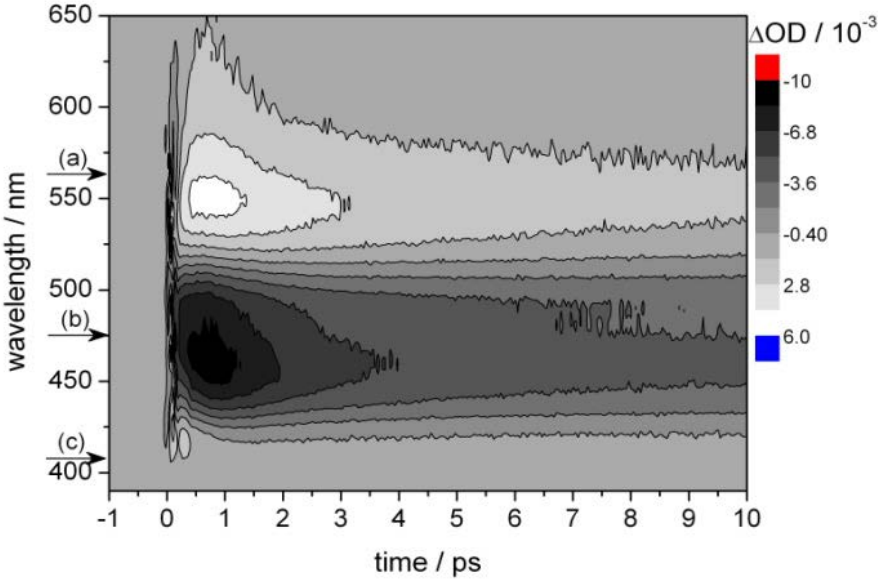

Figure 2.12 Transient change in optical density ΔOD(λ,t) of PhHgHDz in methanol (3.75×10^{-4} mol.dm^{-3}) between 390 nm and 650 nm after excitation with a 40 fs short laser pulse at 470 nm. Dark areas indicate decreased absorption or increased emission, light areas indicate increased absorption.[36]

Under excitation with 480 nm light PhHgHDz exhibits no fluorescence in the wavelength region 480 - 700 nm in either of the solvents DCM and methanol, confirming earlier measurements.[37] The visible absorption spectra of mercury dithizonates in polar and non-polar solvents do not differ significantly, all solutions appear orange.

Apart from the absence of fluorescence, the four components of the transient absorption spectroscopic observations are, (i) the reactant's absorption around 470 nm (see Figure 2.12, arrow **b**), (ii) an excited state absorption of the planar orange form below 430 nm (arrow **c**), (iii) absorption of the orthogonally (90°) twisted intermediate on the excited potential energy surface around 575 nm (shoulder above arrow **a**, see also Figure 2.22, p. 27), and (iv) the product's absorption around 555 nm (arrow **a**).

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[36] H. Schwoerer, K. G. von Eschwege, G. Bosman, P. Krok and J. Conradie, *Phys. Chem. Chem. Phys.*, submitted, 2010

[37] B. Paci, J. Nunzi, N. Sertova and I. Petkov, *J. Photochem. Photobiol.A: Chem.* 2001, **137**, 141

An orthogonally twisted intermediate state was proposed via its excited state absorption (point iii above). Bifurcation along pathways b and c (Figure 2.13) towards the ground states of the orange *cis* and blue *trans* configurations occurs below the funnel of the conical intersection.

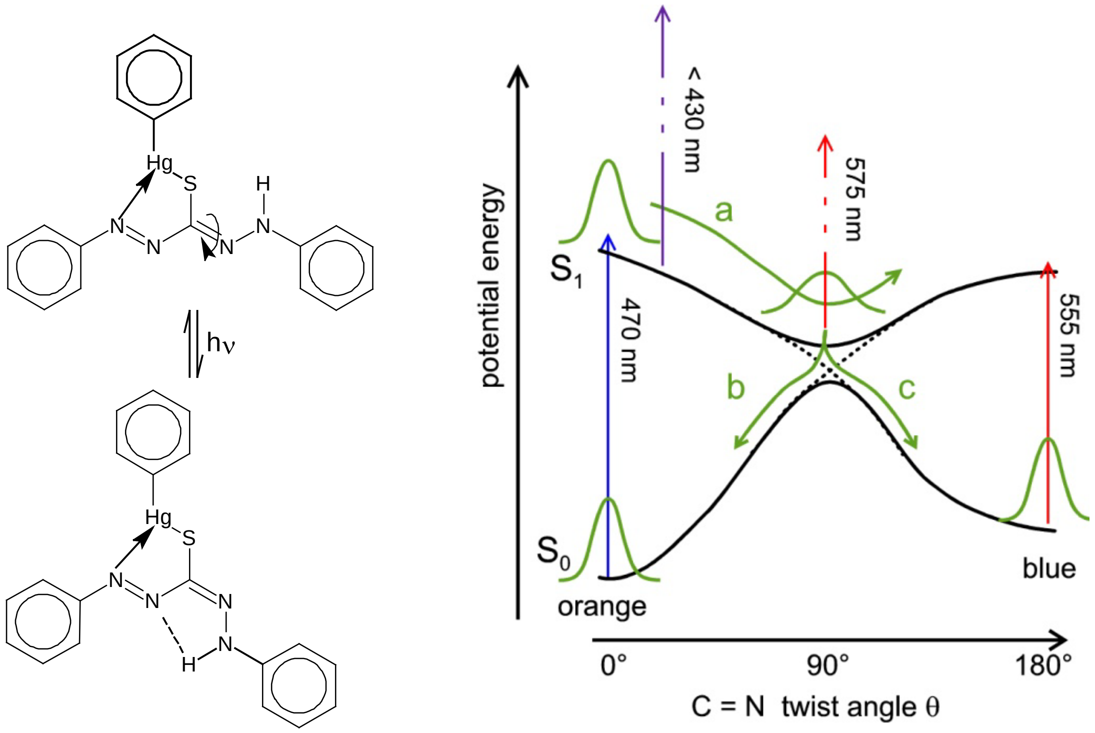

Figure 2.13 Proposed reaction pathway for PhHgHDz after $S_0 \rightarrow S_1$ photo-excitation. After excitation the molecule immediately starts twisting around the C-N bond (left) to minimize its energy. This corresponds to a slope down the S_1 potential energy surface and runs into a region of a conical intersection with S_0. After fast vibrational relaxation it proceeds onto S_0 where it bifurcates in two pathways towards the orange and the blue form ground states.[36]

2.4. Crystal Structures

2.4.1. Dithizone

Laing[17] redetermined and refined the dithizone crystal structure more accurately than first reported by Alsop,[38] see Figure 2.3, page 6. The dithizone ligand is near planar, with the C-S bond lying on the intersection of the two mirror planes. The phenyl rings however are slightly twisted out of the mean plane in opposite directions. The bond lengths indicate that the π-electrons in the N-N-C-N-N backbone are delocalized and that there are no localized single or double bonds.

N-N and N=N bonds are typically 1.45 Å and 1.25 Å respectively and N-C and N=C bonds are 1.47 Å and 1.29 Å respectively, while S-C and S=C bond lengths are 1.82 Å and 1.60 Å

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[38] P. A. Alsop, Ph.D. Thesis, Universiry of London, 1971

respectively.[39,40,41] In the N-N-C-N-N backbone the N-N bond lengths are 1.299 (2) Å and 1.295 (3) Å, while the N-C bond lengths are 1.345 (3) Å and 1.334 (3) Å, indicating extensive delocalization. The S-C bond length is 1.712 (3) Å which shows that delocalisation extends to the S-C bond.

2.4.2. Dehydrodithizone

The first chemical scientists to suggest the meso-ionic structure (Figure 2.14, left) for the yellow crystalline dehydrodithizone, Dz, were Ogilvie and Corwin.[42] The structure was later confirmed by X-ray crystallography.[43] Contrary to the dithizone ligand and complexes, Dz exhibits little or no conjugation in the N-C bond between the tetrazolium and phenyl rings. This is confirmed by the N2-C2 distance (1.443 Å) which is characteristic of single bonds. The N1-N2 bond distance is 1.318(3) Å, which indicates more of a double than a single bond character. The S-C(1) bond has a length of 1.687(5) Å .

The dehydrodithizone crystal has an unusual packing order; each sulphur atom is sandwiched between the planes of two adjacent tetrazole rings. The tetrazole rings are in turn sandwiched between two sulphur atoms, with the crystal thus consisting of alternating tetrazole rings and sulphur atoms. This is, amongst others, indicative of a positive charge on the tetrazole ring and a negative charge on the sulphur atom.

Figure 2.14 The oxidised product of dithizone formally known as dehydrodithizone (Dz, left) and *para*-methyldehydrodithizone (right). Both structures were stylistically changed.

For *para*-methyldehydrodithizone (Figure 2.14, right), the N1-N2 bond distance, 1.313(8) Å, is indicative of some double-bond character. The S-C bond length of 1.686(10) Å is similar to

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[39] Huheey, pps. A-21 to A-34; T. L. Cottell, “The Strengths of Chemical Bonds.” 2nded., Butterworths, London, 1958

[40] B. deB. Darwent, “National Standard Reference Data Series,” National Bureau of Standards, No. 31, Washington, DC, 1970

[41] S. W. Benson, *J. Chem. Educ.*, 1965, **42**, 502

[42] J. W. Ogilvie and A. H. Corwin, *J. Am. Chem. Soc.*, 1961, **83**, 5023

[43] Y. Kushi and Q. Fernando, *J. Chem. Soc.*, 1969, 1240

that found in the unsubstituted dehydrodithizone. The weak electron-donating capacity of *para*-methyldehydrodithizone does not alter the bond distances of the C-N and N-N bonds.[44]

2.4.3. Dithizonatophenylmercury(II)

Published X-ray crystal data of dithizonatomercury complexes include the following: bis(dehydrodithizone)mercury(II) chloride, i.e. monodentate mercury bonded dehydrodithizone,[45] anhydro-5-mercapto-2,3-diphenyltetrazole-dichloromercury(II),[46] (1,5-diphenylthiocarbazonato-N,S)-methylmercury(II),[47] and (dithizonato-N,S)-phenylmercury(II), i.e. dithizonatophenylmercury(II).[48] In all these complexes the dithizonate phenyl rings are mostly planar with slight twists in the dithizone backbone. The mercury metal is bidentately coordinated through the N and S atoms. In the case of the dehydrodithizone complex the metal is only coordinated through the S atom, see Figure 2.15, right.

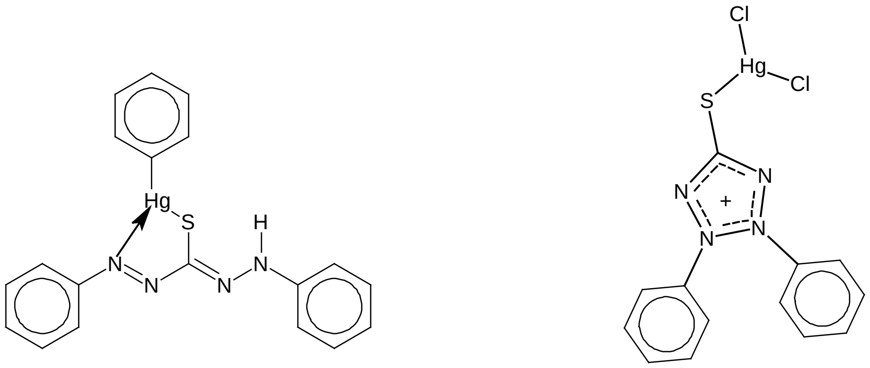

Figure 2.15 Structures of dithizonatophenylmercury(II) (PhHgHDz, left) and the monodentate mercury-bonded dehydrodithizone (right) as determined by X-ray crystallography.

In the PhHgHDz, complex (see Figure 2.15, left) the Hg atom displays planar, irregular three-coordination, the geometry at the Hg atom being almost T-shaped. The strong covalent Hg-S bond length is 2.372(9) Å long. Delocalisation is not as pronounced along the ligand backbone of the metal complex as in the dithizone ligand crystal structure. The formal double bonds, N=C, 1.301(6) Å and N=N, 1.277(5) Å are slightly elongated, while the formal single bonds N-C, 1.415(5) Å and N-N, 1.336(5) Å are shortened. The S-C bond length of 1.731(9) Å lies between a double and single bond length and proves that delocalization found in the Ph-N-N-C-N-N-Ph backbone does extend to the S atom.

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[44] P. S. Zhao, F. F. Jian, H. L. Xiao and Y. X. Hou, *Bull. Korean Chem. Soc.*, 2004, **25**, No. 12

[45] W. J. Kozarek, Q. Fernando, *Inorg. Chem.*, 1973, **12**, 2129

[46] R. E. Marsh, F. H. Herbstein, *Acta Crystallogr.,Sect. B: Struct. Sci.*, 1983, **39**, 280

[47] A. T. Hutton, H. M. N. H. Irving, L. R. Nassimbeni, G. Gafner, *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.*, 1980, **36**, 2064

2.5. Computational Chemistry

2.5.1. Introduction

Computational chemistry is a branch of theoretical chemistry of which the goals are to create efficient mathematical approximations and computer programs to solve the Schrödinger equation. It is a branch of theoretical chemistry and is considered a mathematical description of chemistry. It is convenient to study chemical reactions that are difficult, dangerous, expensive and impossible to do in the laboratory. Computational chemistry can also be used to simulate reaction kinetics, catalysts, medicine, inorganic compounds, organic compounds, etc. Investigations normally start by computing molecular geometries, energies of molecules and transition states, frequencies (IR, NMR and UV/visible), electron distribution (MO, dipole moments, bond orders and charges), ground states, excited states and ionization energies, to mention but a few.[49,50]

Computational chemistry is also a tool in understanding some chemical problems more completely *e.g.* molecular bonding. The best is to combine theory with experiment and to take advantage of synergies between both. Table 2.5 shows a summary of some computational chemistry methods used in chemistry.

In density functional theory (DFT) the energy of a molecule can be determined from electron-density instead of a wavefunction. A density functional is used to obtain the energy from the electron density.[49]

The **density functionals** in use may be divided into three different classes:

- **Local functionals**: A local functional (LDA) treats the density as a uniform electron gas and may account for spin polarization.
- **Gradient corrected functionals**: Gradient corrected methods (GGA), for example BLYP,[51] PW91[52] and OLYP,[53] utilize the electron density and its gradient.

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[48] A. T. Hutton, H. M. N. H. Irving, *Chem.Commun.*, 1979, 1113

[49] E. Lewars, *Computational Chemistry, Introduction to the theory and applications of Molecular and Quantum Mechanics,* Kluver Academic Publishers, Boston, 2003, 1-7

[50] C. J. Cramer, *Essentials of Computational Chemistry, Theories and Models*, John Wiley & Sons, USA, 2004, 5-10

[51] A. D. Becke, *Phys. Rev. A38*,1988, 3098; C. Lee, W. Yang, R.G. Parr, *Phys. Rev. B37*, 1988, 785

[52] J. P. Perdew in: P. Ziesche, H. Eschrig (Ed.) *Electronic Structure of Solids, Akademie, Berlin,* 1991, 11; J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B46,* 1992 6671, Erratum: J. P. Perdew, J. A. Chevary, S. H. Vosko, K. A. Jackson, M. R. Pederson, D. J. Singh, C. Fiolhais, *Phys. Rev. B48*, 1993, 4978

[53] N. C. Handy, A. J. Cohen *Mol. Phys.*, 2001, **99**, 403; C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B37*, 1988, 785

- **Hybrid functionals**: Hybrid methods combine functionals from other methods with pieces of HF calculation, usually the exchange integrals. Examples of hybrid functionals are B3LYP[54] and O3LYP.[55]

Table 2.5 Computational methods used in chemistry.[49]

Tool	Explanation
Molecular mechanics	Newtonian mechanics used to model molecular systems, this is the classic ball (atoms) - spring (bonds) model
Molecular dynamics	used to solve Newton's equations of motion numerically to obtain information of its time-dependant properties
Ab initio calculations	method where a full quantum mechanical calculation is performed from first principles based on the Schrödinger equation
Empirical methods	method is based on a database of experimental observations
Semi empirical calculations	method is a mixture of theoretical (Schrödinger equation) and experimental observations (empirical) methods
Density functional theory (DFT)	method is also based on the Schrödinger equation, instead of the many-body electronic wavefunction, the electron density around the nucleus is calculated

A **basis set** is a set of functions used to describe the shape of the orbitals in an atom. Usually these functions are atomic orbitals, in that they are centered on atoms. When molecular calculations are performed, it is common to use a linear combination of atomic basis functions. Initially, the atomic orbitals were typically Slater-type orbitals (STO), which corresponded to a set of functions which decayed exponentially with distance from the nuclei. Later, it was realized that these Slater-type orbitals could in turn be approximated as linear combinations of Gaussian-type orbitals (GTO) instead. Today, there are hundreds of basis sets composed of Gaussian-type orbitals, (GTOs). The smallest of these are called minimal basis sets, and they are typically composed of the minimum number of basis functions required to represent all the electrons on each atom. The largest of these can contain literally dozens to hundreds of basis functions on each atom. A basis set can roughly be characterized by two factors: its size (single-, double-, triple-zeta; with or without polarization) and by the level of frozen core approximation. The STO basis sets provided by ADF are SZ, DZ, DZP, TZP, and TZ2P. The increasing numbers point to an increase in size and quality. It is not possible to give a formally correct short general classification for each basis set directory. However, generally speaking we can say that SZ is a single-zeta basis set, DZ is a double zeta basis set, DZP is a double zeta polarized basis, TZP is a core double zeta, valence triple zeta, polarized basis set, and finally TZ2P is a

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[54] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem. 98*, 1994, 11623;

M. A. Watson, N. C. Handy, A. J. Cohen, *J. Chem. Phys.*, 2003, **119**, 6475; R. H. Hertwig, W. Koch, *Chem. Phys. Lett.*, 1997, **268**, 345 core double zeta, valence triple zeta, doubly polarized basis. When *ab initio* or DFT calculations are done the basis set must be specified.

Time-dependent density functional theory (TDDFT)[56] can be viewed as an exact reformulation of time-dependent quantum mechanics, where the fundamental variable is no longer the many-body wave-function but the density. TDDFT provides an efficient, elegant, and formally exact way of describing the dynamics of interacting many-body quantum systems, circumventing the need for solving the full time-dependent Schrödinger equation. Today, TDDFT has become the method of choice for calculating excitation energies of complex molecules, and is becoming increasingly popular for describing optical and spectroscopic properties of a variety of materials such as bulk solids, clusters and nanostructures.

The Amsterdam Density Functional (ADF)[57] and Gaussian[58] are two quantum chemistry software packages using Density Functional Theory (DFT) for electronic structure modeling.

Energies of molecules are obtained from DFT calculations. These include the total bonding energy, enthalpy and free energy. When optimizing the geometry of a molecule, the total bonding energy of the molecule is obtained. An indication of the relative stability of different isomers of the same molecule can be obtained by comparing these energies. However, free energies are needed to get the correct relative stability. Zero point energy correction must also be taken into account. Zero point energy, thermal corrections (vibrational, rotational and translational) and entropy S is obtained from a frequency calculation of the optimized molecule. The thermodynamic parameters enthalpy (H) and Gibbs free energy (G) can be calculated from:

$U = E_{\mathrm{TBE}} + E_{\mathrm{ZPE}} + E_{\mathrm{IE}}$

$H = U + \mathrm{R}T$ (gas phase) or $H = U$ (solution)

$G = H - \mathrm{T}S$

where U is the total energy (electronic internal energy), E_{TBE} is total bonding energy, E_{ZPE} is zero point energy, E_{IE} is internal energy (sum of vibrational, rotational and translational

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[55] A. J. Cohen, N. C. Handy, *Mol. Phys.*, 2001, **99**, 607; M. A. Watson, N. C. Handy, A. J. Cohen, *J. Chem. Phys.*, 2003, **119**, 6475

[56] G van Gisbergen, S. J. A., J. G. Snijders, and E. J. Baerends, *Computer Physics Communications*, 1999, **118**, 119

[57] G. Te Velde, F.M Bickelhaupt, E.J. Baerends, C.F. Guerra, S.J.A. Van Gisbergen, J.G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001** (22) 931-967.

[58] Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

energies), R is the gas constant, T is temperature and *S* is entropy (calculated from the temperature dependent partition function in ADF at 298.15 K).

2.5.2. Structure and Spectroscopy

To our knowledge Spevacek and Spevackova[59] were the first scientists to study dithizone and its tautomers using computational chemistry. They used the Pople method with limited configuration interaction (LCI). From the calculations two high energy bands were observed at A (23 000 cm^{-1}) and B (12 000 cm^{-1}), see Figure 2.16. Since theoretical results did not simulate experimental results they concluded that there is no keto-enol tautomer equilibrium in cyclohexane. Nevertheless, because of the high degree of similarity for the enol form, the symmetric structure for dithizone in cyclohexane solution is proposed.

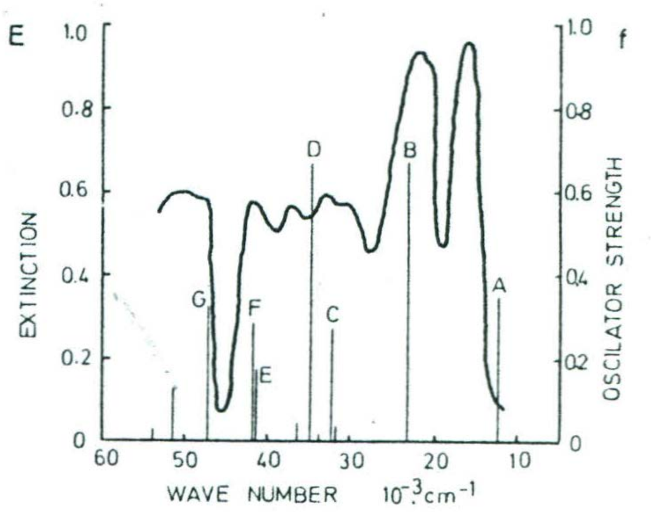

Figure 2.16 Calculated (spikes) and experimental (solid line) spectrum of dithizone (5 x 10^{-5} M) in cyclohexane.[59]

Schonherr *et al.*[60] performed calculations on 3 different isomers (Figure 2.17, top) and its tautomers (Figure 2.17, bottom) of dithizone using the semi empirical methods, MNDO, AM1 and PM3 and using DFT with the functional B3LYP/6-31++G**. They found the ground state energies to differ significantly amongst the tautomers. Energies amongst the different conformers of each tautomer, however, differ only slightly. Planarity is somewhat conserved in the symmetric and enol tautomers, while the keto form deviates significantly from planarity because of electron localisation, see Figure 2.17, top right.

DFT B3LYP/6-31++G** [60] functional calculations show that the symmetric form is lowest in energy. The calculated energy barrier between the enol and symmetric form was found to be less

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[59] V. Spevacek and V. Spevackova, *J. Inorg. Nucl. Chem.*,1974, **34**, 1299

[60] T. Schonherr, V. Schimd, R. Linder and U. Rosellen, *Int. J. Quantum Chem.*, 2002, **86**, 90

than 3 kcal mol^{-1}. Due to the low calculated energy difference between the enol and symmetric form and on the grounds of NMR studies of dithizone in solution it was concluded that there might be an equilibrium between the enol and symmetric tautomers in solution.

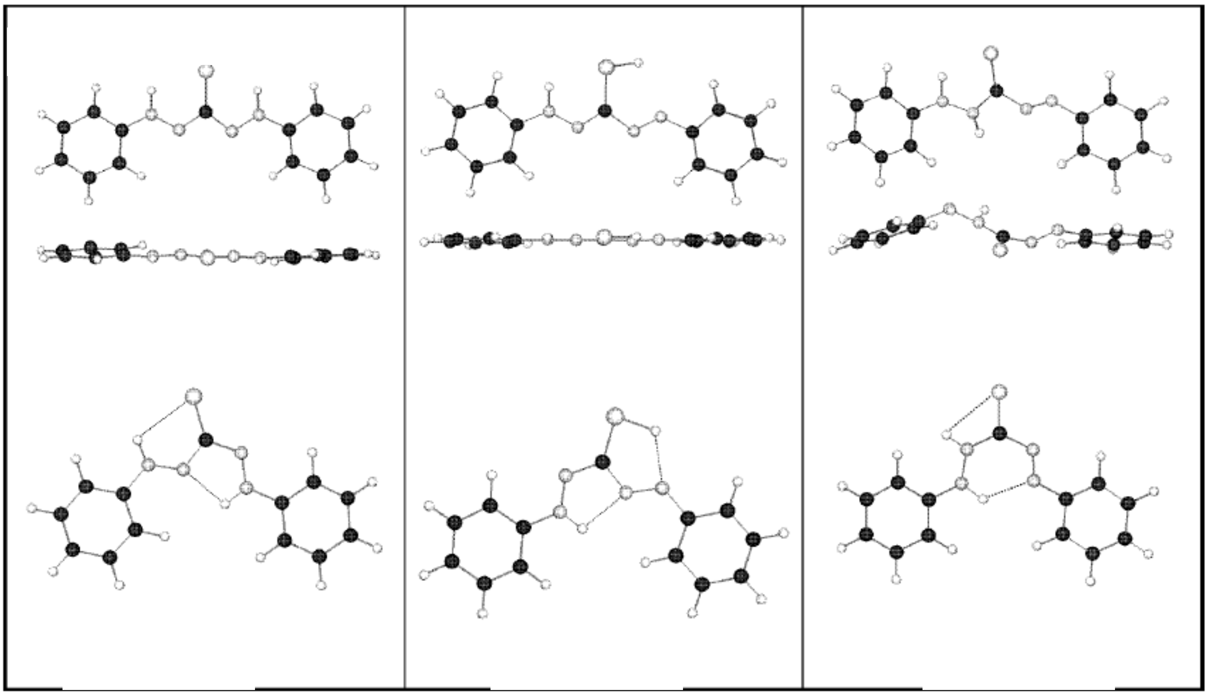

Figure 2.17 Tautomers of dithizone: symmetric (top left), enol (top middle) and keto (top right). Different hydrogen bridges of dithizone HB1 (bottom left), HB2 (bottom middle) and HB3 (bottom right) are indicated. The figure was stylistically changed.[60]

Jian *et al.*[25] performed calculations on dehydrodithizone, using DFT-B3LYP, HF, and MP2 methods and proposed the structure in Figure 2.18. The NPA (natural population analysis) results show both the sulphur atom and the tetrazole ring to carry a *delta*-negative charge. The two phenyl rings on the other hand both carry *delta*-positive charges. They argued that on the basis of this newly proposed structure, the calculated results may explain the experimental observation that it is not just the sulphur atom that gets protonated, but also the nitrogen atoms, because of its relative negative character.

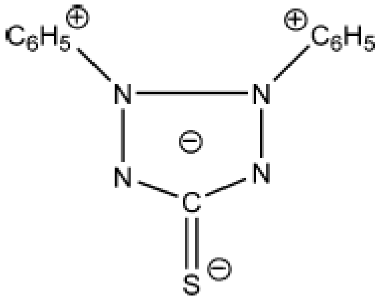

Figure 2.18 A new dehydrodithizone structure proposed by Jian *et al.*[25]

Von Eschwege *et al.*[35] were the first to do an extensive DFT quantum computational study on the photochromism of mercury dithizonate. They calculated the ground state of PhHgHDz (orange in hexane) and the blue excited state (with proposed structures: N2H, S1H and N4H, see next page) when irradiated with light. Calculations were performed with ADF (Amsterdam Density Functional) using DFT with the PW91 exchange and correlation functional and the ZORA/TZP basis set, as well as with Gaussian version 0.3 (G03) with B3LYP functional and the CEP-31G basis set.

Figure 2.19 depicts the bent X-ray crystal structure (a) of the PhHgHDz orange isomer, and (b) the density functional method, ADF/PW91, both giving a bent dithizonato backbone.

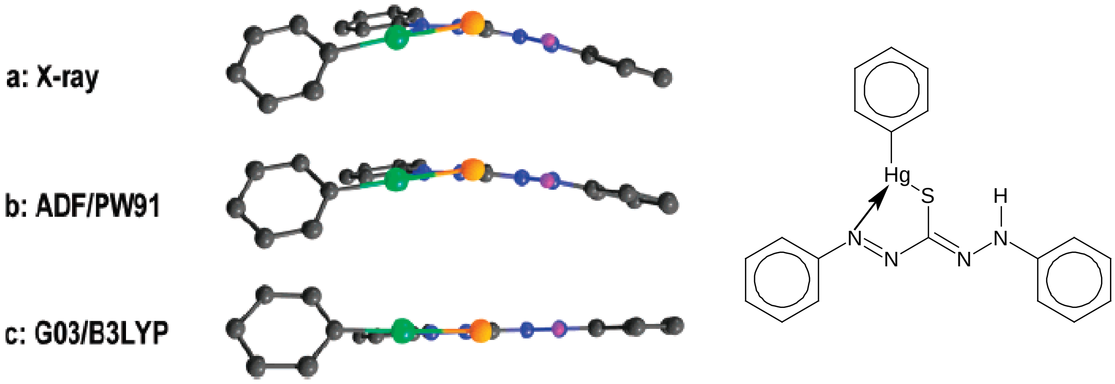

Figure 2.19 Orange isomer of PhHgHDz, comparing the (a) X-ray structure to (b) ADF/PW91, and (c) G03/B3LYP calculated geometries. Phenyl hydrogens are omitted for clarity. (Key: green, Hg; orange, S; blue, N; violet, H; grey, C.)[35]

The Gaussian hybrid functional B3LYP optimized the orange isomer to a planar geometry (c), despite imposing no symmetry limitations on the calculation. ADF/PW91 therefore gives a geometry that resembles the X-ray crystal structure better. The phenyl ring bonded to the Hg atom was found to be nearly perpendicular to the ligand plane, and this is consistent for all three representations. The phenyl rings of the dithizonato ligand are coplanar with the ligand backbone, indicating a high degree of conjugation between the phenyl rings and the adjacent nitrogens in the dithizonato Ph-N-N-C-N-N-Ph backbone. The π-orbitals of the phenyl rings are expected to overlap with adjacent unhybridized nitrogen p-orbitals resulting in the planar character of the dithizonato ligand.

Based on computed results for orange PhHgHDz corresponding closely to experimental results, calculations were extended to include the hypothesized blue form of the mercury dithizonate. Figure 2.20a depicts the classically accepted structure for the blue form of the dithizonate, referred to as N2H. Two other alternatives are S1H (b) and N4H (c). The dithizonato proton is bonded to N4 in tautomer N4H. The difference between N4H and N2H is that the dithizonato proton stays fixed on N4 throughout the proposed reversible photochromic reaction and is not intra- or intermolecularly transferred as previously anticipated.[61,62]

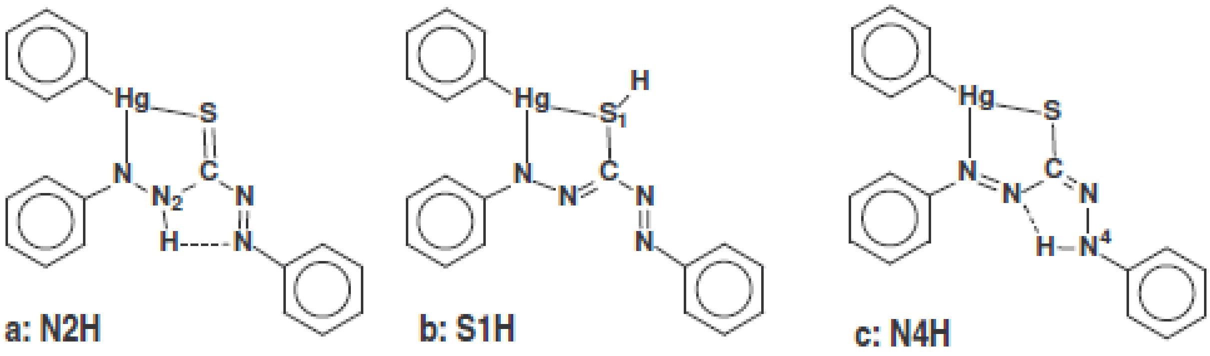

Figure 2.20 Three possible photo-excited tautomers of PhHgHDz (blue form): (a) N2H, (b) S1H and (c) N4H.[35]

The traditional structure, N2H, has the second highest relative energy. N4H has the lowest relative energy, 8.53 kcal mol^{-1} (ADF/PW91) less than the N2H structure. The energy differences between the N4H and N2H geometries are larger (> 8.37 kcal mol^{-1}) than the energy differences between the orange ground state isomer and the photo excited N4H blue isomer (< 5.98 kcal mol^{-1}).

Table 2.6 Energies of the calculated blue structures of PhHgHDz relative to the orange isomer.[35]

	ADF/PW91/ ZORA/TZP/	**ADF/OLYP/ ZORA/TZP/**	**G03/B3LYP/ CEP-31G**
PhHgHDz	**(kcal mol^{-1})**	**(kcal mol^{-1})**	**(kcal mol^{-1})**
Structure N4H	5.74	5.50	5.02
Structure N2H	14.30	14.60	16.30
Structure S1H	26.29	23.90	39.91

Solvent effects were also explored and it was noticed that the effect on both the different isomers as well as PhHgHDz tautomers is minimal. The same degree of delocalization along the entire ligand backbone is observed for the N4H blue isomer, as was previously discussed for the orange isomer.

The UV/visible spectra of the orange and blue forms were theoretically calculated and results compared to experimentally obtained results. Electronic and experimental spectra are

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[61] L. S. Meriwether, E. C. Breitner and C. L. Sloan, *J. Am. Chem. Soc.*, 1965, **87**, 4441

[62] (a) H. Bouas-Laurent and H. Dur, *Pure Appl. Chem.*, 2001, **73**, 639, (b) A. T. Hutton and H. M. N. H. Irving, *J. Chem. Soc., Dalton Trans.*, 1982, 2299

superimposed as shown in Figure 2.21, with calculated spectra depicted as bars. Experimental photo-excited PhHgHDz, middle and right, shows maxima at 275 nm and 604 nm. The shoulder at 450-490 nm of the blue form is a result of partial back conversion to the orange ground state. Theoretical peaks do not match the experimental spectra perfectly, but it shows a similar pattern none the less.

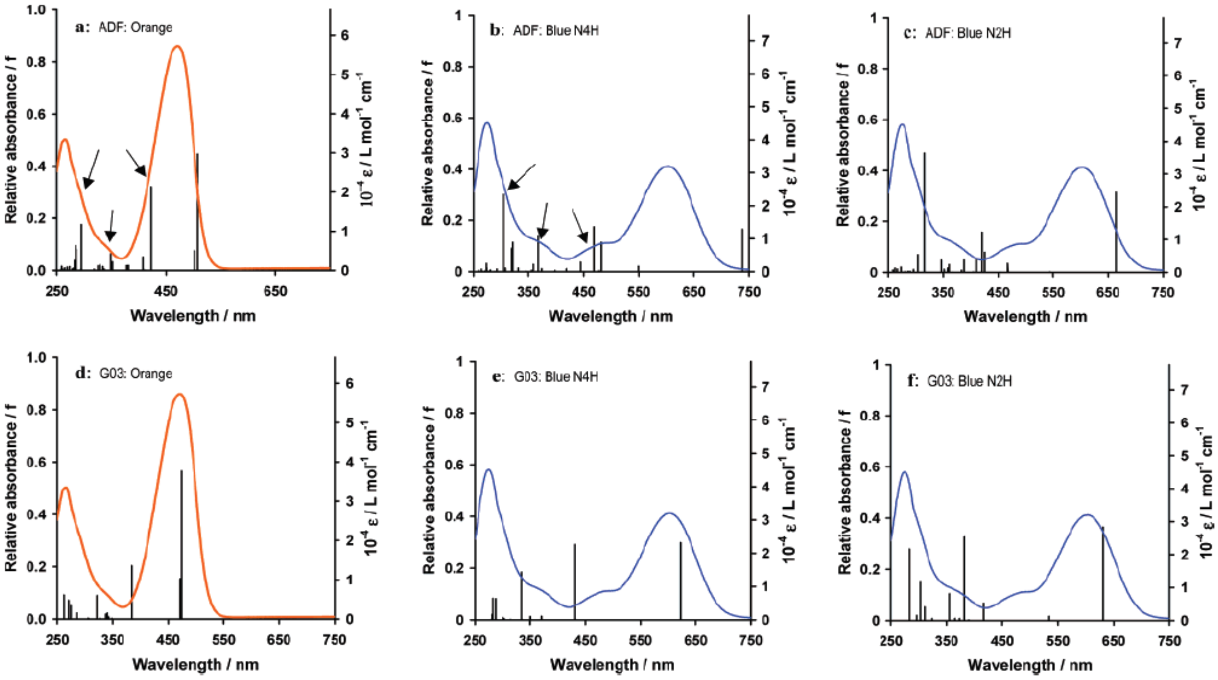

Figure 2.21 ADF (**a**, **b** and **c**) and G03/B3LYP (**d**, **e** and **f**) calculated electronic spectra (bars) and experimental spectra in hexane (lines) of the isomers of PhHgHDz. Left: Orange isomer. Middle: Blue isomer - Structure N4H. Right: Blue isomer - structure N2H. Both the N4H (middle) and N2H (right) oscillators are overlaid with the same experimental blue spectrum. Y-axes give relative absorbance for experimentally determined spectra and f = atomic units for calculated oscillator strengths. Arrows indicate shoulders to the main peaks.[35]

Calculated electronic signals which appear at 472 and 474 nm (G03/B3LYP), and 502 and 508 nm (ADF/PW91) are attributed to mainly the HOMO-1 to LUMO, and HOMO to LUMO transitions respectively. G03/B3LYP gives the best approximation for the experimental maximum at 471 nm see, Figure 2.21d.

2.5.3. Photochromism of Dithizonatophenylmercury(II)

Schwoerer *et al.* investigated the photochromism of dithizonatophenylmercury(II) using computational chemistry and laser studies.[36] The computed change in the S_0 ground state potential energy of PhHgHDz during twisting along the C=N axis of rotation is represented in Figure 2.22. The experimental excitation energy of 2.63 eV, (60.65 kcal mol^{-1}, 471 nm) is, as expected, higher than what is required to overcome the computed barrier of 1.20 eV (27.67 kcal mol^{-1}). The ground state energy of the unstable blue isomer is ca. 0.21 eV (4.84 kcal mol^{-1}) higher than that of the orange resting state. It remains a question why the relatively high energy barrier is so readily overcome in the mere thermal back reaction, the latter being aided by more polar solvents and a change in metal.

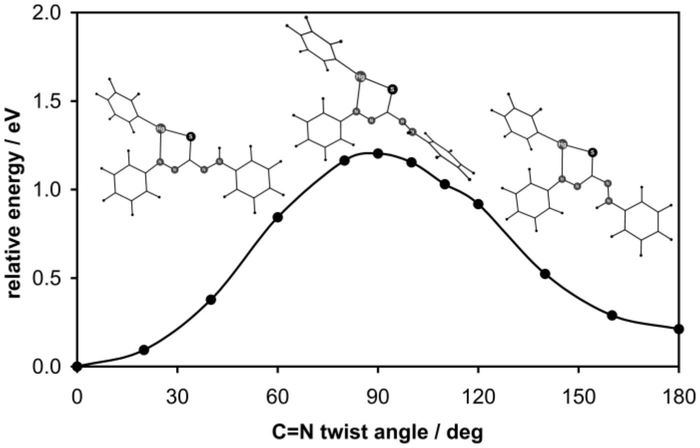

Figure 2.22 ADF calculated potential energy of PhHgHDz along the -C=N- twist coordinate, displaying minima in the planar configurations and a maximum in the orthogonal geometry.[36]

2.6. Electrochemistry

2.6.1. Introduction

Cyclic voltammetry[63,64] (CV) is by far the most effective electroanalytical technique for the study of electroactive species. Because of its versatility and ease of measurements CV's have been extensively used in the fields of electrochemistry, organic chemistry, inorganic chemistry, and biochemistry. CV's are effective in its capability for quickly observing redox behaviour of molecules over a wide potential range. The voltammogram obtained is different from that of a conventional spectrum; it conveys information as a function of an energy scan. Cyclic voltammetry comprises of cycling the potential of the working electrode, which is submerged in an unstirred solution containing the sample, and determining the resulting current.

The potential of the working electrode is controlled with a reference electrode such as a saturated calomel electrode (SCE) or a silver/silverchloride electrode (Ag/AgCl) and referenced against an internal standard such as Fc/Fc^+ as recommended by IUPAC.[65,66] The potential applied across the two electrodes can be considered as an excitation signal.

Figure 2.23 (next page, top) shows the excitation signal that causes the potential to first scan forward from -0.2 V to 0.4 V vs. SCE where the scan direction is reversed, creating a backward scan to the original potential of -0.2 V. The scan rate, as reflected by the slope, is 100 mV s^{-1}.

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[63] P. T. Kissinger and W. R. Heineman, *J. Chem. Ed.*, 1983, **60**, 702

[64] D. H. Evans, K. M. O'Connell, R. A. Peterson and M. J. Kelly, *J. Chem. Ed.*, **1983**, 60, 290

[65] G. Gritzner and J. Kuta, *Pure Appl. Chem.*, 1984, **56**, 461

A second cycle is indicated by the broken line. With modern instruments the switching of potentials and scan rates can easily be varied. By measuring the current at the working electrode during the potential scan a cyclic voltammogram is obtained (Figure 2.23, bottom) as the sample is oxidised and reduced. The current can be considered as the response signal to the potential excitation signal. The voltammogram has a vertical axis (current) vs. a horizontal axis (potential). The potential varies linearly with time and the horizontal axis can then be considered as a time axis.

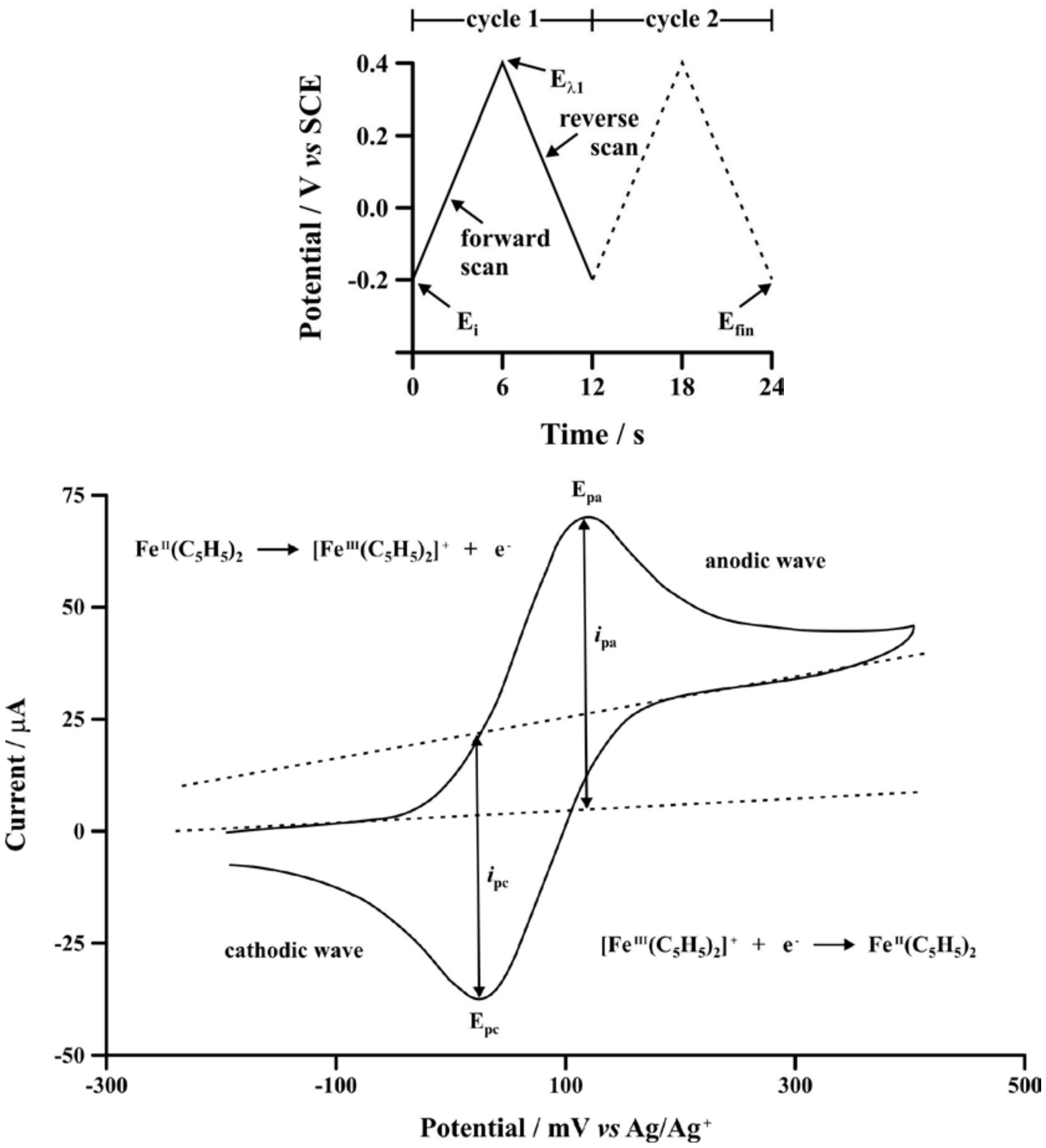

Figure 2.23. Triangular waveform (top) with switching potentials at -0.2 V and 0.4 V vs SCE. Cyclic voltammogram (bottom) of 3.0 mM Fc (ferrocene) measured in 0.1 mM tetrabutylammonium hexafluorophosphate/ acetonitrile at a scan rate of 100 mV.s^{-1} with a glassy carbon working electrode at 25 °C.

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[66] R. R. Gagné, C. A. Koval and G. C. Lisensky, *Inorg. Chem.*, 1980, **19**, 2855

Two important parameters[67] of cyclic voltammetry exists and that is the peak separation and the current ratios. The peak separation, i.e. $\Delta E_p = E_{pa}-E_{pc}$, where E_{pa} and E_{pc} are the peak potentials of the anodic and cathodic scans respectively (see Figure 2.23) associated with an electrochemical process, while the current ratio, i_{pa}/i_{pc}, is associated with a chemical process. The formal reduction potential is defined as $E^0 = (E_{pa}-E_{pc})/2$. A redox couple is said to be electrochemically reversible if the difference in peak potential (ΔE_p) is 59 mV at 25 °C for a one electron transfer process. Because of slow transfer kinetics at the electrode surface, over potentials and high solvent resistance, the peak separation increases to above 59 mV. A redox couple is said to be reversible if i_{pa}/i_{pc} is equal to unity. The redox couple is said to be electrochemically quasi-reversible or irreversible, when both the oxidation and reduction process take place, but there is slow electron exchange between the electrode and the molecule in solution. A peak separation of $90 \text{ mV} \leq \Delta E_p \leq 150 \text{ mV}$ is considered quasi-reversible while, $\Delta E_p > 150$ mV indicates electrochemically irreversible behaviour. A complete chemically irreversible system is where only reduction or oxidation can occur.

2.6.2. Redox Properties of Dithizone

Dithizone[68] can be oxidized and reduced by chemical and electrochemical means. This is possible due to its thiol group and formazan (NH-N=C(SH)-N=N) structure. Scheme 2.2 illustrates the chemical oxidation path of dithizone to the disulphide and dehydrodithizone. Reduction of the completely oxidized form, dehydrodithizone, is accomplished by treatment with dextrose in basic medium. The ionization reaction of dithizone with NaOH, KOH and Na wire to the water soluble derivatives is also shown. The latter may in turn be converted to the NBu_4 salt which is soluble in non-polar solvents.[68]

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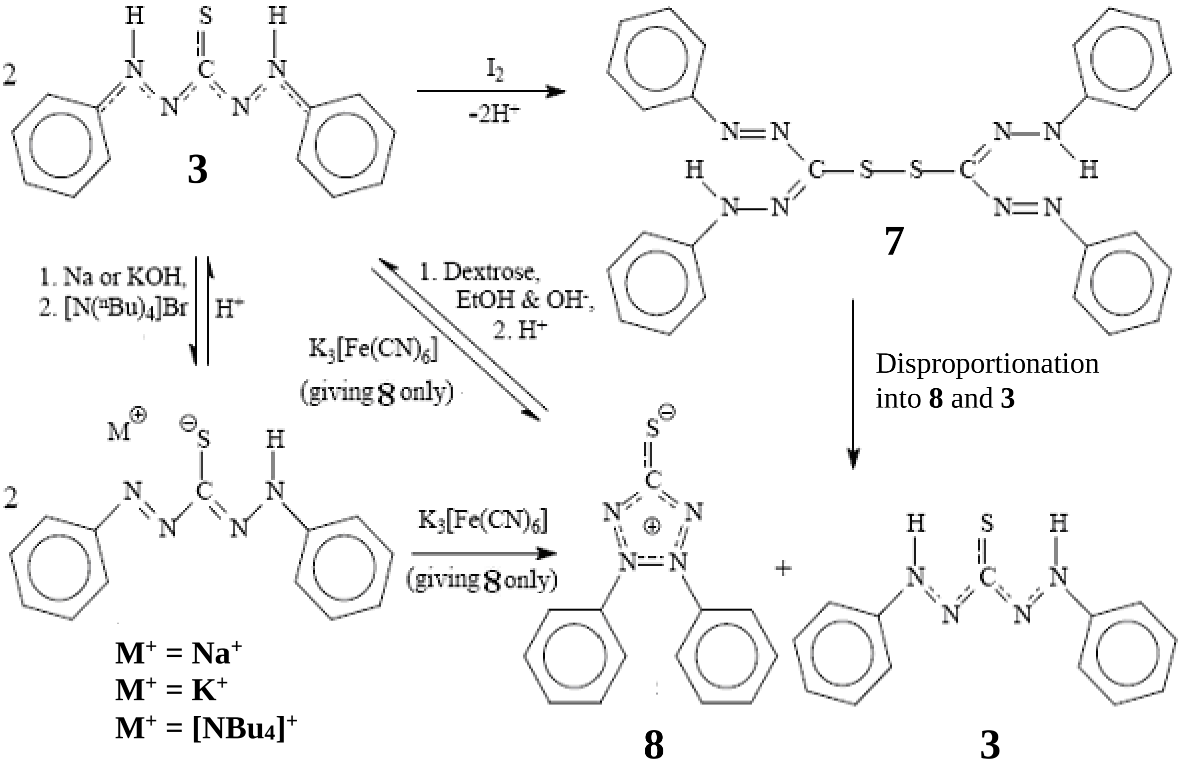
[67] P. A. Christensen and A. Hamnett, *Techniques and Mechanisms in Electrochemistry*, Blackie Academic & Professional, London, 1994, 55, 170

[68] K. G. von Eschwege and J. C. Swarts, *Polyhedron*, 2010, **29**, 1727



Scheme 2.2 Chemical oxidation of dithizone **3**, to dimer **7** and Dz **8**. The reaction of dithizone with NaOH, KOH and sodium wire converts it to water soluble salts, which may again be converted into the NBu_4 salt soluble in non-polar solvents. Figure adapted from reference with stylistic changes.[68]

Tomcsanyi[69] in 1974 was the first to do a limited electrochemical investigation of dithizone. He used a hanging mercury drop electrode (HMDE) in basic media (NaOH, 1M) and a saturated calomel reference electrode at 25 °C, and using two types of electrolytes 1) 0.2 M sodium sulphate-20% ethanol and 2) 1 M ammonia-ammoniumchloride-20% ethanol. Basic medium converts H_2Dz to the HDz^- anion species. He also experimented with a glassy carbon and carbon paste electrodes.

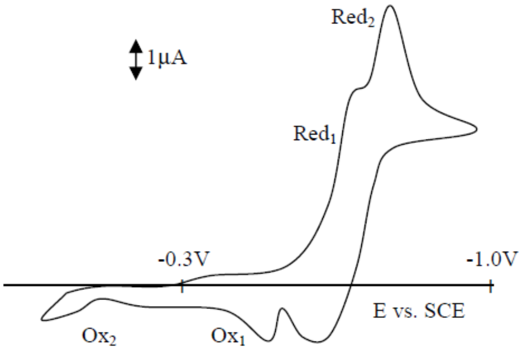


Figure 2.24 Cyclic voltammogram of dehydrodithizone (Dz) solution at a hanging mercury drop electrode (HMDE).[69]

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[69] L. Tomcsanyi, *Anal. Chim, Acta*, 1974, **70**, 1411; 1977, **88**, 371 and 1977, **89**, 409

The disulfide **7**, and dehydrodithizone Dz **8**, compounds were identified during the voltammetric study and the following overall redox scheme was proposed for dithizone:

oxidation $2HDz^{-} \longrightarrow HDz\text{-}HDz + 2e^{-}$

auto-oxidation $HDz\text{-}HDz \longrightarrow Dz + HDz^{-} + H^{+}$

Red1 $HDz^{-} + 2H^{+} + 2e^{-} \longrightarrow H_3Dz^{-}$

Red2 $Dz + H^{+} + 2e^{-} \longrightarrow HDz^{-}$

The above redox processes may be described as follows: two HDz^{-} molecules are oxidised to **7**, with the loss of two electrons and **7** auto-oxidises into **8** and **3** with the loss of a proton. **Red1** is where the HDz^{-} anion is reduced to the trihydrogendithizone anion, with the uptake of two electrons and two protons, and **Red2** is the reduction of dehydrodithizone, Dz to HDz^{-}, with the uptake of two electrons and one proton.

Pemberton and Buck[70,71] in 1982 performed a study on the redox behaviour of HDz^{-} in alkaline NaOH solutions with sample concentrations ranging from 10^{-3} – 10^{-4} M, at Ag, Cu and Au working electrodes, a Ag/AgCl reference electrode, a platinum counter/auxiliary electrode and KCl as electrolyte utilizing the Surface Raman Spectro-electrochemistry technique. For the Cu working electrode (see Figure 2.25, left) the redox behaviour of HDz^{-} is suggested to be governed by the reducible formazan (NH-N) and the oxidizable thiol (C-S) functionality. The redox behaviour of HDz^{-} at Cu was found to be similar to that at Ag.

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[70] J. E. Pemberton and R. P. Buck, *J. Am. Chem. Soc.*, 1982, **104**, 4076

[71] J. E. Pemberton and R. P. Buck, *J. Am. Chem. Soc.*, 1983, **87**, 3336

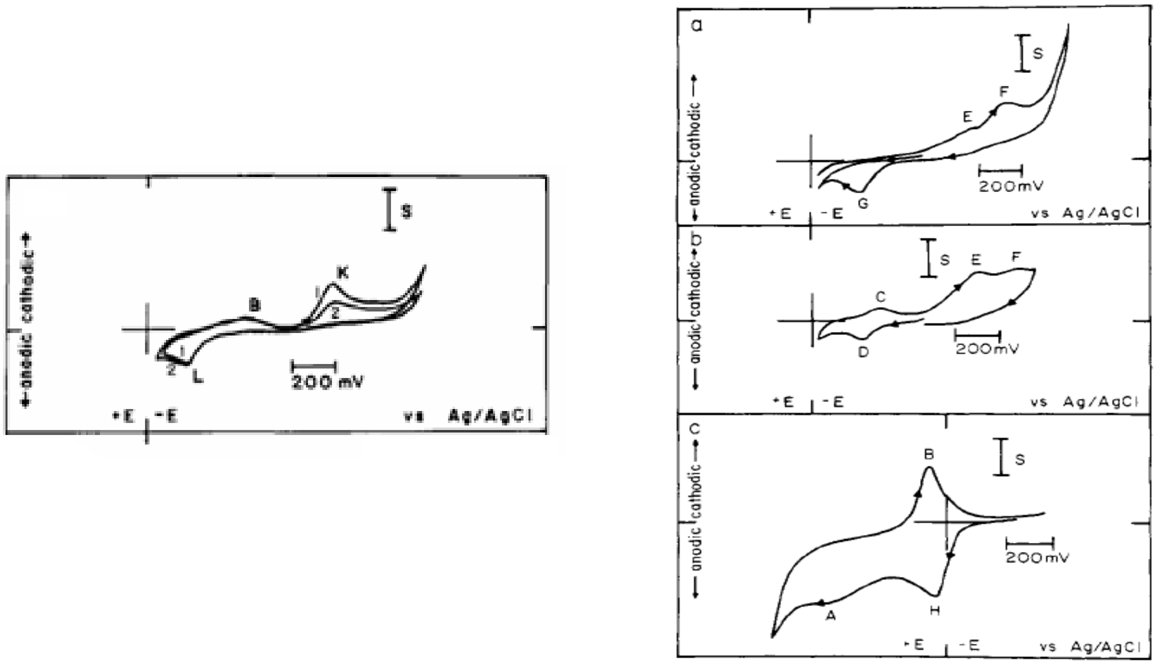


Figure 2.25 Redox behaviour of dithizone at a Cu working electrode (left) and Au working electrode (right). Figure was stylistically changed.[70,71]

The reduction process K in Figure 2.25 (left) is observed at -0.80 V, and represents the reduction of HDz^- at the formazan group with the uptake of two protons and two electrons to form trihydrogendithizone, H_3Dz^-.

reduction $$HDz^- + 2H^+ + 2e^- \longrightarrow H_3Dz^-$$

oxidation $$2HDz^- \longrightarrow HDz\text{-}HDz + 2e^-$$

Process L (Figure 2.25 left) represents the oxidation of HDz^- to the disulphide, HDz-HDz, which occurs at -0.175 V and is coupled to reduction process K.

At the Au working electrode HDz^- is reduced to trihydrogendithizone, H_3Dz^-, as depicted in Figure 2.25a (right). Processes E and F (see Figure 2.25 a and b, right) can be coupled to the reduction of HDz^- in solution and adsorbed HDz^- at the Au working electrode species, respectively. Figure 2.25c (right) depicts the oxidation process H at 0.05 V, where HDz^- is oxidised to the disulphide species.

Mirkalaf *et al.*[13] in 1998, attached dithizone to gold and tin oxide electrodes; and also did a limited exploration on the electrochemical behaviour of dithizone. This was done by synthesising a dicarboxylic acid derivative of dithizone.

$$
\begin{aligned}
&\mathrm{HDz}^{-} \xrightarrow{\text{slow}} \mathrm{HDz}^{0} + \mathrm{e}^{-} \\
&\mathrm{HDz}^{0} + \mathrm{HDz}^{0} \xrightarrow{\text{fast}} \mathrm{HDz-DzH} \\
&\mathrm{HDz-DzH} \xrightarrow{\text{very slow}} \mathrm{Dz} + \mathrm{HDz}^{-} + \mathrm{H}^{+}
\end{aligned}
$$

The first oxidation step is the rate determining step and is slow, where HDz^- is oxidised to neutral HDz. The second step describes the formation of the disulphide (see Figure 2.26). Since the third step is very slow in comparison with voltammetric time response, it was not considered feasible to occur.

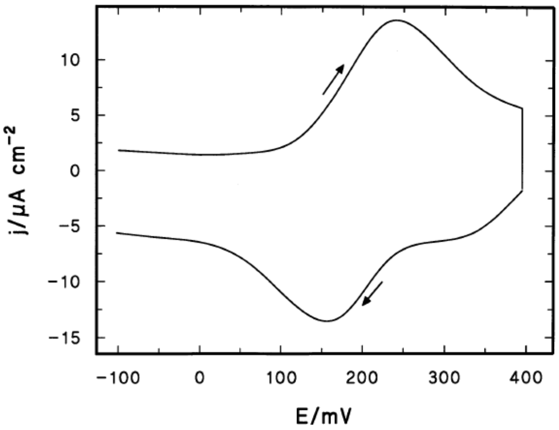


Figure 2.26 CV of dithizone attached to a gold modified electrode in phosphate buffer with a sweep rate of 100 mV s^{-1}.[13]

For the cathodic reduction process the following was proposed:

$$
\begin{aligned}
&\mathrm{HDz-DzH} + \mathrm{e}^{-} + \mathrm{H}^{+} \leftrightarrows \mathrm{H_2Dz} + \mathrm{HDz}^{0} \\
&\mathrm{HDz}^{0} + \mathrm{e}^{-} \rightarrow \mathrm{HDz}^{-}
\end{aligned}
$$

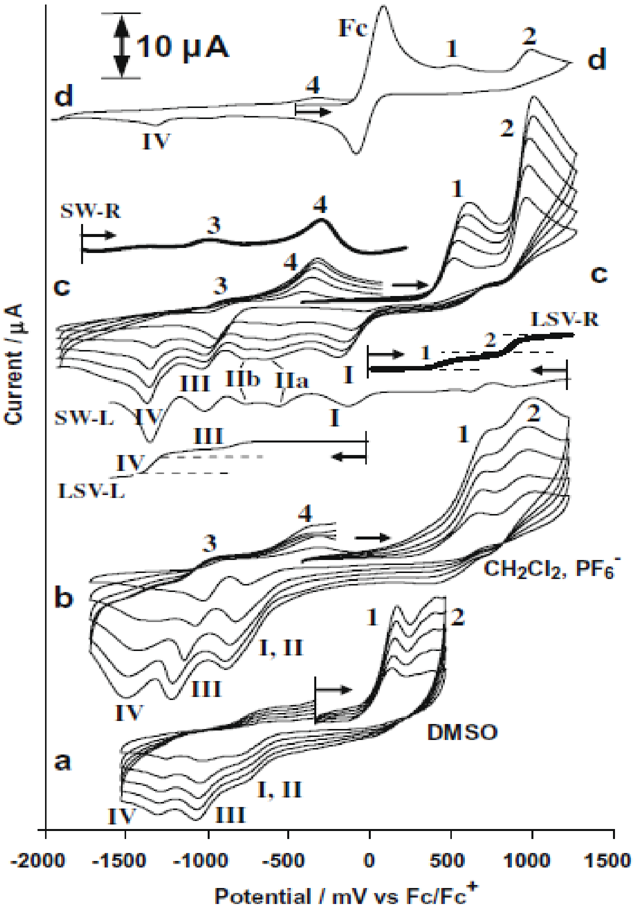
In the above process the cleavage of the disulphide bond with the addition of an electron and proton leads to the formation of dithizone, H_2Dz and neutral HDz. HDz captures an electron and this gives rise to the formation of HDz^-, the overall reaction thus being:

$$
\mathrm{HDz-DzH} + 2\mathrm{e}^{-} + \mathrm{H}^{+} \leftrightarrows \mathrm{H_2Dz} + \mathrm{HDz}^{-}
$$

Von Eschwege and Swarts in 2010,[68] did a complete electrochemistry study of dithizone. Separate cyclic voltammetry experiments were performed in CH_2Cl_2 with $[NBu_4][PF_6]$ as electrolyte, as well as the new non-coordinating electrolyte, $[NBu_4][B(C_6F_5)_4]$. The effect of the solvent was investigated by employing both dimethyl sulfoxide (DMSO) and dichloromethane (DCM, CH_2Cl_2) in a comparative study, with $[NBu_4][PF_6]$ as electrolyte. All scans utilized a standard three electrode system, comprising of a Pt-wire as an Auxiliary electrode, a Ag/AgCl reference electrode and a glassy carbon working electrode, and were referenced against Fc/Fc^+ as internal standard.

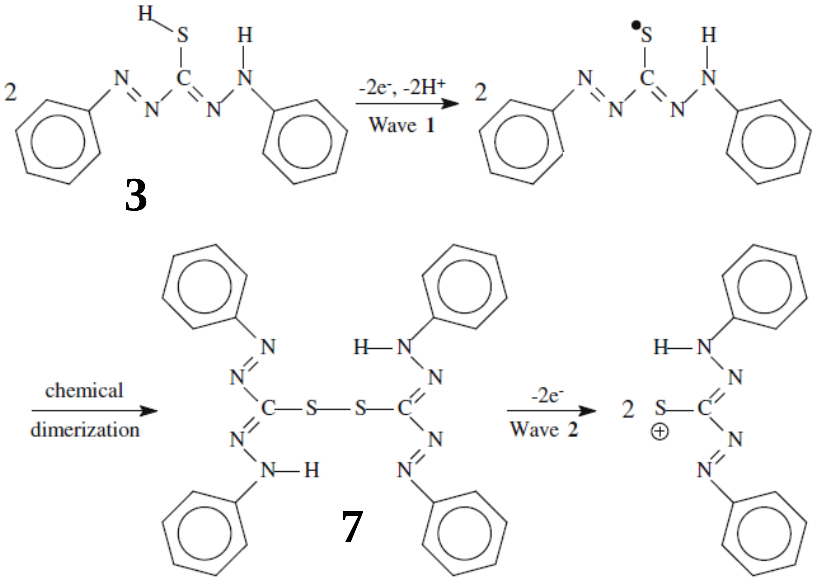
Figure 2.27

Cyclic voltammograms of 1 mmol dm^{-3} solutions of H_2Dz, at scan rates of 100, 200, 300, 400 and 500 mV s^{-1} and 20 °C, at a glassy carbon working electrode, in (a) DMSO/0.1 mol dm^{-3} $[NBu_4][PF_6]$; (b) CH_2Cl_2/0.1 mol dm^{-3} $[NBu_4][PF_6]$; (c) and (d) CH_2Cl_2/0.1mol dm^{-3} $[NBu_4][B(C_6F_5)_4]$, (c) also shows the square wave voltammograms at 100 Hz and linear sweep voltammograms at 2 mV s^{-1}. The trace LSV-L has the special feature of being initiated at potentials where oxidation processes 1 and 2 have not been invoked. As a consequence, peaks I and II were absent. (d) Free ferrocene (Fc) has been added as internal standard. Assigned oxidation (waves 1–4; numbering starts from the resting state of 1) and reduction peaks (waves I–IV) correspond to reactions shown in Scheme 2.3 and Scheme 2.4.**Error! Bookmark not defined.**



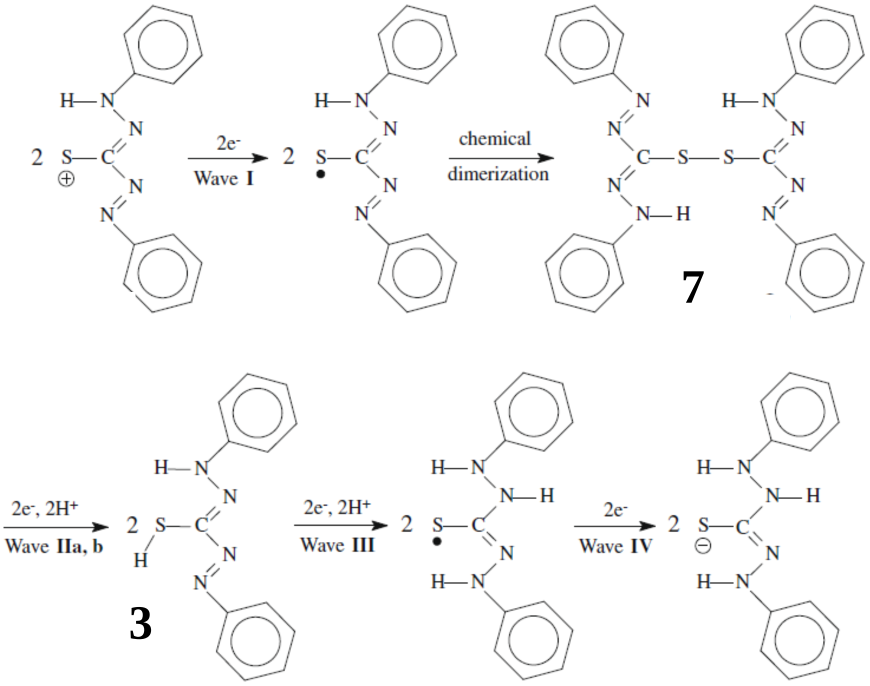
A comparison of the cyclic voltammetry of dithizone between DMSO and DCM in the presence of $[NBu_4][PF_6]$ is given in Figure 2.27 a and b respectively. DMSO, a coordinating polar solvent, was observed to lower the anodic peak potentials 1 & 2, of dithizone. DCM is a non-coordinating solvent and no interaction is expected between the solvent and dithizone. The reduction waves III and IV were shifted to slightly higher potentials (-1058 and -1284 mV) in DMSO compared to DCM (-1083 and -1341 mV). Therefore the result of the DMSO-dithizone interactions was to narrow down the potential range over which oxidation wave 2 and reduction wave IV span, by 610 mV, in comparison with the cyclic voltammogram obtained in DCM.

In the presence of $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte (Figure 2.27 c and d) improved results are evident. $[B(C_6F_5)_4]^-$ anions have a lower charge density compared to $[PF_6]^-$, thus $[B(C_6F_5)_4]^-$ has a lower tendency to form ion pairs with positively charged oxidized species, e.g. $HDz^{+\cdot}{\cdot}[B(C_6F_5)_4]^-$, consequently the cathodic peaks, I, IIa and IIb, could clearly be resolved. Without these peaks an accurate description of the redox cycle of dithizone would have been impossible. Scheme 2.3 was proposed for the oxidation of dithizone. The CV of dithizone reveals two oxidation and reduction electrochemically irreversible one-electron transfer processes. Dithizone has two acidic protons that can be removed chemically or electrochemically. Wave 1 (CV c in Figure 2.27), corresponds to H_2Dz **3** losing one electron and one proton to form the HDz· radical, see Scheme 2.3. The HDz· radical dimerizes to form **7** before the second oxidation takes place. The dimeric species **7** is oxidized at the labile S-S bond. This causes a positive charge on the sulfur during the formation of the HDz^+ cation.



Scheme 2.3 Proposed oxidation of dithizone **3**. CV wave numbers correspond to Figure 2.27. Figure was stylistically changed.

Scheme 2.4 represents the proposed reduction half cycle of dithizone, based on CV c in Figure 2.27. Wave I, at -210 mV corresponds to the HDz cation being reduced to the HDz· radical upon addition of an electron. Waves IIa and IIb (-662 mV and -778 mV respectively, at 500 mV s^{-1}) represents different mixtures of the disulphide and the HDz· radical. Both the disulphide and radical are reduced to **3** in a one-electron transfer process after the uptake of a proton. The trihydrogen radical species, (Figure 2.27, Scheme 2.4, wave III at -1048 mV), is formed upon one-electron reduction of **3**. The trihydrogen ion, H_3Dz^-, forms in the last reduction step represented by wave IV at -1382 mV. H_3Dz^- is the deprotonated form of the four-proton diphenylthiocarbodihydrazide. Waves 3 and 4 represents the re-oxidation of the trihydrogen anion to **3**, in Scheme 2.4.



Scheme 2.4 Proposed reduction of Dithizone. CV wave numbers correspond to Figure 2.27. Figure was stylistically changed.

Apart from the above electrochemical studies done on dithizone Von Eschwege also did electrochemistry on chloro and fluoro substituted dithizone derivatives, see Figure 2.28.[16]. This study was done mainly to quantize imposed oxidation limitations with regard to dithizone. The increase in the first oxidation potential (E_1) of the above series of dithizones lie in the following order (at a scan rate of 300 mV s^{-1}):

$$H_2Dz\ (576\ mV) < (p\text{-}Cl)H_2Dz\ (716\ mV) < (p\text{-}F)H_2Dz\ (717\ mV) < (o\text{-}F)H_2Dz\ (741\ mV)$$

$$< (m\text{-}F)H_2Dz\ (805\ mV)$$

The above order is in good agreement with the pK_a values determined by Al-Salihy and Freiser[72] (see Table 2.7). Both the electrochemical and pK_a studies suggest that the *meta*-substituted derivatives have the best stability against oxidation. The *para*-substituted chloro and fluoro derivatives are comparatively similar in their abilities to stabilise the dithizone ligand, with the *ortho*-Fluoro derivative being only slightly better than the two para substituted derivatives.

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[72] A. R. Al-Salihy and H. Freiser, *Talanta*, 1970, **17**, 182

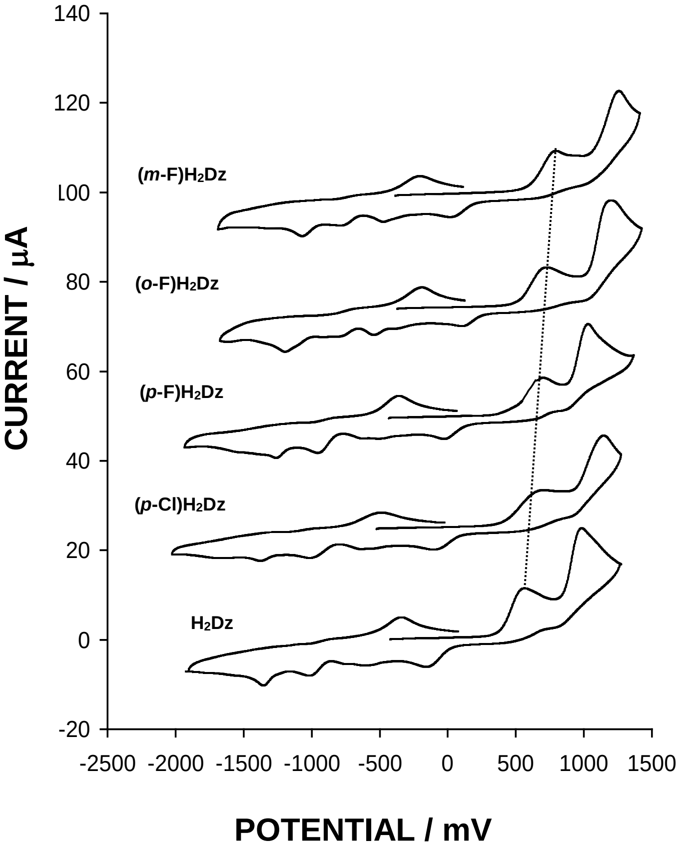


Figure 2.28

Cyclic voltammograms recorded at scan rates of 300 mV s^{-1}, using 0.1 $mol.dm^{-3}$ $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode at 20°C, in CH_2Cl_2, of 1mmol dm^{-3} of H_2Dz, (*p*-Cl)H_2Dz, (*p*-F)H_2Dz, (*o*-F)H_2Dz, and (*m*-F)H_2Dz.

All cyclic voltammograms were referenced against ferrocene as internal standard. The dotted line indicates increase in potential of the first oxidation peak of the series of dithizones.[16]

Halogens are known to be deactivating towards the *ortho*- and *para*-directions in aromatic systems. This might be the reason why the first oxidation potentials (E_1) of the *ortho*- and *para* derivatives lie in close proximity to each other, as seen in Figure 2.28. The *meta*-fluoro dithizone, being the best stabilised against mercaptan oxidation, has an anodic peak potential of 805 mV. This is 229 mV higher than the corresponding H_2Dz value of 576 mV.

Table 2.7 Acid dissociation constants of dithizone and some of its analogues, (R)H_2Dz.[72]

R	**pK_a**
p-CH_3	6.40
o-CH_3	6.23
H	5.77
p-F	4.99
p-Cl	4.63
p-Br	4.40
p-I	4.03
m-CF_3	2.57

3. Results and Discussion

3.1. Introduction

The results and discussion of this research project is presented as follows:

- Synthesis of dithizone derivatives.

  a) Electron donating dithizone ligands with substituents on both phenyl rings include *ortho*, *meta* and *para*-methoxy, and *ortho*, *meta* and *para*-methyl, as well as the *3,4*-dimethyl derivatives. The synthetic procedures are discussed.

  b) Attempts to synthesize dithizones with extended phenyl ring systems are discussed. These compounds have naphthalene, anthracene, pyrene and fluorene instead of benzene rings.

  c) Novel mercury dithizonates of selected dithizone derivatives have been synthesized, characterized and tested for photochromicity.

- Two single crystals, *ortho*-fluorodithizone-disulphide and *ortho*-methoxydehydrodithizone, were grown, and the structures determined by means of X-ray crystallography.

- Comprehensive Amsterdam Density Functional (ADF) quantum computational studies of all the ligand and complex species. Studies include geometry optimizations and energies of isomers and tautomers, Time-Dependent Density Functional Theory (TDDFT) calculations (i.e. theoretically computed UV/visible spectra), as well as molecular orbital presentations.

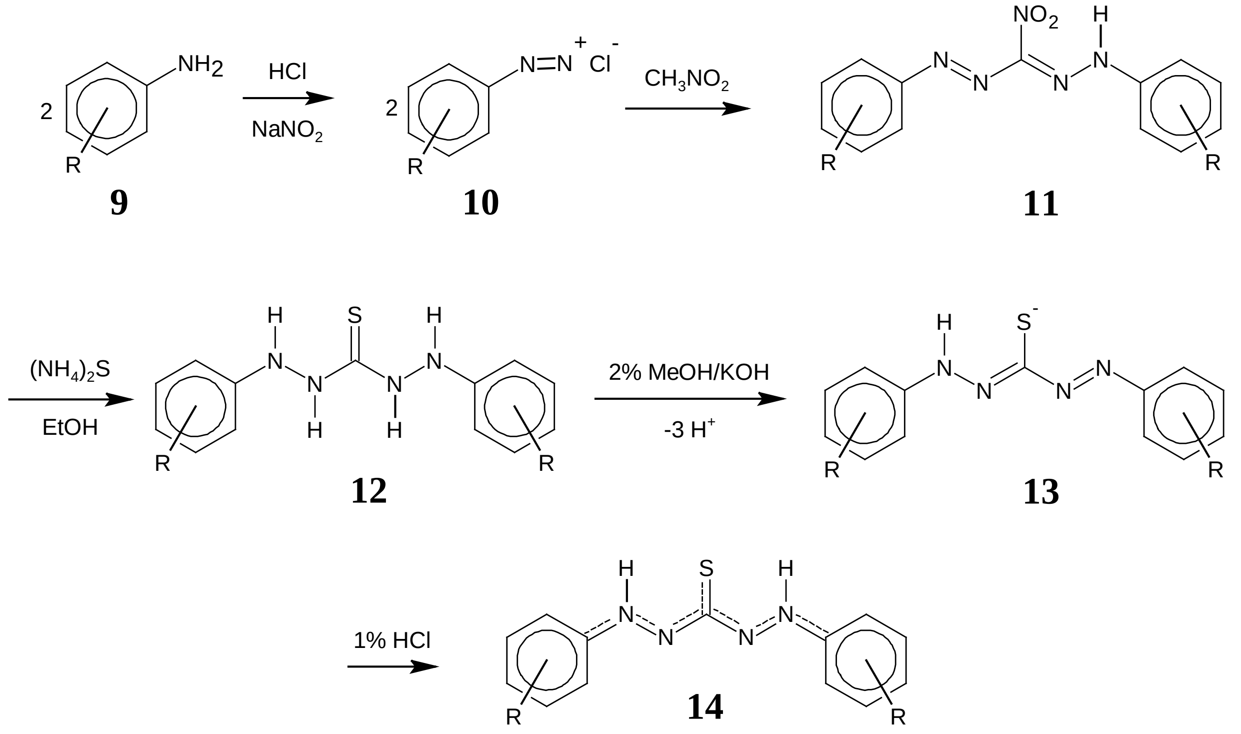
- Electrochemical studies of substituted dithizone derivatives, which also include some electron-withdrawing fluorinated species, and of corresponding mercury dithizonates.

This study was done mainly to explore the borders within which photochromism in altered mercury dithizonates take place, by (a) electronically altering the ligand, and (b) extending the aromatic ring system in the ligand and (c) to explore the borders of oxidation of both the ligands and complexes by making use of electrochemistry.

3.2. Synthesis

3.2.1. Dithizone Derivatives

The synthetic method followed to synthesize all the dithizone derivatives was reported by Pelkis *et al.* [11] and Mirkhalaf *et al.*[13], see Scheme 3.1 (next page). These methods were modified, as discussed on the next page. Ring substituted anilines were dissolved in a mixture of water and hydrochloric acid, cooled to – 10 °C and diazotized with sodium nitrite. This was done to transform the amine group into the azo (N=N) functionality. The diazotized product was added to a mixture of sodium acetate trihydrate and glacial acetic acid, which acts as an acidic buffer (using other than the trihydrated acetate salt gave solubility problems). To this mixture nitromethane was added and a deep red nitroformazan precipitated after about 30 minutes. Water was added and the product filtered off through a Buchner funnel. Nitromethane serves as a coupling agent; two of the azide functionalities couple via one nitromethane molecule, which makes the compound insoluble in water. Washing the nitroformazan with copious amounts of water ensures that the product is washed clean of all salts and water soluble materials. The nitroformazan was then added to a mixture of absolute ethanol and ammonium sulphide and stirred until a colour change was observed, which positively indicates that reduction was successful. Ammonium sulphide (Mirkhalaf) was conveniently used instead of employing the noxious H_2S and NH_3 gas method (Pelkis), to substitute the NO_2 group with S. This solution was then added to a water/ice mixture and filtered through a sintered glass funnel - half filled with silica gel. The latter prevents clogging, which otherwise often occurred. The unstable dirty white thiocarbazide, H_4Dz, was immediately added to a 2 % methanolic potassium hydroxide solution, changing the colour to orange/red - an oxidation process whereby the thiocarbazide was stripped of three of its protons, forming HDz^-. To this mixture was added 1 % hydrochloric acid solution, which protonated HDz^- to form the precipitated black dithizone product, H_2Dz. The acid/base purification step is crucial because on addition of base the product dissolves (orange-red) while insoluble impurities stay undissolved. Addition of the acid separates the then precipitated black product from soluble impurities in solution. Therefore repeating the acid-base process, at least three to five times, yielded pure products, as confirmed by thin layer chromatography.



9 - 14:

a **R = *o*-CH$_3$**
b **R = *m*-CH$_3$**
c **R = *p*-CH$_3$**
d **R = *o*-OCH$_3$**
e **R = *m*-OCH$_3$**
f **R = *p*-OCH$_3$**
g **R = 3,4-(CH$_3$)$_2$**

h **α-napthyl**
i **α-anthracenyl**
j **α-pyrenyl**
k **β-fluorenyl**

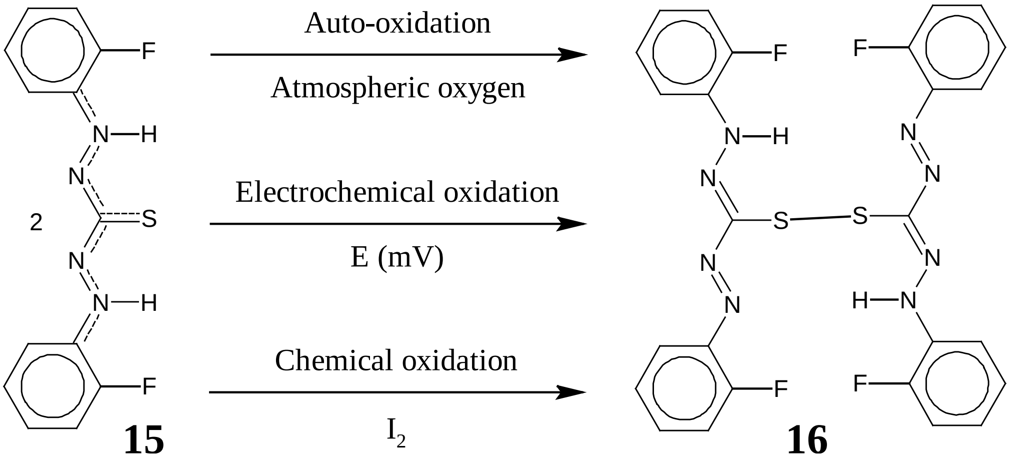
Scheme 3.1 The synthesis of electrondonating (**a** - **g**) and extended ring system (**h** - **k**) dithizones. R is the substituent on the phenyl ring, **a** - **g**. Extended ring systems, **h** - **k**, have the phenyls replaced by the indicated groups.

^{1}H NMR spectra of the dithizones do not reveal much structural information, as it often shows only phenyl ring proton signals, while the imine proton signal is in some cases not observed, most probably due to delocalisation within the dithizone molecule. Signals of aliphatic organic substituents, CH$_3$ and OCH$_3$, that serve as electron donating groups, are however clearly visible between 2 and 4.2 ppm. Being bonded to aromatic phenyl rings causes some degree of deshielding, and thus shifting of the methyl proton signals to slightly higher ppm values, as reported in Chapter 4. All synthesized dithizones are symmetric, i.e. the substituent is on both phenyl rings, with the consequence that ^{1}H NMR signals from both rings overlap perfectly.

By applying reagent ratios as in the method reported by Mirkhalaf *et al.*[13] the deep red nitroformazan product was not obtained. It was therefore decided to change the ratios, with the ideal ratio found to be, 1 aniline: 1.5 sodium nitrite: 5 nitromethane. Using the *ortho*-toluidine derivative as model compound (for the sake of rationalizing), yields of up to 44 % nitroformazan were then obtained. The dithizone yield unfortunately could not be increased as compared to that of Pelkis *et al*, being only about 13 %. The sodium hydroxide method of Hubbard and

Scott[9] (see Par. 2.2.1) was also tried and this method worked fairly well as a very high yield of *ca.* 90 % was obtained for the *ortho*-toluidine nitroformazan. (In this method *alkaline* nitromethane is used instead of only nitromethane).

During the process of recrystalization of fluorinated dithizones (supplied by Dr. von Eschwege) for use in the electrochemical study, the disulphide of *ortho*-fluorodithizone was serendipitously "synthesized". The outcome was surprising as, to our knowledge, no literature reports on the successful preparation of the disulphide via auto-oxidation of a dithizone in solution has been reported. More so even, the product happened to be crystalline, in fact, suitable for single crystal X-ray crystallography. These few orange/red disulfide crystals grew amidst black dithizone precipitate. Solving the structure finally gave conclusive evidence of the disulphide in the redox cycle of dithizone and its derivatives, see Scheme 3.2 and Scheme 3.6.[21]



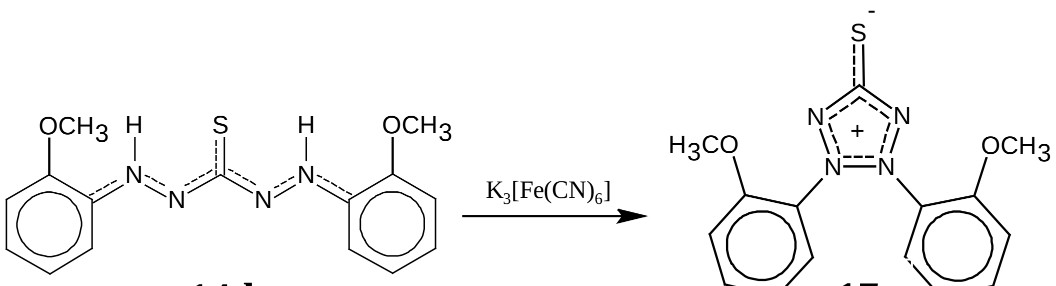
15 **16**

Scheme 3.2 The oxidation of *ortho*-fluorodithizone via three different routes.

Sizeable crystals of the disulphide were obtained by dissolving *ortho*-fluorodithizone in toluene and overlaying it with a few drops of n-hexane. Over a period of 24 hours the characteristic green-coloured dithizone solution converted to dark orange/red, typical for dithizone either losing a proton or being oxidized.

For the reason of obtaining additional characterization data *ortho*-fluorodithizone was also *chemically* oxidised. This was done by dissolving it in dichloromethane, with oxidation taking place during sonication in an iodine-dichloromethane/water mixture.[68] Sonication enhanced dissolution and consequently also the oxidation process of the dithizone. The organic layer (containing some iodine) was removed with a Pasteur pipette and the solvent was removed under reduced pressure at room temperature. For the purpose of leaving unreacted iodine behind, the residue was extracted with diethyl ether and chromatographed through silica gel on a short column packed in a sintered glass funnel. The first red fraction was collected and the solvent removed using a rotary evaporator. Unfortunately no further characterization could be done, as the product proved to be unstable, i.e. very readily re-protonating, converting back to the parent compound, as seen by re-appearing of the green dithizone colour. However, a UV/visible spectrum from the diethyl ether chromatography eluant could be obtained, agreeing perfectly with the spectrum obtained from the crystals of the auto-oxidation process, with λ_{max} = 254, 299 and 405 nm. The *ortho*-fluorodithizone has therefore been oxidised in three ways; auto-oxidation under atmospheric oxygen, chemically by employing iodine, and electrochemically by application of a positive electrical potential (see Scheme 3.2 on previous page and paragraph 3.5).

During continued attempts to further characterize the compounds here synthesized, efforts had been made to grow large enough single crystals for X-ray diffractometry of almost all the products. Failure to do so compelled us to also fully oxidise some of the dithizones, namely to the completely deprotonated tetrazolium salt, dehydrodithizone. Being zwitter-ionic in nature these compounds are known to more readily crystallize in sizeable crystals, as may be noticed from the Cambridge Crystallographic Database. The second crystal structure reported here was grown from the chemical oxidation product of the *ortho*-methoxydithizone derivative. *Ortho*-methoxydehydrodithizone was obtained by stirring a solution of the dithizone in dichloromethane in the presence of the oxidising agent, potassium hexacyanoiron(III), and potassium carbonate which acts as the base, in water.[21] The organic layer was removed, washed with water, and the solvent removed under reduced pressure. The product residue, on recrystallization from a minimum dichloromethane in acetone and water, yielded orange-brown *ortho*-methoxydehydrodithizone crystals, see Scheme 3.3.



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Scheme 3.3 Chemical oxidation of *ortho*-methoxydithizone to *ortho*-methoxydehydrodithizone.

Table 3.1 shows the yields, melting points and UV/visible spectroscopic maxima of all the dithizone derivatives that were synthesized. The highest yield of 35 % obtained for the *meta*-methyldithizone is low compared to that of Pelkis *et al.*[11] who reported a yield of 78 % for the same compound. As earlier mentioned, the procedure followed in the present research project was similar to that reported by Pelkis *et al.*[11] with the main difference being the use of ammonium sulphide (20 % aqueous) instead, as suggested by Mirkhalaf *et al.*[13] replacing the use of noxious gases, NH_3 and H_2S. Mirkhalaf unfortunately did not report yields obtained. It is therefore possible that the use of ammonium sulphide might be the reason for the lower yields.

Table 3.1 Yields of dithizone derivatives (R)H_2Dz, corresponding melting points and UV/visible absorption maxima in DCM. Unsubstituted dithizone (R = H) is added to the table as reference only.

Substituent, R	Nitroformazan yield (%)	Dithizone yield (%)	M.P. (°C)	λ_{max} (nm)
H	-	-	168	450, 608
***o*-OCH_3**	69	23	178 - 179	468, 644
***m*-OCH_3**	76	24	148 - 149	463, 627
***p*-OCH_3**	47	0	-	-
***o*-CH_3**	44	13	162.8	461, 625
***m*-CH_3**	83	35	149 - 151	452, 617
***p*-CH_3**	67	2	98 - 103	456, 623
3,4-$(CH_3)_2$	72	3	129 - 131	461, 629
α-Naphthyl	60	32	176 - 184	370, 680

Although Pelkis *et al.* [11] did manage to synthesize *para*-methoxydithizone, unfortunately this derivative was the only one in the present series for which the synthesis proved to be unsuccessful. Preparing the *para*-methoxynitroformazan, however, was no problem, with a yield of 47 %. Otherwise, nitroformazan yields were in general relatively high, as may be seen in Table 3.1. It is at the second step, i.e. when replacing the nitro group with sulphur, where yields usually dropped dramatically. Further work to try and increase final product yields would certainly be worthwhile investigating in the future.

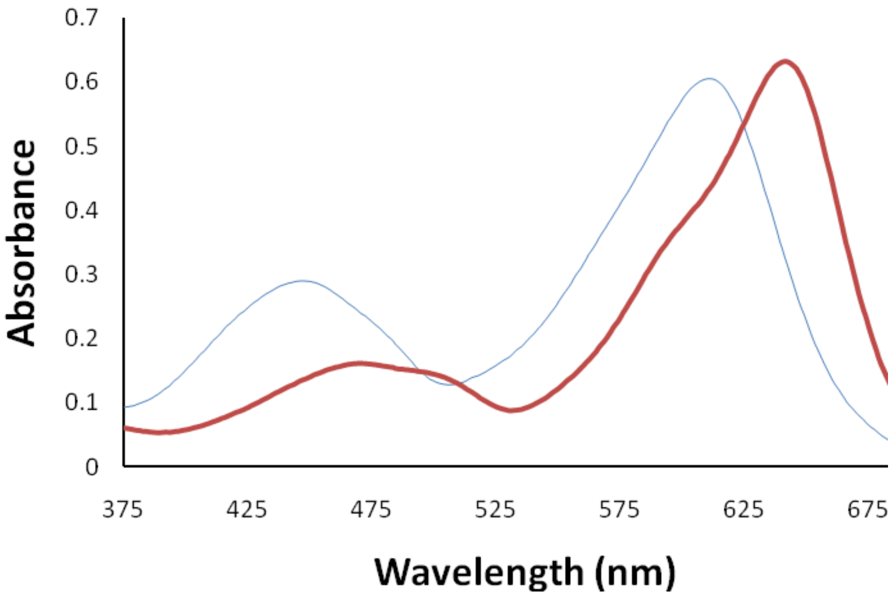


Figure 3.1 UV/visible spectra of dithizone (thin/blue line, C = 1x10^{-5} M, λ_{max} = 450, 608 nm, ε = 61 000 dm^3 mol^{-1} cm^{-1}) and *ortho*-methoxydithizone (thick/red line, C = 3x10^{-5} M, λ_{max} = 468, 644 nm, ε = 21 000 dm^3 mol^{-1} cm^{-1}) in DCM.

Due to the high extinction coefficient (intense colour) of dithizone and its derivatives, UV/visible spectrometry is always a technique of choice, often revealing definite quantitative as well as qualitative information. Figure 3.1, for example, illustrates the red shift occurring due to substitution with an electron-donating *ortho*-methoxy group, as compared to that of unsubstituted dithizone.

Dithizone has maxima at 450 nm and 608 nm while absorbance maxima of *ortho*-methoxy dithizone lie at 468 nm and 644 nm, which represent red shifts of 18 and 36 nm respectively. The entire electron donating series was red-shifted relative to dithizone, with *ortho*-methoxy dithizone being the most pronounced. The order of the red-shifts at lower energy are shown below, with wavelengths at absorbance maxima indicated within brackets, in nanometers.

$$\text{H (608)} < m\text{-CH}_3 \text{ (617)} < p\text{-CH}_3 \text{ (623)} < o\text{-CH}_3 \text{ (625)} < m\text{-OCH}_3 \text{ (627)}$$

$$< 3,4\text{-(CH}_3)_2 \text{ (629)} < o\text{-OCH}_3 \text{ (644)}$$

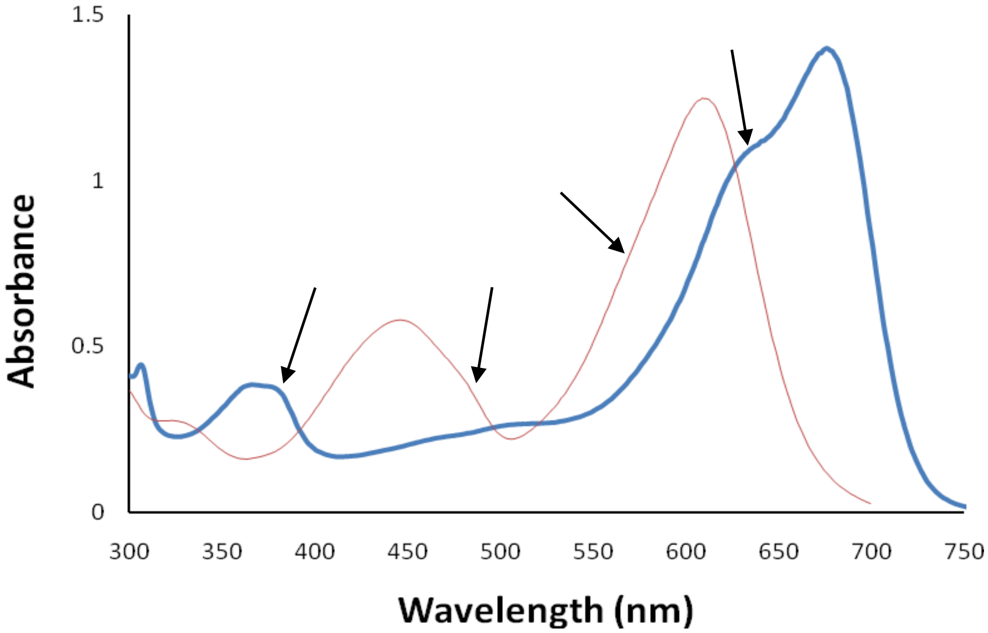
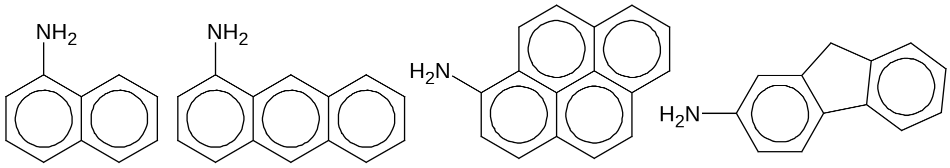


Figure 3.2 UV/visible spectra of dithizone in DCM (thin/pink line, C = 2x10^{-5} M, λ_{max} = 450, 608 nm, ε = 61 000 dm^3 mol^{-1} cm^{-1}) and α-naphthyldithizone in DCM (thick/blue line, C = 5x10^{-5} M, λ_{max} = 370, 680 nm, ε = 28 000 dm^3 mol^{-1} cm^{-1}) in DCM.

The effect of dithizones being substituted with electron donating groups, i.e. electron density being donated into the conjugated dithizone backbone, is that HOMO → LUMO excitation takes place more readily, thus the lowering in absorbance energy, i.e. at longer wavelengths. These derivatives nevertheless all still have a dark colour, almost brown to black as a solid, dissolving in dichloromethane to give the characteristic green colour that is synonymous with these compounds. All UV/visible spectra appear to have two shoulders on the inside of the two main peaks as illustrated in Figure 3.2.

To further extend the study of dithizone chemistry it was decided to synthesize derivatives with starting materials, α-naphthylamine (**9h**), α-aminoanthracene (**9i**), α-aminopyrene (**9j**) and β-aminofluorene (**9k**), i.e. the dithizone benzene rings being replaced by different extended aromatic ring systems, see Figure 3.3. During previous computational chemistry studies[16] it was noted that the HOMO and LUMO orbitals of dithizone stretch along the entire length of the molecule, including the phenyl rings. This raised the question of whether the same would be observed for extended aromatic systems, and what the possible effect there-of might be on the photochromic reaction.



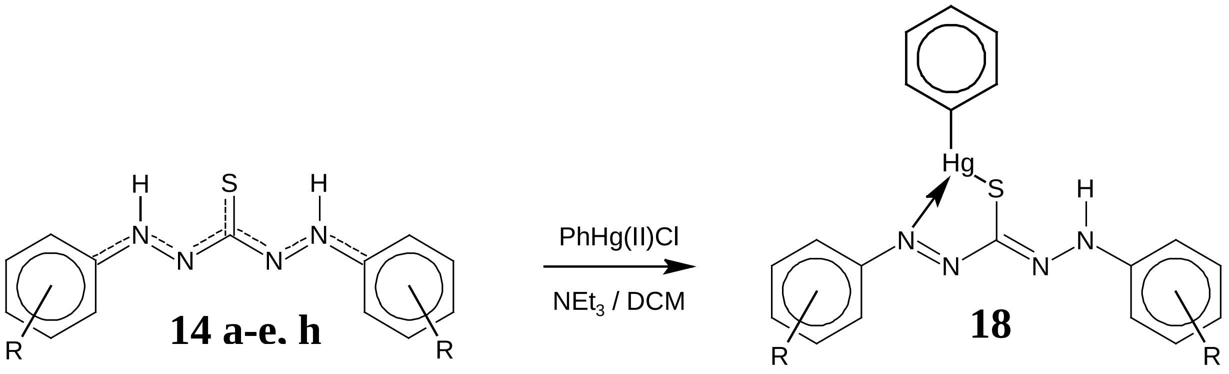
9h **9i** **9j** **9k**

Figure 3.3 Amines used in the synthesis of the extended dithizones.

Although **14h** (Scheme 3.1) had the typical dark green colour, a pure product of **14h** could not be obtained by making use of the alternating acid-base purification method. By passing **14h** through a silica gel column (70% DCM: 30% n-Hexane), however, yielded a purple fraction that has the characteristic two absorption maxima as in the case of dithizone. The UV/visible spectrum of **14h** is nevertheless quite different from the phenyl ring dithizones, see Figure 3.2. Whereas the phenyl ring dithizones have a green colour in solution, the colour of the naphthyl compound **14h** is blue when dissolved in dichloromethane. **14h** on the other hand also has two broad peaks, being spaced much further apart. The major peak (680 nm) is red-shifted and the minor peak (370 nm) blue-shifted relative to dithizone, see Figure 3.2. This result is consistent with a single literature report concerning **14h**.[73] (α-anthracenyl)H_2Dz **14i**, (α-pyrenyl)H_2Dz **14j**, and (β-fluorenyl)H_2Dz **14k**, unfortunately yielded many side products, even after passing though a silica column, which made it very difficult to isolate, especially since some of the by-products appeared either too close or on top of each other on the column. Although reactions did proceed in line with the normal dithizone synthetic procedure, the difficulty to isolate pure final products caused further attempts in this endeavour to be abandoned. Good nitroformazan yields were nevertheless obtained. The possibility for more synthetic attempts in the future is certainly not excluded.

3.2.2. Metal Dithizonates

In order to complex the dithizone ligands to mercury, triethylamine[35] was added to a dithizone dichloromethane solution, together with a small excess of phenylmercury(II) chloride. Triethylamine serves as base, to deprotonate H_2Dz to form the more reactive HDz^- anion. A colour change from green to orange/red was observed during complexation for all the ligand derivatives, while **14h** goes from blue to orange/red. Reaction mixtures were stirred for 15 minutes, with reactions visibly taking place within seconds. After the solvent was removed the product was extracted with DCM, leaving any unreacted mercury and amine chloride salts behind, see Scheme 3.4. Ethanol was added to the DCM solution, for the purpose of recrystallization. The final filtered product was washed with a water/ethanol mixture.



18 **a** **R = *o*-CH_3** **d** **R = *o*-OCH_3**
b **R = *m*-CH_3** **e** **R = *m*-OCH_3**
c **R = *p*-CH_3** **h** **α-Napthyl**

Scheme 3.4 General complexation reaction for all dithizone derivatives.

All the mercury dithizonates synthesized in this study were visibly observed to be photochromic, except **18a** and **18h**. The complexes that are photochromic has the usual colour change in solution of DCM from orange to blue when irradiated with visible light, as observed for PhHgHDz. The exception was found in the photochromic reaction of **18d**, where a dilute DCM solution underwent a colour change from pink to purple. To our knowledge this is the first significant colour deviation in photochromic mercury complexes of this kind, see Figure 3.4. The purple photo-excited state was generated by irradiating a dilute pink dichloromethane solution (3×10^{-5} M) of the photochromic compound **18d** with a 400 W mercury-halide lamp, which radiates mainly in the visible region of the electromagnetic spectrum. The photochromic reaction, however, appeared much more efficient when the complex was exposed to direct sunlight.

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[73] K. S. Math, Q. Fernando and H. Freiser, *J. Anal. Chem.*, 1964, **36**, 1762

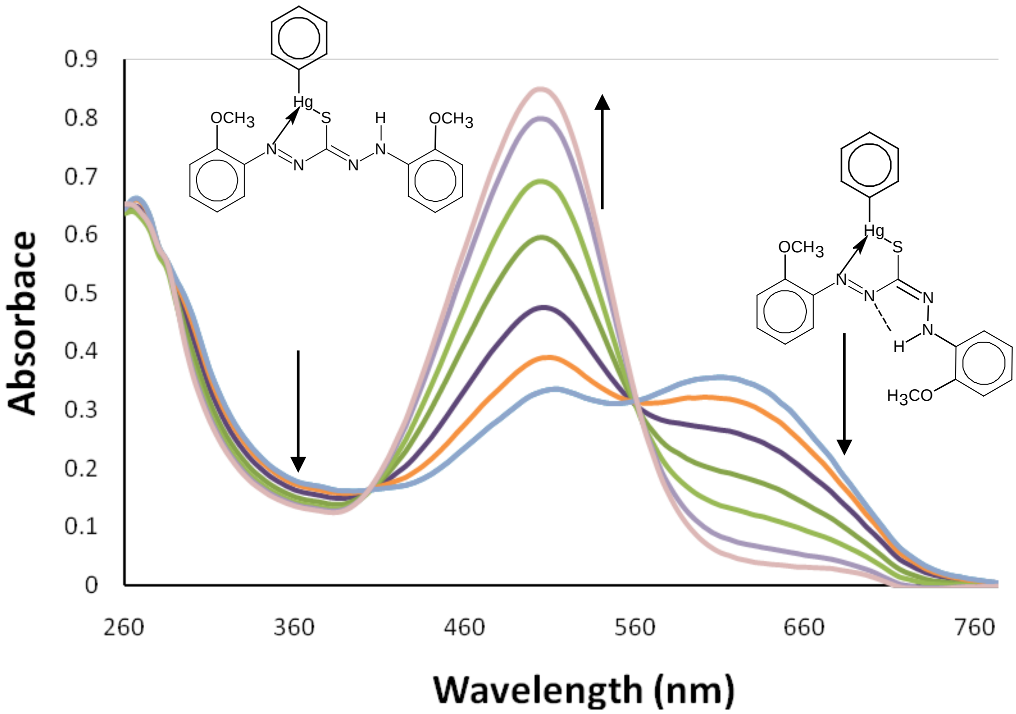


Figure 3.4 The spontaneous radiationless thermal back-reaction of *ortho*-methoxydithizonatophenylmercury(II) in dichloromethane. The purple photo-excited state (λ_{max} = 615 nm, ε = 11 892 dm^3 mol^{-1} cm^{-1}) reverts back to the pink ground state (λ_{max} = 505 nm, ε = 28 346 dm^3 mol^{-1} cm^{-1}), with isosbestic points at 405 nm and 560 nm. Spectra were recorded every 5 seconds for 60 seconds. The proposed ground (left) and photo excited state (right) structures above are equivalent to the PhHgHDz structures.

Following the spontaneous radiationless thermal back-reaction of *ortho*-methoxydithizonatophenylmercury(II) from purple to pink, two isosbestic points are seen at 405 nm and 560 nm, which is an indication of the absence of transition states or secondary processes during the back reaction.

Table 3.2 shows the yields, melting points and UV/visible spectroscopic absorption maxima of all the complexes synthesized. All the photochromic complexes had an approximate return time of 1 minute. The complexation reaction of 3,4-dimethyldithizonatophenylmercury(II) did not yield enough product for characterization purposes and is therefore not included here. Unfortunately no photochromism was observed for the extended naphthyl complex. It must however be pointed out that photochromism being not visible does not imply the absence of it. The possibility still remains that the back-reaction is simply so fast that it is invisible to the eye, as recently observed for PhHgHDz by Von Eschwege and Schwoerer during ultra-fast (femtosecond) laser studies in methanol.[36] During this investigation photochromicity of PhHgHDz in methanol (very polar solvent) was positively proved for the first time.

Table 3.2 Mercury dithizonate yields, melting points and UV/visible absorption maxima of the ground and photo-excited states, in DCM. Values are compared against the unsubstituted complex, PhHg(**R**)HDz with R = H.

R	**Yield (%)**	**M.P. (°C)**	**λ_{max} (nm) Ground state**	**λ_{max} (nm) Excited state**	**Colour change**
H	90	166	471	583	Orange to blue
***o*-OCH_3**	54	212 - 213	505	615	Pink to purple
***m*-OCH_3**	60	137 - 139	485	605	Orange to blue
***o*-CH_3**	68	120 - 122	467	-	Orange, No colour change
***m*-CH_3**	61	170 - 173	480	595	Orange to blue
***p*-CH_3**	94	146 - 148	486	604	Orange to blue
α-Naphthyl	81	229 - 233	509	-	Orange, No colour change

NMR spectra (see Chapter 4) of dithizone and its derivatives and complexes typically reveal very little structural information, as apart from the proton on the nitrogen back bone, hydrogens are otherwise found only on the phenyl rings. The imine protons are highly deshielded; for almost all the free ligands these signals lie at *ca* 13 ppm, except for the naphthyl derivative, which, due to its extended aromaticity, is even more deshielded, namely to 14.13 ppm. The same tendency is observed for the corresponding mercury complexes, where the imine proton signals lie round about 9.5 ppm, while for the naphthyl compound it is at 10 ppm. The dramatic shift of almost 4 ppm in going from the free ligand to the complex is indicative of the large anisotropic effect that is operative in the former.

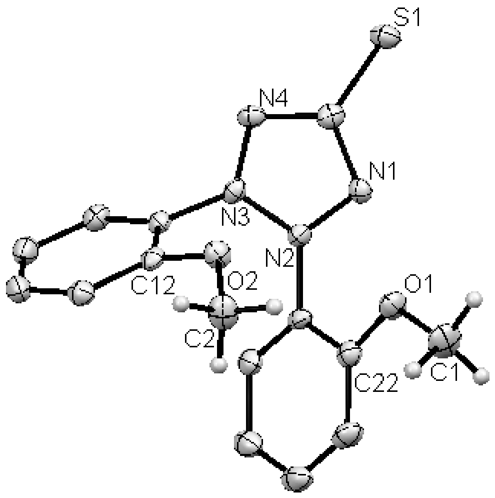
3.3. X-Ray Crystallography

3.3.1. Introduction

Except for two of the oxidation products of dithizone, *ortho*-methoxydehydrodithizone and *ortho*-fluorodithizone-disulphide, all other attempts to grow crystals of intermediates and products synthesized during this study, suitable for X-ray crystallography, were unsuccessful.

Dehydrodithizone is known for readily growing crystals [CCD: DHDTIZ10,[43] DHDTIZ11,[74] DHDTIZ12[25] and DHDTIZ13[75]], which may be explained in terms of the zwitter-ionic nature of this molecule which lends it ideally towards ionic type packing in the crystal lattice. Dithizone itself often only give very fine needles that are too thin for X-ray data-collections. However, the surprise came when, during recrystallization of *ortho*-fluorodithizone during preparation of this compound for use in electrochemical studies, the first known crystal of a dithizone-disulphide was found in the mother liquor. Solving this unique structure provides final evidence not only in support of the structures and redox schemes discussed in the present study, but also supports the long standing hypothesized oxidation mechanism as proposed by Kiwan and Irving[21] (see also the literature survey, p. 9, and the section on electrochemistry, section 2.6).

3.3.2. *Ortho*-Methoxydehydrodithizone



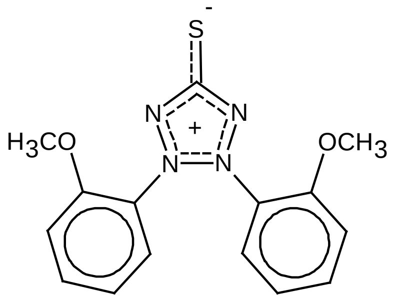


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Figure 3.5 Crystal structure of *ortho*-methoxydehydrodithizone (left). Phenyl hydrogen atoms are omitted.

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[74] T.V. Koksharova, *Zh. Strukt. Khim. (Russ.) (J. Struct. Chem.),* 2004, **45**, 361

[75] H. Slaouti, S. Boutamine, M. Meklati, F. Balegroune, L. Toupet, N. Lokbani, O. Vittori, *Synth. React. Inorg., Met. -Org., Nano-Met. Chem.* 2006, **36**, 633

Figure 3.5 shows the crystal structure and atom labeling applied to *ortho*-methoxydehydrodithizone, as also related to Tables 3.4 (bond lengths), 3.5 (bond angles) and 3.6 (torsion angles). Crystallographic refinement data is summarized in Table 3.3. The crystal structure is in accordance with what is expected for the dehydrodithizone molecule, with the tetrazole forming a 5-membered ring and the phenyl rings twisted at *ca* 30° angles relative to the 5-membered tetrazole plane. The methoxy groups are *cis*-oriented relative to the tetrazole backbone.

Table 3.3 Crystal and structure refinement data.

Empirical formula	$C_{15}H_{14}N_4O_2S\cdot0.4C_3H_6O\cdot0.1CH_2Cl_2$
Formula weight	346.09
Temperature	100 (2) K
Wavelength	0.71073 Å
Crystal system	Orthorhombic
Space group	*Pbcn*
Unit cell dimensions	a = 19.5069 (13) Å, b = 12.5245 (7) Å, c = 13.2780 (10) Å
	$\alpha = \beta = \gamma = 90.0°$
Volume	3244.0 (4) $Å^3$
Z	8
Density	1.417 Mg m^{-3}
Absorption coefficient	0.25 mm^{-1}
F(000)	1448
Crystal size	0.33 × 0.12 × 0.11 mm
Theta range for data collection	2.1° to 28.3°
Index ranges	$h = -15\rightarrow26$, $k = -12\rightarrow16$, $l = -13\rightarrow17$
Reflections collected	10890
Independent reflections	4013
Absorption correction	multi-scan
$R[F^2 > 2\sigma(F^2)]$	0.059
Data / restraints / parameters	4013 / 2 / 238
Largest diff. peak and hole	0.84 e.$Å^{-3}$ and −0.57 e.$Å^{-3}$

Due to the large degree of conjugation that occurs in dithizone and its derivatives, bond lengths along the backbone often deviates significantly from what is generally observed for single and double bond distances. The same is true for dehydrodithizone. N-N single and N=N double bonds are typically 1.45 Å and 1.25 Å respectively, C-N and C=N bonds are 1.47 Å and 1.29 Å, and C-S and C=S bonds are 1.82 Å and 1.60 Å respectively.[39,40,41] Table 3.4 lists the most important bond distances of the electron donating methoxy-substituted dehydrodithizone, in comparison to related bond distances found in the electron-withdrawing fluoro-substituted derivative[76] as well as the unsubstituted compound.[43] In general, bond lengths of all three compounds are rather similar, with the largest difference seen for the N2-N3 bond in (*o*-OCH_3)Dz being 0.026 Å longer than in (*m*-F)Dz. Whereas the bond distances in (*o*-OCH_3)Dz and Dz are most similar, it is seen that the effect of the electron-withdrawing substituent in (*m*-F)Dz is to increase/strengthen the double bond character between the nitrogens that connect the two phenyl rings, N2 and N3, as well as between the tetrazole carbon and the two adjacent nitrogens, N1 and N4.

All three compounds show, as expected, a high degree of delocalization in the tetrazolium rings, with bond lengths that are longer than single, and shorter than double bonds. Delocalization also includes the C-S bond, which is about 1.69 Å, compared to a C-S single bond length of 1.80 Å, as is seen in the disulphide structure discussed in the next section.

Kushi and Fernando[43] reported dehydrodithizone to have a delocalized positive charge in the tetrazole ring and a negative charge on sulphur (see Figure 3.5, right). They also illustrated how, because of the zwitter-ionic nature of dehydrodithizone in the crystal lattice, the sulphur atoms are sandwiched between the planes of two adjacent tetrazole rings which are at a distance of 3.482 Å on either side of the sulfur atom.

Table 3.4 Selected bond lengths (Å) of (*o*-OCH_3)Dz, (*m*-F)Dz and Dz. Numbering relates to Figure 3.5.

Bonds	**(*o*-OCH_3)Dz**	**(*m*-F)Dz**	**Dz**
S1-C3	1.690 (3)	1.687 (3)	1.691 (2)
C3-N1	1.371 (3)	1.361 (2)	1.368 (2)
C3-N4	1.369 (3)	1.361 (2)	1.368 (2)
N1-N2	1.313 (3)	1.318 (2)	1.318 (2)
N3-N4	1.321 (3)	1.318 (2)	1.318 (2)
N2-N3	1.339 (3)	1.313 (3)	1.334 (2)
N2-C21	1.428 (3)	1.434 (2)	1.443 (2)
N3-C11	1.434 (4)	1.434 (2)	1.443 (2)
O1-C22	1.362 (3)		
O2-C12	1.353 (3)		
O1-C1	1.440 (3)		
O2-C2	1.436 (3)		

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[76] K. G. von Eschwege and A. Muller, *Acta Cryst.* 2009, **E65**, o1864

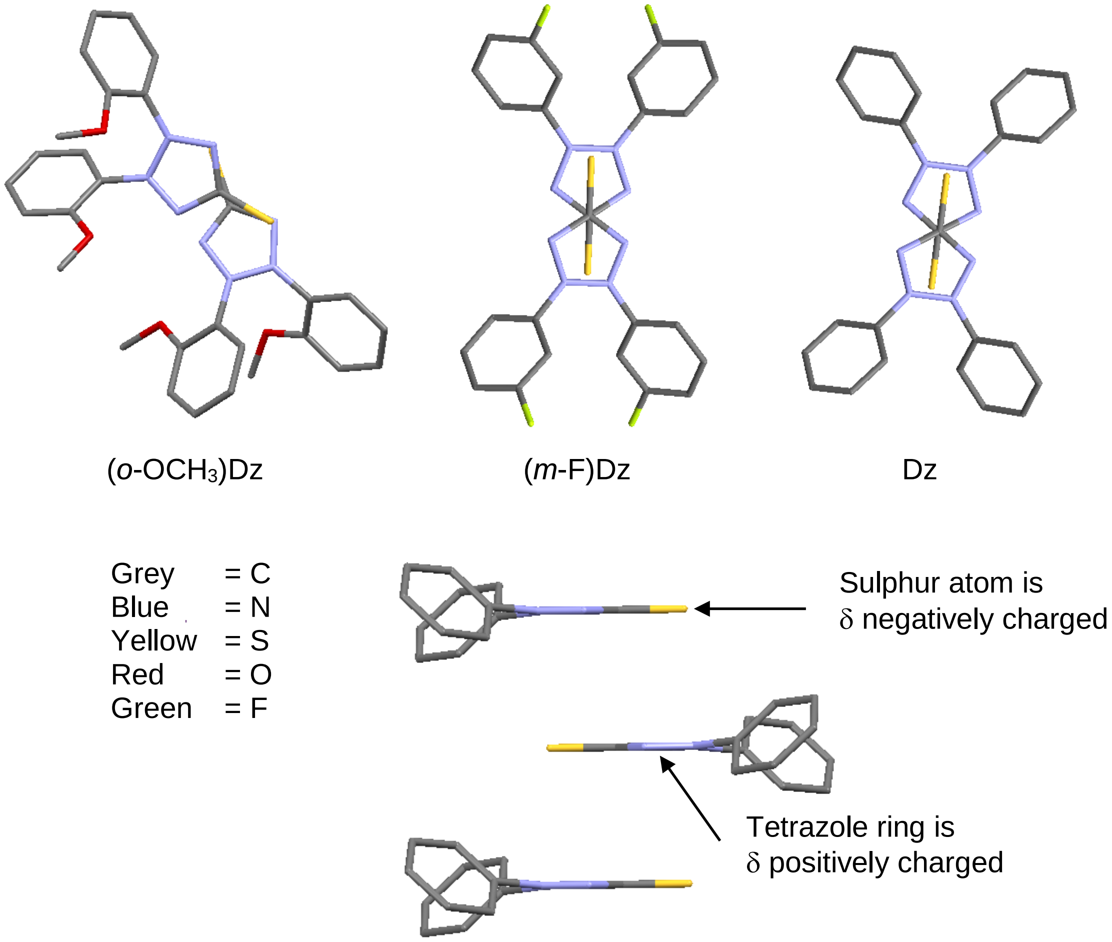


Figure 3.6 Comparative crystal packing top view for (*o*-OCH_3)Dz (top left), (*m*-F)Dz (top middle) and Dz (top right). The sandwich packing of Dz is shown in the bottom picture (side view). In the above illustrations the sulphur atoms are all δ negatively charged, while the tetrazole rings (N-N-N-N-C) are all δ positively charged because of delocalization within the ring.

Figure 3.6 (top left) illustrates the packing of (*o*-OCH_3)Dz to be relatively similar to that of Dz and (*m*-F)Dz (top middle). In the case of (*o*-OCH_3)Dz the sulphur atom is at a distance of 3.775 Å from the neighbouring molecule's N4 nitrogen and 3.561 Å from the plane of the tetrazole ring. In the (*m*-F)Dz crystal the latter distance is 3.518 Å, and 3.550 Å in the Dz crystal. The reason for the slightly twisted packing seen in the (*o*-OCH_3)Dz crystal, as opposed to the other two more symmetrically packed examples, is most probably due to the methoxy groups all being *cis* orientated relative to the C-S bond axes of both neighbouring molecules.

Based on natural population analyses (NPA) calculated at the DFT-B3LYP/6-311G level of theory Jian *et al.*[25] proposed an alternative charge distribution pattern in Dz. *Some* of their results showed both the sulphur and tetrazole ring to be δ-negatively charged while the positive charge is distributed over the two phenyl rings. Based on all crystallographic crystal packing evidence, of which some is presented in Figure 3.6, clearly showing the δ-negative S consistently being paired by a neighbouring tetrazolium ring, and *vice versa*, Jian's result may hardly be supported. The earlier hypothesis makes provision for ionic positive-negative type packing, while that would not be the case in the proposal made by Jian.

Table 3.5 Selected bond angles (°) of (*o*-OCH_3)Dz, (*m*-F)Dz and Dz. Numbering relates to Figure 3.5.

Angles	**(*o*-OCH_3)Dz**	**(*m*-F)Dz**	**Dz**
S1-C3-N1	123.7 (2)	124.3 (8)	124.9 (2)
S1-C3-N4	126.1 (2)	124.3 (8)	124.9 (2)
N1-C3-N4	110.2 (2)	111.2 (4)	110.1 (2)
C3-N1-N2	104.8 (2)	103.6 (5)	104.8 (1)
C3-N4-N3	104.6 (2)	103.6 (5)	104.8 (1)
N1-N2-N3	110.2 (2)	110.7 (3)	110.2 (1)
N4-N3-N2	110.2 (2)	110.7 (3)	110.2 (1)
N1-N2-C21	125.8 (2)	122.8 (1)	121.5 (9)
N4-N3-C11	126.3 (2)	122.8 (1)	121.5 (9)

With the very limited amount of freedom of movement within these molecules bond angles are as expected, in close agreement. Both the ring angles centered around nitrogens N2 and N3, to which the phenyl rings are attached, are 110.2°, which is also exactly similar to the carbon centered angle, N1-C3-N4. The remaining ring angles, i.e. centered around N1 and N4, are slightly smaller, namely 104.8° and 104.6° respectively.

Table 3.6 Selected tortion angles (°) of (*o*-OCH_3)Dz, (*m*-F)Dz and Dz. Numbering relates to Figure 3.5.

Torsion angels	**(*o*-OCH_3)Dz**	**(*m*-F)Dz**	**Dz**
S1-C3-N4-N3	178.6 (2)	179.9 (2)	-179.8 (0)
S1-C3-N1-N2	-178.2 (2)	179.9 (2)	-179.8 (0)
N1-N2-N3-N4	0.5 (3)	-0.5 (2)	0.7 (1)
N3-N2-N1-C3	-1.4 (3)	0.4 (2)	-0.5 (4)
N2-N3-N4-C3	0.6 (3)	0.4 (2)	-0.5 (4)
N1-N2-C21-C22	59.1 (4)	-43.6 (2)	46.4 (3)
N4-N3-C11-C12	-115.2 (3)	-43.6 (2)	46.4 (3)
C21-C22-O1-C1	-179.5 (2)		
C11-C12-O2-C2	-159.1 (2)		

From the list of selected torsion angles in Table 3.6 it may be seen that the molecule is essentially flat, except for the phenyl rings which are twisted due to steric obstruction. The dihedral angles formed by the benzene rings with the central five-membered ring are 59.1 (4)° and -115.2 (3)°. The C11-C12-O2-C2 torsion angle, -159.2°, does not lie in the plane of the phenyl ring it is attached to. The other methoxy group, however, do lie in the plane of its phenyl ring, as is seen in the torsion angle of -179.5°.

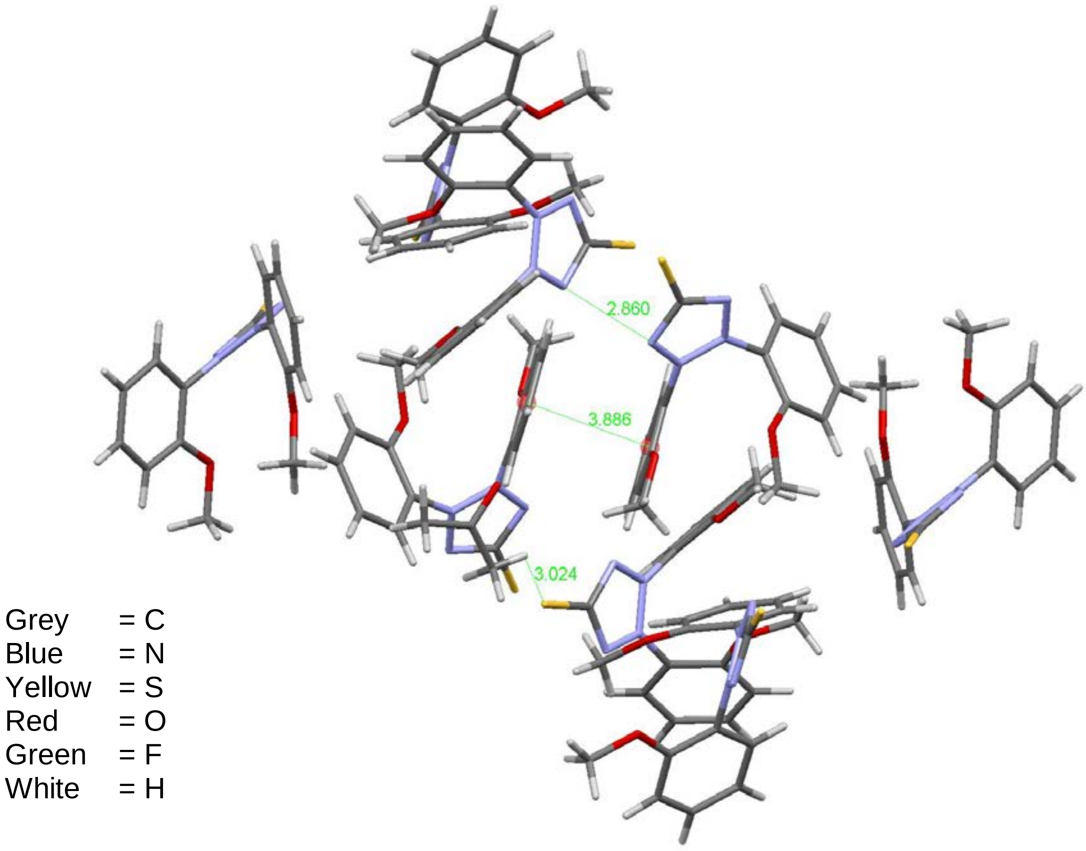
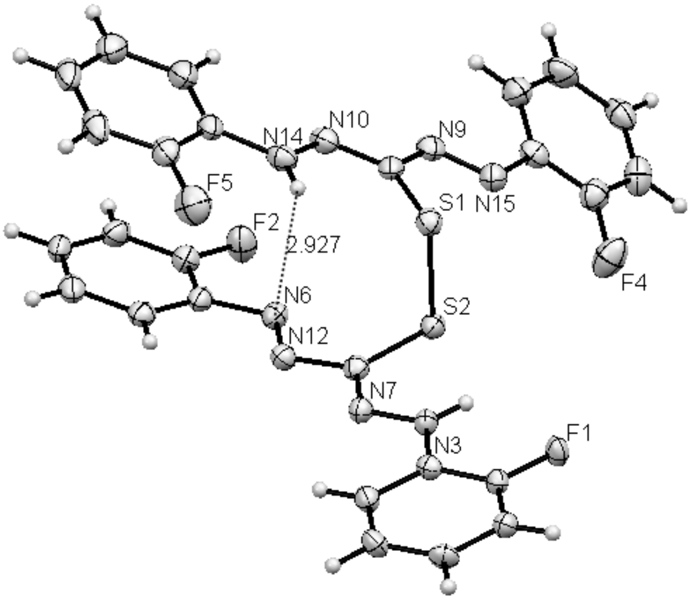


Figure 3.7 Crystal lattice packing of *ortho*-methoxydehydrodithizone. All solvent molecules are omitted for clarity.

Figure 3.7 illustrates the eight (*o*-OCH_3)Dz molecules per unit cell. For every ten of these molecules four molecules of acetone, and one molecule of dichloromethane is trapped inside the lattice - of which the latter is omitted from the packing diagram for clarity sake. Packing in the (*o*-OCH_3)Dz crystal differs from (*m*-F)Dz and Dz in that the tetrazolium ring of every individual molecule is not sandwiched but only paired instead, which may be ascribed to the relatively large methoxy protrusions. In the crystal packing some short contacts are seen in the N1-N1 and S-H2A non-bonding distances of 2.860 Å and 3.024 Å respectively. The relatively short distance of 3.886 Å between the centroids of benzene rings from two neighbouring molecules indicate π–π stacking interactions.

3.3.3. *ortho*-Fluorodithizone-disulphide



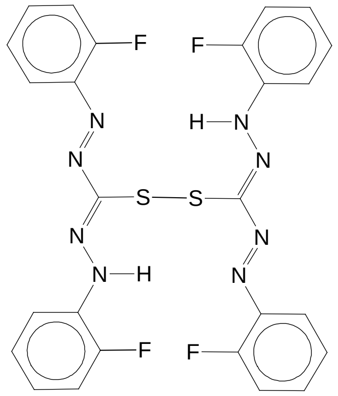


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Figure 3.8 Crystal structure of *ortho*-fluorodithizone disulphide. Hydrogen bonding between the monomers is indicated.

Figure 3.8 shows the structure and atom labeling of *ortho*-fluorodithizone-disulphide, (*o*-FHDz)$_2$, as related to Tables 3.8 (bond lengths), 3.9 (bond angles) and 3.10 (torsion angles). Crystallographic refinement data is summarized in Table 3.7. The crystal structure, packed in the triclinic space group, comprises two largely flat dithizonate monomers which are sideways joined through the sulphur atoms of each monomer.

Table 3.8 includes a comparison between bond distances of the disulphide monomers and those observed in the parent H_2Dz and K^+HDz^- compounds. Since no other dithizone disulphides have up to date been reported, the S-S bond length is compared to disulphides of other related compounds. Two such examples are bis(1-(2,6-Dimethylphenyl)-1,2,3,4-tetrazol-5-yl)disulfane[77] **(i)** and 5,5'-Dithio-bis(1-phenyl-1H-tetrazole)[78] **(ii)**, with S-S bond lengths of 2.013 Å and 2.026 Å respectively. The dithizone disulphide S-S bond distance was measured at 2.083(1) Å. The latter bond distance is about 0.06 to 0.07 Å longer than the former, which is indicative of a slightly weaker S-S bond in this case. In the dithizone disulphide the C-S bond distances are 1.787 Å and 1.802 Å, while for K^+HDz^- it is 1.719 Å and for H_2Dz 1.712 Å. The shorter bond distances in the latter two structures indicate stronger bonds, but also the fact that S here is not bound to a second atom, as is the case in the disulphide.

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[77] Y. Kim, J. Han, S. Kang, W. S. Han, S.W. Lee, *Dalton Trans.* 2003, 3357

[78] I. Brito, A. Cardenas, A. Mundaca, H. Villalobos, M. Lopez-Rodriguez, *Acta Crystallogr., Sect.E: Struct.Rep.Online*, 2007, **63**, o2581

Table 3.7 Crystal and structure refinement data.

Empirical formula	$C_{26}H_{18}F_4N_8S_2{\cdot}0.5(C_6H_{14})$
Formula weight	625.69
Temperature	100 (2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	a = 7.6537 (3) Å, b = 12.4352 (6) Å, c = 16.3279 (7) Å
	α = 73.674 (2)°, β = 85.270 (2)°, γ = 76.176 (2)°
Volume	1447.96 (11) $Å^3$
Z	2
Density	D_x = 1.435 Mg m^{-3}
Absorption coefficient	0.25 mm^{-1}
F(000)	646
Crystal description	red plate
Crystal size	0.05 x 0.30 x 0.35 mm
Theta range for data collection	3.4–24.3°
Index ranges	-10 =< h =< 10, -16 =< k =< 15, -21 =< l =< 21
Reflections collected	26154
Independent reflections	7129 [R(int) = 0.054 R(σ) = 0.0668]
Absorbtion correction	multi-scan *SADABS* (Bruker, 2009)
$R[F^2 > 2\sigma(F^2)]$	0.059
Data / restraints / parameters	7129/0/388
Largest diff. peak and hole	0.64 e.$Å^{-3}$ and −0.44 e.$Å^{-3}$

Table 3.8 Selected bond lengths (Å) of (*o*-F HDz)$_2$, H_2Dz and K^+HDz^-.

Bonds	**(HDz)$_2$ 16a**	**Bonds**	**(HDz)$_2$ 16b**	**H_2Dz**	**KHDz**
S1-S2	2.083 (1)				
S2-C8	1.787 (3)	**S1-C23**	1.802 (4)	1.712 (3)	1.719(6)
N7-C8	1.312 (4)	**N10-C23**	1.308 (5)	1.345 (3)	1.321(7)
N12-C8	1.392 (5)	**N9-C23**	1.377 (4)	1.334 (3)	1.410(7)
N3-N7	1.317 (4)	**N10-N14**	1.310 (3)	1.295 (3)	1.344(5)
N6-N12	1.275 (4)	**N9-N15**	1.257 (4)	1.299 (2)	1.275(5)
N6-C17	1.419 (5)	**N15-C28**	1.438 (4)	1.380 (3)	1.435(7)
N3-C16	1.398 (4)	**N14-C22**	1.424 (5)	1.391 (2)	1.384(7)
F1-C11	1.364 (3)	**F5-C32**	1.382 (4)		
F2-C25	1.357 (4)	**F4-C31**	1.356 (4)		

Regarding the -N=N-C=N-N(H)- monomeric backbones it is clear from Table 3.8 that the double bonds in the disulphide are well defined, e.g. the N6=N12 and N9=N15 bonds are 1.275 Å and 1.257 Å long, which corresponds closely to a similar bond order in the dithizonate anion, K^+HDz^-. Dithizone has -N-N(H)- bond lengths of 1.299 Å and 1.295 Å which are slightly shorter than in the disulphide and anionic species. The C23=N10 (1.308 Å) and C8=N7 (1.312 Å) disulphide double bonds follow a similar trend to the -N=N- bonds. The adjacent N3-N7 (1.317 Å) and N10-N14 (1.310 Å) bonds nevertheless still have more of a double bond character, being much shorter than the typical -N-N- bond distance of 1.45 Å. The same is also true for H_2Dz (1.295 Å), but K^+HDz^- has a slightly longer bond of 1.344 Å. From this it is obvious that delocalization is a major contributor to the unique bond distances found in almost all dithizones and related species. Bond distances between nitrogens and adjacent phenyl carbons are typically about 0.03 to 0.08 Å shorter than in typical C-N single bonds, which is less than in H_2Dz (0.08 - 0.09 Å) and KHDz. Conjugation that includes the phenyl rings is therefore less pronounced in the disulphide than in dithizone itself. π-Delocalization along the linear and planar molecule is typical of sp^2 hydridization of nitrogen atoms in the molecule backbone.

Bond lengths of the fluorines in the disulphide are as follows: C11-F1 (1.364 Å), C25-F2 (1.357 Å), C32-F5 (1.382 Å) and C31-F4 (1.356 Å), which compares closely to the bond lengths of the *meta*-fluoro-dehydrodithizone which are 1.352 Å and 1.352 Å.

Table 3.9 Selected bond angles (°) of (*o*-F HDz)$_2$.

(HDz)$_2$ 16b		**(HDz)$_2$ 16a**	
S2-S1-C23	102.0 (1)	**S1-S2-C8**	100.2 (1)
S1-C23-N9	122.7 (2)	**S2-C8-N12**	124.0 (2)
N15-N9-C23	114.8 (3)	**N6-N12-C8**	114.6 (2)
N14-N10-C23	117.6 (3)	**N3-N7-C8**	119.3 (3)
N10-N14-C22	119.6 (2)	**N7-N3-C16**	118.0 (2)
N9-N15-C28	113.3 (2)	**N12-N6-C17**	113.1 (2)

Bond angles involving the S-S fusion reaction, S2-S1-C23 and S1-S2-C8, as shown in Table 3.9, are 102.0° and 100.2°. These values compare very closely with what was observed for other disulphides, e.g. the previously mentioned disulfane **(i)** and dithio **(ii)** compounds, with corresponding angles of 100.5° & 100.4°, and 102.12° & 102.83° respectively. These values are 7 to 9° less than typical tetrahedral angles of 109°, which may be ascribed to the fact that only two bonds are formed with sulphur, while the remaining positions on the S atoms are occupied by non-bonding electron pairs. Packing effects and the hydrogen bond between the two monomers (see Figure 3.8) may additionally play a role here. In a comparison between the two monomers in the disulphide other bond angles in general do not differ by more than 2°. Bond angles also agree closely to related angles in the parent compound.

Table 3.10 Selected torsion angles (°) of (*o*-F HDz)$_2$.

(HDz)$_2$ 16a		**(HDz)$_2$ 16b**	
C8-S2-S1-C23	-104.1 (2)	**C8-S2-S1-C23**	-104.1 (2)
N12-N6-C17-C25	-175.0 (3)	**N9-N15-C28-C31**	-164.5 (3)
N7-N3-C16-C11	179.6 (3)	**N10-N14-C22-C32**	174.8 (3)

Selected torsion angles, as seen in Table 3.10, show that, apart from the twist between the two monomers, each of the latter are still rather planar, as was also observed for the parent dithizone compound. The largest deviation from planarity is seen in the N9-N15-C28-C31 angle, i.e. the phenyl ring being rotated away more than 15° from the 180° plane. Interestingly, the corresponding angle in the other monomer is rotated by only 5°, a difference which must be ascribed to packing and/or steric effects. The dihedral angle C8-S2-S1-C23 of -104.1°, observed at the S-S bond also corresponds closely to the *bond angles* at these points, and thus also to an almost tetrahedral conformation.

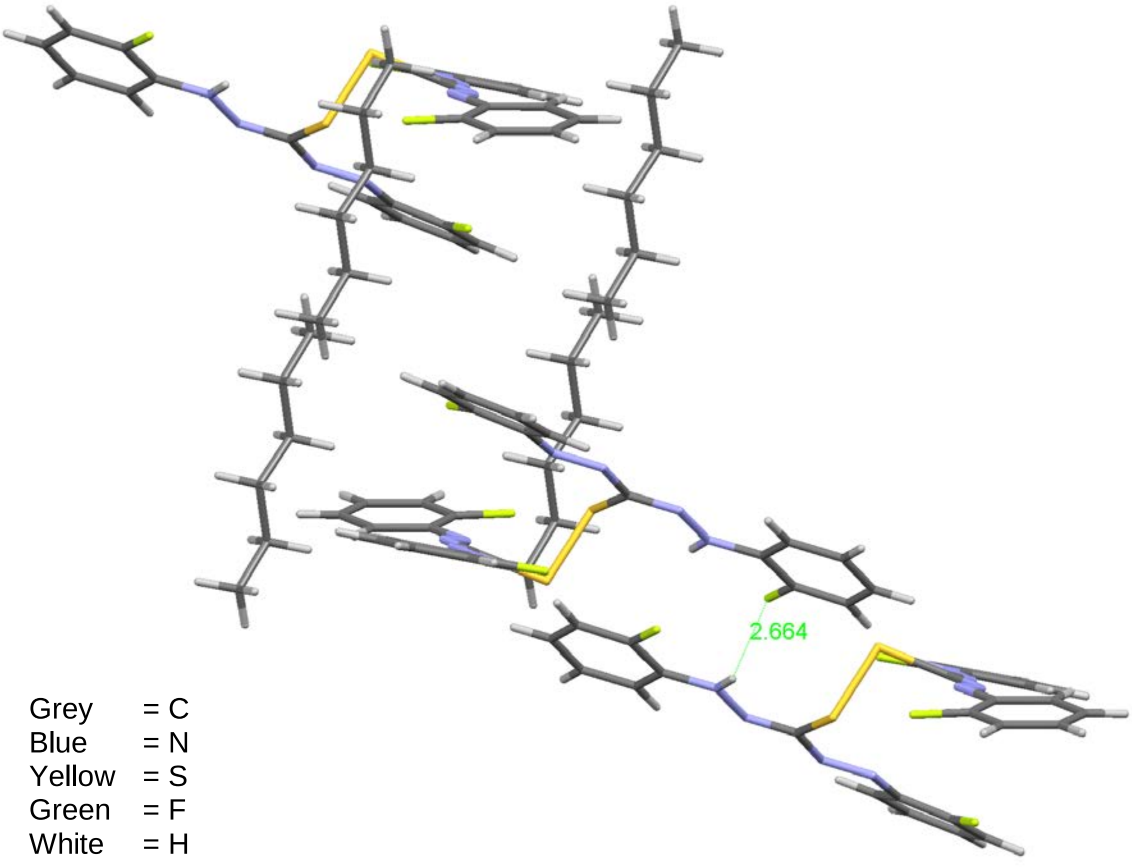

Figure 3.9 Crystal lattice packing of (*o*-F HDz)$_2$. The four n-hexane solvent molecules are shown.

The unit cell, as illustrated in Figure 3.9, contains two molecules of *ortho*-fluorodithizone disulphide, together with four n-hexane solvent molecules. The two disulphide monomers are twisted in such a way that the imine proton of one monomer lies directly above the N6 nitrogen of the other monomer, i.e. almost perpendicular on N6 in the plain of the other monomer. This weak H-bond interaction, at a distance of 2.927 Å (see Figure 3.8), explains the observed twisted conformation. Additionally, there is also a short contact between fluorine and the imine proton (the imine proton that is not involved in the above-mentioned H-bond) of a molecule in a neighbouring cell, with a distance of 2.664 Å. This shortest of intermolecular contacts (apart from some H-H contacts) most probably contributes towards the relative ease with which the present *ortho*-fluorinated compound crystallized into crystals large enough for an X-ray data collection to be performed.

3.4. Computational Chemistry

3.4.1. Introduction

As mentioned in Chapter 1, the purpose of this study is amongst others, to vary electronic and steric properties on the dithizone ligand by investigating the effect different substituents and extended ring systems have on the photochromic properties of corresponding mercury complexes. In our quest to do so, computational chemistry was found to be a suitable tool, significantly contributing towards greater understanding of the species under investigation. Geometry optimizations of selected isomeric and tautomeric forms of the ligands and mercury complexes were performed. Additionally, the Time Dependant Density Functional Theory (TDDFT)[79] oscillators which correspond to experimental UV/visible spectra, as well as molecular orbital calculations of all species were done.

DFT calculations were carried out using the Amsterdam Density Functional (ADF) 2007 and 2009 software,[80] with the Generalized Gradient Approximation (GGA) functional PW91**[81]** and the hybrid functional B3LYP.[82] The Triple ζ polarized (TZP) basis set, with a fine mesh for numerical integration, a spin-restricted formalism and a full geometry optimization with tight convergence criteria was used for minimum energy searches. All calculations have been performed with no symmetry constraint and all structures have been calculated as singlet states. Solvent effects were taken into account for all optimized structures reported here. The COSMO (Conductor like Screening Model) model of solvation[83,84,85] was used as implemented in ADF.[86] The COSMO model is a dielectric model in which the solute molecule is embedded in a molecule-shaped cavity surrounded by a dielectric medium with a given dielectric constant (ε_0). The type of cavity used is Esurf[87] and the solvents used are methanol (ε_0 = 32.6) and dichloromethane (ε_0 = 8.9). Where applicable, scalar relativistic effects were used with the ZORA[88,89,90,91,92] (Zero Order Regular Approximation) formalism. The energies used in this

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[83] A. Klamt, G. Schüürmann, *J. Chem. Soc., Perkin Trans. 2* 1993, 799

[84] A. Klamt, *J. Phys. Chem.*, 1995, **99**, 2224

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[87] J. L. Pascual-Ahuir, E. Silla, I. Tuñon, *J. Comput. Chem.*, 1994, **15**, 1127

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[89] E. van Lenthe, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.*, 1993, **99**, 4597

[90] E. van Lenthe, E.J. Baerends, J.G. Snijders, *J. Chem. Phys.*, 1994, **101**, 9783

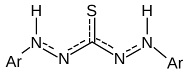
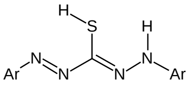
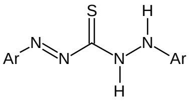
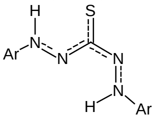
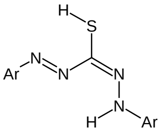
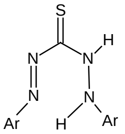
[91] E. van Lenthe, J.G. Snijders, E.J. Baerends, *J. Chem. Phys.*, 1996, **105**, 6505

section are the total bonding energy (electronic internal energy) of the optimized molecules. No frequency analysis to obtain free energy corrections has been done.

3.4.2. Dithizone Derivatives

Six different isomers and tautomers of all seven different substituted phenyl dithizones were geometry optimized in gas phase, in a polar solvent (methanol), as well as a non-polar solvent (DCM), in order to establish the energetically favoured geometry of each. Table 3.11 lists all the optimized relative energies of the methyl and methoxy derivatives.

Table 3.11 ADF PW91/TZP (1st line) and B3LYP/TZP (3rd line) calculated relative energies of different stereo isomers and tautomers of dithizone derivatives. The energies were calculated in gas phase (no brackets), dichloromethane (round brackets) and methanol [square brackets] as solvents (2nd line). Ar represents the *ortho*, *meta* or *para* substituted phenyl ring variants. The symmetric form in each case was assigned the value of zero (population analysis 99.99 %) as this is the only structure that has been determined by X-ray crystallography for the parent dithizone compound, see section 2.4.1.

Structure	**Relative Energies (kcal mol^{-1})**						
Ar:	***o*-OCH$_3$**	***m*-OCH$_3$**	***p*-OCH$_3$**	***o*-CH$_3$**	***m*-CH$_3$**	***p*-CH$_3$**	**3,4-(CH$_3$)$_2$**
 (symmetric)	0 (0) [0] 0	0 (0) [0] 0	0 (0) [0] 0	0 (0) [0] 0	0 (0) [0] 0	0 (0) [0] 0	0 (0) [0] 0
 (enol)	8 (16) [12] 7	8 (10) [9] 5	8 (11) [11] 6	9 (10) [11] 6	9 (10) [10] 8	8 (11) [11] 6	9 (11) [12] 6
 (keto)	16 (20) [18] 13	16 (14) [12] 10	16 (14) [14] 10	16 (14) [14] 10	15 (14) [13] 12	15 (14) [14] 10	15 (14) (14) 10
 (Hydrogen-bridge-1)	14 (11) [10] 15	14 (12) [9] 15	14 (11) [10] 15	14 (12) [11] 15	15 (11) [11] 17	14 (11) [10] 15	14 (11) [10] 15
 (Hydrogen bridge-2)	12 (20) [15] 10	15 (14) [13] 8	11 (14) [15] 8	12 (14) [14] 9	12 (14) [14] 8	11 (14) [15] 8	11 (14) [15] 8
 (Hydrogen bridge-3)	28	19	19	24	19	20	20

The symmetric form of all the dithizones were assigned a zero value, as this geometry consistently optimized to the lowest DFT calculated energy, also in solution environments. Gas phase calculations of the enol form of all derivatives gave the 2nd lowest energy, closely followed by the hydrogen bridge-2 (HB2) isomer. It is interesting to note that both solvents gave similar lowest (apart from the symmetric form) values for the enol and HB1 isomers, as opposed

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[92] E. van Lenthe, R. van Leeuwen, E.J. Baerends, J.G. Snijders, *Int. J. Quantum Chem.*, 1996, **57**, 281

to the *ca* 3 kcal mol^{-1} higher solvent values seen for the keto and HB2 isomers. Furthermore, for the keto (apart from *o*-OCH_3) and HB1 isomers, the solvent has a definite stabilization effect over the gas phase environments, as seen in the lower energies here. HB3 is obviously not a favoured geometry. Giving the highest energy values, further calculations for this isomer was deemed excessive. Table 3.12 contains all the calculated relative energies of isomers and tautomers of the extended ring systems dithizone series. The symmetric form has been assigned the zero value, as again, this form consistently gave the lowest energy for all four derivatives. Otherwise, tendencies in relative energy values are roughly similar to that seen above. It is however obvious from the data that the larger difference amongst these four compounds is responsible for more exceptions in the energy distribution pattern, e.g. methanol solutions of the HB1 and HB2 pyrenyl compound gave a much lower (2nd lowest) energy than gas and solvent phase enol solutions of the same. This, for instance, is not the case for the naphthyl compound, proving that larger structural differences play a definite role in the preferred conformer in solution.

Table 3.12 PW91/TZP (1st line) and B3LYP/TZP (3rd line) calculated relative energies of different stereo isomers and tautomers of dithizone derivatives. The energies were calculated in gasphase (no brackets), dichloromethane (round brackets) and methanol (square brackets) as solvent (2nd line). Ar represent the extended rings: α-naphthyl, α-anthracenyl, α-pyrenyl and β-fluorenyl. The symmetric form in each case was assigned the value of zero (population analysis 99.99 %) as this is the only structure that has been determined by X-ray crystallography for the parent dithizone compound, see section 2.4.1. Calculations that did not converge are left blank.

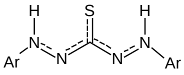
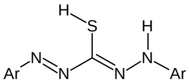
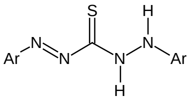
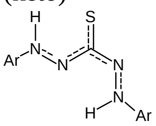
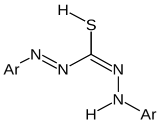
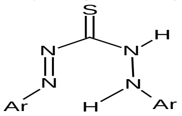
Structure	**Relative energies (kcal mol^{-1})**			
Ar	**α-naph**	**α-anth**	**α-pyr**	**β-fluor**
 (symmetric)	0 (0) [0] 0	0 (0) [0] 0	0 (0) [0] 0	0 (0) [0] 0
 (enol)	8 (10) [10] 7	9 (12) [10] 7	12 (10) [10] 8	8 (11) [11] 5
 (keto)	14 (13) [12] 9	14 (12) [10] 9	17 (19) [18] 9	15 (14) [14] 11
 (Hydrogen bridge-1)	16 (14) [12] 15	13 (10) [9] -	11 (7) [7] 15	14 (11) [10] 14
 (Hydrogen bridge-2)	12 (12) [14] 8	10 (11) [11] -	10 (7) [12] -	11 (14) [14] 7
 (Hydrogen bridge-3)	24	-	20	19

Figure 3.10 (left) gives the PW91/TZP calculated TDDFT oscillators of the symmetric form and experimental UV/visible superimposed spectra of the symmetric form of unsubstituted dithizone in a series of solvents. The experimental spectra all show two main absorption bands; one peak at 400-550 nm and another at 550-650 nm. Figure 3.10 (right) gives the calculated spectra (Gaussian broadening of oscillators) of the symmetric form of unsubstituted dithizone in these solvents. The calculated spectra also exhibit two main bands, one at 400-500 nm and the lower energy band at 600-800 nm. The calculated high energy bands, in both gas and solvent phase, correspond excellently to the experimental λ_{max}, e.g. for toluene (blue) the difference is less than 5 nm. At the low energy band this is not the case; with the gas phase λ_{max} being the furthest removed, namely to wavelengths higher than 800 nm. This may however not be considered to be wrong, as no experimental gas phase UV/visible spectrum of the compounds under investigation has as yet been obtained. Solvent calculations are thus more applicable, with the calculated oscillator in DMSO being only about 45 nm higher than the experimental λ_{max} value of 620 nm.

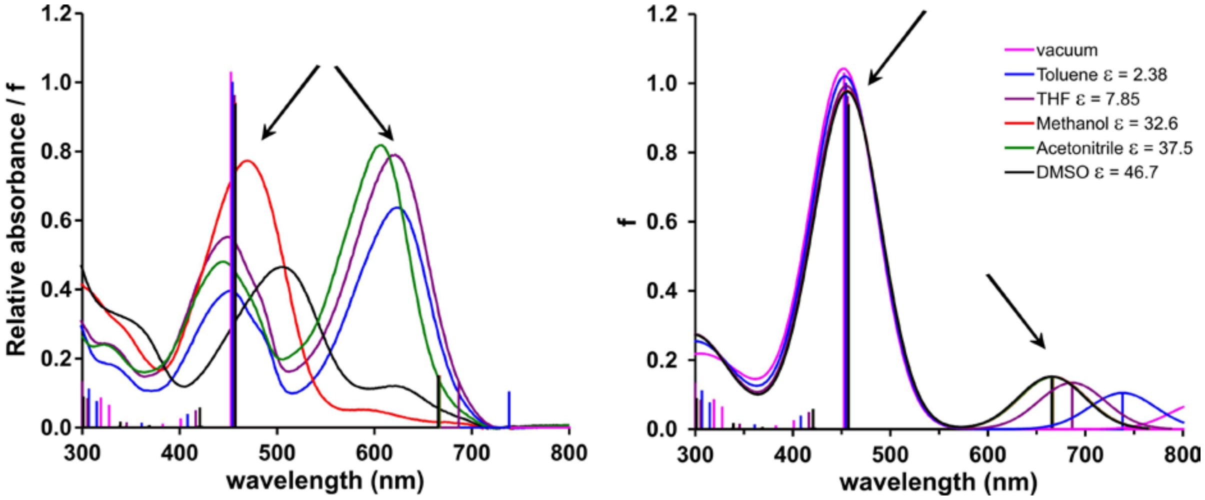


Figure 3.10 ADF/PW91 calculated electronic spectra (spikes) overlaid with experimentally measured spectra of dithizone (curves) in the indicated solvents (left). ADF/PW91 calculated electronic spectra (spikes) overlaid with artificial TDDFT-based electronic absorption spectra of dithizone (curves), in the indicated solvents (right, dielectric constants indicated). Artificial spectra were generated by line broadening with half-width 80 nm, using Gaussian functions. Arrows indicate high (low λ) and low energy (high λ) absorption peaks. (Red & green behind black.)

Figure 3.11 and Figure 3.12 below give the gas phase PW91/TZP TDDFT calculated oscillators and superimposed experimentally obtained UV/visible spectra in DCM of *ortho*-methoxydithizone and α-napthtyldithizone respectively. The experimental UV/visible spectrum of unsubstituted dithizone consists of two broad absorption bands, with peaks at 450 nm and 608 nm and a trough at 502 nm between the two peaks, see Figure 3.2. The experimental spectrum of the *ortho*-methoxydithizone ligand in DCM is similar to that of the unsubstituted parent compound, but has shoulders on the facing side of the peaks. The visible region is also dominated by two broad bands both situated between 400 and 700 nm. The two main bands, with λ_{max} at 468 nm (ε = 5 215 dm^3 mol^{-1} cm^{-1}) and 644 nm (ε = 20 897 dm^3 mol^{-1} cm^{-1}) have shoulders at 503 and 590 nm respectively. The trough between the two maxima is situated at 530 nm.

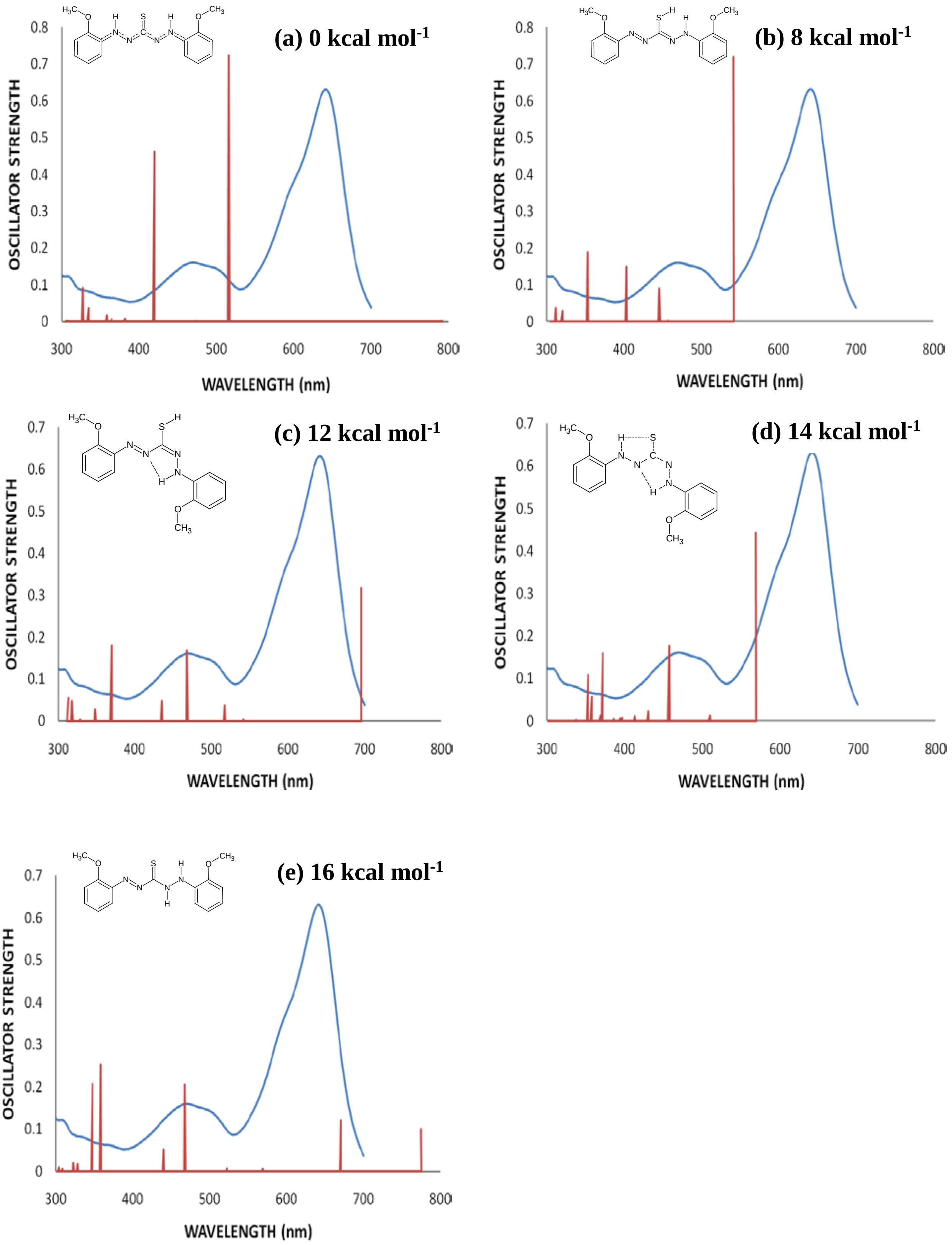


Figure 3.11 ADF/PW91 calculated electronic spectra (spikes) and experimentally measured spectra in DCM (curves) [λ_{max} (DCM) = 468, 644 nm (20 897 dm^3 mol^{-1} cm^{-1})] of indicated isomers of *ortho*-methoxydithizone. (Due to computational expense and time constraints solvent phase calculations were not performed here.)

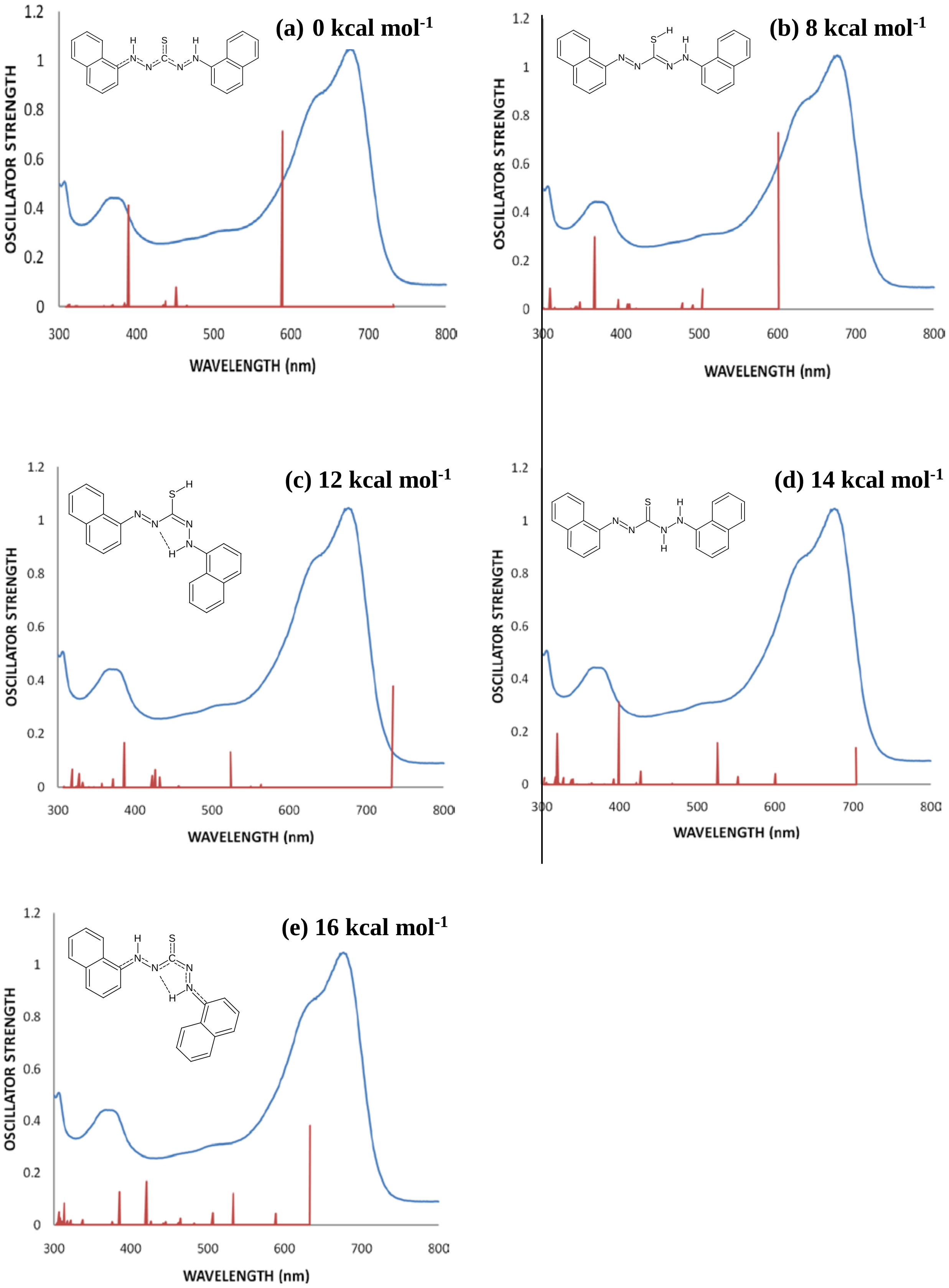


Figure 3.12 ADF/PW91 calculated electronic spectra (spikes) and experimentally measured spectra in DCM (curves) [λ_{max} (DCM) = 370, 383 (shoulder), 624 (shoulder), 680 nm (ε = 27 796 dm^3 mol^{-1} cm^{-1})] of indicated isomers of α-naphthyldithizone.

The visible region of the experimental spectrum of the α-naphthyldithizone ligand is dominated by a broad asymmetric band with λ_{max} = 680 nm (ε = 27 796 dm^3 mol^{-1} cm^{-1}) and a shoulder at 624 nm, while the UV region is dominated by a band with λ_{max} = 370 nm (ε = 8 752 dm^3 mol^{-1} cm^{-1}) and a shoulder at 383 nm. The trough between the two maxima stretches from 420 to 520 nm. Because the absorbance is not zero in this region some theoretical oscillators should be observed.

Using Boltzman distribution, the relative calculated energies from Table 3.11 and Table 3.12 together with Figure 3.10, indicates the symmetric form in all cases to contribute more than 99.9 % to the UV/visible spectra. On the contrary, TDDFT calculated spectra do not simulate the symmetric form very well, but agree better with some of the other isomers/tautomers, especially the keto form. Theoretical prediction of the UV/visible spectrum of unsubstituted dithizone in *solvent* (Fig.3.10) is therefore much more accurate. (The entire ensemble of calculated spectra for all the derivatives may be viewed in Appendix A.)

Figure 3.13 PW91/TZP calculated HOMO orbitals of the symmetric form of all the methoxy and methyl substituted dithizone derivatives.

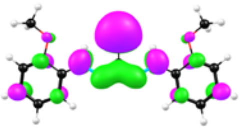
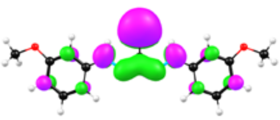
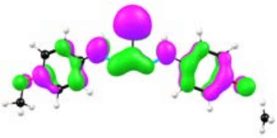
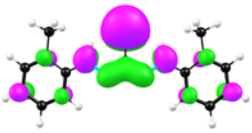
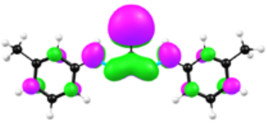
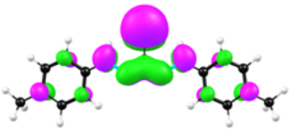
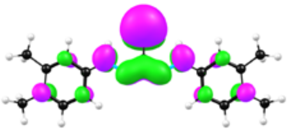
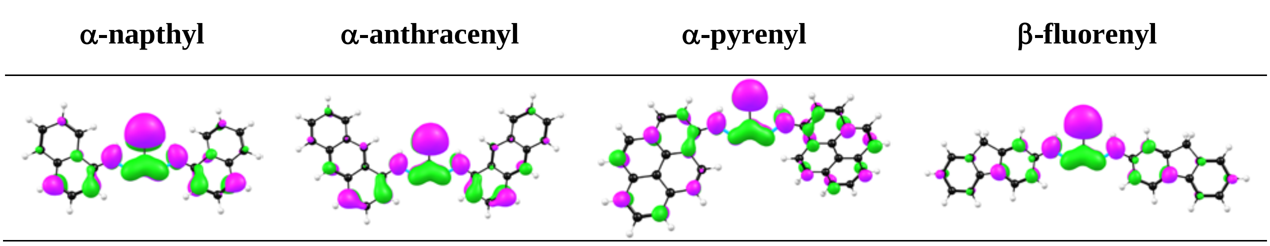
***o*-OCH$_3$**	***m*-OCH$_3$**	***p*-OCH$_3$**	***o*-CH$_3$**
			
***m*-CH$_3$**	***p*-CH$_3$**	**3,4-(CH$_3$)$_2$**	
			

Figure 3.13 and Figure 3.14 give a presentation of the HOMO of the symmetric form of the ring substituted and extended ring dithizones of this study. Extensive π electron delocalization throughout the entire Ar-N-N-C(S)-N-N-Ar backbone (excluding aliphatic substituents) of the dithizone derivatives is observed. This is in agreement with the conjugated character in the Ph-N-N-C(S)-N-N-Ph backbone of the experimental crystal structures of dithizone, see Chapter 2, Section 2.4.1. Otherwise, no significant difference between all the tabulated species with regards to electron distribution along the back bone is observed visually. This is expected, since the electronic influence of the substituents or altered ring systems is not strong enough to result in any profound change in electron distribution. Differences are however readily detected

electrochemically, as will later be seen when comparing cyclic voltammograms of some of these compounds.

Figure 3.14 PW91/TZP calculated HOMO orbitals of the symmetric form of the extended ring dithizones.



3.4.3. Mercury Dithizonates

The complexes of dithizone and its derivatives form a very interesting class of compounds. The metals that can be complexed to dithizone and its derivatives span through almost the entire periodic table. What makes the complexes unique is its ability to exhibit photochromism in a variety of colours. The full potential of computational chemistry applied to these complexes has not yet been fully exploited; computational chemistry is a useful tool to explore the phenomenon of photochromism. From the laser studies, as discussed in the literature survey, it was determined that dithizonatophenylmercury(II), when irradiated with blue-green or sun light, does not momentarily remain in the photo-excited blue state but temporally relaxes into the 180° rotated blue ground state.[36]

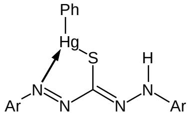
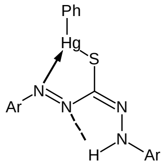
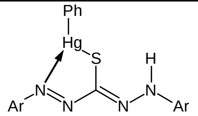
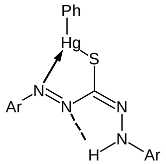
The quantum computational relative energies for the two photo-isomers of selected mercury dithizonato complexes are listed in Table 3.13. The higher energy isomer (blue) is the ground state of the proposed photo-excitation product of the lower energy ground state of the mercury dithizonato complexes (orange).[36] The geometry of the proposed product of photo-excitation (blue isomer) corresponds to *syn-anti* isomerization around the C=N bond of the ground state molecule. In the process the C=N double bond weakens to a single bond, which then allows free rotation around the same.

Two functionals were used when computing the optimized structures, namely PW91 and B3LYP, both with the TZP basis set. The energy difference between the two isomeric forms of the ring-substituted mercury dithizonato complexes is between 7 and 8 kcal mol^{-1} for both functionals. The implication is that upon photo-excitation the lower energy ground state (orange isomer) can readily be converted to the proposed blue isomeric form. Based only on these computational results all methoxy and methyl substituted dithizonates are expected to be photochromic, even though photochromism is not visibly observed for *ortho*-

methyldithizonatophenylmercury(II). In the case of the latter the radiationless thermal back reaction may just be too fast to be observed with the naked eye.

Table 3.13 also lists the energies of the optimized structures of the extended dithizone derivatives which could not be experimentally isolated. The only product with an extended ring that was successfully synthesized is α-naphthyldithizonatophenylmercury(II). A dilute solution irradiated with direct bright African sun light unfortunately did not reveal this compound to be photochromic, at least, visibly.

Table 3.13. PW91/TZP (first line) and B3LYP/TZP (second line) calculated relative energies (total bonding energies) of the ground state (orange isomer) and the photo-isomer (blue) of some mercury dithizonato complexes. Energies represent gas phase calculations. Ar indicates the substituted phenyl ring in *ortho*, *meta* and *para* positions and also the α-naphthyl, α-anthracenyl, α-pyrenyl and β-fluorenyl derivatives.

Complex	**Relative energies (kcal mol^{-1})**					
Ar	**H**	***o*-OCH$_3$**	***m*- OCH$_3$**	***p*- OCH$_3$**	***o*- CH$_3$**	**m- OH$_3$**
	0 0	0 0	0 0	0 0	0 0	0 0
	8 *-	7 8	7 8	7 8	7 7	8 7
Ar	***p*- CH$_3$**	**3,4-(CH$_3$)$_2$**	**α-naph**	**α-anth**	**α-pyr**	**β-fluor**
	0 0	0 0	0 0	0 0	0 0	0 0
	8 8	8 8	7 8	9 -	6 -	8 9

* Blank spaces represent calculations that did not converge.

Figure 3.15 depicts the calculated electronic spectra of the two ground state isomers of photochromic *ortho*-methoxydithizonatophenylmercury(II), overlaid with its experimental spectra. A DCM solution of the ground resting state is pink, while the photo-isomer ground state solution is purple. A fairly good simulation is obtained for the UV/visible spectrum of the pink ground state (Fig.3.15, left). The two strong calculated peaks at 472 nm and 535 nm are attributed mainly to transitions from HOMO-3 to LUMO and HOMO to LUMO respectively (see Figure 3.15), and correspond to the broad experimental ground state peak with λ_{max} = 505 nm (ε = 28 300 dm^3 mol^{-1} cm^{-1}). A third strong oscillator stands out, namely at

495 nm, which might be the transition responsible for the asymmetric shape (accentuated by dashed line in Fig.3.15) of the visible band. The two low lying peaks, at 292 nm and 306 nm, simulates the shouldered peak that appears around 250 nm fairly well.

The experimental spectrum of the photo-isomer (purple, Figure 3.15, right) of *ortho*-methoxydithizonatophenylmercury(II) shows two peaks. The peak at 505 nm appears due to regeneration (radiationless thermal back reaction) of the pink resting state, while the peak at 615 nm represents the purple photo-isomer. The lowest energy peak of the theoretical TDDFT of the purple isomer is red-shifted by 304 nm (from 535 to 839 nm), while the experimental spectrum is red shifted by only 110 nm (from 505 to 615 nm). Although the calculated red-shift *tendency* is correct, it shifted too much. By analogy, based on earlier observations and discussions related to the ligand-alone spectra, one may conclude that solvent phase calculations would have performed better here – a matter which may certainly be investigated further once better computational facilities become available to us. A larger degree of accuracy is observed for the high energy (short λ) calculated oscillators (as again with dithizone itself), when corrected by a blue-shift of about 60 nm. It should be pointed out that only ground state and not excited state calculations for the two isomeric forms of *ortho*-methoxydithizonatophenylmercury(II) are presented here.

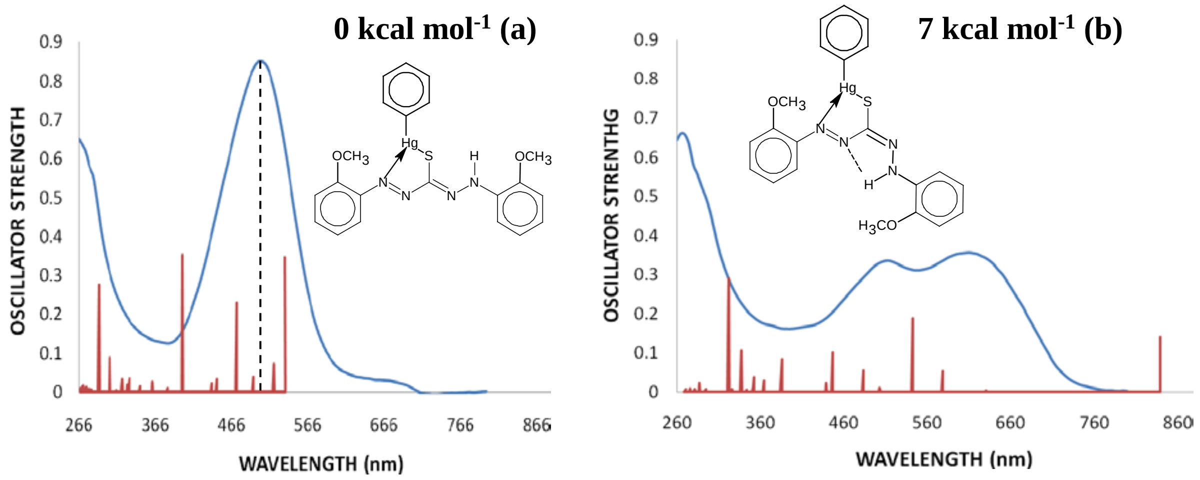


Figure 3.15 PW91/TZP calculated electronic spectra (spikes) and experimentally determined spectra (curves) in DCM [λ_{max} (DCM) = 505 nm (pink, ε = 28 346 dm^3 mol^{-1} cm^{-1}), and 615 nm (purple, ε = 11 840 dm^3 mol^{-1} cm^{-1})] of the resting state and photo-isomers of *ortho*-methoxydithizonatophenylmercury(II).

Table 3.14 relates to Figure 3.15, and gives information related to the ground and photo-excited states of *ortho*-methoxydithizonatophenylmercury(II). Percentage contributions are given as measure of how much each transition from the indicated HOMO to the LUMO contributes to the photo-excitation process. For the ground state the HOMO to LUMO contribution is 64 %. The process of photochromism is discussed below, with reference to PhHgHDz.

Table 3.14 Main transition TDDFT (PW91/TZP) results for the ground and photo-excited states of *ortho*-methoxydithizonatophenylmercury(II).

***ortho*-methoxydithizonatophenylmercury(II) resting state**

E (kcal mol^{-1})	λ (nm)	f	From	To	% contribution
53	535	0.347	HOMO	LUMO	64
54	521	0.0736	HOMO-2	LUMO	82
57	494	0.0396	HOMO-2	LUMO	50
			HOMO-3	LUMO	27
60	472	0.229	HOMO-3	LUMO	52
			HOMO-1	LUMO	31

***ortho*-methoxydithizonatophenylmercury(II) photo product**

E (kcal mol^{-1})	λ (nm)	f	From	To	% contribution
34	839	0.141	HOMO	LUMO	90
45	631	0.00366	HOMO-1	LUMO	67
			HOMO-2	LUMO	33
49	578	0.0529	HOMO-2	LUMO	41
			HOMO-3	LUMO	26
52	543	0.189	HOMO-3	LUMO	59

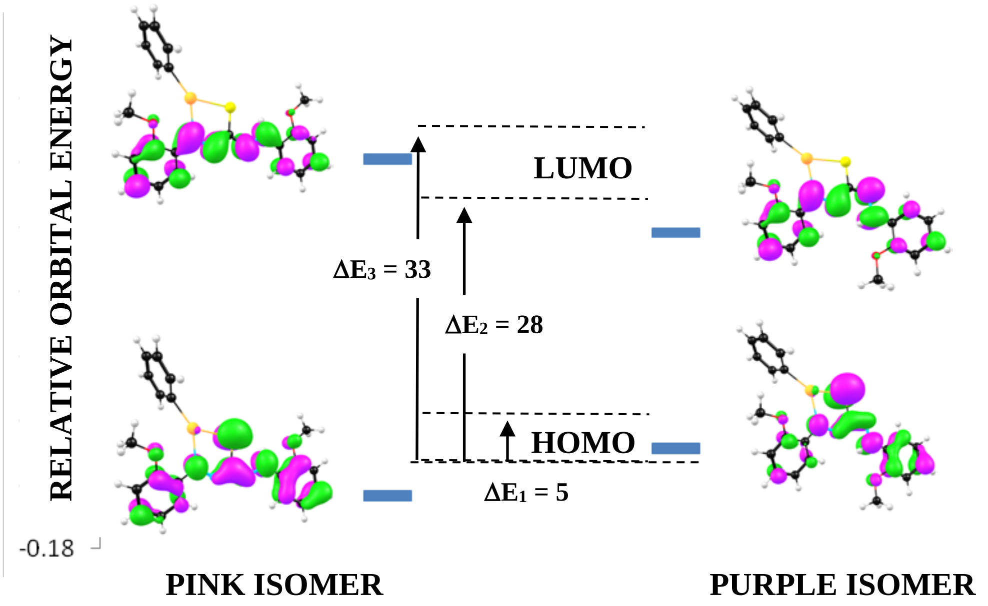


Figure 3.16 Relative orbital energies of the pink and purple isomers of *ortho*-methoxydithizonatophenylmercury(II). All energies are reported in kcal mol^{-1}.

Figure 3.16 gives a presentation of how photochromism takes place in the molecule under discussion. The HOMO orbital has pi character in the C1=N2 bond (see atom numbering in Figure 3.17 below). The C1=N2 double bond degenerates into a single bond on irradiation with blue-green light, around which free rotation can then take place. The change in C1=N2 bond character may be seen in the orbital presentation above, i.e. the strong orbital overlap in the pink ground state (bottom, left), is absent in the vertically excited state molecule (top, left). Rotation now takes place around this bond, going to the 180°-twist excited state (right, top), which then relaxes into the purple ground state isomer (right, bottom) – with the C1=N2 double bond restored. From here further slow thermal relaxation takes place, restoring the original pink resting state. Vibrational energy (heat) appears to be sufficient to overcome the intermediate energy barrier, the latter which is shown for PhHgHDz, in par. 2.5.3.

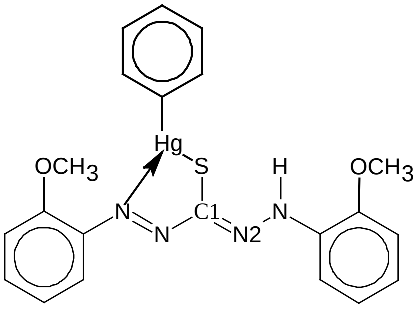


Figure 3.17 Atom labeling of *ortho*-methoxydithizonatophenylmercury(II).

By inspecting Figure 3.16 it is evident that the delocalization of the electrons does not just include the N-N-C(S)-N-N backbone but spans to the phenyl ring and its substituents also. This indicates that the phenyl rings and its substituents (see Figure 3.4, Table 3.2 and Figure 3.23) play a crucial role in the photo-isomerisation process and that the substituents on the phenyl ring might influence the excitation process. Also for this reason it was decided to attempt synthesis of extended aromatic system dithizonates, investigating its influence on the photochromic process.

Table 3.15 Calculated ΔE (molecular orbital energy, kcal mol^{-1}) and experimental λ_{max} for PhHg(R)HDz complexes relative to the HOMO of the lowest energy ground state. ΔE_1, ΔE_2 and ΔE_3 are indicated in Figure 3.16. R is the substituent on the phenyl ring.

R	**ΔE_1 (kcal mol^{-1})**	**ΔE_2 (kcal mol^{-1})**	**ΔE_3 (kcal mol^{-1})**	**λ_{max} (nm)**	**colour change observed upon photo excitation**
		calculated			**experimental**
***o*-CH$_3$**	6	29	36	467	none observed
***m*-OCH$_3$**	6	28	36	485	orange to blue
H	6	28	35	471	orange to blue
***m*-CH$_3$**	5	27	35	480	orange to blue
***p*-CH$_3$**	5	27	34	486	orange to blue
***3,4*-(CH$_3$)$_2$**	3	27	34	-	-
***o*-OCH$_3$**	**5**	**25**	**33**	**505**	**pink to purple**
***p*-OCH$_3$**	4	25	33	-	-
α-naphthyl	4	25	31	509	none observed
β-fluorenyl	4	25	32	-	-
α-anthracenyl	2	23	28	-	-
α-pyrenyl	3	22	27	-	-
***o*-F**	-	-	34	-	orange to blue
***m*-F**	-	-	35	-	orange to blue
***p*-F**	-	-	35	-	orange to blue

The results in Table 3.15 are interesting, because the complexes that were found to be photochromic have the highest ΔE values, right through except for *o*-OCH_3 dithizonate. Not only is the energy difference between the two ground state isomers of these complexes the highest, but also the energy barrier that needs to be overcome photochemically. Admittedly, these values do not include full 3-dimensional modelling of the energy landscape, which would finally have given a complete picture of all energies related to the transitional twist coordinates. It nevertheless indicates that less energy would in principle be required for isomerisation in the large extended, and *ortho* and *para*-methoxy complexes. In general, the trend that is observed for the λ_{max} values lie, as expected, also in the same order (except for the *m*-OCH_3 derivative), with longest wavelengths corresponding to low energies, confirming relative accuracy of the former theoretical results.

With these results available it must be concluded that, although the photochromic reaction might for the above reasons be favoured in the latter compounds, its steric bulkiness might pose an insurmountable obstacle. Apart from that, more kinetic energy would be required to promote rotation, which evidently has little to do with the vertical excitation energy supplied by the absorbed photon.

The *o*-CH_3 dithizonate, on the other hand, also has a high ΔE_3 (HOMO→LUMO) value of 36 kcal mol^{-1}, and was found not to be visibly photochromic, the reason for which is unknown at this stage. The photochromic complexes all have ΔE_3 values between 33 to 36 kcal mol^{-1}. The extended ring system dithizonates generally have low ΔE_3 values, with the α-pyrenyldithizonate being the lowest, at 27 kcal mol^{-1}.

Since the TDDFT calculated lowest energy oscillator corresponds mainly to a HOMO-LUMO excitation (ΔE_3 in Table 3.15), it is expected that the HOMO-LUMO energy difference relates to the corresponding experimental UV/visible maximum, as illustrated in Figure 3.18 (related to Table 3.15). Although the calculated energy difference of the HOMO-LUMO transition does not simulate the experimental wavelength accurately a correlation was found nonetheless, as indicated by the R^2 value of 0.76.

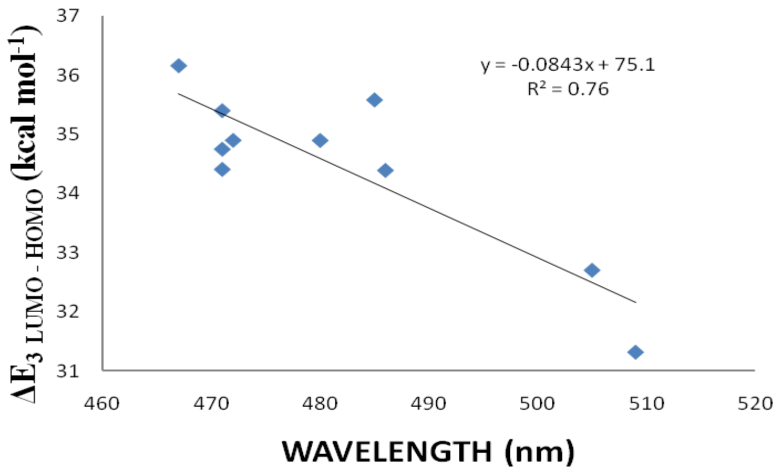
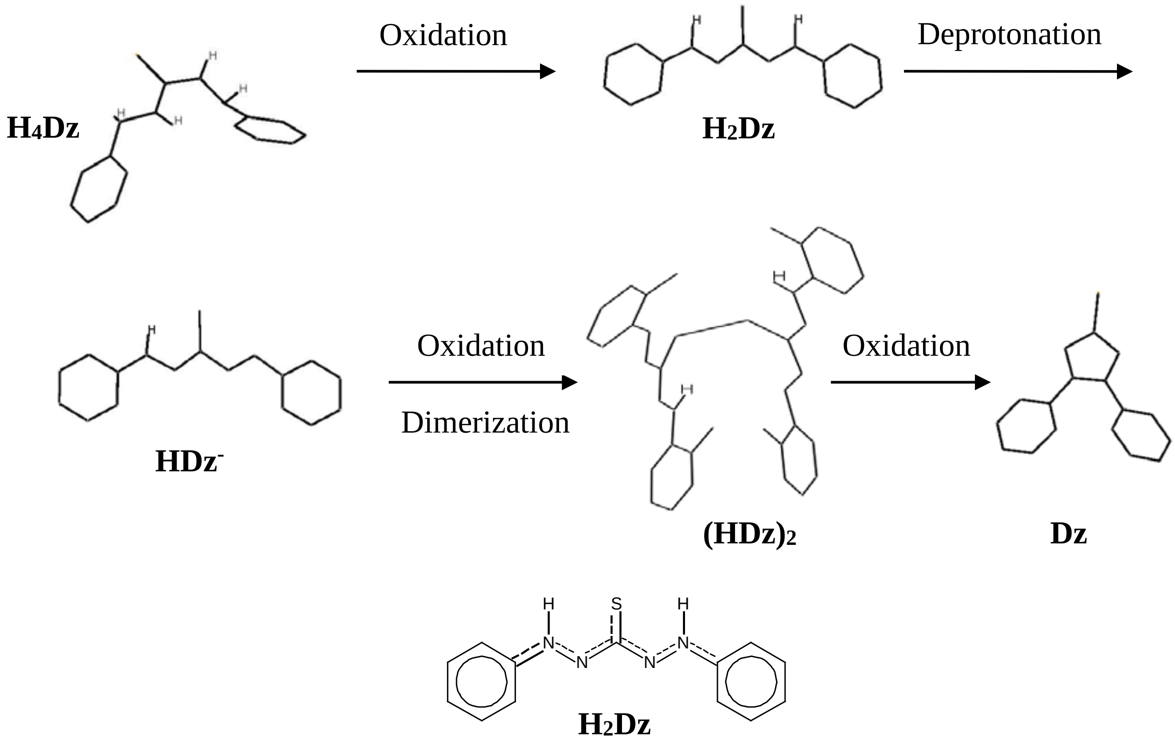


Figure 3.18 Correlation of the HOMO-LUMO energy differences with experimental UV/visible maxima of PhHg(R)HDz complexes. R is the substituent on the phenyl ring. Data in Table 3.15. Corresponding data for *ortho, meta & para*-fluoro complexes[16] are additionally added for purpose of widening the correlation.

3.5. Electrochemistry

3.5.1. Introduction

The redox schemes of unsubstituted dithizone, with all redox waves assigned to related species in solution, are discussed in the literature survey section (Chapter 2). Most of the identified species in the *electrochemical* redox cycle of dithizone are well supported by its analogue *chemical* redox processes and the X-ray crystallographically resolved[93] species resulting from it, see Scheme 3.5.



Scheme 3.5 X-ray crystallographically determined structures of dithizone, H_2Dz, and its chemical oxidation and reduction products. All the compounds' geometries are related to the basic structure of dithizone (bottom), where nitrogen, sulphur and imine hydrogen atoms are labelled, while the phenyl ring carbons and hydrogens, and the sulphur-bonded carbon is not labelled.

The redox behaviour of *electronically altered* dithizone derivatives and complexes is however for the first time reported here. Apart from ultimately studying the effects the substituents have on the photochromic reaction of its mercury complexes using computational chemistry, its varied potential to stabilize dithizone against oxidation is also placed under the magnifying glass in this section. Electrochemistry, specifically cyclic voltammetry, is an ideal technique to quantify the effect of electronically altered species. Dichloromethane, generally considered as being aprotic by nature, was used as solvent. The extremely non-coordinating (and expensive!) electrolyte, $[NBu_4][B(C_6F_5)_4]$, was employed, ensuring better resolution of individual redox waves. The

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[93] Cambridge Crystallographic Database August 2010 update: **H_4Dz** – DPTCBZ01, **H_2Dz** - DITHIZ, **KHDz** – DIFMUA, **$(HDz)_2$** – this thesis, **Dz** – DHDTIZ10.

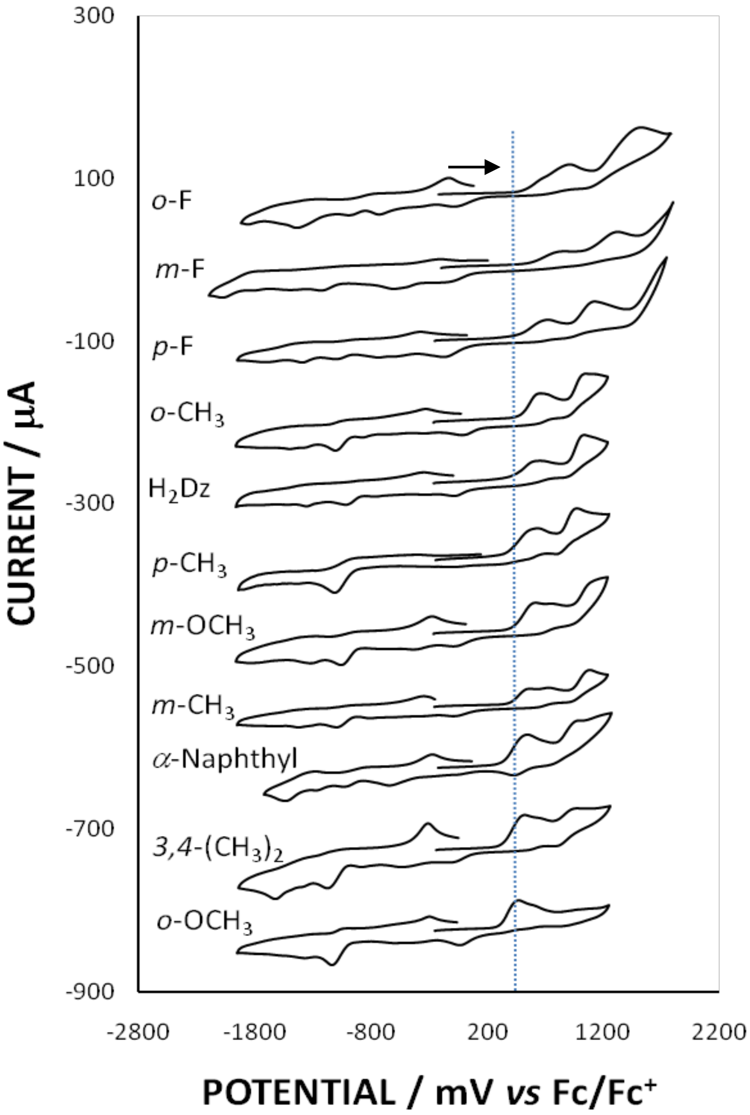
reference electrode is an in-house constructed Ag/AgNO$_3$ electrode, while all potentials were referenced against Fc/Fc$^+$, as recommended by IUPAC.[94]

3.5.2. Dithizone Derivatives

For the purpose of exploring the widest possible borders within which the first oxidation potential of dithizone may be shifted, cyclic voltammograms of all the dithizones substituted with electron-donating groups, as synthesized during this investigation, were compared to the unsubstituted parent compound, as well as to some fluorinated derivatives.[95] The series includes dithizones with substituents on the phenyl rings; *o*-OCH$_3$, *m*-OCH$_3$, *o*-CH$_3$, *m*-CH$_3$, *p*-CH$_3$, 3,4-(CH$_3$)$_2$, H, *o*-F, *m*-F and *p*-F, as well as α-naphtyldithizone.

Figure 3.19

Cyclic voltammograms recorded at a scan rate of 400 mV s^{-1}, using 0.1 M [NBu$_4$][B(C$_6$F$_5$)$_4$] as supporting electrolyte, and a glassy carbon working electrode at 25 °C in dichloromethane, of 1 mM solutions of eleven different dithizones. All cyclic voltammograms were referenced against ferrocene as internal standard. The vertical dotted line lies at 473 mV, corresponding to **E$_1$** for (*o*-OCH$_3$)H$_2$Dz. Scan direction is as indicated. (Cyclic voltammograms of the individual ligands at a series of scan rates can be seen in Appendix A from page IX. Complete cyclic voltammetry data at all scan rates are presented in Table 3.19 on page 87.)



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[94] G. Gritzer and J. Kuta, *Pure Appl. Chem.*, 1984, **56**, 461

[95] Provided by Dr. K. G. von Eschwege.

Table 3.16 Cyclic voltammetry data obtained from voltammograms (*vs* Fc/Fc$^+$) of substituted dithizones (R)H_2Dz, in CH_2Cl_2/0.1 mol dm^{-3} / $[NBu_4][B(C_6F_5)_4]$, utilizing a glassy carbon working electrode, at 25 °C, and scan rate of 400 mV s^{-1}. First anodic (E_1, E_2) and cathodic peak potentials (E_I) are given.

R	**E_1**	**E_2**	**E_{2a}**	**E_{2b}**	**E_I**
***o*-F**	917	1489	-	-	-51
***m*-F**	765	1281	-	-	-95
***p*-F**	723	1097	-	-	-143
***o*-CH_3**	700	1016	-	-	32
H	639	1023	-	-	-37
***p*-CH_3**	638	954	-	-	-66
***m*-OCH_3**	613	-	737	*1113*	-67
***m*-CH_3**	577	-	715	1067	-*55*
α-Naphthyl	552	960	-	-	462
3,4-$(CH_3)_2$	524	-	636	928	-64
***o*-OCH_3**	473	-	641	991	-15

From Figure 3.19 and Table 3.16 above it is evident that the electron-withdrawing fluorinated dithizones have the highest first oxidation potentials, **E_1** (major waves), as was expected. On the other hand, the dimethylated and *o*-OCH_3 compounds have the lowest oxidation potentials. It is interesting to note that the series here considered is bordered by *ortho*-substituted compounds, i.e. the electronic influences, whether electron-withdrawing (*o*-F) or electron-donating (*o*-OCH_3), is most profound where the substituent lies the closest to the reactive N-rich ligand chain. The effect diminishes with substituents systematically being placed further away, via *meta* to *para*-substituent. The E_1 of the very weakly electron-donating –CH_3 derivatives lies inbetween. As expected, the reference parent compound, H_2Dz (**E_1** = 639 mV), essentially separates the electron-withdrawing and electron-donating derivatives, lying 278 mV below the highest value of 917 mV (*o*-F), and 166 mV above the lowest value of 473 mV (*o*-OCH_3). The total range over which **E_1** could therefore be altered by chemical modifications applied symmetrically to the phenyl rings of dithizone, is 444 mV. (We found that the synthetic yields of dithizones are significantly reduced when using stronger electron-donating substituents, while the intensely coloured dithizones are depleted of its colour when two or more fluoro substituents are employed.[16])

Incorporation of the extended naphthyl ring system is electronically of lesser importance, as the initial goal with the extended aromatic systems was to investigate its steric influence and to establish its effect on transition energies during photochromism – which unfortunately was eventually not observed. The anisotropic electron-withdrawing effect of the double-ringed naphthyl ring system is nevertheless significant, with **E_1** = 552 mV, being 87 mV lower than that of the reference compound, H_2Dz (639 mV).

Figure 3.20 gives the cyclic voltammogram of H_2Dz, as reference. Numbering of redox waves refers to corresponding species in the oxidation and reduction processes represented in Schemes 2.3 and 2.4 in the literature survey, see Chapter 2, section 2.6.2. Figure 3.21 and Figure 3.22 are the 400 mV s^{-1} cyclic voltammograms of (*o*-OCH_3)H_2Dz (numbering corresponds to Schemes 3.6 and 3.7) and (α-Naphthyl)H_2Dz, the former being used as model throughout this study, while the latter is the only compound with extended ring system successfully prepared.

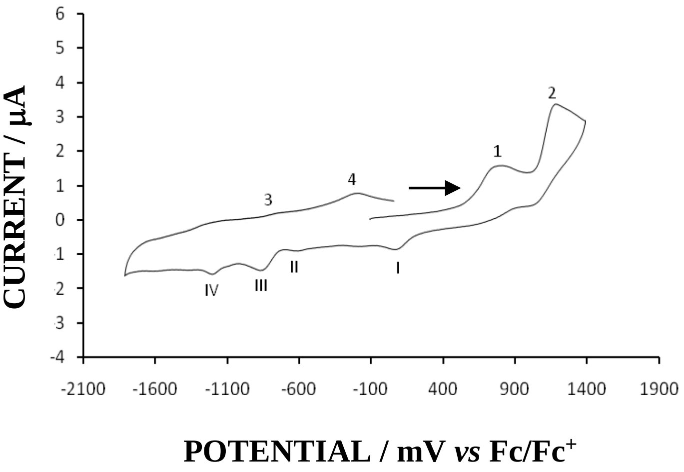


Figure 3.20

Cyclic voltammogram of 1 mM **H_2Dz** recorded at a scan rate of 400 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

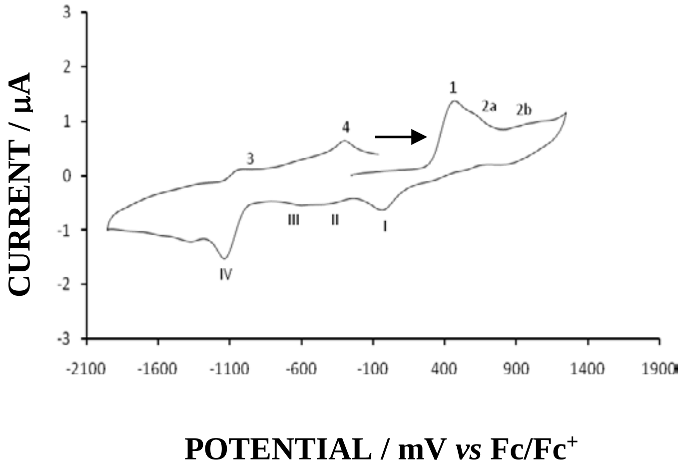


Figure 3.21

Cyclic voltammogram of 1 mM, **(*o*-OCH_3)H_2Dz** recorded at a scan rate of 400 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

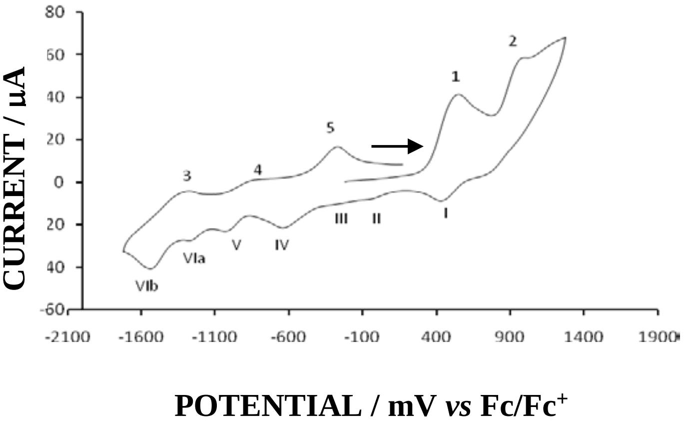


Figure 3.22

Cyclic voltammogram of 1 mM, **(α-Naphthyl)H_2Dz** recorded at a scan rate of 400 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

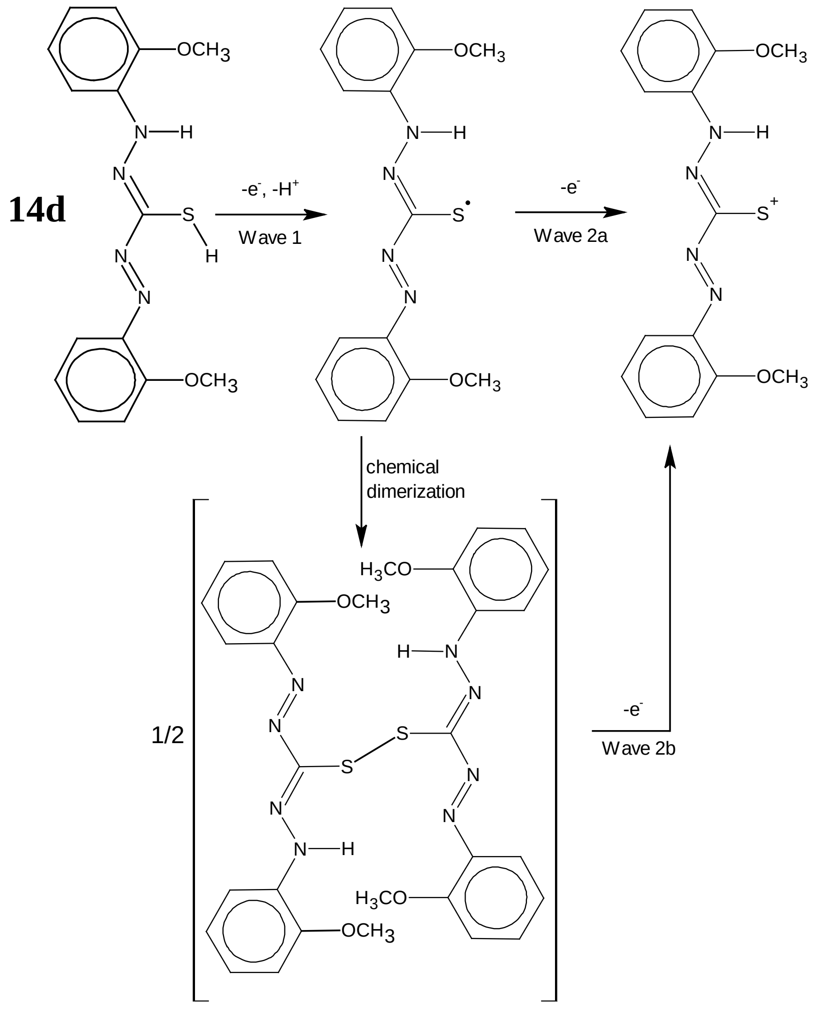
In the cyclic voltammogram of (*o*-OCH_3) H_2Dz (Figure 3.21) the main difference compared to the H_2Dz CV that is immediately observed, is the 1st oxidation wave having a shoulder towards higher potential, here indicated as waves **1** and **2a**, and the 2nd oxidation wave being largely reduced in amplitude. The shoulder is observed for all the derivatives with lowest $\mathbf{E_1}$ values (except (Naph)H_2Dz), e.g. *m*-OCH_3, *m*-CH_3, 3,4-$(CH_3)_2$, and of course, the *o*-OCH_3 derivative. This is accompanied by a systematic decrease in the amplitude of the 2nd oxidation wave, as may be seen in the CV's lower down in Figure 3.19.

This may not be attributed to an initial $H_2Dz \leftrightarrow HDz^-$ equilibrium giving rise to the closely lying waves, as HDz^- would evidently oxidize more readily than unsubstituted H_2Dz. The implication would then be that **Waves 1** and **2a** result from HDz^- and H_2Dz respectively, each loosing an electron. That cannot be, since it would imply that the four above-mentioned derivatives, (with lowest $\mathbf{E_1}$) in its undissociated form, are then more difficult to oxidize than H_2Dz itself, based on the fact that shoulders in these CV's lie at potentials larger than $\mathbf{E_1}$ for H_2Dz.

The proposal now instead is that; on the relatively fast CV time scale, the disulphide is only partially formed in these compounds, thus resulting in a free radical $HDz\cdot$ species that is more readily oxidized further (**Wave 2**) than would otherwise be the case for the disulphide. This proposal is further supported by both crystal structures reported in this thesis, i.e. (a) the larger methyl and methoxy substituents (compared to the fluoro substituent) pose a steric hindrance towards dimerization, although not preventing it (see structure in par. 3.3.2), and (b) compounds with stronger electron-withdrawing groups usually form stronger acids, i.e. more readily lose its protons, thus the unrestricted (due to loss of H) ease by which dimerization can take place as observed for the fluorinated derivative (see structure in par. 3.3.3). In general then, it is seen that although the $\mathbf{E_1}$ oxidation potential of the fluorinated derivatives lie at higher values, it nevertheless form the disulphide more readily.

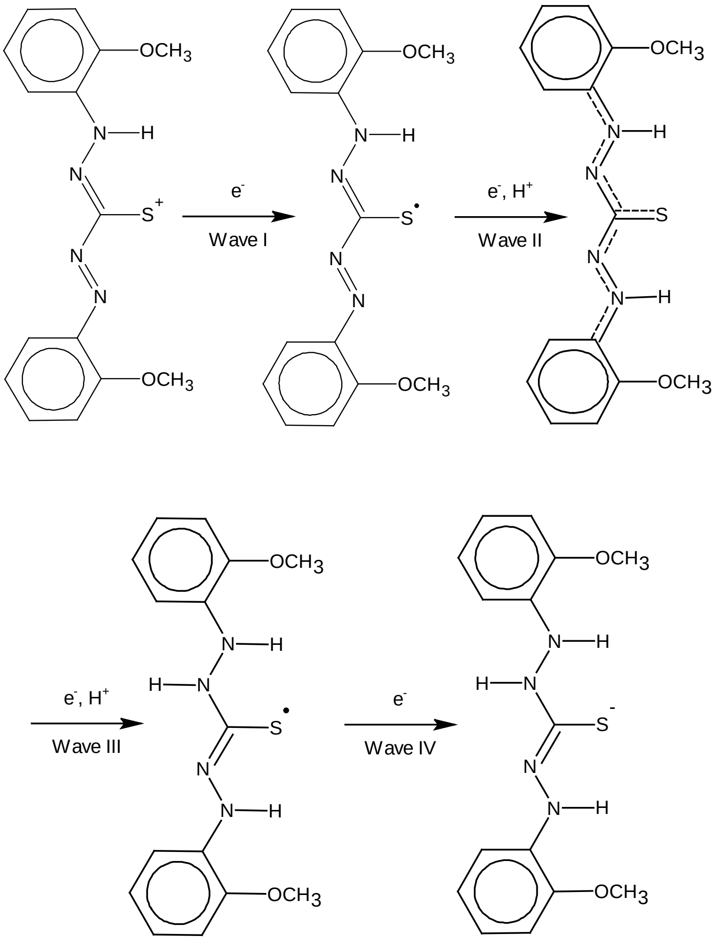
Based on the above arguments therefore, conclusion is reached why **Wave 2** (**2b** in case of *o*-OCH_3) systematically decreases on progressing towards the derivative with the strongest electron-donating substituent. In fact, as may be seen in Figure 3.19 and Figure 3.21, this 2nd wave has almost vanished. Here dimerization is so slow that within scan rates of 100 to 500 mV s^{-1} hardly any dimerization has taken place and the 2nd oxidation step proceeds quickly and mostly directly from the S-radical species. On the other hand, in the case of H_2Dz and its fluorinated derivatives dimerization is fast, resulting in the pronounced 2nd oxidation wave lying at 900+ mV potentials.

Scheme 3.6 is the proposed oxidation process for $(o\text{-OCH}_3)\text{H}_2\text{Dz}$ (and the other three associated derivatives mentioned here above). It differs from the reported scheme for H_2Dz (Scheme 2.3) in that two **Wave 2** pathways are proposed, with the pathway that excludes the disulphide, being the favoured route. Cyclization of the fully oxidized $(o\text{-OCH}_3)\text{HDz}^+$ cation accompanied by loss of a proton to form the *ortho*-methoxydehydrodithizone tetrazolium salt is not considered feasible during the relative fast time scale of the cyclic voltammogram.



Scheme 3.6 Proposed oxidation of *ortho*-methoxydithizone, **14d**. Wavenumbers correspond to Figure 3.21. For the sake of clarity the S-H tautomer of **14d** is shown.

The reduction of the above electrochemical oxidation product, $(o\text{-OCH}_3)\text{HDz}^+$, is presented in Scheme 3.7. The cation is reduced to the $(o\text{-OCH}_3)\text{HDz}\cdot$ radical during a one electron transfer process **(Wave I**, -35 mV**)**. With the uptake of an additional electron (**Wave II**, -429 mV) and a proton the original $(o\text{-OCH}_3)\text{H}_2\text{Dz}$, **14d**, is formed. The symmetric form is then further reduced with the uptake of a proton and electron (**Wave III**, -577 mV), resulting in the formation of the trihydrogenated *ortho*-methoxydithizone, $(o\text{-OCH}_3)_2\text{H}_3\text{Dz}\cdot$ radical. In view of the proton shortage in solution the added proton is anticipated to come from two sources; either a neighbouring dithizone molecule, or else an abstracted solvent proton. The (*o*-OCH$_3$)H$_3$Dz· radical is lastly reduced to the (*o*-OCH$_3$)H$_3$Dz$^-$ anion **(Wave IV**, -1111 mV)**,** which is similar to the thiocarbazide, H$_4$Dz, but without one proton.



14d

Scheme 3.7 Oxidation of *ortho*-methoxydithizone cation. Wavenumbers correspond to Figure 3.21

The last part of the redox cycle is the re-oxidation to **14d**. **Waves 3** and **4** (Figure 3.21) represent the reversal of reduction processes **IV** and **III**, generating the original product again. A difference between the reduction processes of H$_2$Dz and (*o*-OCH$_3$)H$_2$Dz is seen in the reduction at **Wave II**. In the H$_2$Dz reduction process reported in literature two waves were observed for the reduction process observed with the oxidation **Wave 2** namely **Wave IIa** and **Wave IIb**.[68] these two reduction waves were ascribed to the reduction of the disulphide and the HDz radical. This was not observed only for the *m*-F and *p*-F derivatives of this study.

3.5.3. Mercury Dithizonates

Only seven phenylmercury(II) complex derivatives could successfully be synthesized during this investigation, either due to complete or partial failure (very low yield) in the afore-going ligand syntheses steps of the other derivatives.

Figure 3.23 compares the CV's of unsubstituted PhHgHDz **19** and complex derivatives containing the *o*-CH_3, *m*-CH_3, *p*-CH_3, *o*-OCH_3 and *m*-OCH_3 substituents, as well as the α-naphthyl derivative. Corresponding first oxidation, $\mathbf{E_1}$, and reduction potentials, $\mathbf{E_I}$, are given in Table 3.17, arranged from most to least positive $\mathbf{E_1}$ values.

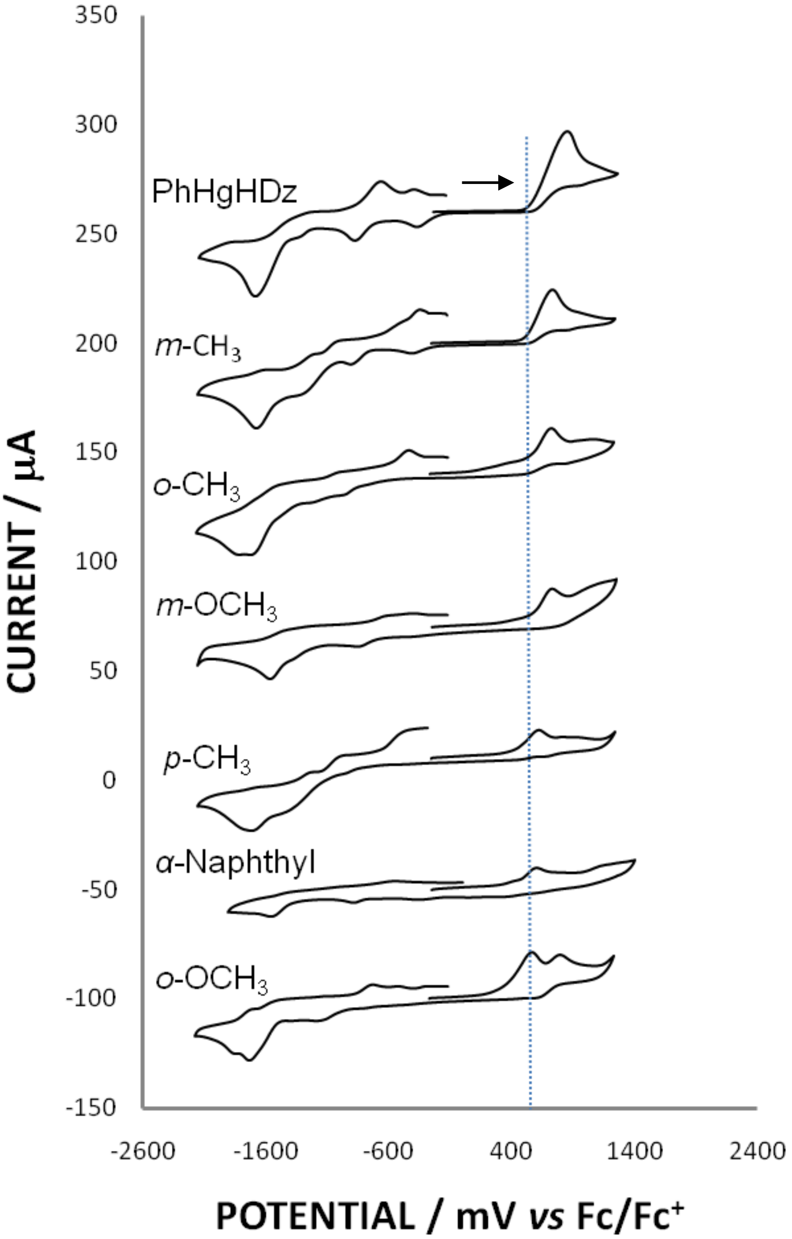


Figure 3.23

Cyclic voltammograms recor-ded at scan rates of 400 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working elec-trode, at 25 °C, in dichloro-methane, of 1 mM of seven different phenylmercury(II) dithizonato complexes.
All cyclic voltammograms were referenced against ferrocene as internal standard.
The vertical dotted line lies at 564 mV, i.e. corresponding to $\mathbf{E_1}$ for PhHg(*o*-OCH_3)HDz. Scan direction is as indicated. (Cyclic voltammograms of the individual complexes at a series of scan rates can be seen in Appendix A from page XII. Complete cyclic voltammetry data at all scan rates are presented in Table 3.20 on page 89.)

Table 3.17 Cyclic voltammetry data obtained from voltammograms (*vs* Fc/Fc^+) of dithizonatophenylmercury(II) complex derivatives, in CH_2Cl_2/0.1 mol dm^{-3} $[NBu_4][B(C_6F_5)_4]$ with a glassy carbon working electrode, at 25 °C. Scan rates, 400 mV s^{-1}. First anodic peak potentials (E_1, mV) and first cathodic peak potentials (E_I, mV) are given. PhHg(R)HDz where R is the substituent.

R	**E_1**	**E_I**
H	846	-340
***m*-CH_3**	731	-393
***o*-CH_3**	726	-
***m*-OCH_3**	721	-373
***p*-CH_3**	624	-488
α-Naphthyl	592	-68
***o*-OCH_3**	504	-408

A total potential shift of 342 mV between the highest (PhHgHDz, 846 mV) and the lowest $\mathbf{E_1}$ values (PhHg(*o*-OCH_3)HDz, 504 mV) is observed. The *enhancing* effect of the metal is demonstrated in the fact that this difference is 176 mV more than in the corresponding free ligands, where the corresponding difference is only 166 mV. Although more than 100 mV lower than in PhHgHDz, $\mathbf{E_1}$ for the next three complexes, *m*-CH_3, *o*-CH_3 and *m*-OCH_3, varies only within 10 mV, illustrating the electrochemical similarity between these complexes. The electronic influence of the naphthyl variant is once again significant, being 254 mV lower than that of PhHgHDz.

Assignment of the observed redox waves of PhHgHDz, PhHg(*o*-OCH_3)HDz and α-PhHg(Naph)HDz as represented in **Figure 3.24**, **Figure 3.25** and **Figure 3.26**, is done in accordance with Scheme 3.8 and Scheme 3.9.

In contrast to the free ligand PhHgHDz do not have a free mercaptan (-C-SH) group that can be oxidized to form disulphide bridges. Upon complexation with mercury the free mercaptan becomes a stable “metal thioether”, Hg-S-C, which effectively prevents disulphide formation. Thus, the mercury complexes have only one proton per dithizonato ligand that can be removed upon oxidation during **Wave 1** (**Figure 3.24**, Scheme 3.8), rather than a disulphide bridge.

Reversal of the dithizonato oxidation process takes place during the cathodic scan at -340 mV (**Wave II**), at a scan rate of 400 mV s^{-1}, Table 3.20. This process regenerate the original dithizonato ligand in an electrochemical irreversible step. For the reduction of PhHgHDz **19** a single wave, **Wave III** at -850 mV vs Fc/Fc^+, corresponds to dithizonato ligand reduction to give $PhHgHDz^-$, as shown in Scheme 3.8. An additional one-electron reduction process takes place at -1656 mV (**Wave IV**). In analogy to the free ligand this process probably generates H_3Dz^- anionic ligands while still coordinated to PhHg(II).

Re-oxidation of the fully reduced species, $PhHgH_2Dz^-$, at **Wave 3** (*ca.* -1292 mV) is followed by oxidation of the intermediate species, $PhHgH_2Dz \leftrightarrow PhHgHDz^-$, at **Waves 4a & 4b** (-704 & -422 mV) to reform **19**. **Wave 3** was not as well resolved as **Waves 4a & 4b**. Electrochemical data for all the described processes are summarized in Table 3.20. All the above redox processes are electrochemically irreversible because ΔE values are substantially larger than 59 mV.[96]

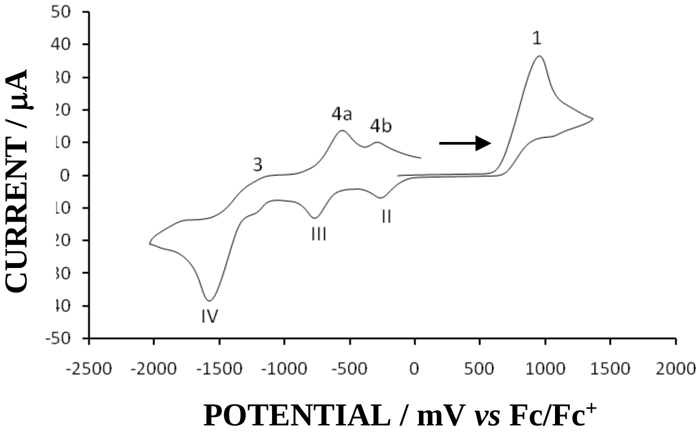


Figure 3.24

Cyclic voltammogram of 1 mM **PhHgHDz** recorded at a scan rate of 400 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane. Scan direction is as indicated.

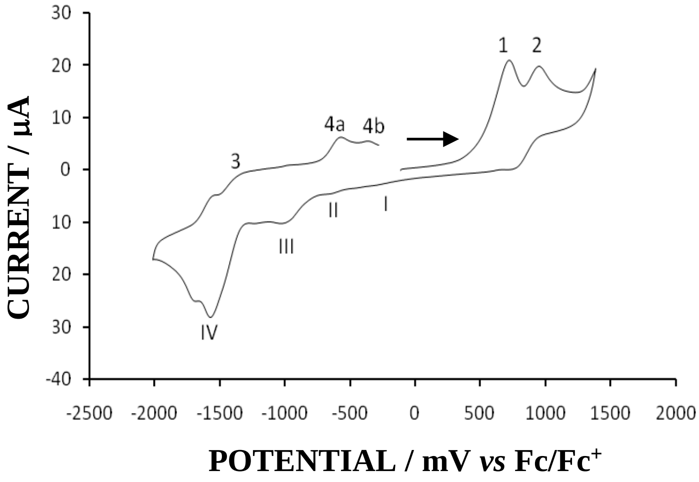


Figure 3.25

Cyclic voltammogram of 1 mM, **PhHg(*o*-OCH$_3$)HDz** recorded at a scan rate of 400 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane. Scan direction is as indicated.

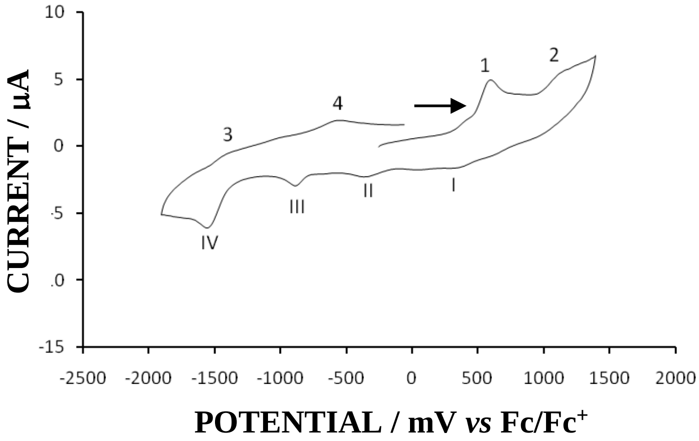


Figure 3.26

Cyclic voltammogram of 1 mM, **PhHg(Naph)HDz** recorded at a scan rate of 400 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane. Scan direction is as indicated.

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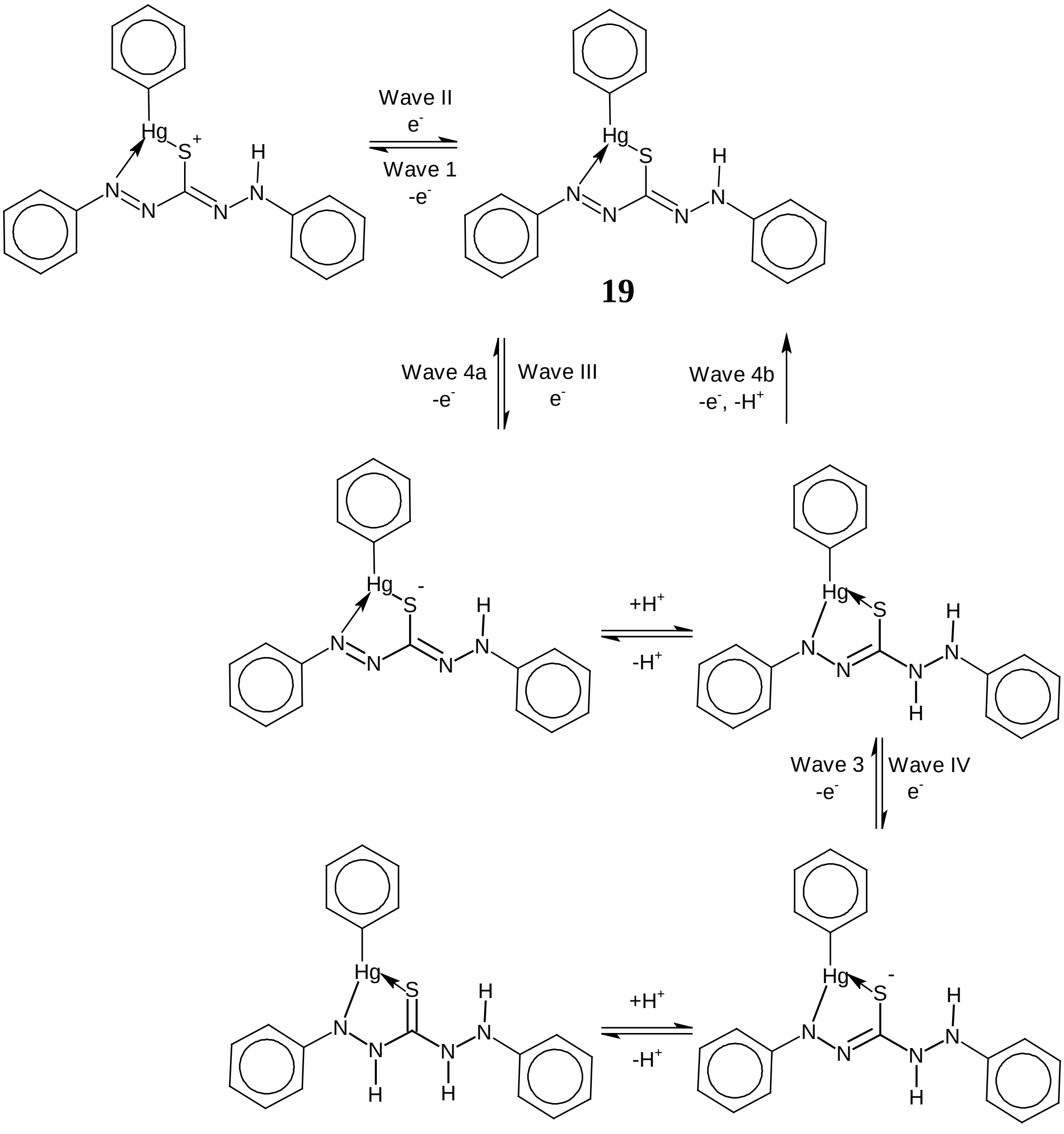
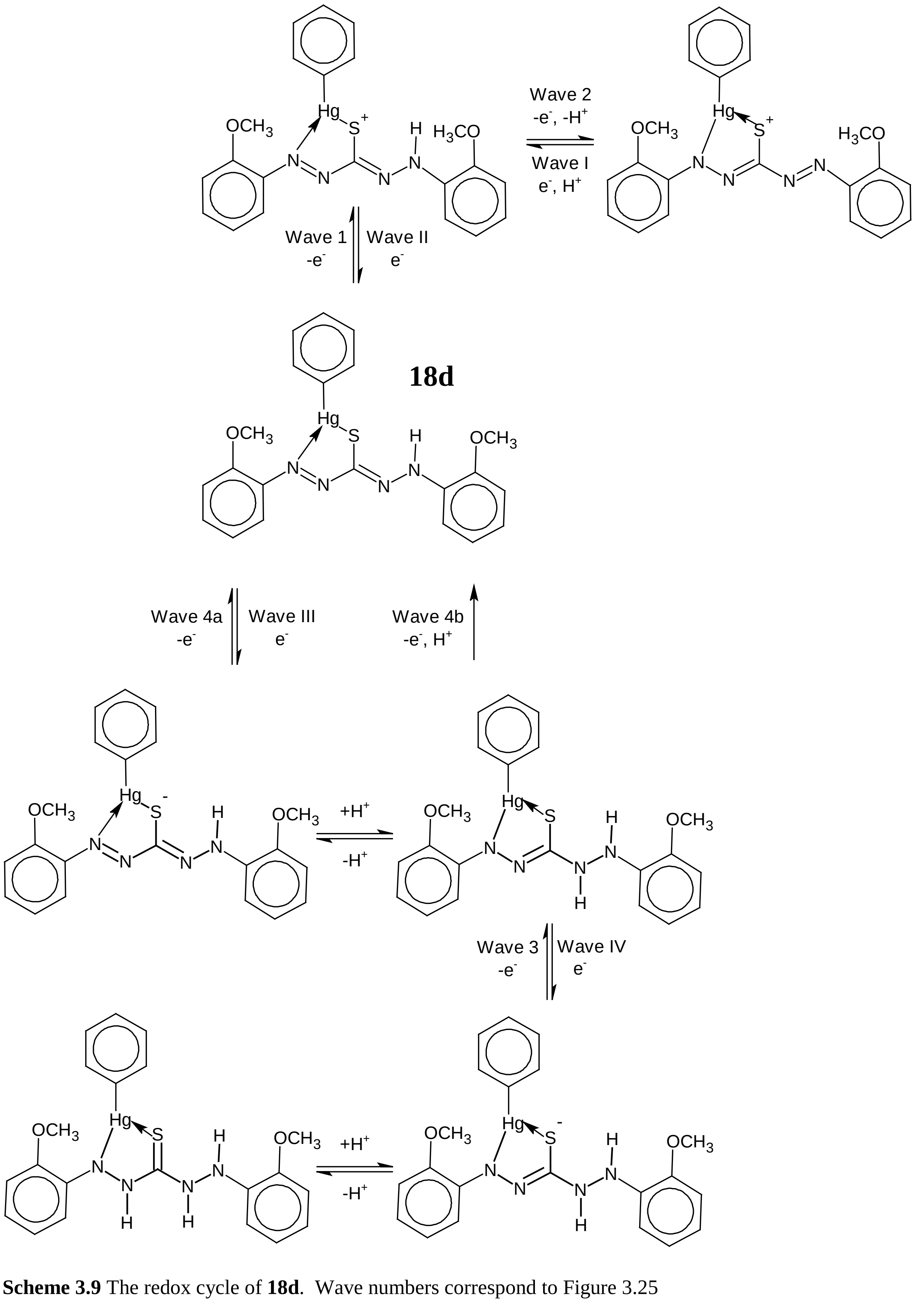
[96] H. J. Gericke, N. I. Barnard, E. Erasmus, J. C. Swarts, M. J. Cook and M A. S. Aquino, *Inorg. Chim. Acta,* 2010, **363**, 2222.



Scheme 3.8 The redox cycle of dithizonatophenylmercury(II). Wave numbers correspond to Figure 3.24.

The redox cycle (Figure 3.25) of PhHg(*o*-OMe)HDz **18d** differs mainly from that of **19** in that two initial oxidation waves are observed, implying the loss of two electrons and inevitably also one proton, as indicated in Scheme 3.9. **Wave 1** agrees with what is seen for **19** above, although as expected, at the much lower potential of 504 mV.

With the second oxidation wave, at 774 mV, the backbone imine proton is expected to dissociate from the complex cation, with simultaneous loss of a second electron. On basis of the relatively fast CV time scale, and in line with the proposed free ligand oxidation scheme (see Scheme 3.6) ring closure may most probably be ruled out for the complex as well. The effect of the electron-donating methoxy groups here is to shift the otherwise higher second oxidation wave to within the observable window that is electrochemically allowed by the dichloromethane solvent.



Scheme 3.9 The redox cycle of **18d**. Wave numbers correspond to Figure 3.25

Due to the two initial oxidation steps taking place **18d** is expected to have an additional reduction wave as well, which is indeed seen, although poorly resolved. Through **Waves I** & **II** (-408 & -780 mV) the original neutral parent compound **18d** is retrieved. These waves lie, as expected, at lower potentials than the corresponding wave for **19** (**Wave II** at -340 mV), since higher electron density on the **18d** ligand resists reduction. **Waves III** & **IV** (-1102 & -1698 mV) correspond to similar processes as described for **19** (also marked **III** & **IV**). The same is true for re-oxidation **Waves 3** & **4**. No proposal may as yet be made with regard to the almost-reversible redox process observed immediately to the left (lower potential) of **Wave IV**.

The last complex to be considered is PhHg(α-Naphthyl)HDz, the cyclic voltammogram of which is shown in Figure 3.26. This CV resembles the PhHg(*o*-OCH_3)HDz CV more closely than that of PhHgHDz, as also here additional oxidation and reduction waves are observed. Based on the fact that the naphthyl and *ortho*-methoxy complexes have the lowest $\mathbf{E_1}$ values (Figure 3.23, Table 3.20), their close resemblance is expected. As for PhHg(α-Naphthyl)HDz, its second oxidation wave is notably higher, namely at 1276 mV, which almost coincides with the upper border of what is observable within the dichloromethane CV window. The first reduction **Wave I** lies also higher, at 68 mV, implying a much less stable PhHg(α-Naphthyl)Dz^+ second oxidation species. Lastly it may be noted that at oxidation **Wave 4**, no proton equilibrium appears to be present, however, these waves are poorly resolved and not much may be concluded from this observation.

Figure 3.27 shows cyclic voltammograms performed at different scan rates, 100 – 500 mV s^{-1}, as was done for all the free ligands and complexes here presented. The *ortho*-methoxy derivatives alone are shown here, with the rest given in the Supporting Information. As all potentials are referenced against ferrocene, a typical CV that includes ferrocene is also shown for each of the data sets below. Corresponding corrections based on the ferrocene reduction potential was $E^0(Fc/Fc^+)$ vs. Ag/$AgNO_3$ = 274 mV. No Oster Young Square Wave or Linear Sweep voltammograms were performed, as it was already proven that individual dithizone redox waves relate to single electron transfers.[72]

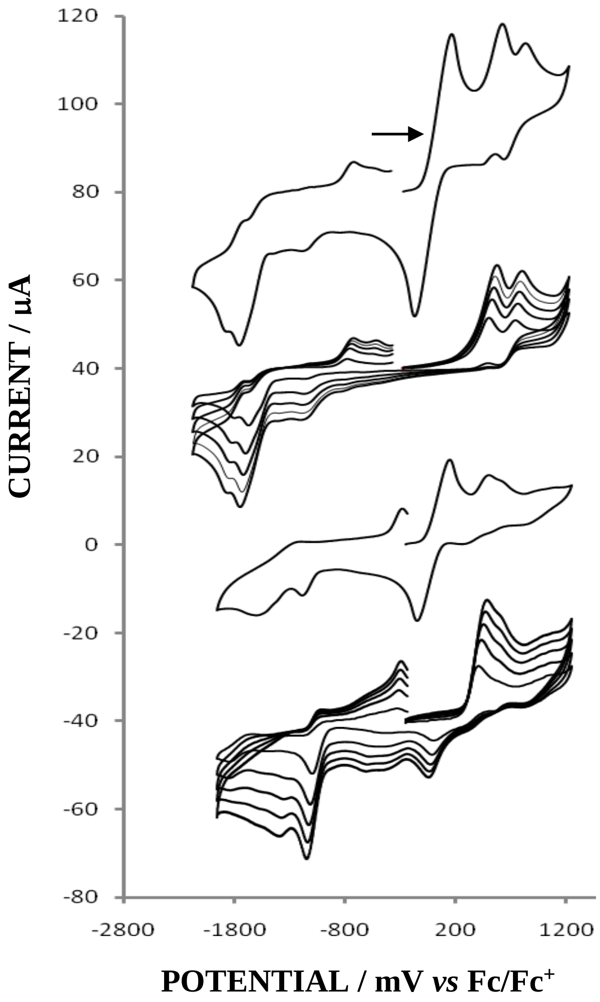


Figure 3.27 Cyclic voltammograms recorded at scan rates 100, 200, 300, 400 and 500 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode at 25 °C, in dichloromethane, of 1 mM of PhHg(*o*-OCH_3)HDz (top) and (*o*-OCH_3)H_2Dz (bottom). All cyclic voltammograms are referenced against ferrocene as internal standard. Scan direction is as indicated.

The UV/visible absorption of a molecule corresponds mainly to excitation of an electron from the HOMO into the LUMO, whereas electro-oxidation corresponds only to the removal of an electron from the HOMO. A correlation might thus be drawn between oxidation and the HOMO energy and the reduction potential and the LUMO energy.

Figure 3.28 shows the relation between the experimental oxidation potential and the calculated HOMO energy, left, as well as the relation between the experimental reduction potential and the calculated LUMO energy, right, of the series of dithizonatophenylmercury(II) complex derivatives, the data in Table 3.18 gives these values. The correlation between the experimental oxidation potential and the calculated HOMO energy of the complexes gives a much better comparison then that of the experimental reduction and calculated LUMO energies, with R^2 values of 0.8895 and 0.5378 respectively. The poor relation between E_{II} (reduction) and E (LUMO) may be ascribed to the electrochemically irreversible nature of these complexes. The extra oxidation wave observed for the complex in Figure 3.27 (top) may also play a role in the value of E_{II} (reduction) as obtained here after E_I (reduction). The good relationship between E_1 (Oxidation) and E (HOMO) enable us to design complexes with a specific oxidation potential.

Table 3.18 Experimental and theoretical data for dithizonatophenylmercury(II) and its derivatives, PhHg(R)HDz, with R being the substituent.

R	λ_{max}	HOMO (kcal mol^{-1})	LUMO (kcal mol^{-1})	E_1 (mV)	E_I (mV)	E_{II} (mV)
H	471	-116.36	-80.95	846	-	-340
***o*-CH$_3$**	467	-114.31	-78.14	726	-408	-938
***m*-CH$_3$**	480	-113.82	-78.92	731	-393	-881
***p*-CH$_3$**	486	-112.04	-77.65	624	-488	-948
***o*-OCH$_3$**	505	-107.78	-75.08	504	-408	-780
***m*-OCH$_3$**	485	-113.63	-78.05	721	-373	-805
α-naphthyl	509	-112.63	-81.32	592	-68	-280
***o*-F**	471	-118.65	-84.24	-	-	-
***m*-F**	472	-122.21	-87.31	-	-	-
***p*-F**	471	-118.82	-84.07	-	-	-

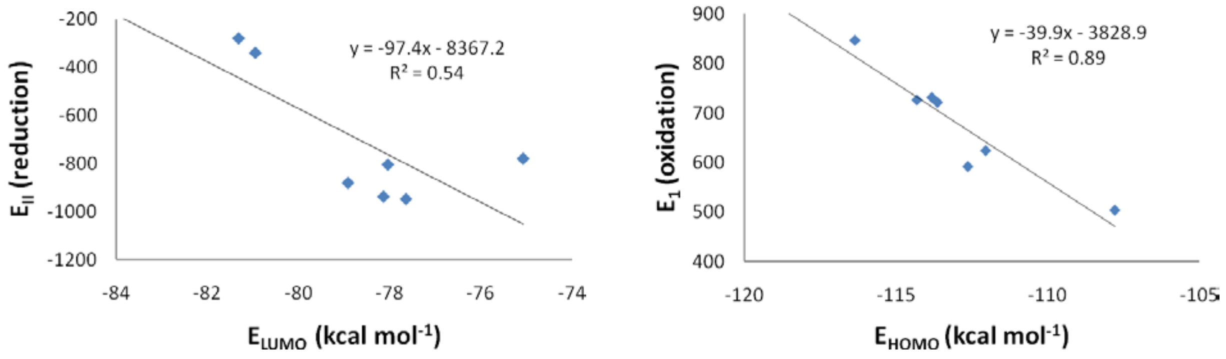


Figure 3.28 Correlation between the experimental oxidation and calculated HOMO energies and the experimental reduction and calculated LUMO energies. R^2 values are indicated.

It may therefore be concluded that for dithizonatophenylmercury(II) and its derivatives the experimental oxidation potentials relates to calculated HOMO energies, and the experimental reduction potentials relates to calculated LUMO energies, although the latter does not correlate as well, as seen in the R^2 value. This relation will make it possible to predict the first oxidation potential and possibly also to determine if a dithizonato complex derivative will be photochromic or not.

Table 3.19 Cyclic voltammetry data obtained from voltammograms (*vs* Fc/Fc$^+$) of **dithizone** and its derivatives (R)H$_2$Dz (R is the substituent), in CH$_2$Cl$_2$/0.1 mol dm^{-3} [NBu$_4$][B(C$_6$F$_5$)$_4$] with a glassy carbon working electrode at 25 °C. Scan rates (ν), cathodic and anodic peak potentials (E) are given. The values in italics are estimated.

		Oxidation and Re-oxidation potentials					
R	**mV s^{-1}**	**E$_1$**	**E$_2$**	**E$_{2a}$**	**E$_{2b}$**	**E$_3$**	**E$_4$**
H	**100**	571	987	-	-	-939	-405
	200	573	987	-	-	-855	-401
	300	617	1017	-	-	-893	-395
	400	639	1023	-	-	-929	-371
	500	-	-	-	-	-879	-449
***o*-OCH$_3$**	**100**	405	-	*637*	*943*	*-1023*	-361
	200	435	-	*627*	*963*	*-1067*	-335
	300	451	-	*631*	*963*	*-1057*	-335
	400	473	-	*641*	*991*	*-1067*	-331
	500	489	-	*639*	*991*	*-1073*	-323
***m*-OCH$_3$**	**100**	609	-	671	*1113*	-935	-349
	200	603	-	725	*1097*	-959	-323
	300	597	-	741	*1107*	-973	-323
	400	613	-	737	*1113*	-973	-309
	500	607	-	735	*1105*	-973	-309
***o*-CH$_3$**	**100**	684	970	-	-	*-1334*	-380
	200	698	1002	-	-	*-1334*	-362
	300	712	1016	-	-	*-1334*	-348
	400	700	1016	-	-	*-1068*	-350
	500	700	1030	-	-	*-1068*	-350
***m*-CH$_3$**	**100**	483	-	705	1031	*-953*	-429
	200	519	-	725	1051	*-993*	-385
	300	525	-	701	1051	*-997*	-391
	400	577	-	715	1067	*-1001*	-391
	500	557	-	721	1077	*-1001*	-377
***p*-CH$_3$**	**100**	622	898	-	-	*-992*	-412
	200	642	934	-		*-1014*	-386
	300	632	962	-	-	*-960*	*-372*
	400	638	954	-	-	*-962*	*-372*
	500	670	982	-	-	*-1018*	-358
3,4-(CH$_3$)$_2$	**100**	432	-	600	916	*-1010*	-380
	200	480	-	618	916	*-1042*	-346
	300	486	-	626	918	*-1076*	-342
	400	524	-	636	928	*-1092*	-328
	500	516	-	654	928	*-1082*	-324
***o*-F**	**100**	735	1267	-	-	*-801*	-303
	200	795	1335	-	-	*-805*	-237
	300	857	1453	-	-	*-805*	-181
	400	917	1489	-	-	*-805*	-163
	500	903	1531	-	-	*-805*	-143
***m*-F**	**100**	683	1155	-	-	*-1829*	-321
	200	737	1207	-	-	*-1845*	-311
	300	757	1249	-	-	*-1857*	-233
	400	765	1281	-	-	*-1855*	-243
	500	779	1287	-	-	*-1835*	-217
***p*-F**	**100**	543	1015	-	-	*-937*	-479
	200	601	1045	-	-	*-957*	-445
	300	673	1079	-	-	*-957*	-421
	400	723	1097	-	-	*-957*	-407
	500	730	1117	-	-	*-957*	-361

		Reduction potentials										
R	**mV s^{-1}**	**E_{I}**	**E_{II}**	**E_{IIa}**	**E_{IIb}**	**E_{III}**	**E_{IIIa}**	**E_{IIIb}**	**E_{IV}**	**E_{IVa}**	**E_{IVb}**	**E_{V}**
H	**100**	31	-663	-	-	-937	-	-	-1285	-	-	-
	200	1	-683	-	-	-949	-	-	-1289	-	-	-
	300	-3	-673	-	-	-957	-	-	-1295	-	-	-
	400	-37	-733	-		-977	-	-	-1315	-	-	-
	500	-	-	-	-	-	-	-	-		-	-
***o*-OCH₃**	**100**	1	*-401*	-	-	-	-	-	-1073	-	-	-
	200	-45	*-429*	-	-	-	-	-	-1089	-	-	-
	300	-53	*-421*	-	-	-565	-	-	-1011	-	-	-
	400	-35	*-429*	-	-	-577	-	-	-1111	-	-	-
	500	-49	*-421*	-	-	-587	-	-	-1127	-	-	-
***m*-OCH₃**	**100**	-	-407		-	-999	-	-	-	*-1297*	*-1399*	-
	200	-43	-389	-	-	-1017	-	-	-	-1267	*-1389*	-
	300	-53	-395	-	-	-1025	-	-	-	-1283	-1367	-
	400	-67	-389	-	-	-1033	-	-	-	-1287	-1367	-
	500	-67	-399	-	-	-1037	-	-	-	-1293	-1385	-
***o*-CH₃**	**100**	84	*-864*	-	-	-1034	-	-	-	*-1344*	*-1466*	-
	200	82	*-798*	-	-	-1046	-	-	-	*-1378*	*-1488*	-
	300	94	*-810*	-	-	-1056	-	-	-	*-1382*	*-1506*	-
	400	32	*-842*	-	-	-1080	-	-	-	*-1348*	*-1472*	-
	500	28	*-838*	-	-	-1078	-	-	-	*-1348*	*-1460*	-
***m*-CH₃**	**100**	*27*	*-791*	-	-	-1013	-	-	-	-	-1383	-
	200	*1*	*-765*	-	-	-1033	-	-	-	-1267	-1401	-
	300	*-37*	*-775*	-	-	-1069	-	-	-	-1291	-1387	-
	400	*-55*	*-785*	-	-	-1069	-	-	-	-1291	-1393	-
	500	*-63*	*-789*	-	-	-1083	-	-	-	-1301	-1403	-
***p*-CH₃**	**100**	*10*	*-762*	-	-	-1056	-	-	-	-	-	-
	200	*-6*	*-780*	-	-	-1070	-	-	-	-	-1394	-
	300	*-50*	*-782*	-	-	-1083	-	-	-	-	-	-
	400	*-62*	*-790*	-	-	-1090	-	-	-	-	-	-
	500	*-78*	*-820*	-	-	-1114	-	-		-1328	-1432	-
3,4-(CH₃)₂	**100**	-30	-406	-	-	-	-	-	-1102	-	-	-1514
	200	-30	-482	-	-	-836	-	-	-1118	-	-	-1552
	300	-52	-490	-	-	-850	-	-	-1134	-	-	-1578
	400	-64	-496	-	-	-850	-	-	-1152	-	-	-1598
	500	-78	-504	-	-	-868	-	-	-1150	-	-	-1600
***o*-F**	**100**	61	-	-	-	-881	-	-	-	-	-	-
	200	41	-603	-	-	-871	-	-	-	-1315	-1483	-
	300	29	-645	-	-	-963	-	-	-	-955	-1337	-
	400	-51	-699	-	-	-963	-	-	-	-1421	-1551	-
	500	-89	-733	-	-	-959	-	-	-	-1455	-1593	-
***m*-F**	**100**	-27	-	-	-539	-	-827	-1127	-	-1429	-1723	-
	200	-11	-	-455	-561	-	-849	-1157	-	-1435	-1749	-
	300	-99	-	-461	-571	-	-801	-1173	-	-1461	-1755	-
	400	-95	-	-455	-571	-	-807	-1183	-	-1455	-1765	-
	500	-99	-	-	-565	-	-837	-1165	-	-1445	-1759	-
***p*-F**	**100**	35	-	-	-	-1007	-	-	-	-	-1595	-
	200	-69	-	-399	-679	-1031	-	-	-	-1329	-1613	-
	300	-113	-	-477	-691	-1047	-	-	-	-1349	-1639	-
	400	-143	-	-537	-705	-1051	-	-	-	-1369	-1643	-
	500	-147	-	-533	-699	-1051	-	-	-	-1367	-1667	-

Oxidation, reduction and Re-oxidation potentials

R	**mV s^{-1}**	**E_{1}**	**E_{2}**	**E_{I}**	**E_{II}**	**E_{III}**	**E_{IV}**	**E_{V}**	**E_{VIa}**	**E_{VIb}**	**E_{3}**	**E_{4}**	**E_{5}**
α-Naphthyl	**100**	458	900	390	-	-	-418	-938	-	-1438	*-1374*	*-846*	*-368*
	200	488	930	484	32	-144	-518	-968	-1192	-1444	*-1288*	*-856*	*-334*
	300	504	950	468	-2	-204	-616	-986	-1218	-1480	*-1276*	*-832*	*-318*
	400	552	960	462	-18	-264	-624	-990	-1238	-1506	*-1310*	*-856*	*-308*
	500	530	972	458	-32	-302	-650	-1024	-1256	-1536	*-1280*	*-884*	*-209*

Table 3.20 Cyclic voltammetry data obtained from voltammograms (*vs* Fc/Fc$^+$) of **dithizonatophenylmercury(II)** and its derivatives, PhHg(R)HDz (R is the substituent), in CH_2Cl_2/0.1 mol dm^{-3} [NBu_4][$B(C_6F_5)_4$] with a glassy carbon working electrode at 25 °C. Scan rates (ν), cathodic and anodic peak potentials (E) are given. Values in italics are estimated.

R	mV s^{-1}	Oxidation, reduction and Re-oxidation potentials								
		E_1	E_2	E_I	E_{II}	E_{III}	E_{IV}	E_3	E_{4a}	E_{4b}
H	**100**	718	-	-	-284	-774	-1554	*-1278*	-770	-446
	200	768	-	-	-314	-810	-1594	*-1266*	-730	-452
	300	794	-	-	-334	-836	-1640	*-1282*	-714	-436
	400	846	-	-	-340	-850	-1656	*-1292*	-704	-422
	500	840	-	-	-350	-856	-1686	*-1302*	-684	-422
***o*-OCH₃**	**100**	474	704	*-404*	-794	-1112	-1634	*-1488*	-812	-
	200	498	724	*-408*	-754	-1106	-1668	*-1488*	-782	-566
	300	514	740	*-408*	-770	-1106	-1688	*-1494*	-776	-550
	400	504	774	*-408*	-780	-1102	-1698	*-1434*	-760	-546
	500	544	770	*-414*	-790	-1160	-1716	*-1494*	-754	-546
***m*-OCH₃**	**100**	635	-	-339	-821	-1493	-	*-1443*	-665	-
	200	659	-	-343	-801	-1499	-	*-1459*	-675	-
	300	675	-	-359	-811	-1521	-	*-1459*	-661	-429
	400	721	-	-393	-805	-1539	-	*-1439*	-651	-419
	500	709	-	-383	-811	-1533	-	*-1489*	-653	-425

R	mV s^{-1}	Oxidation, reduction and Re-oxidation potentials											
		E_1	E_2	E_I	E_{II}	E_{III}	E_{IIIa}	E_{IIIb}	E_{IV}	E_3	E_4	E_{4a}	E_{4b}
***o*-CH₃**	**100**	630	-	-	-876	-	-1594	-1728	-	*-1042*	-	-	-
	200	660	-	-	-880	-	-1634	-1764	-	*-1014*	-494	-	-
	300	670	-	-	-910	-	-1668	-1768	-	*-1026*	-480	-	-
	400	726	-	-	-938	-	-1680	-1798	-	*-1020*	-464	-	-
	500	718	-	-	-976	-	-1698	-1824	-	*-1002*	-460	-	-
***m*-CH₃**	**100**	629	-	-339	-825	-1593	-	-	-	*-1029*	-	-595	-415
	200	665	-	-353	-855	-1599	-	-	-	*-1009*	-	-545	-409
	300	685	-	-373	-871	-1633	-	-	-	*-1011*	-	-527	-395
	400	731	-	-393	-881	-1649	-	-	-	*-1019*	-	-511	-379
	500	709	-	-403	-901	-1679	-	-	-	*-1045*	-	-479	-371
***p*-CH₃**	**100**	524	-	-498	-910	-1628	-	-	-	*-1045*	-494	-	-
	200	534	-	-494	-896	-1692	-	-	-	*-1045*	-434	-	-
	300	580	-	-494	-946	-1742	-	-	-	*-1045*	-512	-	-
	400	624	-	-488	-948	-1698	-	-	-	*-1045*	-494	-	-
	500	594	-	-464	-940	-1704	-	-	-	*-1045*	-490	-	-
α-Naphthyl	**100**	538	1234	-	-	-	-	-	-1404	*-1284*	-	-	-
	200	552	1252	24	-252	-780	-	-	-1434	*-1382*	*-612*	-	-
	300	558	1276	-26	-276	-800	-	-	-1458	*-1458*	*-634*	-	-
	400	592	1276	-68	-280	-814	-	-	-1470	*-1410*	*-650*	-	-
	500	576	1288	-80	-294	-822	-	-	-1480	*-1382*	*-626*	-	-

4. Experimental

4.1. Introduction

Experimental procedures, reaction conditions and techniques used during the course of this investigation are reported in this chapter.

4.2. Materials

Solid and liquid reagents were purchased from Sigma-Aldrich, and used without further purification. UniLAB grade solvents were purchased from Merck. Double-distilled water was used where necessary. Melting points (uncorrected) of products were determined with an Olympus BX51 polarized microscope, fitted with a LINKAM THRM 600 heating stage. The upper temperature limit of this instrument is 300 °C.

4.3. Spectrometry

Nuclear magnetic resonance ^1H spectra were recorded on a 300 MHz Bruker Avance DPX NMR spectrometer, at 298 K. Chemical shifts are reported relative to $SiMe_4$ (0 ppm). Spectral processing was done by means of the MestReNova v. 5.3.0.4469 NMR software for Windows. Ultraviolet and visible spectra were recorded on a Varian Cary 50 UV/visible spectrophotometer. Spectra were drawn from dilute solutions in quartz cuvettes. All relevant compounds obey Beer's law at the experimental concentrations utilized. Spectral processing was done with Microsoft Excel.

4.4. Electrochemistry

Measurements on *ca* 1.0 mM solutions of the ligands and complexes in dry air-free dichloromethane containing 100 times excess of tetrabutylammonium tetrakis(pentafluorophenyl)borate as supporting electrolyte were conducted under a blanket of purified argon at 25°C utilizing a BAS 100 B/W electrochemical workstation interfaced with a personal computer. A three electrode cell, using a Pt auxiliary electrode, a glassy carbon working electrode (surface area 0.0707 cm^2) and an in-house constructed $Ag/AgNO_3$ reference electrode were employed. Temperatures were kept constant to within 0.5 °C. Experimental potentials were referenced against the $Ag/AgNO_3$ reference electrode, but results presented are referenced against ferrocene as an internal standard, according to internationally accepted IUPAC standards. To achieve this, each experiment was performed first in the absence of ferrocene and then repeated in the presence of < 1 mM ferrocene. Data was manipulated on a Microsoft Excel worksheet to set the formal reduction potentials of Fc/Fc^+ couple at 0 V.

4.5. Synthesis

4.5.1. Dithizone Derivatives

4.5.1.1. *ortho*-Methoxydithizone, (*o*-$OCH_3PhNHN)_2CS$

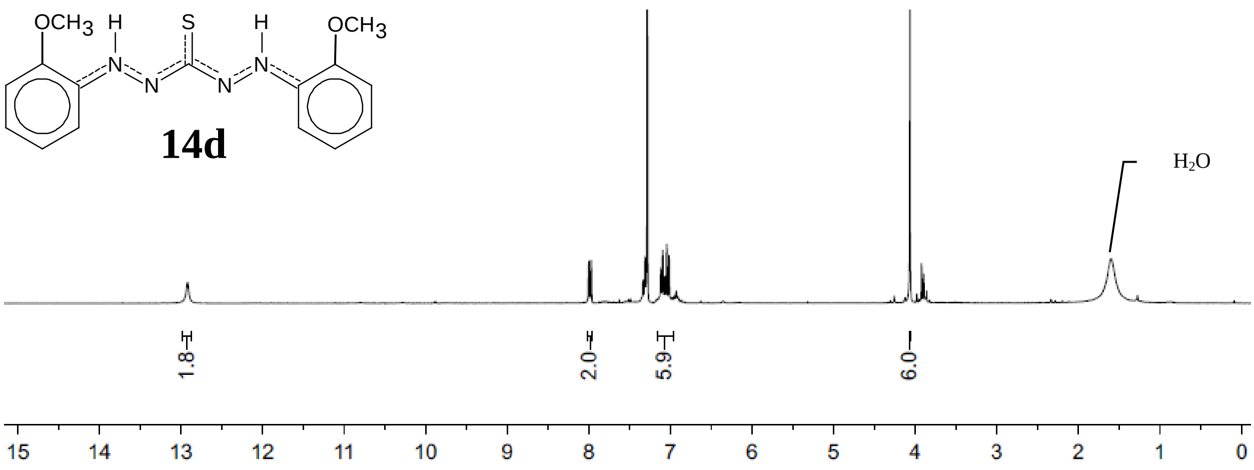
Nitroformazan: In a 100 ml beaker, *ortho*-methoxy aniline (3.0126 g, 24.46 mmol) was added to a mixture of concentrated hydrochloric acid (13 ml) and water (25 ml) and cooled to -10 ^{o}C on a cold plate while stirring. Sodium nitrite (2.5316 g, 36.69 mmol) dissolved in water (5 ml) was slowly added. In a 500 ml beaker the diazo solution was added to a mixture of sodium acetate trihydrate (40 g), glacial acetic acid (25 ml) and water (10 ml) and stirred at room temperature for 5 minutes. Nitromethane (7.4627 g, 122.3 mmol) was added and stirred for 1 hour, followed by 400 ml of water and stirring for another 30 minutes. The precipitate was filtered with a Buchner funnel and washed with copious amounts of water. The nitroformazan solid was dried over night in an oven at 70 °C. (2.767 g, 69 %)

Thiocarbazone: The nitroformazan (1.5012 g, 4.5585 mmol) was dissolved in a mixture of absolute ethanol (90 ml) and ammoniumsulfide solution (10 ml) in a 250 ml stoppered round bottom flask and stirred for 1 hour. After reduction was complete the red solution was added to a water/ice mixture (500 ml). The dirty-white/yellow carbazide was filtered off on a Buchner funnel containing silica gel (better filtration) and washed with water. The unstable thiocarbazide was immediately oxidized to the dark red thiocarbazone by the addition of cold 2 % methanolic potassium hydroxide (50 ml). Stirring was continued until complete dissolution.

Dithizone: The dark green dithizone derivative was precipitated by the addition of the thiocarbazone to dilute hydrochloric acid (1 %, 100 ml). The product was filtered and again precipitated from an alcoholic alkali solution to which diluted hydrochloric acid was added.

The crude product sample was dissolved in DCM and passed through a short silica column using toluene as eluent. A yellow impurity ran ahead of the green product band, while some impurities stayed behind at the origin. Alternatively, instead of running a column, repeating the aforementioned precipitation procedure five times, yielded pure (0.3 g, 22.7 %) *ortho*-methoxydithizone, as monitored by the use of TLC plates and NMR spectroscopy.

M.p. 178 – 179 °C, λ_{max}/nm (dichloromethane) 468 & 644, δ_H (300 MHz, $CDCl_3$)/ppm: 4.00 (6 H, s, $OC\underline{H}_3$), 6.97 – 7.17 (6 H, m, 2 × $C_6\underline{H}_4$), 7.95 – 8.02 (2 H, d, 2 × $C_6\underline{H}_4$), 12.92 (2H, s, 2 × $N\underline{H}$). (See NMR spectrum on page here following.)



14d

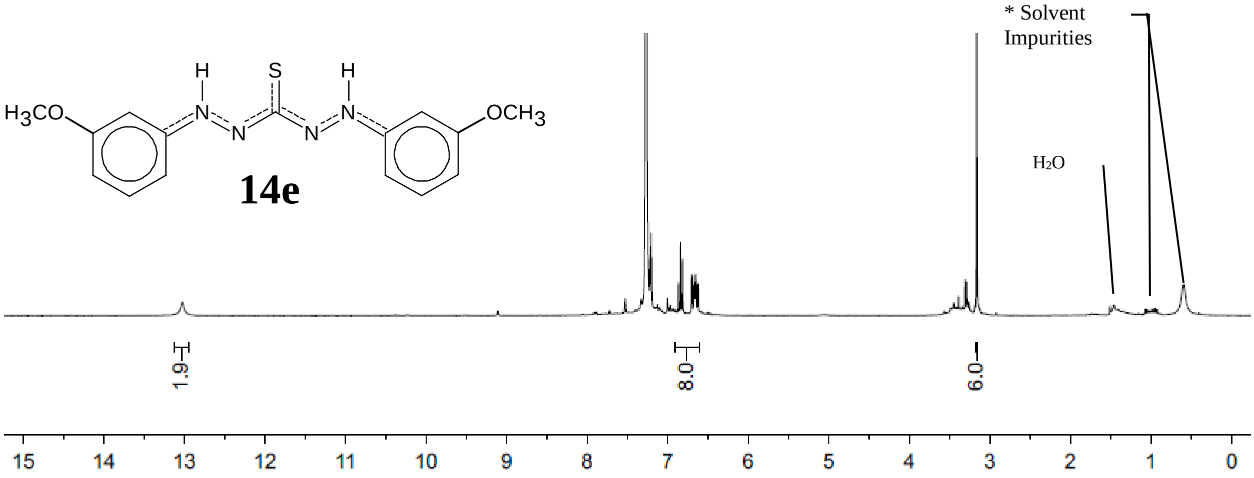
4.5.1.2. *meta*-Methoxydithizone, (*m*-$OCH_3PhNHN)_2CS$

Synthetic procedure as for *ortho*-methoxydithizone (4.5.1.1)

Nitroformazan yield, 2.6 g (76 %)

Dithizone yield, 0.3 g (24 %) 1.1 g of nitroformazan reagent was used.

M.p. 148 - 149 °C, λ_{max}/nm (dichloromethane) 463 & 627, δ_H (300 MHz, C_6D_6)/ppm: 3.17 (6 H, s, 2 × $OC\underline{H}_3$), 6.60 – 6.92 (8 H, m, 2 × $C_6\underline{H}_4$), 13.03 (2H, s, 2 × $N\underline{H}$)



14e

* Typical water and solvent impurities in new deuterated chloroform are seen below 2 ppm. For clarity sake this part of the spectrum is henceforth omitted.

4.5.1.3. *para*-Methoxydithizone, (*p*-$OCH_3PhNHN)_2CS$

Synthetic procedure as for *ortho*-methoxydithizone (4.5.1.1)

Nitroformazan yield, 2.1 g (47 %)

Dithizone yield, 0 g (0 %) 1.0 g of nitroformazan reagent was used.

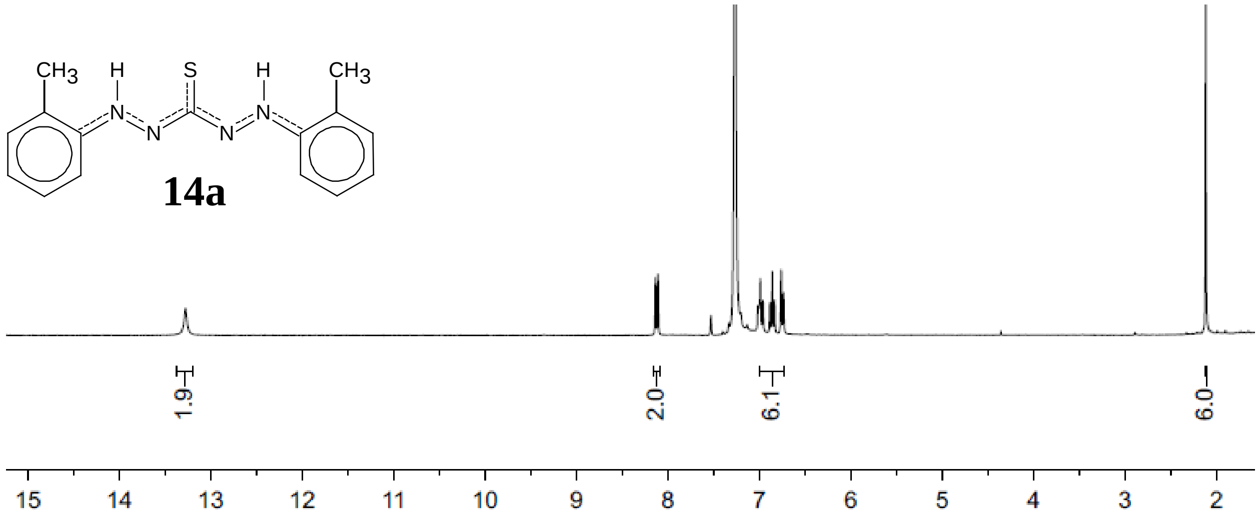
4.5.1.4. *ortho*-Methyldithizone, (*o*-$CH_3PhNHN)_2CS$

Synthetic procedure as for *ortho*-methoxydithizone (4.5.1.1)

Nitroformazan yield, 3 g (44 %)

Dithizone yield, 0.07 g (13.3 %) 1.1 g of nitroformazan reagent was used.

M.p. 162.8 °C, λ_{max}/nm (dichloromethane) 461 & 625, δ_H (300 MHz, C_6D_6)/ppm: 2.12 (6 H, s, 2 × $C\underline{H}_3$), 6.72 – 6.99 (6 H, m, 2 × $C_6\underline{H}_4$), 8.09 – 8.16 (2 H, d, 2 × $C_6\underline{H}_4$), 13.28 (2H, s, 2 × $N\underline{H}$).



14a

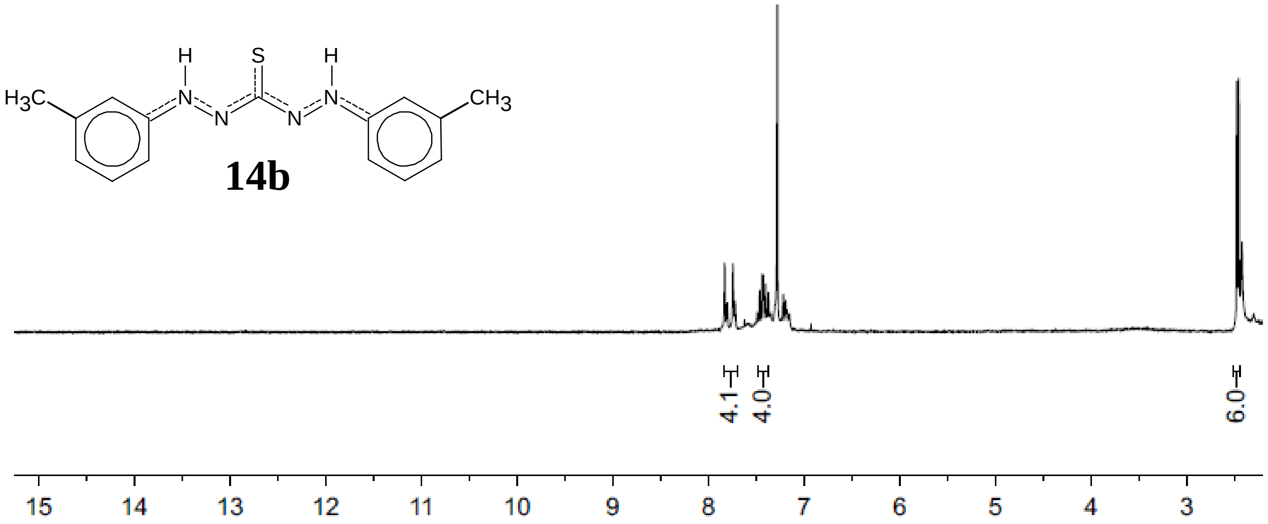
4.5.1.5. *meta*-Methyldithizone, (*m*-$CH_3PhNHN)_2CS$

Synthetic procedure as for *ortho*-methoxydithizone (4.5.1.1)

Nitroformazan yield, 2.9 g (83 %)

Dithizone yield, 0.3 g (35 %) 1 g of nitroformazan reagent was used.

M.p. 149 - 151 °C, λ_{max}/nm (dichloromethane) 452 & 617, δ_H (300 MHz, $CDCl_3$)/ppm: 2.46, 2.48 (6 H, d, 2 × $C\underline{H}_3$), 7.37 – 7.49 (4 H, m, 2 × $C_6\underline{H}_4$), 7.70 – 7.85 (4 H, dd, 2 × $C_6\underline{H}_4$).



14b

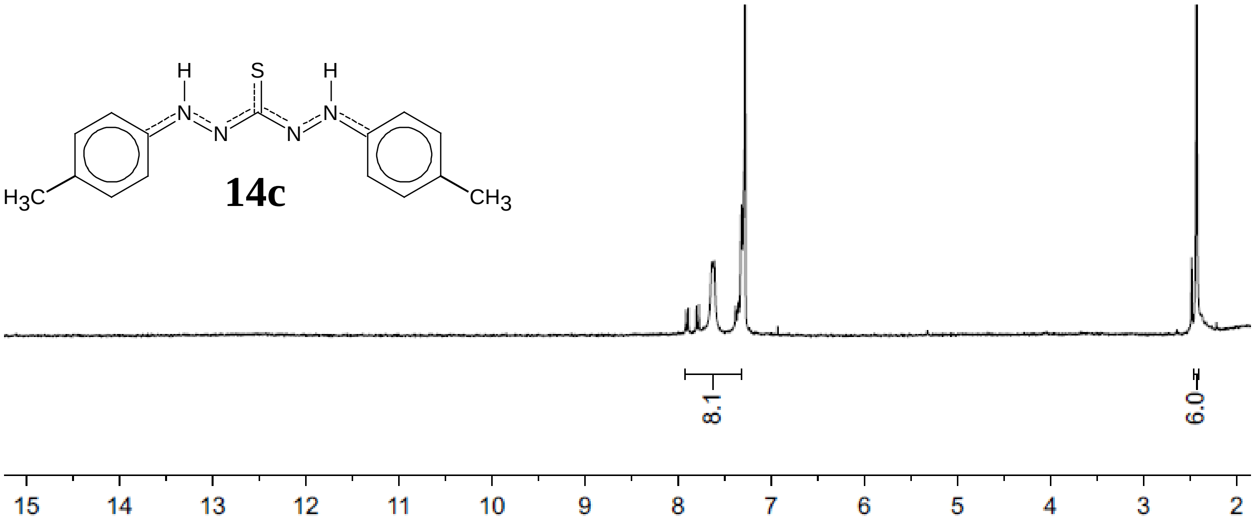
4.5.1.6. *para*-Methyldithizone, (*p*-$CH_3PhNHN)_2CS$

Synthetic procedure as for *ortho*-methoxydithizone (4.5.1.1)

Nitroformazan yield, 2.3 g (67 %)

Dithizone yield, 0.01 g (1.5 %) 1 g of nitroformazan reagent was used.

M.p. 98 - 103 °C, λ_{max}/nm (dichloromethane) 456 & 623, δ_H (300 MHz, $CDCl_3$)/ppm: 2.43 (6 H, s, 2 × $C\underline{H}_3$), 7.32 – 7.92 (8 H, m, 2 × $C_6\underline{H}_4$).



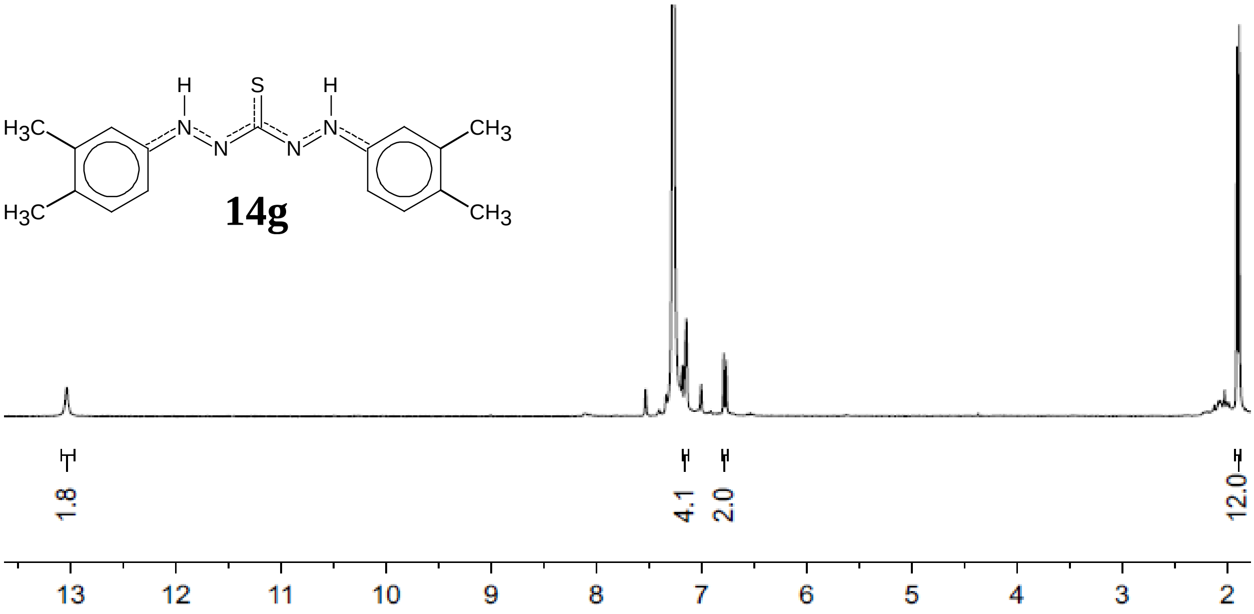
4.5.1.7. 3,4-Dimethyldithizone, (3,4-$CH_3PhNHN)_2CS$

Synthetic procedure as for *ortho*-methoxydithizone (4.5.1.1)

Nitroformazan yield, 4.8 g (72 %)

Dithizone yield, 0.005 g (3.2 %) 0.5 g of nitroformazan reagent was used.

M.p. 129 - 131 °C, λ_{max}/nm (dichloromethane) 461 & 629, δ_H (300 MHz, C_6D_6)/ppm: 1.89-1.91 (12 H, d, 4 × $C\underline{H}_3$), 6.76 - 6.79 (2H, d, 2 × $C_6\underline{H}_3$), 7.11 – 7.19 (4H, 2 x s, 2 × $C_6\underline{H}_3$), 13.04 (2H, s, 2 × $N\underline{H}$).



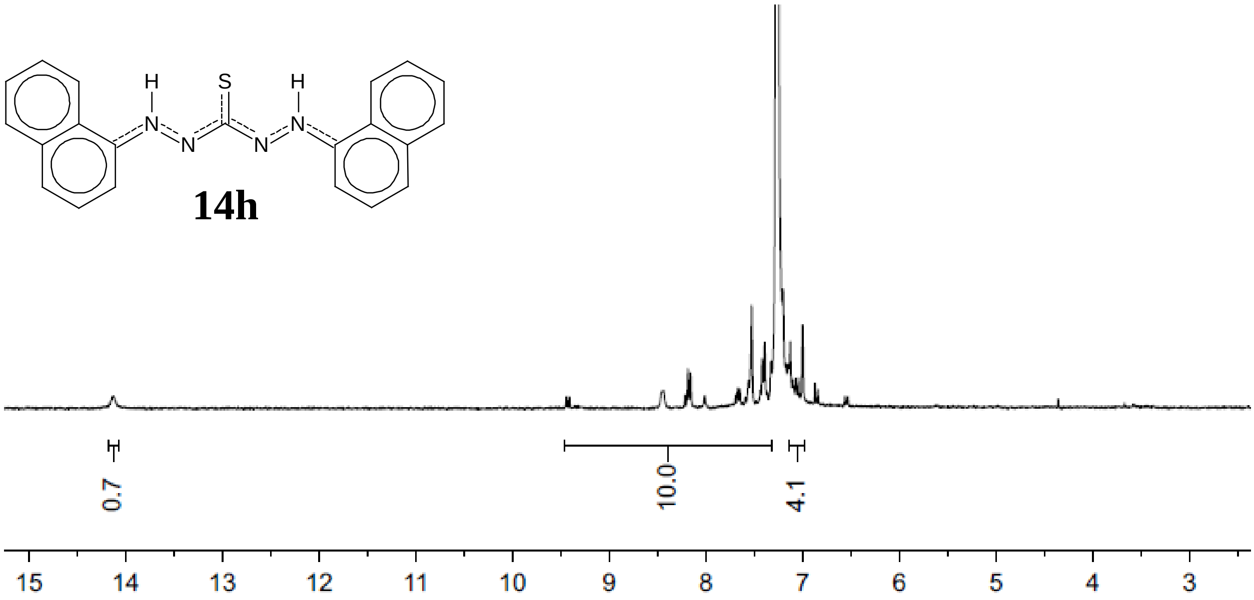
4.5.1.8. *α*-Naphthyldithizone, $(\alpha\text{-NaphNHN})_2CS$

Synthetic procedure as for *ortho*-methoxydithizone (4.5.1.1)

Nitroformazan yield, 2.3 g (60 %)

Dithizone yield, 0.3 g (32 %) 1 g of nitroformazan reagent was used.

M.p. 176 - 184 °C, λ_{max}/nm (dichloromethane) 370 & 383, shoulder 641 & 680, δ_H (300 MHz, C_6D_6)/ppm: 6.98 – 9.49 (14 H, m, 2 × $C_{10}\underline{H}_7$), 14.13 (2H, s, 2 × N$\underline{H}$).



14h

4.5.1.9. *β*-Fluorenyldithizone, $(\beta\text{-FluorNHN})_2CS$

Synthetic procedure as for *ortho*-methoxydithizone (4.5.1.1)

Nitroformazan yield, 1.2 g (40 %)

Dithizone yield, 0 g (0 %) 1.0 g of nitroformazan reagent was used, inseparable product obtained.

4.5.1.10. *α*-Pyrenyldithizone $(\alpha\text{-PyrNHN})_2CS$

Synthetic procedure as for *ortho*-methoxydithizone (4.5.1.1)

Nitroformazan yield, 1.7 g (72 %)

Dithizone yield, 0 g (0 %) 1.1 g of nitroformazan reagent was used, inseparable product obtained.

4.5.1.11. *α*-anthracenyldithizone (α-AnthNHN)$_2$CS

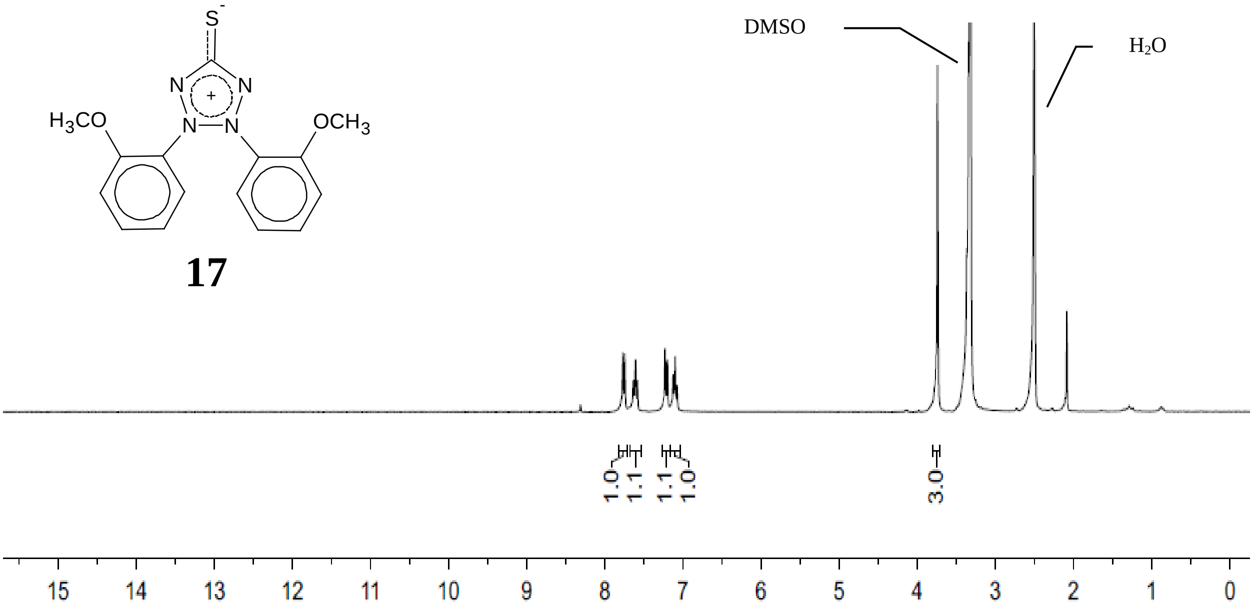
Synthetic procedure as for *ortho*-methoxydithizone (4.5.1.1)

Nitroformazan yield, 2.0 g (84 %)

Dithizone yield, 0 g (0 %) 1.0 g of nitroformazan reagent was used, inseparable product obtained.

4.5.1.12. *ortho*-Methoxydehydrodithizone, (*o*-OCH$_3$PhNN)$_2$CS

A solution of *ortho*-methoxydithizone (0.2 g, 0.6 mmol) in dichloromethane (60 ml) was stirred for 2 hours with a solution of potassium hexacyanoiron (III) (0.48 g) and potassium carbonate (0.46 g) in water (20 ml). The organic layer was removed, washed with water, and the solvent removed under reduced pressure. The product residue, on recrystallization from a minimum dichloromethane in acetone and water, gave 0.098 g orange-brown crystals of the dehydrodithizone. Yield, 49 %, M.p. 192 °C, λ_{max}/nm (acetone) 445, δ_H (300 MHz, $(CD_3)_2SO$ /ppm: 3.74 (3 H, s, *o*-C$\underline{H}_3$), 7.10 (1 H, t, *p*-$C_6\underline{H}_5$), 7.21 (1H, d, *m*-$C_6\underline{H}_5$), 7.61 (1H, t, *m*-$C_6\underline{H}_5$), 7.76 (1H, d, *o*-$C_6\underline{H}_5$).



17

4.5.1.13. *ortho*-Fluorodithizone disulphide, (*o*-FPhNHN)$_4$(CS)$_2$

Chemical oxidation

ortho-Fluorodithizone* (0.05 g, 0.2 mmol) was dissolved in dichloromethane (20 ml), and oxidized under sonication (12 min) together with a dichloromethane solution (5 ml) of iodine (0.25 g, 2 mmol) and water (15 ml). The organic layer was removed and the solvent was removed under reduced pressure at room temperature. The residue was dissolved in ether (leaving I_2 behind) and chromatographed through silica gel in a sintered glass funnel. The first red fraction was collected and the solvent evaporated at 36 °C on a rotary evaporator. The oily/tar solid was left to stand overnight. λ_{max}/nm (diethyl ether) 254, 299 and 405. (Further work-up for the purpose of purification and accurate characterization resulted in product fission, with the green color of the parent dithizone appearing.)

Auto oxidation

Ortho-fluorodithizone was dissolved in toluene and a few drops of n-hexane layered on top of the solution. Over a 24 hour period, while exposed to atmospheric oxygen, a colour change from green to red was observed, indicating auto-oxidation of the reagent has occurred.

M.p. 128-129 °C, λ_{max}/nm (diethyl ether) 254, 299 and 405. X-ray crystal structure (par.3.3.3)

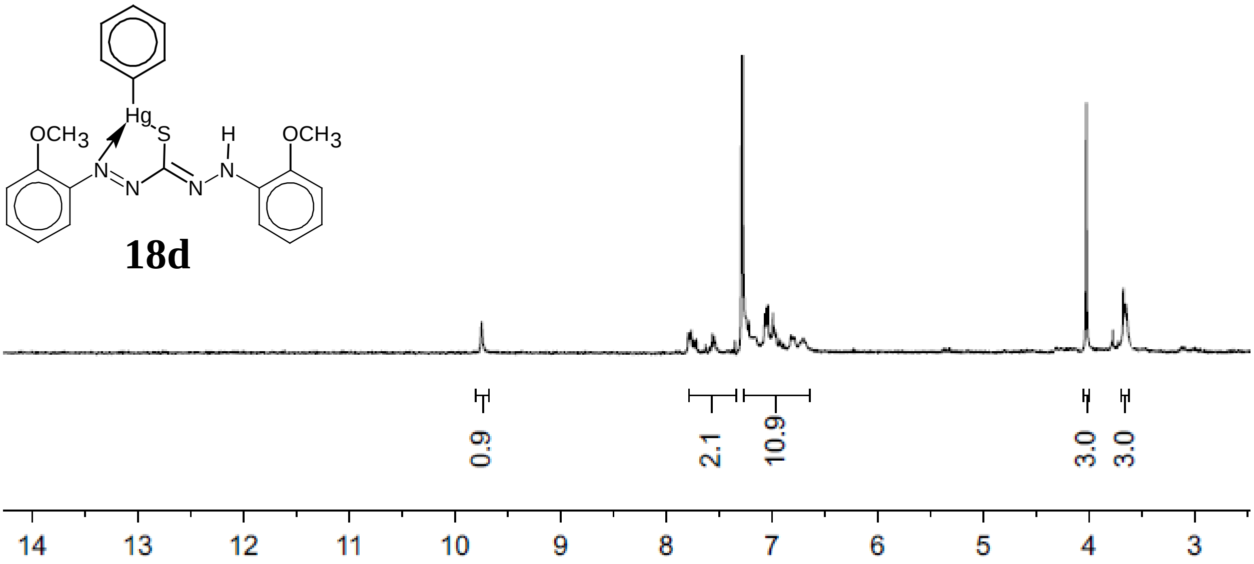
* supplied by Dr. K. G. von Eschwege

4.5.2. Mercury Dithizonates

4.5.2.1. *ortho*-Methoxydithizonatophenylmercury(II), PhHg(*o*-OCH_3)HDz

Triethylamine (0.0400 g, 0.4447 mmol) was added to a solution of *ortho*-methoxydithizone (0.1036 g, 0.3278 mmol) and phenylmercury(II) chloride (0.1480 g, 0.479 mmol) in dichloromethane (30 ml), and stirred for 15 minutes. The solution was overlaid with absolute ethanol (15 ml) to liberate 0.1048 g (54 %) of pure crystalline product.

M.p. 212 - 213 °C, λ_{max}/nm (dichloromethane) 505, δ_H (300 MHz, $CDCl_3$)/ppm: 3.68, 4.03 (6 H, 2 × s, 2 × C$\underline{H}_3$), 6.57 – 7.89 (13 H, m, 2 × $C_6\underline{H}_4$, 1 × $C_6\underline{H}_5$), 9.75 (1H, s, 1 × N$\underline{H}$).



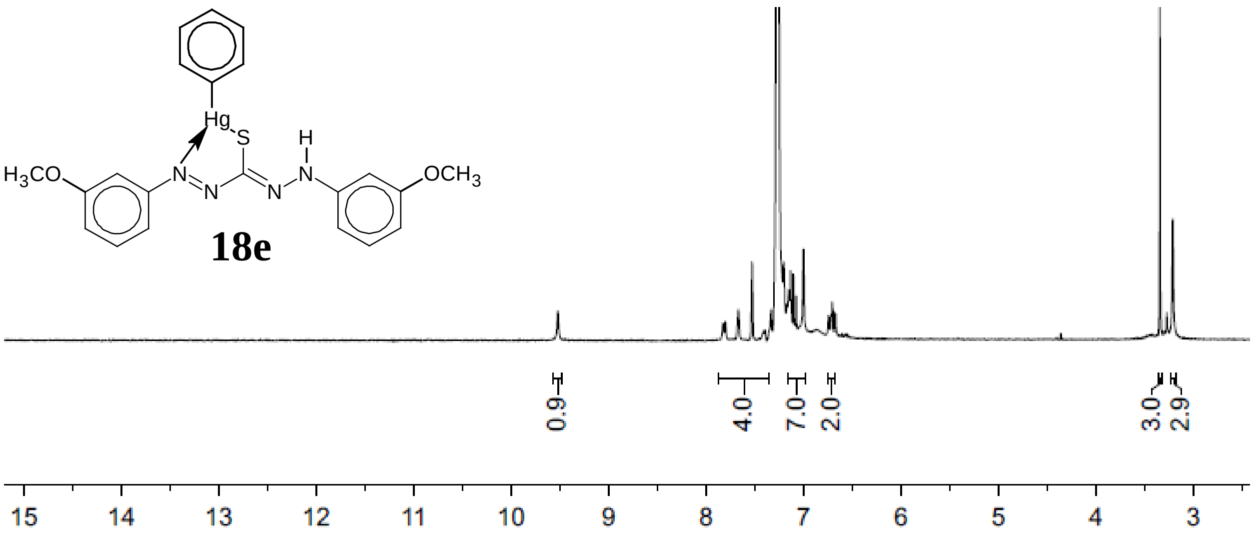
18d

4.5.2.2. *meta*-Methoxydithizonatophenylmercury(II), PhHg(*m*-OCH$_3$)HDz

Synthetic procedure as for *ortho*-methoxydithizonatophenylmercury(II) (4.5.2.1)

Complex yield, 0.112 g (60 %). 0.1 g *meta*-methoxydithithizone was used.

M.p. 137 - 139 °C, λ_{max}/nm (dichloromethane) 485, δ_H (300 MHz, C_6D_6)/ppm: 3.21, 3.34 (6 H, 2 × s, 2 × $C\underline{H}_3$), 6.67 – 7.87 (13 H, m, 2 × $C_6\underline{H}_4$, 1 × $C_6\underline{H}_5$), 9.52 (1H, s, 1 × $N\underline{H}$).



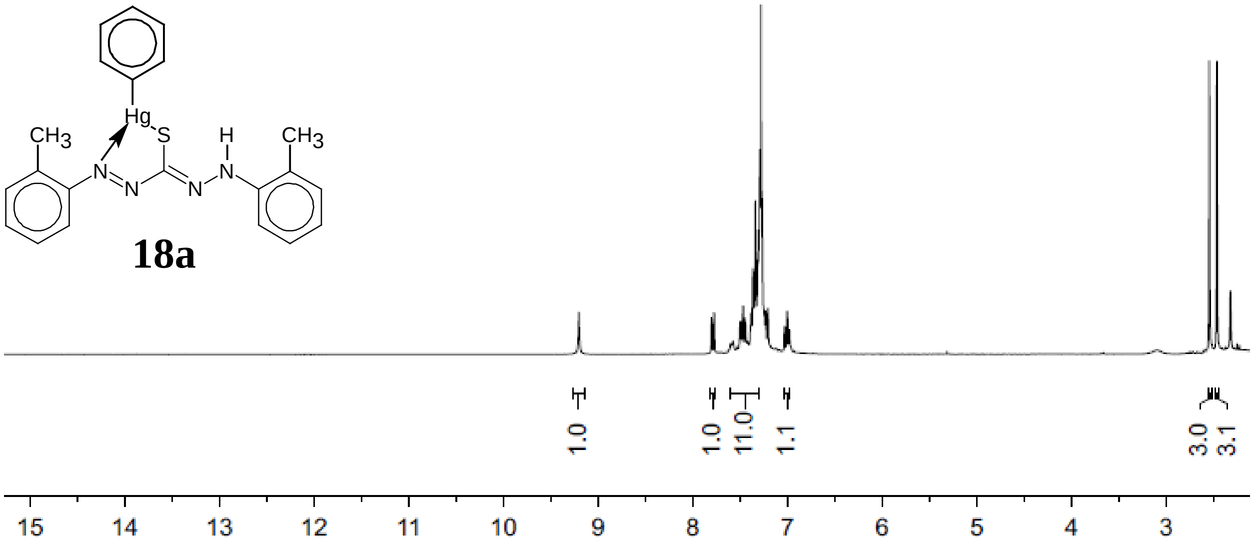
18e

4.5.2.3. *ortho*-Methyldithizonatophenylmercury(II), PhHg(*o*-CH$_3$)HDz

Synthetic procedure as for *ortho*-methoxydithizonatophenylmercury(II) (4.2.3.1)

Complex yield, 0.027 g (68 %). 0.02 g *ortho*-toluidinedithizone was used.

M.p. 120 - 122 °C, λ_{max}/nm (dichloromethane) 467, δ_H (300 MHz, $CDCl_3$)/ppm: 2.46, 2.54 (6 H, 2 × s, 2 × $C\underline{H}_3$), 6.98 – 7.82 (13 H, m, 2 × $C_6\underline{H}_4$, 1 × $C_6\underline{H}_5$), 9.20 (1H, s, 1 × $N\underline{H}$).



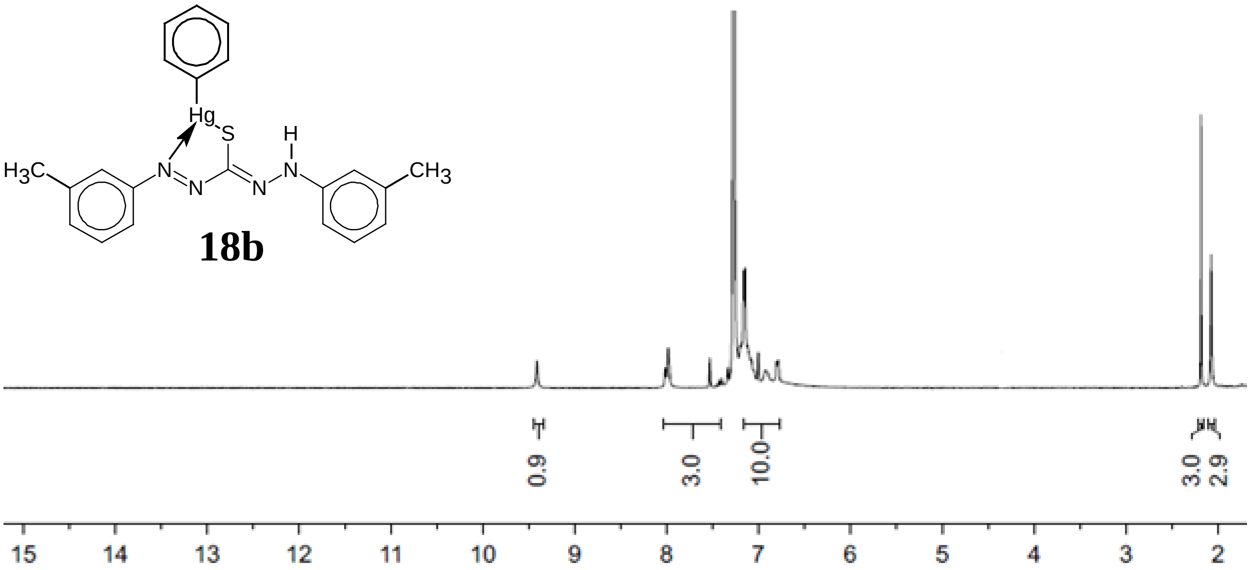
18a

4.5.2.4. ***meta*-Methyldithizonatophenylmercury(II), PhHg(*m*-CH_3)HDz**

Synthetic procedure as for *ortho*-methoxydithizonatophenylmercury(II) (4.2.3.1)

Complex yield, 0.121 g (61 %). 0.1 g *meta*-toluidinedithithizone was used.

M.p. 170 - 173 °C, λ_{max}/nm (dichloromethane) 480, δ_H (300 MHz, C_6D_6)/ppm: 2.08, 2.19 (6 H, 2 × s, 2 × $C\underline{H}_3$), 6.76 – 8.04 (13 H, m, 2 × $C_6\underline{H}_4$, 1 × $C_6\underline{H}_5$), 9.41 (1H, s, 1 × $N\underline{H}$).

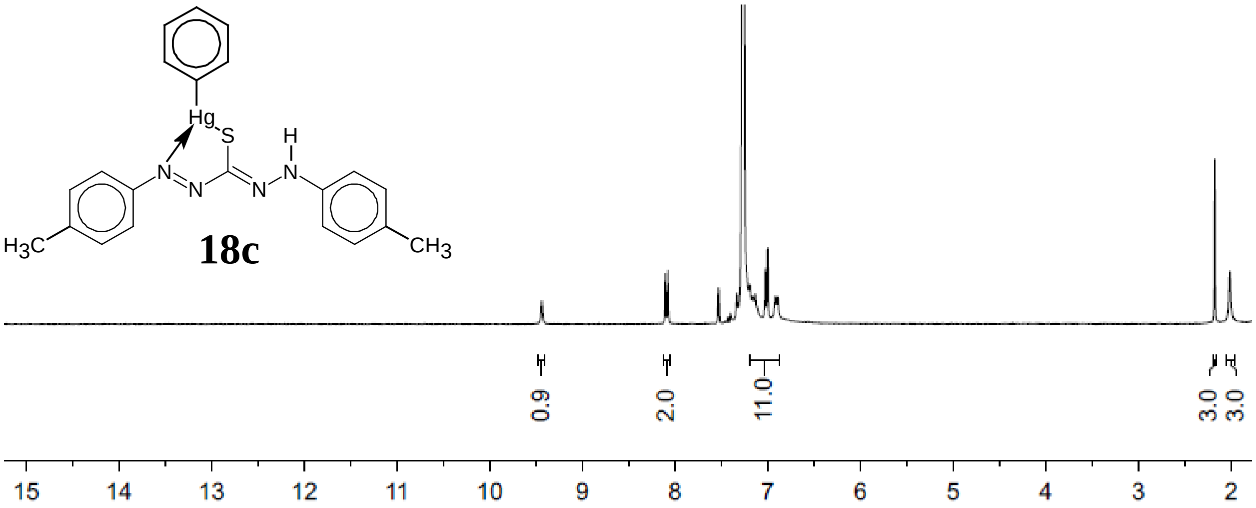

18b

4.5.2.5. ***para*-Methyldithizonatophenylmercury(II), PhHg(*p*-CH_3)HDz**

Synthetic procedure as for *ortho*-methoxydithizonatophenylmercury(II) (0.2.3.1)

Complex yield, 0.0078 g (94 %). 0.004 g *para*-toluidinedithithizone was used.

M.p. 146 - 148 °C, λ_{max}/nm (dichloromethane) 486, δ_H (300 MHz, C_6D_6)/ppm: 2.02, 2.18 (6 H, 2 × s, 2 × $C\underline{H}_3$), 6.87 – 8.12 (13 H, m, 2 × $C_6\underline{H}_4$, 1 × $C_6\underline{H}_5$), 9.44 (1H, s, 1 × $N\underline{H}$).

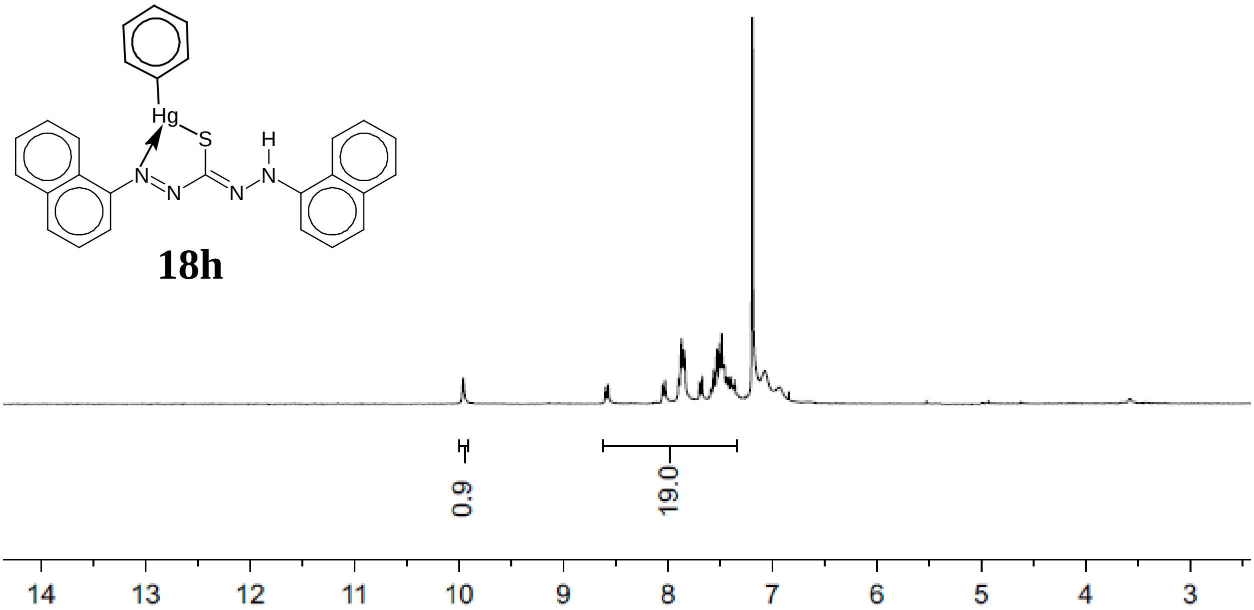

18c

4.5.2.6. *α*-Naphthyldithizonatophenylmercury(II), PhHg(*α*-Naph)HDz

Synthetic procedure as for *ortho*-methoxydithizonatophenylmercury(II) (4.2.3.1)

Complex yield, 0.144 g (81 %). 0.1 g *alpha*-naphthyldithizone was used.

M.p. 229 - 233 °C, λ_{max}/nm (dichloromethane) 509, δ_H (300 MHz, $CDCl_3$)/ppm: 7.36 – 8.60 (19 H, m, 2 × $C_{10}\underline{H}_7$, 1 × $C_6\underline{H}_5$), 9.96 (1H, s, 1 × N$\underline{H}$).



18h

5. Summary and Future Perspectives

Fundamental understanding of substituted or extended dithizones, its mercury complexes and the corresponding photochromic reactions is incomplete. Apart from its intermittent synthesis, little attention has been given to this field, as seen in the virtual absence of published related literature. Dithizone is mostly used in metal analyses. Apart from an earlier investigation into some electron-withdrawing fluoro and chloro substituted dithizones,[16] this investigation focused on electron-donating and extended aromatic ring system dithizones. Techniques that were employed are: comparative synthetic procedures, UV/visible spectrophotometry, NMR spectroscopy, X-ray crystallography, electrochemistry and quantum computational chemistry.

Of the seven methyl and methoxy substituted dithizones, only five mercury complexes were successfully synthesized, and of the four envisaged extended systems, only the naphthyl derivative was successful. Quantum computational chemistry, including geometry optimization of the most important tautomers and isomers, oscillator calculations, molecular orbital representations and orbitals energies, was however done for all eleven complexes, including their precursors, as well as unsubstituted dithizone itself – as point of reference. Cyclic voltammograms of the ligands and complexes helped to quantify the effect of altering ligand structures. X-ray crystallography ultimately confirmed some proposed structures and schemes, especially the successfully grown dithizone disulphide.

Although synthesis up to the nitroformazan is mostly quite successful, the final step, i.e. synthesis of the dithizone product, often fails to give good yields. Some attention to increase yields was given here, and to make the synthesis more convenient. More work may however still be done on this step, in order to try and increase yields. The possibility of substituted/altered dithizone synthesis is by far not depleted, and will thus be pursued to greater extremes in the immediate future. The same is true for a many-metal approach, as opposed to only mercury that was involved here. Naturally, spectroscopy, electrochemistry, crystallography and computational chemistry are tools that will have continued application.

With increased fundamental understanding of the system at hand, possible future applications in polymers and/or molecular switching devices might be pursued.

6. ABSTRACT

For the purpose of investigating the influence on the photochromic reaction of its phenylmercury complexes, a series of dithizone derivatives were at first synthesized. This includes symmetrical dithizone derivatives with electron-donating ability; *ortho*, *meta* & *para*-methyl and methoxy, as well as the *3,4*-dimethyl derivative, including some of its disulphide and dehydrodithizone oxidation products. The synthesis of extended aromatic ring dithizone derivatives was attempted, i.e. instead of a phenyl ring the dithizone was extended to have napthyl, fluorenyl, anthracenyl and pyrenyl functional groups. Synthetic procedures were optimized, while conveniently utilizing ammoniumsulphide instead of NH_3(g) and H_2S(g) as reagent. Phenylmercury(II) complexes were prepared from the successfully synthesized *ortho* and *meta*-methoxy, and *ortho*, *meta* and *para*-methyl, and napthyldithizone derivatives. All except the *ortho*-methyl and naphthyl dithizonates were observed to be photochromic. The *ortho*-methoxy dithizonate, for the first time, exhibited an alternative color reaction; instead of the usual orange to blue, this compound changed from pink to purple.

From the corresponding substituted dithizone the disulphide of *ortho*-fluorodithizone was synthesized through auto-oxidation, chemical oxidation and electrochemical oxidation. Successful growth of a sizeable crystal of the latter compound ended in solving, for the first time, the X-ray crystal structure of a dithizone disulphide, giving conclusive evidence in support of the long standing proposal of an unstable disulphide intermediate in the oxidation reaction of dithizone. Solving also the X-ray crystal structure of *ortho*-methoxydehydrodithizone gave indirect structural evidence in support of the foregoing synthesis product.

A comprehensive ADF DFT quantum computational study included the successfully and unsuccessfully prepared dithizones and dithizonatophenylmercury complexes. Results unambiguously showed the symmetric form of dithizone and its analogues to be the most stable. TDDFT calculations simulate the trends seen in experimental UV/visible spectra. Graphical representations show molecular orbitals (HOMO & LUMO) extending over the entire length of the ligand, confirming the molecule's structural importance in the photochromic reaction. Extended dithizonates pose a steric hindrance for photochromism to take place.

Electrochemical studies were performed on the above successfully synthesized ligands and complexes, as well as some fluoro-substituted dithizones, exploring the electronic borders within which photochromism ultimately takes place. Complete redox schemes are proposed for the observable redox waves in the cyclic voltammograms of all species involved. An approximate linear relation between experimental oxidation data of the dithizonates and the calculated HOMO energies was found ($R^2 = 0.89$).

7. SAMEVATTING

’n Reeks ditisoon derivate is gesintetiseer, om uiteindelik die effek van die fotochromiese reaksie van die fenielkwikkomplekse daarvan te bestudeer. Dit sluit in simmetriese ditisoon derivate met die vermoë om elektrone te doneer; *orto*-, *meta*- en *para*-metiel en -metoksie, so wel as die 3,4-dimetiel derivaat, insluitend sommige disulfied en dehidroditisoon oksidasie produkte. Die sintese van verlengde aromatiese ringsisteme was ook probeer; in plaas van ’n fenielring het die verlengde ditisone naftiel, fluoreniel, antraseniel en pireniel gedeeltes. Sintetiese metodes is geoptimiseer, terwyl ammoniumsulfied gerieflikheidshalwe as reagens in plaas van $NH_3(g)$ en $H_2S(g)$ gebruik is. Fenielkwik(II) komplekse is berei van die suksesvol gesintetiseerde *orto*- en *meta*-metoksie-, en *orto*-, *meta*- en *para*-metiel- en naftielditisoon derivate. Fotochromisme is by almal behalwe die *orto*-metiel en naftiel ditisonate waargeneem. Die *orto*-metoksie ditisonaat het, vir die eerste keer, ’n ander kleur reaksie gegee; in plaas van die gewone oranje na blou verander hierdie verbinding se kleur van pienk na pers.

Die disulfied van *orto*-fluoroditisoon is van die ooreenstemmende gesubstitueerde ditisoon gesintetiseer deur outo-, chemiese- en elektrochemiese oksidasie. Die suksesvolle groei van ’n groot genoeg kristal van die voorafgenoemde verbinding het geeindig in die opklaring, vir die eerste keer, van die X-straalkristalstruktuur van ’n ditisoondisulfied, wat oortuigende bewys gee van die langstaande voorstel van ’n onstabiele disulfied oorgangsvorm in die oksidasi reaksie van ditisoon. Deur die X-straalkristalstruktuur van *orto*-metoksiedehidroditisoon op te los gee indirekte bewys ter ondersteuning van die voorafgaande sintese produk.

’n Uitgebreide ADF DFT kwantumberekeningsstudie het die suksesvolle en onsuksesvol bereide ditisone en ditisoonfenielkwikkomplekse ingesluit. Die resultate het duidelik bewys dat die simmetriese vorm van ditisoon en sy derivate die mees stabiele vorm is. TDDFT berekeninge simuleer die tendens gesien in die eksperimenteel bepaalde spektra. Grafiese voorstellings wys molekulere orbitale (HOMO en LOMO) strek oor die hele lengte van die ligand en dien as bewys dat die molekuul se struktuur ’n belangrike rol in die fotochromiese reaksie speel. Die verlengde ditisonate veroorsaak steriese hindernis wat oënskynlik die fotochromiese reaksie belemmer.

Elektrochemiese studies is uitgevoer op bogenoemde suksesvol gesintetiseerde ligande en komplekse, so wel as op fluoor-gesubstitueerde ditisone, waardeur die elektroniese grense waarbinne fotochromisme plaasvind ondersoek is. Volledige redoksskemas is voorgestel vir die waargenome redokspieke in die sikliese voltamogramme van die verbindings wat ondersoek is. ’n Benaderde lineêre verhouding is tussen die eksperimentele oksidasie data van die ditisonate en die berekende HOMO energieë gevind ($R^2 = 0.89$).

Appendix A

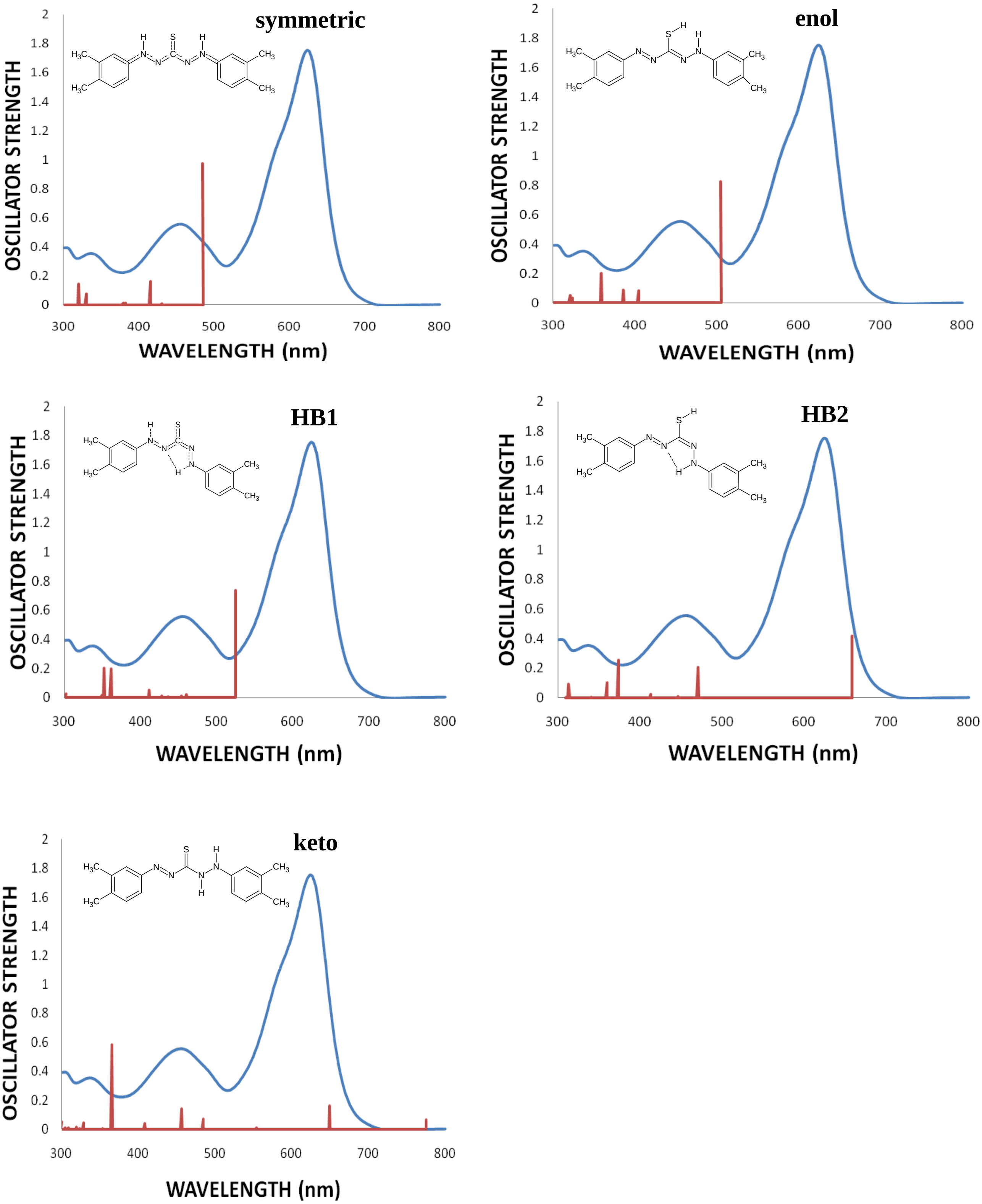


Figure A.1 ADF/PW91 calculated electronic spectra (spikes) and experimentally determined spectra of different isomers of *3,4*-dimethyldithizone in DCM. C = 2 x 10^{-5} M, ε = 85 883 dm^3 mol^{-1} cm^{-1} at λ_{max} = 461, 629 nm.

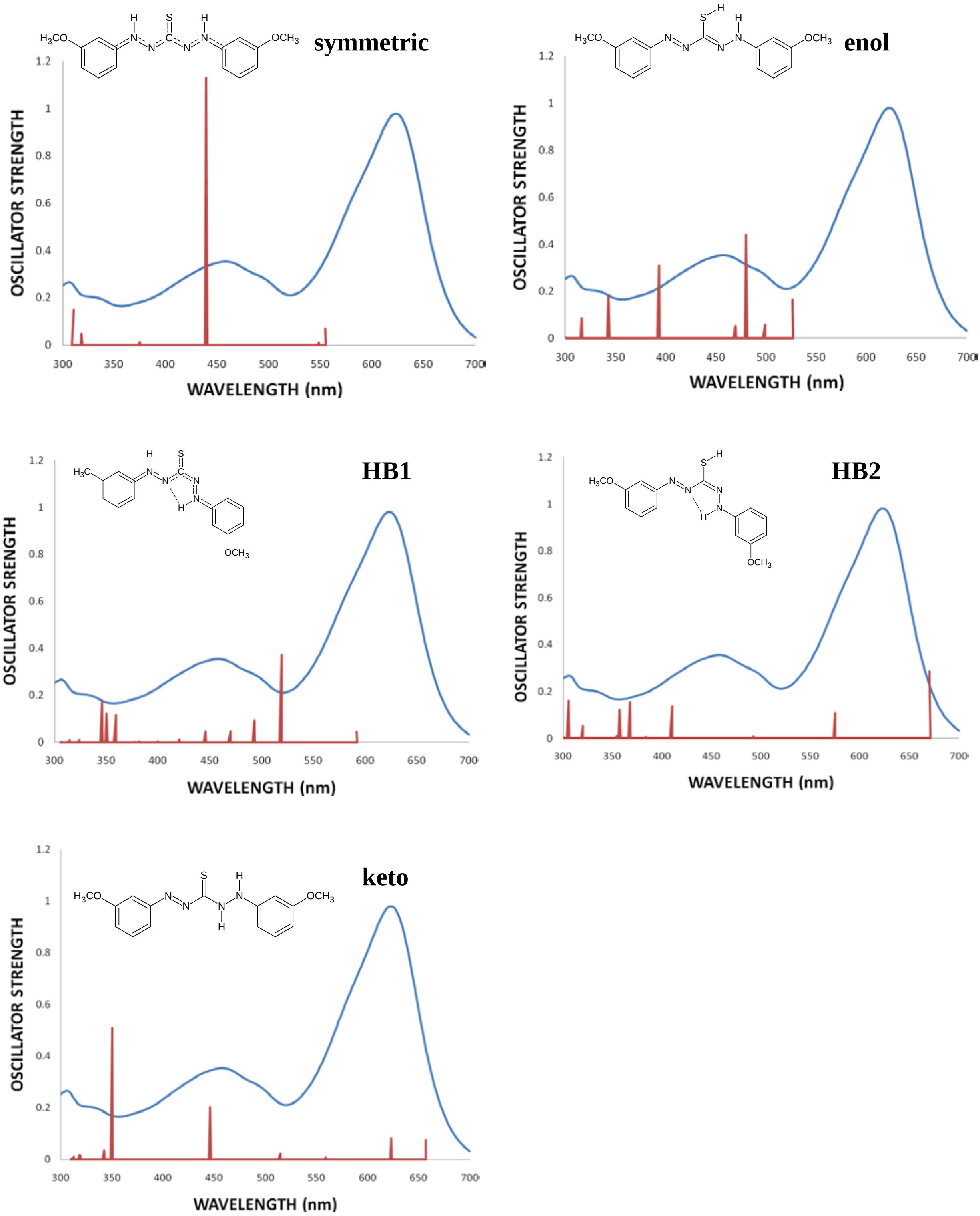


Figure A.2 ADF/PW91 calculated electronic spectra (spikes) and experimentally determined spectra of different isomers of *meta*-methoxydithizone in DCM. C = 10 x 10^{-5} M, ε = 9 699 dm^3 mol^{-1} cm^{-1} at λ_{max} = 463, 627 nm.

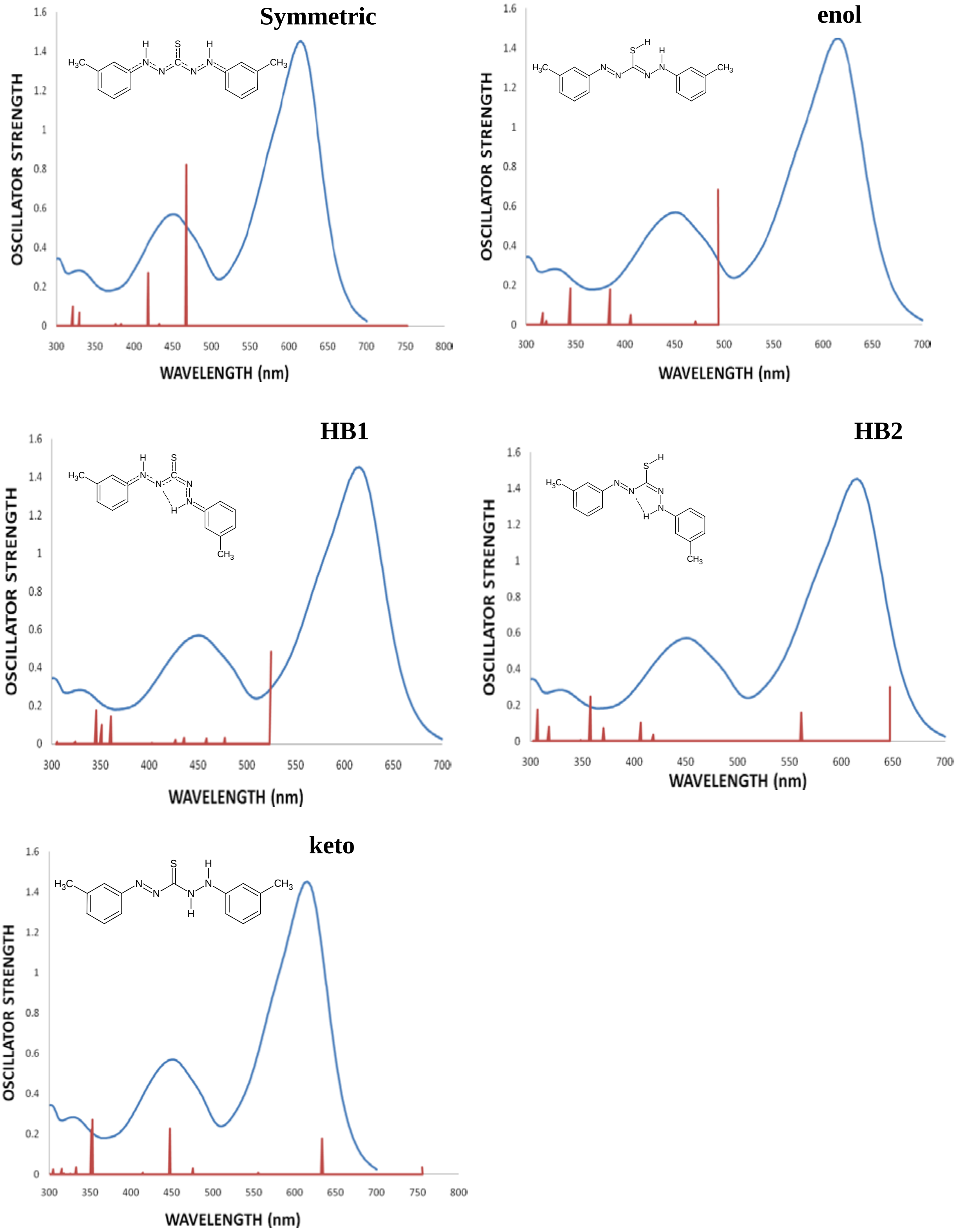


Figure A.3 ADF/PW91 calculated electronic spectra (spikes) and experimentally determined spectra of different isomers of *meta*-methyldithizone in DCM. $C = 3 \times 10^{-5}$ M, $\varepsilon = 48\ 020\ dm^3\ mol^{-1}\ cm^{-1}$ at $\lambda_{max} = 452, 617$ nm.

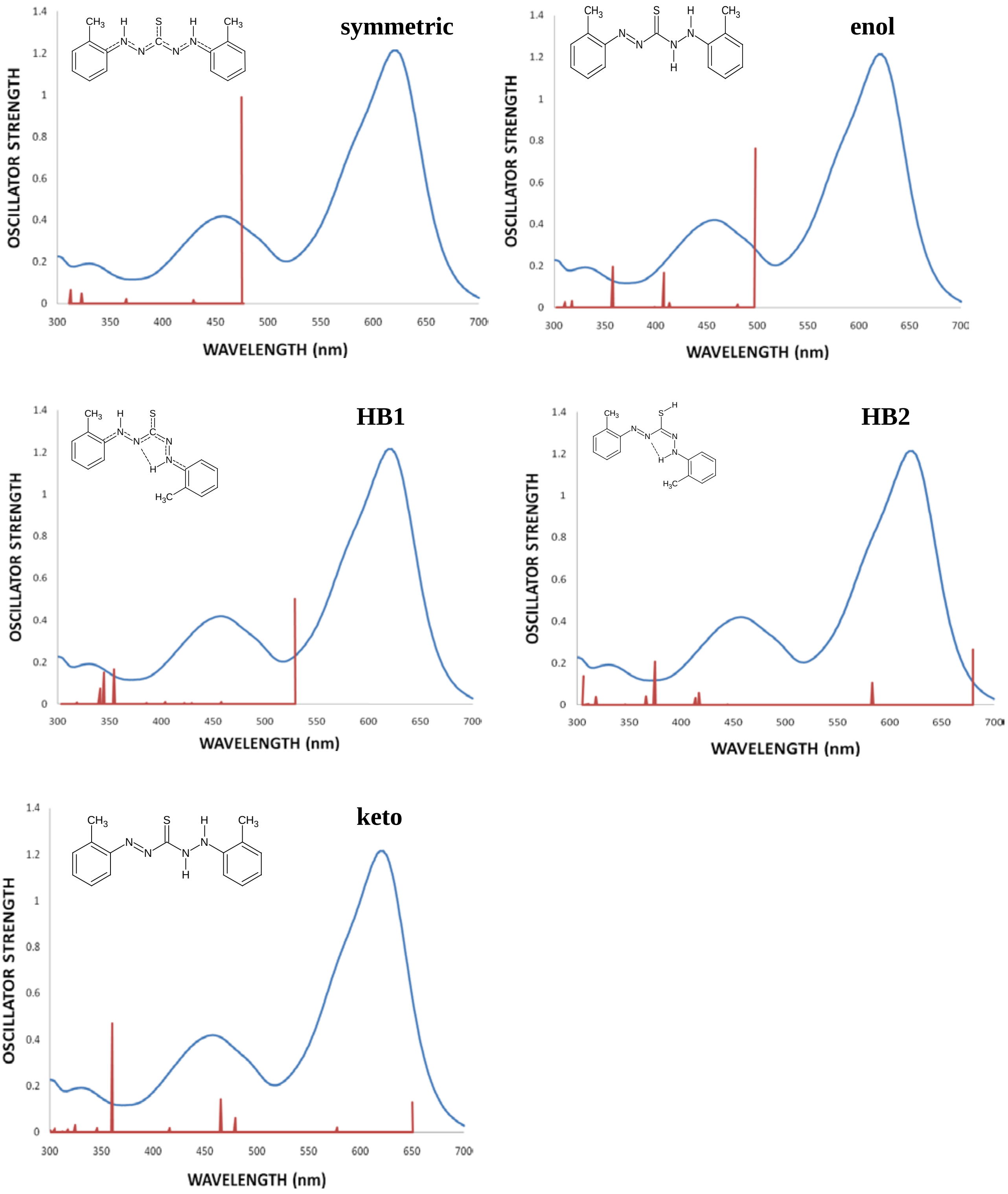


Figure A.4 ADF/PW91 calculated electronic spectra (spikes) and experimentally determined spectra of different isomers of *ortho*-methyldithizone in DCM. C = 3 x 10^{-5} M, ε = 40 085 dm^3 mol^{-1} cm^{-1} at λ_{max} = 461, 625 nm.

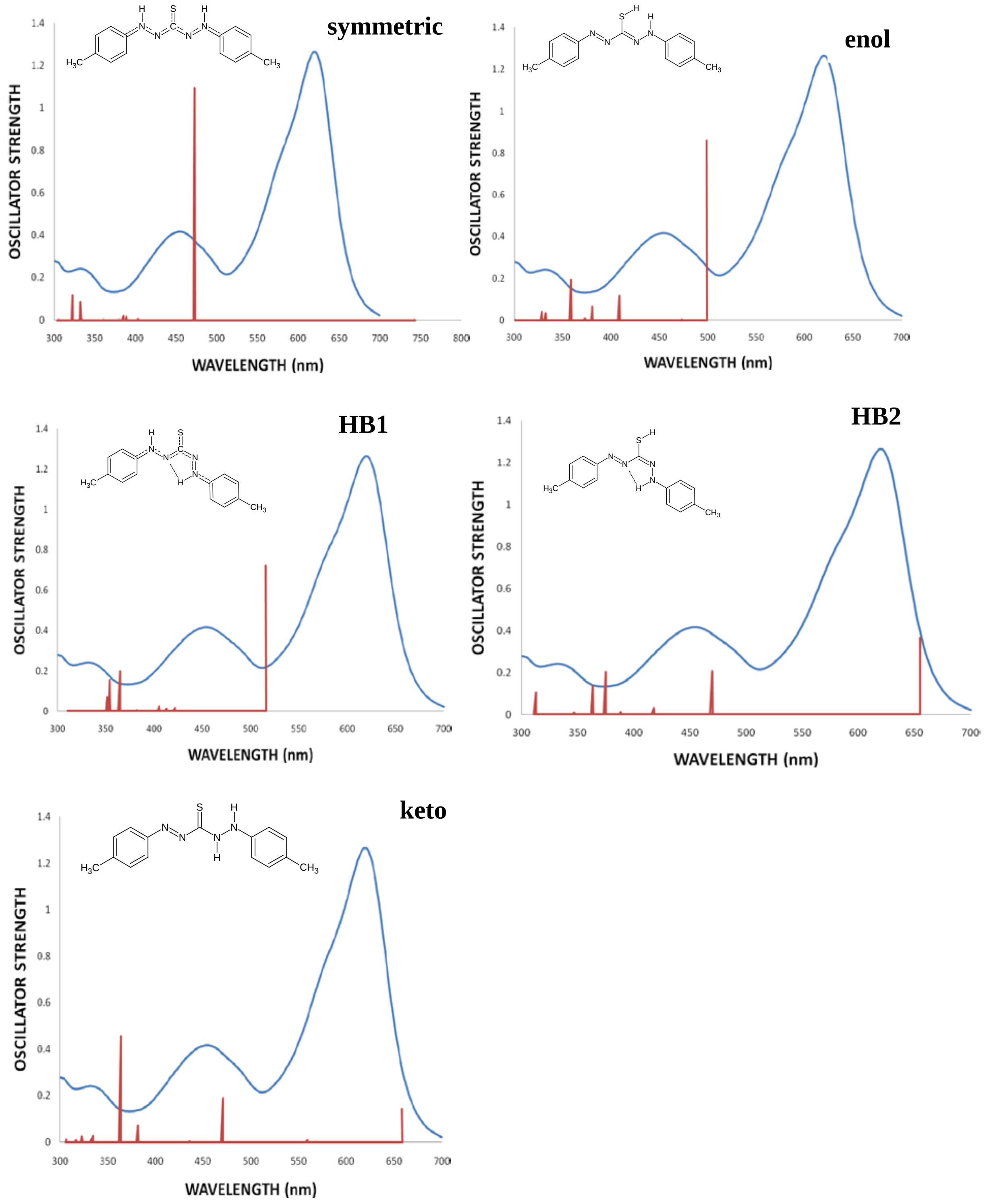


Figure A.5 ADF/PW91 calculated electronic spectra (spikes) and experimentally determined spectra of different isomers of *para*-methyldithizone in DCM. C = 3×10^{-5} M, ε = 41 985 dm^3 mol^{-1} cm^{-1} at λ_{max} = 456, 623 nm.

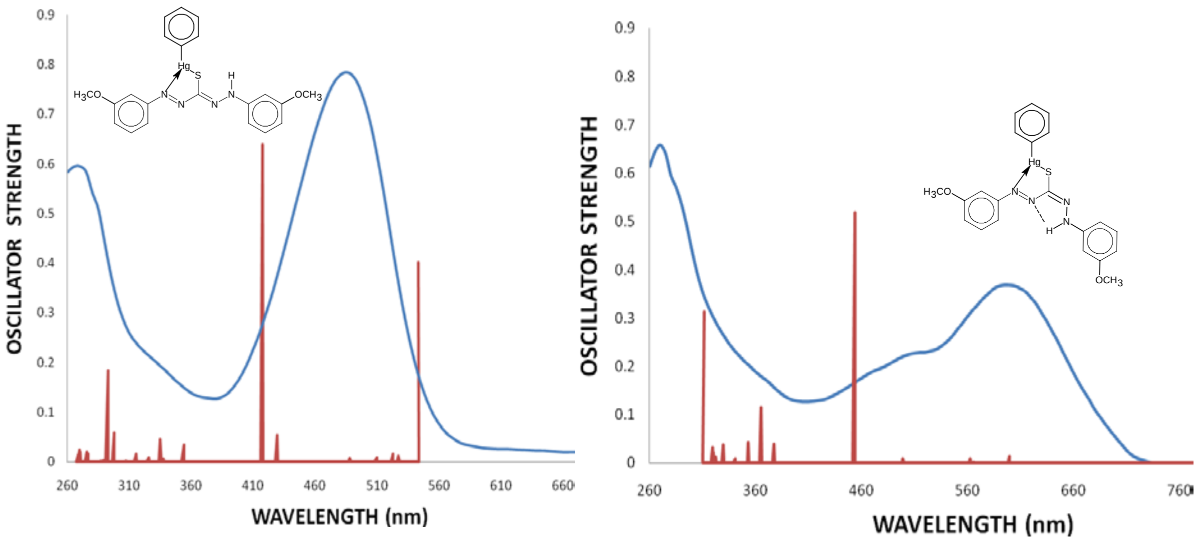


Figure A.6 ADF/PW91 calculated electronic spectra (spikes) and experimentally determined spectra of *meta*-methoxydithizonatophenylmercury(II) in dichloromethane. The blue photo-excited state (right, λ_{max} = 605 nm, ε = 12 256 dm^3 mol^{-1} cm^{-1}) and the orange ground state (left, λ_{max} = 485 nm, ε = 26 113 dm^3 mol^{-1} cm^{-1}). The proposed ground and excited state structures above are due to analogy of PhHgHDz.

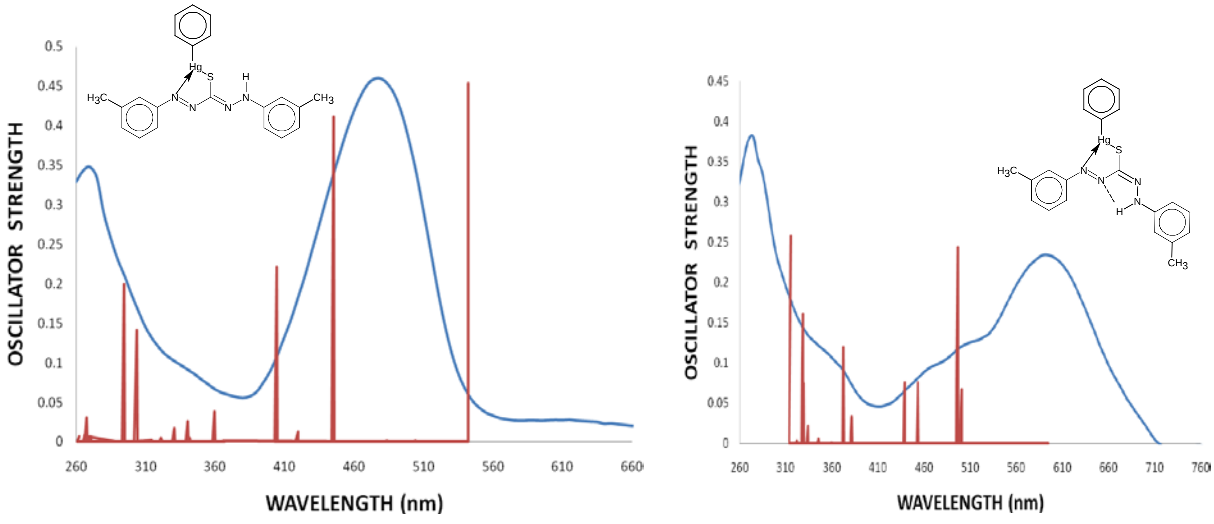


Figure A.7 ADF/PW91 calculated electronic spectra (spikes) and experimentally determined spectra of *meta*-methyldithizonatophenylmercury(II) in dichloromethane. The blue photo-excited state (λ_{max} = 595 nm, ε = 7 789 dm^3 mol^{-1} cm^{-1}) and the orange ground state (λ_{max} = 480 nm, ε = 15 167 dm^3 mol^{-1} cm^{-1}). The proposed ground and excited state structures above are due to analogy of PhHgHDz.

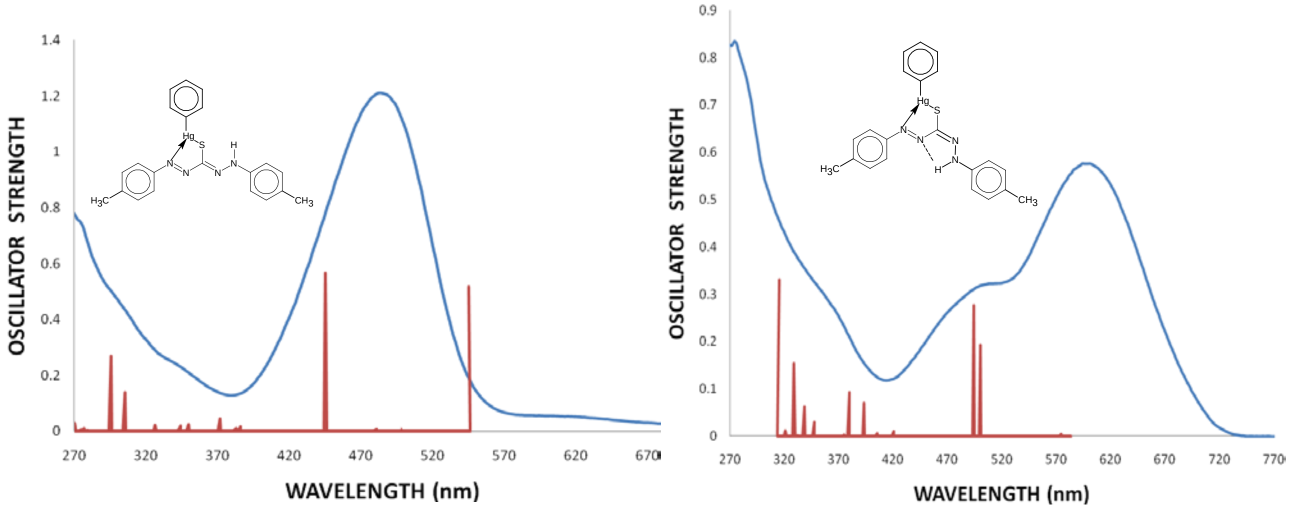


Figure A.8 ADF/PW91 calculated electronic spectra (spikes) and experimentally determined spectra of *para*-methyldithizonatophenylmercury(II) in dichloromethane. The blue photo-excited state (λ_{max} = 604 nm, ε = 19 175 dm^3 mol^{-1} cm^{-1}) and the orange ground state (λ_{max} = 486 nm, ε = 40 298 dm^3 mol^{-1} cm^{-1}). The proposed ground and excited state structures above are due to analogy of PhHgHDz.

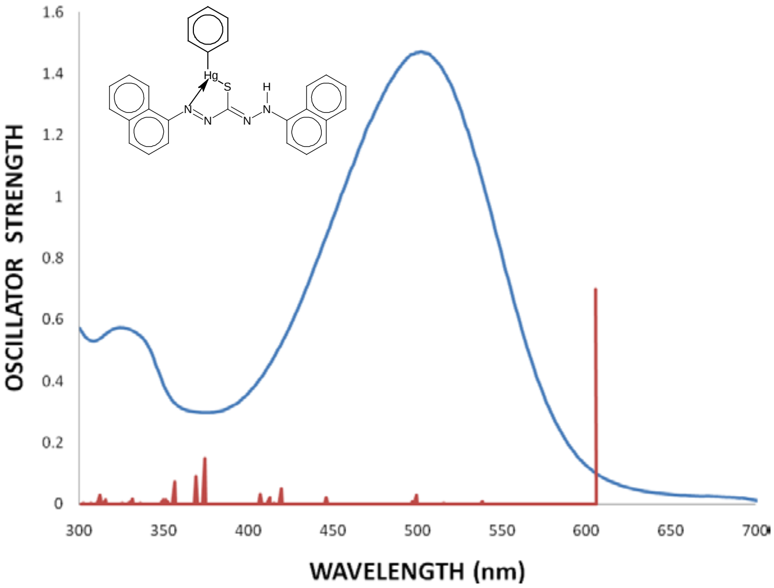


Figure A.9 ADF/PW91 calculated electronic spectra (spikes) and experimentally determined spectra of *α*-naphthyldithizonatophenylmercury(II) in dichloromethane. The orange ground state (λ_{max} = 509 nm, ε = 48 477 dm^3 mol^{-1} cm^{-1}). The proposed ground state structure above is due to analogy of PhHgHDz.

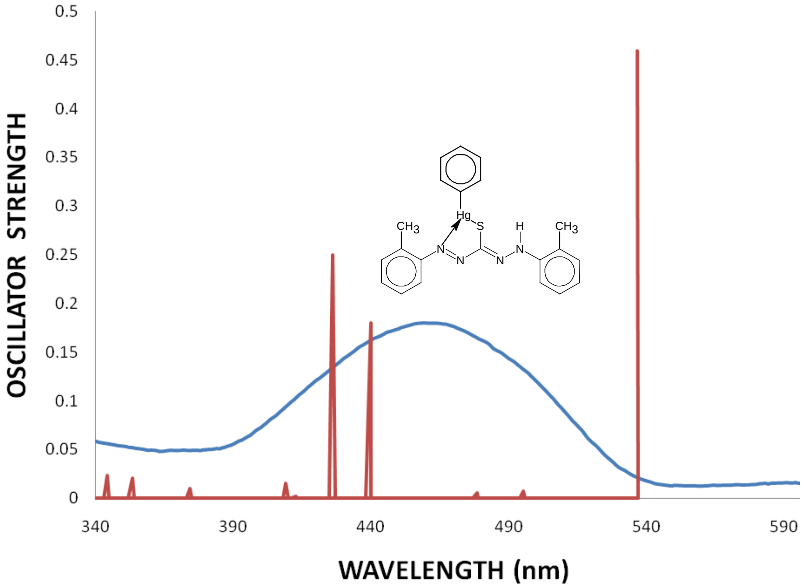


Figure A.10 ADF/PW91 calculated electronic spectra (spikes) and experimentally determined spectra of *ortho*-methyldithizonatophenylmercury(II) in dichloromethane. The orange ground state (λ_{max} = 467 nm, ε = 6 003 dm^3 mol^{-1} cm^{-1}). The proposed ground state structure above is due to analogy of PhHgHDz.

Figure A.11

Cyclic voltammogram of 1 mM **$\mathrm{H_2Dz}$** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M $[\mathrm{NBu_4}][\mathrm{B(C_6F_5)_4}]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

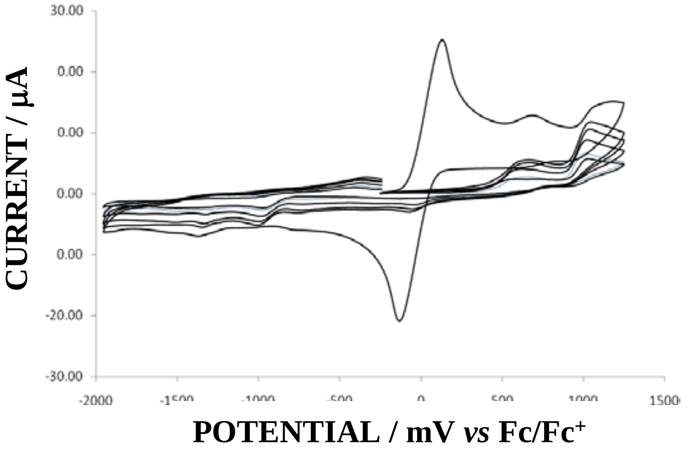


Figure A.12

Cyclic voltammogram of 1 mM, ***3,4*-$\mathbf{(CH_3)_2H_2Dz}$** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M $[\mathrm{NBu_4}][\mathrm{B(C_6F_5)_4}]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

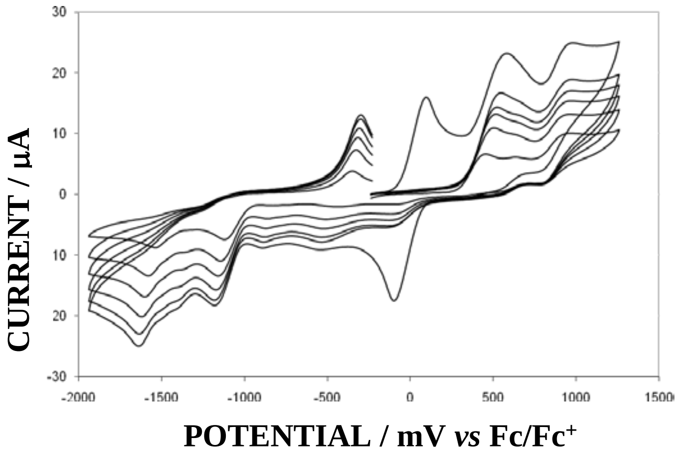


Figure A.13

Cyclic voltammogram of 1 mM, **(*m*-$\mathbf{OCH_3)H_2Dz}$** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M $[\mathrm{NBu_4}][\mathrm{B(C_6F_5)_4}]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

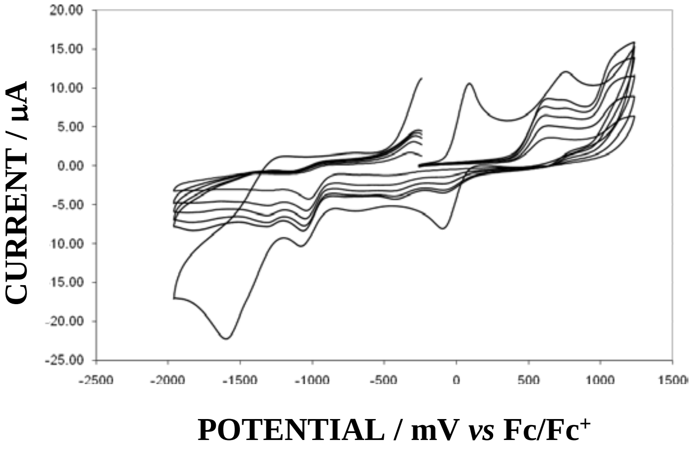


Figure A.14

Cyclic voltammogram of 1 mM **(*o*-CH$_3$)H$_2$Dz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M [NBu$_4$][B(C$_6$F$_5$)$_4$] as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

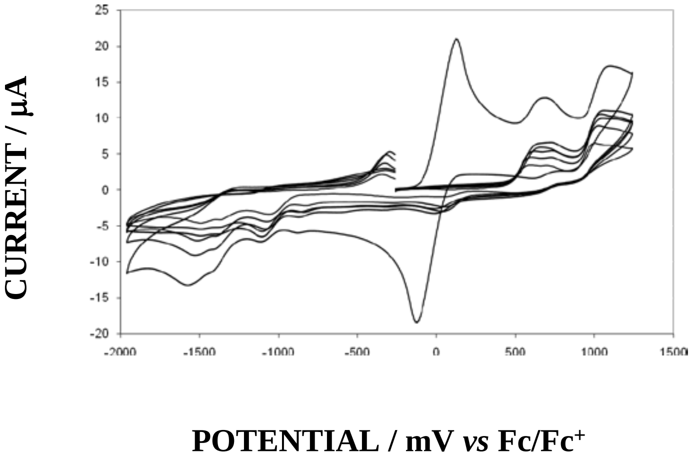


Figure A.15

Cyclic voltammogram of 1 mM, **(*m*-CH$_3$)H$_2$Dz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M [NBu$_4$][B(C$_6$F$_5$)$_4$] as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

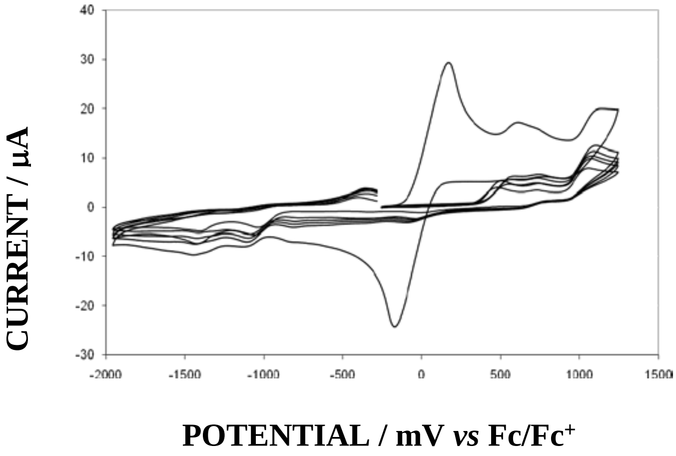


Figure A.16

Cyclic voltammogram of 1 mM, **(*p*-CH$_3$)H$_2$Dz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M [NBu$_4$][B(C$_6$F$_5$)$_4$] as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

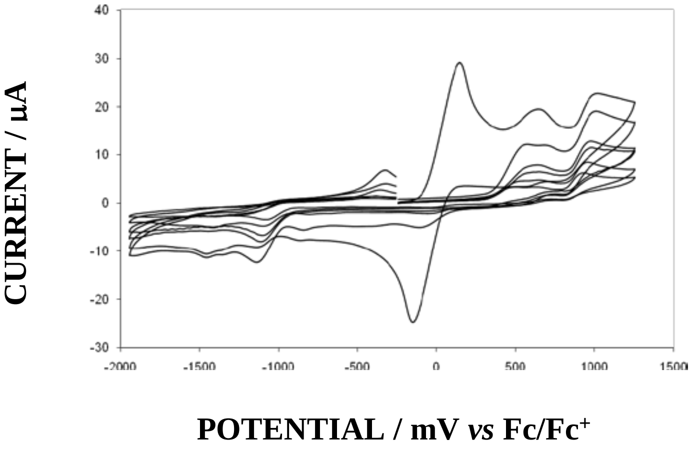


Figure A.17

Cyclic voltammogram of 1 mM **(*o*-F)H_2Dz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

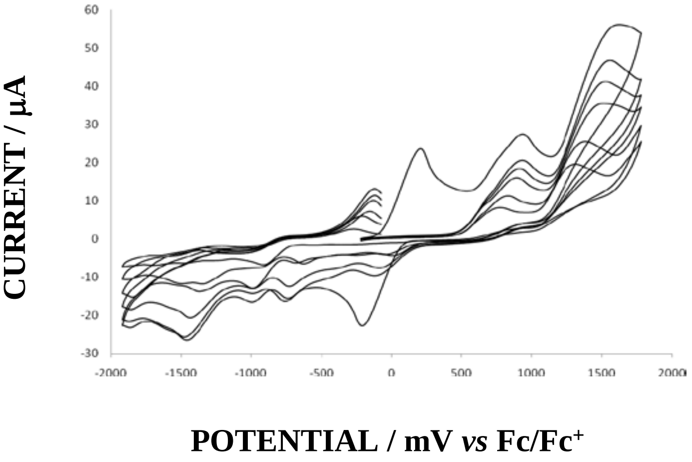


Figure A.18

Cyclic voltammogram of 1 mM, **(*m*-F)H_2Dz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

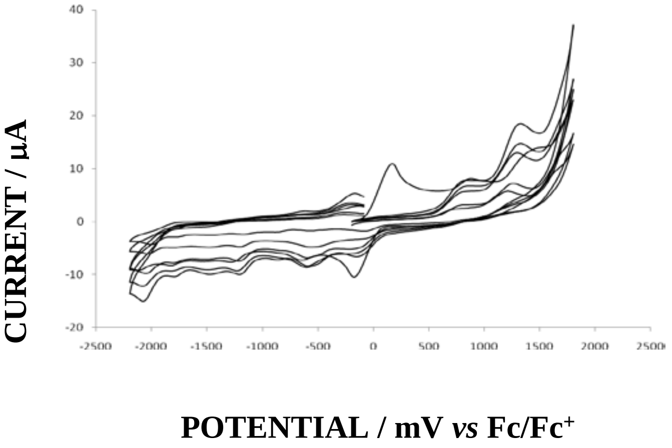


Figure A.19

Cyclic voltammogram of 1 mM, **(*p*-F)H_2Dz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

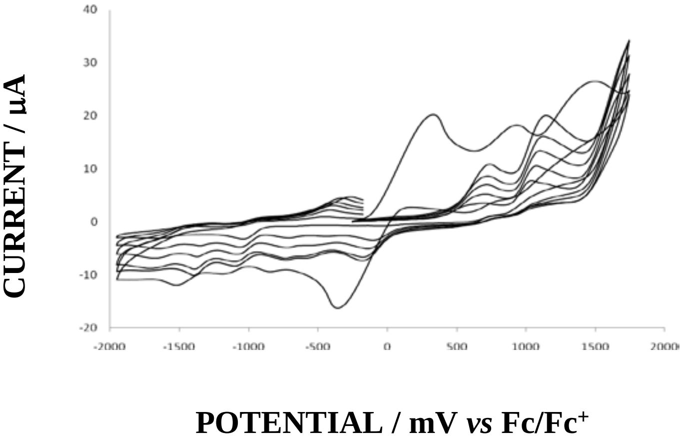


Figure A.20

Cyclic voltammogram of 1 mM **(*α*-naphthyl)H$_2$Dz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M [NBu$_4$][B(C$_6$F$_5$)$_4$] as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

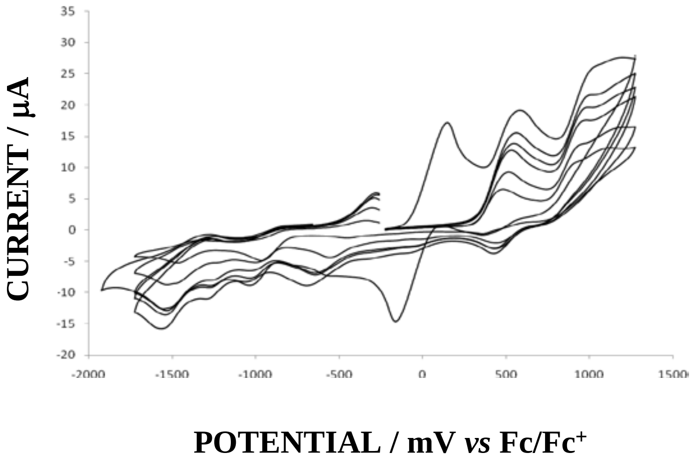


Figure A.21

Cyclic voltammogram of 1 mM **PhHgHDz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M [NBu$_4$][B(C$_6$F$_5$)$_4$] as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

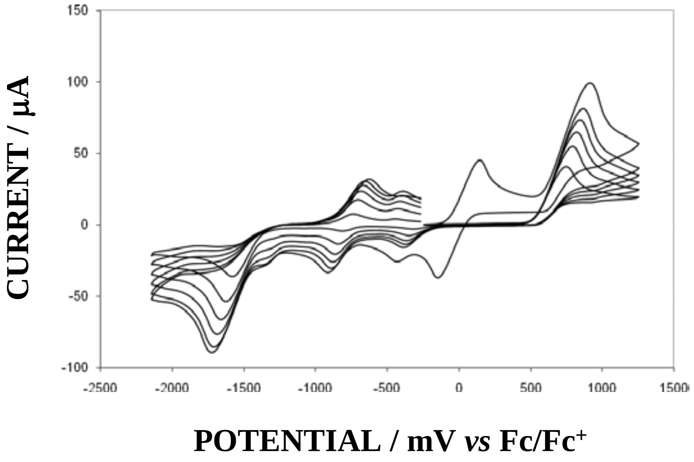


Figure A.22

Cyclic voltammogram of 1 mM, **PhHg(*m*-OCH$_3$)HDz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M [NBu$_4$][B(C$_6$F$_5$)$_4$] as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

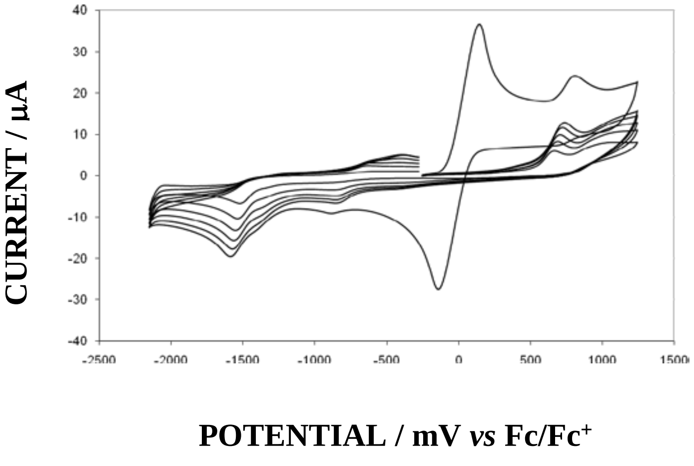


Figure A.23

Cyclic voltammogram of 1 mM, **PhHg(*α*-naphthyl)HDz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

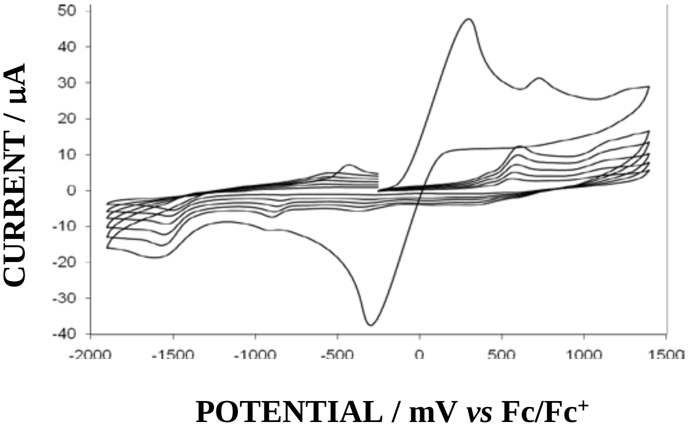


Figure A.24

Cyclic voltammogram of 1 mM **PhHg(*o*-CH₃)HDz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

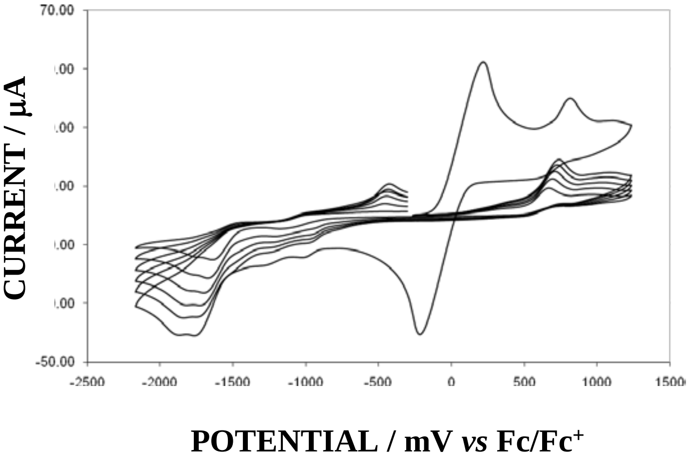


Figure A.25

Cyclic voltammogram of 1 mM, **PhHg(*m*-CH₃)HDz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.

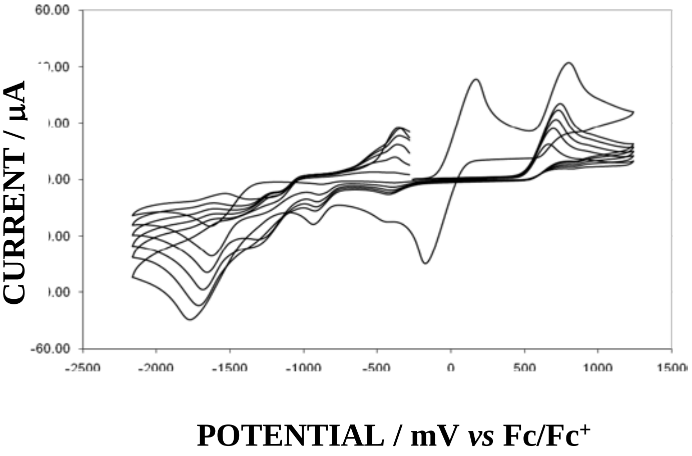
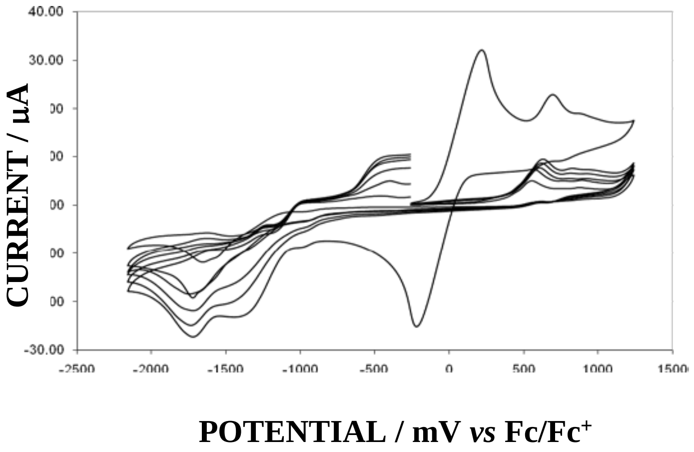


Figure A.26

Cyclic voltammogram of 1 mM, **PhHg(*p*-CH_3)HDz** recorded at scan rates of 100, 200, 300, 400, 500 and fer500 mV s^{-1}, using 0.1 M $[NBu_4][B(C_6F_5)_4]$ as supporting electrolyte, and a glassy carbon working electrode, at 25 °C, in dichloromethane.



Appendix B

Coordinates for all optimized dithizone derivatives studied in this research project.

o-methoxydithizone (Symmetric form)

	x	y	z
N	-0.015126000	2.168071000	0.423882000
N	-0.378223000	1.888660000	-0.796445000
C	-1.439914000	2.641580000	-1.208122000
N	-1.734515000	2.340865000	-2.506590000
N	-2.722246000	3.054290000	-2.969437000
S	-2.260264000	3.813468000	-0.247471000
C	1.047149000	1.549610000	1.065495000
C	1.776334000	0.505310000	0.485587000
H	1.488113000	0.168507000	-0.507208000
C	1.389984000	2.020374000	2.359018000
C	2.457254000	1.436699000	3.042299000
C	2.837054000	-0.070193000	1.177856000
C	3.176396000	0.394189000	2.450681000
H	3.400543000	-0.883250000	0.723772000
H	2.731449000	1.791904000	4.032426000
H	4.006804000	-0.053839000	2.993942000
C	-3.178699000	2.970098000	-4.275977000
C	-2.613238000	2.105086000	-5.219975000
H	-1.787717000	1.471506000	-4.905209000
C	-4.254706000	3.816379000	-4.645661000
C	-4.738380000	3.782165000	-5.954058000
C	-3.105488000	2.078224000	-6.521129000
C	-4.163006000	2.914347000	-6.886777000
H	-2.661092000	1.405806000	-7.252757000
H	-5.560266000	4.429349000	-6.249563000
H	-4.547886000	2.897725000	-7.905175000
H	-0.571256000	2.918044000	0.898280000
H	-3.142146000	3.734355000	-2.292702000
O	-4.732772000	4.618374000	-3.647844000
O	0.617080000	3.044592000	2.828374000
C	-5.807364000	5.504691000	-3.972676000
C	0.949027000	3.587567000	4.109284000
H	-6.033751000	6.043656000	-3.049810000
H	0.849931000	2.829656000	4.898291000
H	0.231673000	4.393021000	4.282561000
H	1.969339000	3.995067000	4.111369000
H	-5.508265000	6.217927000	-4.753058000
H	-6.694673000	4.945947000	-4.300475000

o-methoxydithizone (Enol form)

	x	y	z
N	-3.038637000	1.416625000	-4.679772000
N	-2.184210000	1.760100000	-5.566375000
C	-2.058132000	3.122588000	-5.730733000
N	-1.199425000	3.481294000	-6.658733000
N	-1.043681000	4.779022000	-6.867352000
S	-3.033764000	4.239829000	-4.735983000
C	-0.186840000	5.271586000	-7.845718000
C	0.563473000	4.445282000	-8.686793000
H	0.471792000	3.368721000	-8.567078000
C	-0.092426000	6.678035000	-7.975625000
C	0.745630000	7.231122000	-8.940504000
C	1.400011000	5.008263000	-9.649498000
C	1.491703000	6.393922000	-9.778065000
H	1.980474000	4.358377000	-10.302014000
H	0.821331000	8.310597000	-9.045150000
H	2.143662000	6.835134000	-10.530005000
C	-3.211216000	0.046372000	-4.477422000
C	-2.460537000	-0.946095000	-5.130519000
H	-1.696693000	-0.617308000	-5.831706000
C	-4.217814000	-0.343639000	-3.552815000
C	-4.444785000	-1.704843000	-3.313965000
C	-2.691811000	-2.292915000	-4.886069000
C	-3.686225000	-2.669260000	-3.977695000
H	-2.102415000	-3.051303000	-5.399280000
H	-5.214130000	-2.016884000	-2.612739000
H	-3.877024000	-3.723394000	-3.780923000
H	-1.572119000	5.463389000	-6.318556000
H	-3.554114000	3.053424000	-4.180303000
O	-0.875103000	7.389576000	-7.096069000
C	-0.794074000	8.815332000	-7.159220000
H	-1.123867000	9.187909000	-8.139140000
H	0.229446000	9.160876000	-6.958155000
H	-1.465473000	9.187438000	-6.381575000
O	-4.915501000	0.664167000	-2.955452000
C	-5.964091000	0.289435000	-2.059980000
H	-5.574627000	-0.269716000	-1.197829000
H	-6.730391000	-0.309857000	-2.571866000
H	-6.406562000	1.227402000	-1.716255000

o-methoxydithizone (Keto form)

	x	y	z
N	2.755896000	8.442196000	-1.379541000
N	2.131551000	9.396739000	-0.810068000
C	1.284579000	8.967634000	0.231239000
N	0.679113000	10.074342000	0.749515000
N	-0.003527000	9.994131000	1.936311000
S	1.004064000	7.430461000	0.831823000
C	3.600563000	8.794735000	-2.424243000
C	4.312891000	7.748300000	-3.086648000
C	3.789303000	10.129986000	-2.863964000
H	3.235020000	10.903957000	-2.337507000

C	4.633755000	10.435654000	-3.908547000
C	5.165849000	8.085723000	-4.159629000
C	5.325500000	9.396927000	-4.562309000
H	5.695224000	7.271742000	-4.652182000
H	4.765859000	11.468256000	-4.228260000
H	5.995026000	9.623629000	-5.391101000
C	-1.129416000	10.795279000	2.148982000
C	-1.877544000	10.534807000	3.325049000
C	-1.513009000	11.850556000	1.317472000
H	-0.968764000	12.031971000	0.391891000
C	-2.611455000	12.649659000	1.648361000
C	-2.973257000	11.331545000	3.644551000
C	-3.337599000	12.394664000	2.807139000
H	-3.548678000	11.129817000	4.544877000
H	-2.900019000	13.463821000	0.986239000
H	-4.195376000	13.011747000	3.068280000
H	-0.048449000	9.001517000	2.221955000
H	1.100601000	10.972714000	0.517633000
O	4.286310000	6.423007000	-2.826673000
C	3.546661000	5.841420000	-1.730857000
H	2.471444000	6.010601000	-1.837648000
O	-1.427233000	9.466510000	4.059439000
C	-2.169237000	9.124105000	5.231008000
H	-3.208188000	8.866263000	4.981966000
H	-1.667197000	8.251612000	5.656373000
H	-2.158325000	9.945777000	5.960994000
H	3.786758000	4.775560000	-1.785176000
H	3.860242000	6.265742000	-0.772007000

o-methoxydithizone (Hydrogen bridge 1 form)

	x	y	z
N	0.244038000	2.485266000	0.382881000
N	-0.063463000	2.101416000	-0.834171000
C	-1.294881000	2.569139000	-1.220773000
N	-1.680126000	2.193858000	-2.474289000
N	-0.993073000	1.224987000	-3.020883000
S	-2.305753000	3.557576000	-0.252961000
C	1.481595000	2.266443000	0.949590000
C	2.508449000	1.587398000	0.276407000
H	2.316294000	1.245638000	-0.737440000
C	1.704730000	2.743084000	2.271302000
C	2.940879000	2.526473000	2.881186000
C	3.732639000	1.372855000	0.897974000
C	3.949559000	1.840962000	2.196682000
H	4.523288000	0.844699000	0.367724000
H	3.121717000	2.889559000	3.889789000
H	4.908617000	1.677701000	2.685256000
C	-1.176679000	0.793588000	-4.325501000
C	-2.174982000	1.301983000	-5.164338000
H	-2.834803000	2.072257000	-4.771893000
C	-0.291020000	-0.207682000	-4.799317000
C	-0.418976000	-0.680414000	-6.103529000

C	-2.297775000	0.815913000	-6.462226000
C	-1.423807000	-0.168521000	-6.930774000
H	-3.076465000	1.209603000	-7.112759000
H	0.258714000	-1.443455000	-6.479054000
H	-1.516890000	-0.544830000	-7.947952000
H	-0.519426000	3.051624000	0.849878000
H	-0.212152000	0.822146000	-2.485113000
O	0.650471000	-0.623964000	-3.892089000
O	0.650585000	3.393336000	2.839944000
C	1.600855000	-1.599191000	-4.330193000
C	0.833818000	3.923945000	4.155833000
H	2.255404000	-1.780110000	-3.473992000
H	1.045020000	3.123585000	4.878122000
H	-0.110645000	4.409547000	4.411277000
H	1.646082000	4.663370000	4.172631000
H	1.103221000	-2.535629000	-4.615738000
H	2.193157000	-1.219914000	-5.174015000

o-methoxydithizone (Hydrogen bridge 2 form)

	x	y	z
N	0.124504000	2.616499000	0.469610000
N	-0.170860000	2.161290000	-0.696254000
C	-1.383561000	2.538661000	-1.208779000
N	-1.746265000	2.117177000	-2.410194000
N	-0.930368000	1.259929000	-3.009785000
S	-2.511771000	3.598097000	-0.333464000
C	1.388474000	2.272625000	0.944830000
C	2.335202000	1.518659000	0.223477000
H	2.058434000	1.182303000	-0.773338000
C	1.735163000	2.737801000	2.246699000
C	2.996480000	2.434475000	2.776921000
C	3.580257000	1.223862000	0.757193000
C	3.908918000	1.683464000	2.037407000
H	4.300065000	0.643658000	0.182075000
H	3.271592000	2.784459000	3.768435000
H	4.885105000	1.460151000	2.465590000
C	-1.115220000	0.809482000	-4.305248000
C	-2.138507000	1.259881000	-5.145451000
H	-2.828381000	2.008883000	-4.763777000
C	-0.195497000	-0.161006000	-4.779175000
C	-0.314703000	-0.660329000	-6.072523000
C	-2.250981000	0.751356000	-6.438828000
C	-1.345596000	-0.202588000	-6.903238000
H	-3.048987000	1.108370000	-7.087655000
H	0.388396000	-1.404733000	-6.438579000
H	-1.431032000	-0.597535000	-7.913936000
H	-0.094605000	0.954158000	-2.505810000
O	0.769526000	-0.529734000	-3.868164000
O	0.792293000	3.464863000	2.904759000
C	1.692614000	-1.543796000	-4.268048000
C	1.129768000	3.948311000	4.206916000
H	2.347169000	-1.707334000	-3.407777000
H	1.336058000	3.120220000	4.899303000

H	0.252841000	4.501418000	4.551885000
H	1.996982000	4.622348000	4.169808000
H	1.169835000	-2.478615000	-4.513557000
H	2.292695000	-1.218692000	-5.129289000
H	-1.599631000	3.669353000	0.691112000

m-methoxydithizone (Symmetric form)

	x	y	z
N	0.063103000	2.168735000	0.383090000
N	-0.317357000	1.857983000	-0.819784000
C	-1.352981000	2.633334000	-1.252903000
N	-1.678628000	2.289581000	-2.531893000
N	-2.642193000	3.017838000	-3.010120000
S	-2.115151000	3.878256000	-0.332910000
C	1.109155000	1.540330000	1.054235000
C	1.808824000	0.460016000	0.491675000
H	1.531722000	0.096927000	-0.493951000
C	1.437900000	2.033760000	2.320296000
C	2.481275000	1.448405000	3.041898000
C	2.838459000	-0.108944000	1.227332000
C	3.188993000	0.367856000	2.497163000
H	3.391520000	-0.949013000	0.809984000
H	4.002404000	-0.102000000	3.043855000
C	-3.134932000	2.899446000	-4.307105000
C	-2.629699000	1.947403000	-5.207762000
H	-1.838171000	1.275255000	-4.889077000
C	-4.151402000	3.781183000	-4.682850000
C	-4.673149000	3.725252000	-5.977430000
C	-3.164615000	1.906413000	-6.487188000
C	-4.180156000	2.783040000	-6.890377000
H	-2.785061000	1.176847000	-7.201121000
H	-4.571987000	2.725020000	-7.902521000
H	-0.476398000	2.954836000	0.821030000
H	-3.012115000	3.741424000	-2.346773000
H	-4.540545000	4.520927000	-3.983659000
H	0.897236000	2.874703000	2.753399000
O	2.730624000	2.008749000	4.266843000
O	-5.658665000	4.637064000	-6.250442000
C	3.794660000	1.442666000	5.034027000
C	-6.183726000	4.644564000	-7.579003000
H	-5.397922000	4.863415000	-8.315757000
H	-6.932421000	5.440345000	-7.597754000
H	-6.662634000	3.686720000	-7.826065000
H	4.755902000	1.527125000	4.507548000
H	3.834683000	2.023292000	5.958929000
H	3.597572000	0.387935000	5.272487000

m-methoxydithizone (enol form)

	x	y	z
N	-3.000254000	1.388437000	-4.660275000

N	-2.172204000	1.764435000	-5.551587000
C	-2.048885000	3.127001000	-5.707872000
N	-1.204684000	3.478661000	-6.647469000
N	-1.011981000	4.766854000	-6.863439000
S	-2.988796000	4.256965000	-4.690128000
C	-0.163788000	5.220840000	-7.878157000
C	0.461614000	4.322583000	-8.757885000
H	0.288837000	3.256404000	-8.647177000
C	0.037511000	6.597349000	-7.997770000
C	0.868474000	7.091909000	-9.007099000
C	1.282697000	4.836202000	-9.752999000
C	1.498234000	6.211212000	-9.896221000
H	1.770923000	4.150645000	-10.444426000
H	2.145544000	6.577684000	-10.688343000
C	-3.109214000	-0.005829000	-4.491874000
C	-2.274275000	-0.939391000	-5.137853000
H	-1.497907000	-0.581436000	-5.808768000
C	-4.109870000	-0.437797000	-3.618900000
C	-4.298589000	-1.805096000	-3.388930000
C	-2.466071000	-2.289079000	-4.892403000
C	-3.472613000	-2.739268000	-4.024483000
H	-1.824611000	-3.022586000	-5.379535000
H	-3.596953000	-3.805473000	-3.854350000
H	-1.498947000	5.461183000	-6.289960000
H	-3.517684000	3.107054000	-4.102908000
H	-0.440236000	7.301337000	-7.316143000
H	-4.750075000	0.289601000	-3.123269000
O	1.002134000	8.457178000	-9.037909000
O	-5.316192000	-2.126818000	-2.525981000
C	1.825925000	8.999671000	-10.070659000
C	-5.529126000	-3.515918000	-2.274781000
H	1.811827000	10.082764000	-9.925018000
H	-5.779602000	-4.056080000	-3.198840000
H	-6.373279000	-3.569000000	-1.582819000
H	-4.646208000	-3.977973000	-1.810104000
H	2.859433000	8.634118000	-9.992468000
H	1.426727000	8.758724000	-11.066360000

m-methoxydithizone (enol form)

	x	y	z
N	-3.000254000	1.388437000	-4.660275000
N	-2.172204000	1.764435000	-5.551587000
C	-2.048885000	3.127001000	-5.707872000
N	-1.204684000	3.478661000	-6.647469000
N	-1.011981000	4.766854000	-6.863439000
S	-2.988796000	4.256965000	-4.690128000
C	-0.163788000	5.220840000	-7.878157000
C	0.461614000	4.322583000	-8.757885000
H	0.288837000	3.256404000	-8.647177000
C	0.037511000	6.597349000	-7.997770000
C	0.868474000	7.091909000	-9.007099000

C	1.282697000	4.836202000	-9.752999000
C	1.498234000	6.211212000	-9.896221000
H	1.770923000	4.150645000	-10.444426000
H	2.145544000	6.577684000	-10.688343000
C	-3.109214000	-0.005829000	-4.491874000
C	-2.274275000	-0.939391000	-5.137853000
H	-1.497907000	-0.581436000	-5.808768000
C	-4.109870000	-0.437797000	-3.618900000
C	-4.298589000	-1.805096000	-3.388930000
C	-2.466071000	-2.289079000	-4.892403000
C	-3.472613000	-2.739268000	-4.024483000
H	-1.824611000	-3.022586000	-5.379535000
H	-3.596953000	-3.805473000	-3.854350000
H	-1.498947000	5.461183000	-6.289960000
H	-3.517684000	3.107054000	-4.102908000
H	-0.440236000	7.301337000	-7.316143000
H	-4.750075000	0.289601000	-3.123269000
O	1.002134000	8.457178000	-9.037909000
O	-5.316192000	-2.126818000	-2.525981000
C	1.825925000	8.999671000	-10.070659000
C	-5.529126000	-3.515918000	-2.274781000
H	1.811827000	10.082764000	-9.925018000
H	-5.779602000	-4.056080000	-3.198840000
H	-6.373279000	-3.569000000	-1.582819000
H	-4.646208000	-3.977973000	-1.810104000
H	2.859433000	8.634118000	-9.992468000
H	1.426727000	8.758724000	-11.066360000

m-methoxydithizone (keto form)

	x	y	z
N	2.706863000	8.480740000	-1.323023000
N	2.077155000	9.464524000	-0.835588000
C	1.237824000	9.105705000	0.251694000
N	0.703026000	10.254369000	0.757845000
N	0.091099000	10.209059000	1.988009000
S	0.913885000	7.603345000	0.900363000
C	3.546163000	8.771350000	-2.414019000
C	4.316662000	7.681377000	-2.829817000
C	3.648244000	10.014142000	-3.072626000
H	3.034898000	10.849160000	-2.743264000
C	4.530512000	10.129993000	-4.134782000
C	5.212045000	7.815463000	-3.894817000
C	5.318425000	9.045653000	-4.554617000
H	4.622380000	11.078178000	-4.663410000
H	6.000671000	9.172836000	-5.391957000
C	-1.061145000	10.972904000	2.240524000
C	-1.763711000	10.666618000	3.408342000
C	-1.481441000	12.032400000	1.420715000
H	-0.961719000	12.261086000	0.492455000
C	-2.603533000	12.765935000	1.797103000
C	-2.893217000	11.404880000	3.762440000
C	-3.321016000	12.472455000	2.959225000

H	-2.938274000	13.586103000	1.163436000
H	-4.195868000	13.061322000	3.221405000
H	0.051941000	9.204544000	2.248114000
H	1.162531000	11.125795000	0.494474000
H	-1.442813000	9.848572000	4.053094000
H	4.215056000	6.731083000	-2.309265000
O	5.929229000	6.691595000	-4.209945000
O	-3.512715000	11.000181000	4.917726000
C	6.852401000	6.794507000	-5.294371000
C	-4.685205000	11.713107000	5.310868000
H	-4.463205000	12.770911000	5.510465000
H	-5.027885000	11.233845000	6.231708000
H	-5.472477000	11.642263000	4.546729000
H	7.616683000	7.559985000	-5.098357000
H	7.331600000	5.815542000	-5.371281000
H	6.336228000	7.023572000	-6.237439000

m-methoxydithizone (Hydrogen bridge 1 form)

	x	y	z
N	0.244785000	2.295593000	0.370060000
N	-0.011479000	1.969147000	-0.874842000
C	-1.215048000	2.493622000	-1.282386000
N	-1.581209000	2.184353000	-2.553599000
N	-1.018125000	1.134297000	-3.085680000
S	-2.224218000	3.482418000	-0.311362000
C	1.475137000	2.119873000	0.982938000
C	2.581218000	1.578935000	0.301334000
H	2.487437000	1.313979000	-0.747798000
C	1.577520000	2.493586000	2.329241000
C	2.785745000	2.324777000	3.007483000
C	3.772406000	1.418317000	0.994865000
C	3.895206000	1.782251000	2.341975000
H	4.639029000	1.005108000	0.480818000
H	4.844335000	1.646357000	2.853977000
C	-1.205219000	0.763970000	-4.418316000
C	-2.023761000	1.510535000	-5.271692000
H	-2.516773000	2.402334000	-4.895274000
C	-0.545378000	-0.396517000	-4.862495000
C	-0.712896000	-0.807988000	-6.185224000
C	-2.177466000	1.074219000	-6.585951000
C	-1.533519000	-0.068528000	-7.051980000
H	-2.811809000	1.641827000	-7.264928000
H	-1.647775000	-0.408667000	-8.079407000
H	-0.547733000	2.848507000	0.812442000
H	-0.336463000	0.616925000	-2.513200000
H	0.082372000	-0.954932000	-4.170199000
O	-0.119959000	-1.917447000	-6.725438000
C	0.706816000	-2.699697000	-5.862608000
H	1.561161000	-2.116205000	-5.490273000
H	0.133621000	-3.096750000	-5.012596000
H	1.073218000	-3.529418000	-6.471837000
H	0.723416000	2.914975000	2.858450000

O	2.781453000	2.718692000	4.319197000
C	3.993442000	2.546327000	5.055060000
H	4.285958000	1.487762000	5.100412000
H	4.812769000	3.136210000	4.620623000
H	3.781333000	2.908069000	6.064174000

m-methoxydithizone (Hydrogen bridge 2 form)

	x	y	z
N	0.157476000	2.674093000	0.459328000
N	-0.124168000	2.221783000	-0.705950000
C	-1.321724000	2.608676000	-1.252210000
N	-1.671496000	2.147189000	-2.439323000
N	-0.857857000	1.283928000	-3.026598000
S	-2.458623000	3.716860000	-0.446829000
C	1.406383000	2.277706000	0.968087000
C	2.394945000	1.593046000	0.228500000
H	2.217098000	1.358554000	-0.817016000
C	1.641177000	2.610287000	2.306793000
C	2.839103000	2.241758000	2.927722000
C	3.582703000	1.247006000	0.851880000
C	3.818963000	1.556638000	2.199084000
H	4.355875000	0.723883000	0.290051000
H	4.760997000	1.267128000	2.659262000
C	-1.094601000	0.761488000	-4.293293000
C	-2.210446000	1.136917000	-5.056835000
H	-2.913307000	1.859600000	-4.650736000
C	-0.168909000	-0.165458000	-4.800689000
C	-0.361117000	-0.706599000	-6.068302000
C	-2.381383000	0.580801000	-6.320684000
C	-1.467662000	-0.341325000	-6.839823000
H	-3.241586000	0.878938000	-6.918908000
H	-1.589392000	-0.764308000	-7.835741000
H	-0.008735000	1.016154000	-2.521625000
H	-1.592211000	3.811170000	0.609787000
H	0.708271000	-0.459269000	-4.222500000
O	0.592740000	-1.578406000	-6.579820000
C	0.287078000	-2.958632000	-6.328259000
H	0.250336000	-3.164422000	-5.247298000
H	-0.675494000	-3.241715000	-6.780195000
H	1.092219000	-3.542850000	-6.784656000
H	0.878452000	3.143227000	2.871875000
O	2.957058000	2.593739000	4.247796000
C	4.147451000	2.180576000	4.921256000
H	4.256454000	1.086949000	4.902876000
H	5.040626000	2.644530000	4.479453000
H	4.037551000	2.517381000	5.955224000

p-methoxydithizone (Symmetric form)

	x	y	z
N	0.101551000	2.197777000	0.384142000

N	-0.249827000	1.912506000	-0.837541000
C	-1.353921000	2.602432000	-1.238867000
N	-1.644175000	2.302719000	-2.535777000
N	-2.688103000	2.945652000	-2.975084000
S	-2.243711000	3.709662000	-0.254602000
C	1.174333000	1.604283000	1.037709000
C	1.900366000	0.551595000	0.467404000
H	1.622046000	0.193012000	-0.520388000
C	1.520609000	2.081406000	2.315100000
C	2.569397000	1.508144000	3.010576000
C	2.952774000	-0.027821000	1.168613000
C	3.290613000	0.442741000	2.446922000
H	3.501367000	-0.849441000	0.714049000
H	2.849923000	1.866337000	3.999060000
C	-3.156842000	2.858685000	-4.279828000
C	-2.498053000	2.101906000	-5.256973000
H	-1.596871000	1.558002000	-4.984553000
C	-4.322519000	3.570754000	-4.614953000
C	-4.816280000	3.529099000	-5.906131000
C	-2.993081000	2.062026000	-6.556582000
C	-4.153745000	2.777406000	-6.890415000
H	-2.465941000	1.474685000	-7.304878000
H	-5.716844000	4.074826000	-6.180865000
H	-0.505846000	2.910563000	0.855791000
H	-3.138623000	3.575819000	-2.268046000
H	-4.835401000	4.156321000	-3.852053000
H	0.960502000	2.907730000	2.753052000
O	-4.714718000	2.808132000	-8.138102000
O	4.294364000	-0.069527000	3.222864000
C	-4.044971000	2.083589000	-9.172020000
C	5.011708000	-1.191395000	2.704495000
H	-4.007973000	1.008373000	-8.947179000
H	5.558122000	-0.927581000	1.788237000
H	4.337267000	-2.034278000	2.499819000
H	5.722323000	-1.476342000	3.483946000
H	-3.024774000	2.462527000	-9.325990000
H	-4.633750000	2.245375000	-10.078069000

p-methoxydithizone (Enol form)

	x	y	z
N	-3.020825000	1.357225000	-4.736993000
N	-2.195671000	1.734874000	-5.636970000
C	-2.081506000	3.093055000	-5.807876000
N	-1.208146000	3.450660000	-6.720095000
N	-1.009107000	4.741134000	-6.925245000
S	-3.057772000	4.227221000	-4.823965000
C	-0.100618000	5.198539000	-7.884382000
C	0.573289000	4.313911000	-8.732448000
H	0.387753000	3.247142000	-8.637611000
C	0.132728000	6.579308000	-7.996619000
C	1.021714000	7.063144000	-8.942877000
C	1.466488000	4.801206000	-9.685031000

C	1.695254000	6.178489000	-9.798688000
H	1.976420000	4.094516000	-10.335508000
H	1.210528000	8.130730000	-9.038192000
C	-3.115653000	-0.027758000	-4.548200000
C	-2.349778000	-0.972305000	-5.253567000
H	-1.641492000	-0.617187000	-5.998681000
C	-4.030977000	-0.480449000	-3.580538000
C	-4.178481000	-1.832468000	-3.323043000
C	-2.490931000	-2.329902000	-5.000547000
C	-3.408141000	-2.769422000	-4.030016000
H	-1.885075000	-3.041436000	-5.557083000
H	-4.883600000	-2.193617000	-2.576372000
H	-1.502049000	5.431423000	-6.352012000
H	-3.562669000	3.076919000	-4.215085000
H	-0.385633000	7.274855000	-7.335145000
H	-4.621402000	0.255661000	-3.036839000
O	2.549799000	6.756037000	-10.705974000
O	-3.616973000	-4.081991000	-3.704872000
C	-2.846568000	-5.059182000	-4.410321000
C	3.210451000	5.875410000	-11.615327000
H	3.822654000	6.512454000	-12.258796000
H	-1.769948000	-4.916488000	-4.241927000
H	-3.152111000	-6.027700000	-4.006903000
H	-3.056402000	-5.029305000	-5.488647000
H	3.858795000	5.162535000	-11.085444000
H	2.487236000	5.321613000	-12.231106000

p-methoxydithizone (Keto form)

	x	y	z
N	2.661903000	8.535723000	-1.444847000
N	2.093509000	9.532901000	-0.896047000
C	1.210419000	9.168617000	0.145744000
N	0.733844000	10.316287000	0.715531000
N	0.132006000	10.240216000	1.952696000
S	0.786183000	7.654338000	0.712283000
C	3.568948000	8.826104000	-2.465018000
C	4.230178000	7.702566000	-3.002042000
C	3.882353000	10.105451000	-2.962653000
H	3.367662000	10.971542000	-2.551064000
C	4.836802000	10.258985000	-3.957617000
C	5.184233000	7.845607000	-3.990344000
C	5.499363000	9.126804000	-4.472744000
H	5.708683000	6.987326000	-4.406476000
H	5.069956000	11.253687000	-4.331065000
C	-1.000539000	11.036777000	2.229190000
C	-1.594154000	10.870594000	3.493897000
C	-1.524940000	11.989857000	1.354093000
H	-1.099045000	12.111746000	0.359453000
C	-2.627160000	12.768142000	1.730223000
C	-2.692740000	11.626219000	3.861288000
C	-3.218609000	12.587257000	2.983431000
H	-3.162636000	11.492729000	4.834141000

H	-3.021220000	13.496361000	1.025545000
H	0.035097000	9.223260000	2.148498000
H	1.253677000	11.169849000	0.510191000
H	3.970772000	6.723387000	-2.603534000
H	-1.179116000	10.138056000	4.185872000
O	-4.307762000	13.285076000	3.451283000
O	6.461196000	9.170344000	-5.437673000
C	-4.876168000	14.252888000	2.572197000
C	6.829083000	10.453681000	-5.954007000
H	7.615447000	10.261572000	-6.687737000
H	-5.718477000	14.691790000	3.113318000
H	5.977916000	10.941533000	-6.448000000
H	7.219625000	11.104577000	-5.160431000
H	-5.241630000	13.787264000	1.645214000
H	-4.152294000	15.042324000	2.322465000

p-methoxydithizone (Hydrogen bridge 1 form)

	x	y	z
N	-3.219224000	10.841031000	-1.874435000
N	-2.463200000	11.909002000	-1.755897000
C	-2.700942000	12.796132000	-2.777701000
N	-1.997687000	13.955680000	-2.721786000
N	-1.457468000	14.262397000	-1.570531000
S	-3.802749000	12.510199000	-4.065209000
C	-3.061958000	9.690435000	-1.127574000
C	-3.972656000	8.633659000	-1.338883000
C	-2.044454000	9.543212000	-0.172413000
H	-1.334458000	10.353512000	-0.027085000
C	-1.939957000	8.367130000	0.563967000
C	-3.866300000	7.465418000	-0.611201000
C	-2.849281000	7.319976000	0.349173000
H	-4.560980000	6.642026000	-0.766030000
H	-1.141889000	8.269748000	1.296037000
C	-0.625275000	15.363995000	-1.395620000
C	-0.310806000	16.219040000	-2.459648000
C	-0.108145000	15.622451000	-0.112877000
H	-0.351704000	14.956525000	0.716042000
C	0.705865000	16.720097000	0.100369000
C	0.501872000	17.326165000	-2.242584000
C	1.015880000	17.584889000	-0.962273000
H	0.732107000	17.981962000	-3.078769000
H	1.113754000	16.933901000	1.086385000
H	-3.875175000	10.911525000	-2.711881000
H	-1.599466000	13.609799000	-0.787516000
H	-0.715479000	16.003783000	-3.445369000
H	-4.761378000	8.746798000	-2.082373000
O	-2.828271000	6.124110000	1.012924000
O	1.822655000	18.644622000	-0.650826000
C	-1.812995000	5.944433000	2.002614000
C	2.158907000	19.541458000	-1.712678000
H	-0.809367000	5.999736000	1.558079000
H	-1.902393000	6.690342000	2.804756000

H	-1.973367000	4.945404000	2.415072000
H	1.261031000	20.015596000	-2.132945000
H	2.709854000	19.024254000	-2.510614000
H	2.798465000	20.305763000	-1.264952000

p-methoxydithizone (Hydrogen bridge 2 form)

	x	y	z
N	-0.553230000	11.285018000	-6.803666000
N	-0.102959000	10.277558000	-7.466316000
C	0.072387000	10.453569000	-8.811689000
N	0.502322000	9.450988000	-9.557922000
N	0.791797000	8.309756000	-8.951439000
S	-0.270366000	11.988360000	-9.651847000
C	1.190409000	7.171346000	-9.645175000
C	1.540300000	6.025088000	-8.919334000
H	1.496683000	6.038258000	-7.829250000
C	1.248924000	7.143528000	-11.049471000
C	1.656550000	5.991443000	-11.699806000
C	1.951169000	4.865257000	-9.574979000
C	2.015125000	4.843861000	-10.973796000
H	2.218824000	3.991647000	-8.986019000
H	1.704802000	5.954941000	-12.787076000
C	-0.761293000	11.070266000	-5.440852000
C	-0.463190000	9.873814000	-4.748540000
H	-0.018776000	9.045176000	-5.294439000
C	-1.325262000	12.137317000	-4.722736000
C	-1.609410000	12.026787000	-3.365516000
C	-0.735751000	9.756821000	-3.400995000
C	-1.320414000	10.828250000	-2.697012000
H	-0.514072000	8.840943000	-2.854920000
H	-2.055187000	12.867741000	-2.840223000
H	-0.662575000	12.529036000	-8.455561000
H	0.674620000	8.269273000	-7.935906000
H	0.969327000	8.033658000	-11.607154000
H	-1.548091000	13.057755000	-5.260209000
O	-1.566006000	10.596081000	-1.373141000
O	2.410567000	3.761707000	-11.722009000
C	2.825036000	2.601235000	-11.002692000
C	-2.199899000	11.642938000	-0.632138000
H	2.004501000	2.189160000	-10.397050000
H	-3.182563000	11.890030000	-1.057395000
H	3.120287000	1.868745000	-11.758385000
H	3.683887000	2.820822000	-10.351861000
H	-1.573863000	12.545399000	-0.602098000
H	-2.328392000	11.254397000	0.381131000

o-methyldithizone (Symmetric form)

	x	y	z
N	0.049412000	2.184396000	0.406269000
N	-0.301604000	1.932866000	-0.821668000

C	-1.367507000	2.679396000	-1.227488000
N	-1.668964000	2.379046000	-2.522427000
N	-2.678175000	3.064890000	-2.975527000
S	-2.201700000	3.834809000	-0.253713000
C	1.109717000	1.549943000	1.051603000
C	1.845650000	0.548338000	0.399354000
H	1.570756000	0.278911000	-0.617525000
C	1.416062000	1.945773000	2.374948000
C	2.480715000	1.299541000	3.008244000
C	2.897215000	-0.071570000	1.061309000
C	3.218858000	0.302051000	2.369664000
H	3.467772000	-0.849632000	0.556293000
H	2.734028000	1.590741000	4.028173000
H	4.042719000	-0.181801000	2.891881000
C	-3.166955000	2.951803000	-4.276250000
C	-2.559952000	2.080145000	-5.193536000
H	-1.702868000	1.495675000	-4.867782000
C	-4.284046000	3.741070000	-4.638091000
C	-4.759368000	3.619506000	-5.946311000
C	-3.060724000	1.986166000	-6.485328000
C	-4.163229000	2.756517000	-6.866954000
H	-2.589113000	1.311307000	-7.198121000
H	-5.619559000	4.219250000	-6.245585000
H	-4.557964000	2.686247000	-7.879309000
H	-0.534602000	2.912628000	0.880677000
H	-3.095227000	3.727883000	-2.280816000
C	0.629977000	3.023512000	3.075980000
C	-4.939083000	4.675717000	-3.654095000
H	-5.316571000	4.140393000	-2.770750000
H	-0.431211000	2.754079000	3.180747000
H	0.667979000	3.977858000	2.530854000
H	1.030112000	3.196993000	4.080321000
H	-4.240699000	5.444096000	-3.291426000
H	-5.786436000	5.189269000	-4.120115000

o-methyldithizone (Enol form)

	x	y	z
N	-3.080560000	1.432808000	-4.666102000
N	-2.235878000	1.805278000	-5.546553000
C	-2.126785000	3.165319000	-5.724460000
N	-1.259189000	3.517415000	-6.643322000
N	-1.085528000	4.807240000	-6.876779000
S	-3.116076000	4.292985000	-4.752145000
C	-0.194358000	5.262012000	-7.855436000
C	0.514098000	4.346926000	-8.647297000
H	0.355027000	3.284041000	-8.484369000
C	-0.029167000	6.654644000	-8.025417000
C	0.864960000	7.085707000	-9.009080000
C	1.395705000	4.812246000	-9.616120000
C	1.576411000	6.184579000	-9.802697000
H	1.942890000	4.097231000	-10.229417000
H	1.003749000	8.158202000	-9.151111000

H	2.266074000	6.551604000	-10.561086000
C	-3.184853000	0.043573000	-4.469499000
C	-2.343426000	-0.879591000	-5.119170000
H	-1.587183000	-0.494377000	-5.799481000
C	-4.181181000	-0.403032000	-3.569593000
C	-4.300745000	-1.780805000	-3.358164000
C	-2.483288000	-2.239390000	-4.886406000
C	-3.467693000	-2.694854000	-4.002574000
H	-1.826624000	-2.948315000	-5.389788000
H	-5.066816000	-2.141719000	-2.670637000
H	-3.583824000	-3.761800000	-3.815204000
H	-1.615365000	5.495347000	-6.336266000
H	-3.631104000	3.131299000	-4.165946000
C	-0.787402000	7.642249000	-7.174933000
C	-5.091465000	0.564508000	-2.861287000
H	-0.559013000	7.524475000	-6.104539000
H	-4.521821000	1.254430000	-2.225102000
H	-0.525972000	8.668485000	-7.453863000
H	-1.877020000	7.538890000	-7.294189000
H	-5.654374000	1.180160000	-3.574215000
H	-5.806451000	0.025009000	-2.230174000

o-methyldithizone (Keto form)

	x	y	z
N	2.729942000	8.510383000	-1.343936000
N	2.128191000	9.465581000	-0.765649000
C	1.247525000	9.048300000	0.260411000
N	0.696201000	10.169723000	0.802470000
N	-0.033049000	10.077674000	1.960720000
S	0.873476000	7.515132000	0.810478000
C	3.575711000	8.871346000	-2.404122000
C	4.365385000	7.819702000	-2.935838000
C	3.643062000	10.167777000	-2.953429000
H	3.007889000	10.942482000	-2.528583000
C	4.490278000	10.432882000	-4.017356000
C	5.211202000	8.118713000	-4.009809000
C	5.279135000	9.402936000	-4.546885000
H	5.824654000	7.322959000	-4.433899000
H	4.537356000	11.433435000	-4.445946000
H	5.942776000	9.602487000	-5.387791000
C	-1.153947000	10.904448000	2.156268000
C	-1.959871000	10.633693000	3.287098000
C	-1.446984000	11.986924000	1.316255000
H	-0.846581000	12.167880000	0.425811000
C	-2.536036000	12.812886000	1.596157000
C	-3.045490000	11.473752000	3.533064000
C	-3.339982000	12.561281000	2.706218000
H	-3.676012000	11.265730000	4.398664000
H	-2.759624000	13.646359000	0.931835000
H	-4.194888000	13.198579000	2.925199000
H	-0.127880000	9.063539000	2.161015000
H	1.151547000	11.057901000	0.597736000

C	-1.647479000	9.464619000	4.182934000
C	4.320850000	6.433721000	-2.354280000
H	4.747874000	5.707956000	-3.055805000
H	-1.698042000	8.508680000	3.638657000
H	-2.359535000	9.409304000	5.012934000
H	-0.633737000	9.539918000	4.602393000
H	3.298561000	6.142409000	-2.093473000
H	4.901621000	6.387822000	-1.422289000

o-methyldithizone (Hydrogen bridge 1 form)

	x	y	z
N	0.244966000	2.459041000	0.380313000
N	-0.045653000	2.067777000	-0.837372000
C	-1.282519000	2.523541000	-1.227394000
N	-1.666023000	2.151803000	-2.479070000
N	-0.972803000	1.197549000	-3.041276000
S	-2.299257000	3.500197000	-0.248338000
C	1.476679000	2.268601000	0.982521000
C	2.508469000	1.579891000	0.317880000
H	2.328815000	1.220471000	-0.692172000
C	1.664516000	2.774972000	2.294792000
C	2.904504000	2.557377000	2.897474000
C	3.725699000	1.376992000	0.952523000
C	3.929336000	1.865118000	2.247643000
H	4.521139000	0.841221000	0.436578000
H	3.067895000	2.942288000	3.904620000
H	4.883763000	1.711109000	2.748336000
C	-1.158846000	0.775696000	-4.357322000
C	-2.170745000	1.332761000	-5.154871000
H	-2.806392000	2.105219000	-4.728492000
C	-0.294947000	-0.228930000	-4.855784000
C	-0.486014000	-0.646988000	-6.174323000
C	-2.333997000	0.885827000	-6.459907000
C	-1.491708000	-0.104416000	-6.975527000
H	-3.119883000	1.314576000	-7.080178000
H	-1.615754000	-0.452347000	-7.999862000
H	-0.551503000	3.018482000	0.811938000
H	-0.190323000	0.810421000	-2.497990000
H	0.172523000	-1.416744000	-6.577984000
C	0.795587000	-0.824089000	-4.000026000
H	0.391387000	-1.328840000	-3.110115000
H	1.364478000	-1.567578000	-4.567826000
H	1.509261000	-0.061192000	-3.653448000
C	0.568037000	3.519585000	3.007680000
H	0.225292000	4.391551000	2.431071000
H	-0.313489000	2.883079000	3.173264000
H	0.916312000	3.874661000	3.983138000

o-methyldithizone (Hydrogen bridge 2 form)

	x	y	z
N	0.173163000	2.617940000	0.474548000
N	-0.111385000	2.150494000	-0.687820000
C	-1.317851000	2.525852000	-1.218878000
N	-1.680713000	2.086056000	-2.410583000
N	-0.871700000	1.233643000	-3.022282000
S	-2.450976000	3.614957000	-0.385312000
C	1.433538000	2.280753000	0.984079000
C	2.406323000	1.564048000	0.256339000
H	2.169514000	1.253750000	-0.758828000
C	1.714950000	2.722138000	2.302591000
C	2.968213000	2.417567000	2.844761000
C	3.638788000	1.274917000	0.820333000
C	3.923729000	1.702308000	2.123063000
H	4.385464000	0.723890000	0.248999000
H	3.197592000	2.752908000	3.857120000
H	4.892008000	1.483934000	2.571515000
C	-1.097814000	0.770928000	-4.316246000
C	-2.201901000	1.210917000	-5.061293000
H	-2.886300000	1.925562000	-4.610206000
C	-0.175588000	-0.155335000	-4.859591000
C	-0.400300000	-0.610017000	-6.160548000
C	-2.395504000	0.733251000	-6.352735000
C	-1.495435000	-0.178033000	-6.910941000
H	-3.253416000	1.079594000	-6.928202000
H	-1.643421000	-0.549901000	-7.923394000
H	-0.019249000	0.961733000	-2.528150000
H	-1.566698000	3.692234000	0.659498000
H	0.304567000	-1.322582000	-6.591241000
C	1.008503000	-0.636536000	-4.058464000
H	0.698510000	-1.141369000	-3.130877000
H	1.600756000	-1.351916000	-4.639015000
H	1.679744000	0.190021000	-3.776839000
C	0.697956000	3.484228000	3.107852000
H	0.283855000	4.324501000	2.538254000
H	-0.148989000	2.841456000	3.383821000
H	1.149137000	3.870160000	4.028682000

m-methyldithizone (Symmetric form)

	x	y	z
N	0.033667000	2.138179000	0.421931000
N	-0.335790000	1.884607000	-0.798453000
C	-1.403424000	2.630500000	-1.200495000
N	-1.689893000	2.325877000	-2.498061000
N	-2.677250000	3.020549000	-2.979551000
S	-2.235262000	3.790150000	-0.236349000
C	1.119954000	1.512970000	1.031571000
C	1.860867000	0.528215000	0.365008000
H	1.578644000	0.242503000	-0.644928000
C	1.460599000	1.906804000	2.335864000
H	0.870497000	2.679289000	2.832787000

C	2.546967000	1.328328000	2.991317000
C	2.942448000	-0.048110000	1.021510000
C	3.286817000	0.344147000	2.316778000
H	3.529440000	-0.812807000	0.514652000
H	4.143001000	-0.116155000	2.811577000
C	-3.122176000	2.897782000	-4.295180000
C	-2.535573000	1.980080000	-5.178538000
H	-1.722174000	1.350165000	-4.828042000
C	-4.169956000	3.730051000	-4.717240000
H	-4.606180000	4.440164000	-4.011497000
C	-4.648109000	3.661944000	-6.027085000
C	-3.012090000	1.915501000	-6.481545000
C	-4.053971000	2.745154000	-6.906572000
H	-2.562776000	1.212000000	-7.181129000
H	-4.408652000	2.683857000	-7.935938000
H	-0.534588000	2.868759000	0.912287000
H	-3.104811000	3.703065000	-2.309987000
C	2.918558000	1.742405000	4.392718000
C	-5.790558000	4.537697000	-6.474516000
H	2.346049000	2.617435000	4.719056000
H	-5.757575000	5.520363000	-5.989112000
H	-5.772712000	4.689294000	-7.559536000
H	-6.756526000	4.078216000	-6.220872000
H	3.986056000	1.988029000	4.460712000
H	2.726077000	0.928958000	5.105699000

m-methyldithizone (Enol form)

	x	y	z
N	-3.091044000	1.443147000	-4.639012000
N	-2.307400000	1.859437000	-5.552704000
C	-2.203197000	3.222812000	-5.703503000
N	-1.366914000	3.568051000	-6.650622000
N	-1.132842000	4.844586000	-6.891041000
S	-3.124373000	4.347692000	-4.664683000
C	-0.224196000	5.219942000	-7.890201000
C	0.354621000	4.250955000	-8.722150000
H	0.087643000	3.206549000	-8.585064000
C	0.104249000	6.573367000	-8.042534000
H	-0.348507000	7.316868000	-7.381717000
C	1.017275000	6.979269000	-9.021787000
C	1.261254000	4.657114000	-9.693592000
C	1.595389000	6.004799000	-9.845829000
H	1.717862000	3.908964000	-10.340497000
H	2.314922000	6.303485000	-10.608608000
C	-3.121788000	0.037866000	-4.504499000
C	-2.247623000	-0.818816000	-5.196241000
H	-1.511888000	-0.386357000	-5.869831000
C	-4.070542000	-0.496353000	-3.619671000
H	-4.731536000	0.191950000	-3.091630000
C	-4.175807000	-1.875401000	-3.423413000
C	-2.340619000	-2.188562000	-4.995853000
C	-3.295365000	-2.715201000	-4.120608000

H	-1.661045000	-2.858604000	-5.521655000
H	-3.353650000	-3.794591000	-3.972978000
H	-1.566781000	5.572660000	-6.317136000
H	-3.625976000	3.214508000	-4.038353000
C	-5.218616000	-2.461101000	-2.504265000
C	1.358253000	8.437654000	-9.197091000
H	0.597365000	8.948169000	-9.804721000
H	-5.643135000	-1.701033000	-1.839208000
H	-4.795644000	-3.262466000	-1.885260000
H	-6.045356000	-2.899274000	-3.081623000
H	2.321392000	8.558036000	-9.705785000
H	1.412315000	8.957992000	-8.233052000

m-methyldithizone (Keto form)

	x	y	z
N	2.762792000	8.489257000	-1.331940000
N	2.079123000	9.424779000	-0.818756000
C	1.234208000	9.014953000	0.239595000
N	0.637837000	10.138960000	0.728664000
N	-0.056869000	10.080300000	1.906955000
S	0.938472000	7.498806000	0.873609000
C	3.582324000	8.873743000	-2.411041000
C	4.436783000	7.866893000	-2.883730000
H	4.397223000	6.897238000	-2.385592000
C	3.584190000	10.143571000	-3.018867000
H	2.909327000	10.912329000	-2.649015000
C	4.445419000	10.378679000	-4.080250000
C	5.312320000	8.099146000	-3.948230000
C	5.303813000	9.369551000	-4.538048000
H	4.458227000	11.354445000	-4.565024000
H	5.976967000	9.575341000	-5.371728000
C	-1.149573000	10.930830000	2.129761000
C	-1.884970000	10.733147000	3.308306000
H	-1.607033000	9.912639000	3.973075000
C	-1.482542000	11.988405000	1.270359000
H	-0.946375000	12.136343000	0.334441000
C	-2.537311000	12.833550000	1.612272000
C	-2.950456000	11.569355000	3.642226000
C	-3.266931000	12.633543000	2.784062000
H	-2.797504000	13.655214000	0.946497000
H	-4.089432000	13.303226000	3.036020000
H	-0.132285000	9.077232000	2.159928000
H	1.055747000	11.032463000	0.471930000
C	6.216901000	7.005835000	-4.457932000
C	-3.745853000	11.316527000	4.899106000
H	-3.087483000	11.146171000	5.760213000
H	5.657938000	6.296275000	-5.084445000
H	6.655306000	6.433813000	-3.631256000
H	7.032965000	7.413304000	-5.065287000
H	-4.402362000	12.162043000	5.131866000
H	-4.376646000	10.423156000	4.789972000

m-methyldithizone (Hydrogen bridge 1 form)

	x	y	z
N	0.219310000	2.466694000	0.368742000
N	-0.104408000	2.096786000	-0.845211000
C	-1.337132000	2.571671000	-1.218324000
N	-1.726088000	2.196158000	-2.471613000
N	-1.054858000	1.212063000	-3.003274000
S	-2.329416000	3.561295000	-0.235411000
C	1.469817000	2.240684000	0.919699000
C	2.480162000	1.583645000	0.197086000
H	2.287267000	1.274513000	-0.826284000
C	1.704000000	2.666526000	2.239861000
C	2.935602000	2.440172000	2.852747000
C	3.702730000	1.350229000	0.813436000
C	3.933546000	1.769259000	2.126198000
H	4.489988000	0.835578000	0.264067000
H	4.899222000	1.575484000	2.594262000
C	-1.199443000	0.777521000	-4.317501000
C	-2.186670000	1.284728000	-5.171261000
H	-2.871278000	2.047079000	-4.807715000
C	-0.298734000	-0.205569000	-4.762511000
C	-0.359537000	-0.693624000	-6.064950000
C	-2.254003000	0.785355000	-6.468307000
C	-1.355188000	-0.187253000	-6.916370000
H	-3.018227000	1.163531000	-7.145831000
H	-1.424156000	-0.556713000	-7.940520000
H	-0.547687000	3.032872000	0.836741000
H	-0.287074000	0.819336000	-2.438503000
H	0.465608000	-0.578412000	-4.076896000
C	0.626141000	-1.727602000	-6.546414000
H	1.308931000	-2.032070000	-5.745253000
H	0.112253000	-2.625290000	-6.913748000
H	1.231898000	-1.336447000	-7.375118000
H	0.906544000	3.176543000	2.783309000
C	3.202494000	2.927680000	4.253648000
H	2.273799000	3.050745000	4.821501000
H	3.851100000	2.231519000	4.798795000
H	3.711040000	3.902106000	4.234230000

m-methyldithizone (Hydrogen bridge 2 form)

	x	y	z
N	0.149721000	2.608863000	0.486091000
N	-0.155895000	2.164176000	-0.678058000
C	-1.368304000	2.537161000	-1.192896000
N	-1.723431000	2.107099000	-2.393217000
N	-0.912010000	1.250363000	-2.992554000
S	-2.508086000	3.602944000	-0.337276000
C	1.431848000	2.259450000	0.940358000
C	2.382229000	1.547193000	0.182817000
H	2.132236000	1.234912000	-0.828209000
C	1.758117000	2.679546000	2.241013000
C	3.005566000	2.401621000	2.803875000

C	3.621857000	1.264378000	0.737689000
C	3.933148000	1.683682000	2.036316000
H	4.361742000	0.712691000	0.158529000
H	4.912528000	1.451435000	2.457169000
C	-1.099225000	0.794902000	-4.293215000
C	-2.133395000	1.266714000	-5.112027000
H	-2.818568000	2.019240000	-4.729792000
C	-0.199575000	-0.172768000	-4.774790000
C	-0.315707000	-0.682521000	-6.066530000
C	-2.246958000	0.756052000	-6.402493000
C	-1.355011000	-0.205262000	-6.882145000
H	-3.045416000	1.119203000	-7.048597000
H	-1.463312000	-0.589281000	-7.896998000
H	-0.073013000	0.964424000	-2.479974000
H	-1.615878000	3.691494000	0.698399000
H	0.597753000	-0.532903000	-4.120049000
H	1.003613000	3.230811000	2.803556000
C	0.653074000	-1.721352000	-6.574553000
H	1.352379000	-2.034935000	-5.791142000
H	0.123198000	-2.613879000	-6.932476000
H	1.242428000	-1.333598000	-7.417030000
C	3.362927000	2.886578000	4.186682000
H	2.472229000	3.009697000	4.812799000
H	4.044217000	2.189130000	4.689208000
H	3.870157000	3.861013000	4.138091000

p-methyldithizone (Symmetric form)

	x	y	z
N	0.030861000	2.151988000	0.451949000
N	-0.345553000	1.892792000	-0.765247000
C	-1.419824000	2.629869000	-1.164882000
N	-1.708937000	2.319681000	-2.460140000
N	-2.705278000	3.003411000	-2.941102000
S	-2.255519000	3.786970000	-0.201143000
C	1.120089000	1.525864000	1.054167000
C	1.851677000	0.532928000	0.383746000
H	1.555075000	0.248947000	-0.622483000
C	1.480030000	1.903549000	2.355570000
H	0.908806000	2.673472000	2.875104000
C	2.566475000	1.292751000	2.973806000
C	2.929623000	-0.063526000	1.020717000
C	3.314155000	0.302181000	2.322445000
H	3.491156000	-0.837983000	0.496019000
H	2.839333000	1.592849000	3.985845000
C	-3.136347000	2.882600000	-4.260198000
C	-2.526027000	1.981609000	-5.146486000
H	-1.711700000	1.358442000	-4.786513000
C	-4.194117000	3.691709000	-4.700066000
H	-4.670379000	4.386369000	-4.007599000
C	-4.622648000	3.605968000	-6.020741000
C	-2.971708000	1.911809000	-6.458269000
C	-4.019434000	2.723334000	-6.927237000

H	-2.491992000	1.210548000	-7.142924000
H	-5.442427000	4.241972000	-6.355838000
H	-0.537295000	2.880523000	0.944980000
H	-3.138347000	3.683082000	-2.272325000
C	-4.453810000	2.658237000	-8.368394000
C	4.508143000	-0.338971000	2.979191000
H	-4.551681000	1.619689000	-8.709553000
H	5.445043000	0.083990000	2.587255000
H	4.503020000	-0.182843000	4.063834000
H	4.536606000	-1.418963000	2.786971000
H	-5.414151000	3.162664000	-8.522630000
H	-3.713729000	3.143971000	-9.021441000

p-methyldithizone (Enol form)

	x	y	z
N	-3.046936000	1.412445000	-4.668519000
N	-2.198378000	1.802592000	-5.537092000
C	-2.092373000	3.163688000	-5.707194000
N	-1.230011000	3.514178000	-6.631002000
N	-1.058155000	4.798655000	-6.886820000
S	-3.075528000	4.296588000	-4.730295000
C	-0.162335000	5.229682000	-7.871494000
C	0.586581000	4.313972000	-8.622486000
H	0.466163000	3.250598000	-8.433102000
C	-0.012734000	6.605024000	-8.102182000
H	-0.589802000	7.322212000	-7.516140000
C	0.875783000	7.051400000	-9.075333000
C	1.468292000	4.783621000	-9.590221000
C	1.633140000	6.153606000	-9.841828000
H	2.048064000	4.061504000	-10.167404000
H	0.983597000	8.124125000	-9.240774000
C	-3.131787000	0.017372000	-4.503724000
C	-2.300761000	-0.902833000	-5.168995000
H	-1.545462000	-0.525805000	-5.854755000
C	-4.110121000	-0.460633000	-3.618856000
H	-4.751289000	0.258427000	-3.110794000
C	-4.257691000	-1.827378000	-3.407298000
C	-2.456090000	-2.262798000	-4.944383000
C	-3.432927000	-2.755269000	-4.061234000
H	-1.807027000	-2.968369000	-5.466018000
H	-5.027595000	-2.184551000	-2.721914000
H	-1.599408000	5.502055000	-6.376582000
H	-3.619146000	3.151697000	-4.151732000
C	2.569918000	6.640549000	-10.917863000
C	-3.567205000	-4.233569000	-3.805893000
H	3.072987000	7.570062000	-10.623358000
H	-4.616908000	-4.527617000	-3.683350000
H	-3.039208000	-4.521057000	-2.884289000
H	-3.137895000	-4.821368000	-4.625599000
H	3.339152000	5.892674000	-11.143561000
H	2.026744000	6.845271000	-11.852539000

p-methyldithizone (Keto form)

	x	y	z
N	2.748819000	8.511652000	-1.359053000
N	2.120067000	9.469594000	-0.814750000
C	1.245061000	9.067981000	0.222245000
N	0.707120000	10.201166000	0.758988000
N	0.032098000	10.129243000	1.952373000
S	0.871380000	7.544604000	0.794461000
C	3.613965000	8.876291000	-2.403687000
C	4.387037000	7.825849000	-2.926030000
H	4.256141000	6.833573000	-2.497182000
C	3.756992000	10.169846000	-2.939967000
H	3.151258000	10.979359000	-2.537822000
C	4.662386000	10.391835000	-3.966857000
C	5.295211000	8.063359000	-3.949271000
C	5.450319000	9.348732000	-4.489044000
H	5.897437000	7.241135000	-4.338237000
H	4.772011000	11.395787000	-4.380546000
C	-1.087896000	10.953893000	2.171317000
C	-1.784400000	10.788342000	3.377314000
H	-1.460809000	10.022755000	4.082532000
C	-1.499861000	11.950863000	1.275965000
H	-0.995705000	12.072212000	0.318302000
C	-2.588283000	12.761621000	1.594393000
C	-2.876037000	11.598124000	3.669439000
C	-3.299517000	12.605855000	2.791589000
H	-3.410221000	11.446099000	4.608125000
H	-2.900446000	13.525677000	0.880757000
H	-0.061172000	9.118412000	2.170471000
H	1.179796000	11.078572000	0.543010000
C	-4.475700000	13.490155000	3.122002000
C	6.422915000	9.597351000	-5.611523000
H	-4.162926000	14.533311000	3.273775000
H	6.036955000	9.192443000	-6.558461000
H	6.605663000	10.667850000	-5.756726000
H	7.384680000	9.104792000	-5.419693000
H	-5.217772000	13.488644000	2.312350000
H	-4.977002000	13.156844000	4.037905000

p-methyldithizone (Hydrogen bridge 1 form)

	x	y	z
N	-3.173760000	10.779691000	-1.867429000
N	-2.481787000	11.885425000	-1.747749000
C	-2.771868000	12.763245000	-2.768266000
N	-2.098765000	13.941878000	-2.731373000
N	-1.417903000	14.217036000	-1.652586000
S	-3.885709000	12.428023000	-4.032089000
C	-3.005757000	9.662623000	-1.070417000
C	-3.784729000	8.524459000	-1.354992000
H	-4.488115000	8.550652000	-2.187054000
C	-2.094618000	9.629655000	-0.001862000
H	-1.491910000	10.508905000	0.209320000

C	-1.973350000	8.473257000	0.759005000
C	-3.643173000	7.380279000	-0.586063000
C	-2.735815000	7.326814000	0.486626000
H	-4.245548000	6.502721000	-0.824362000
H	-1.261887000	8.454442000	1.585524000
C	-0.631170000	15.359531000	-1.520015000
C	-0.547785000	16.319083000	-2.539141000
H	-1.106689000	16.164665000	-3.459027000
C	0.080446000	15.541039000	-0.323137000
H	0.013541000	14.792883000	0.468091000
C	0.865169000	16.674563000	-0.152272000
C	0.240089000	17.446272000	-2.343513000
C	0.962187000	17.650656000	-1.155944000
H	0.296488000	18.193859000	-3.135631000
H	1.412354000	16.806077000	0.782090000
H	-3.822923000	10.812448000	-2.716543000
H	-1.424150000	13.524342000	-0.891915000
C	-2.596143000	6.078212000	1.316690000
C	1.830510000	18.866826000	-0.969225000
H	-3.489740000	5.912274000	1.936216000
H	1.571045000	19.656641000	-1.683126000
H	1.733608000	19.275304000	0.044807000
H	2.891868000	18.620190000	-1.119743000
H	-2.475355000	5.190239000	0.682177000
H	-1.731692000	6.138041000	1.987301000

p-methyldithizone (Hydrogen bridge 2 form)

	x	y	z
N	-0.595670000	11.313208000	-6.847822000
N	-0.154770000	10.264561000	-7.445320000
C	0.069916000	10.392094000	-8.794069000
N	0.507180000	9.367623000	-9.499979000
N	0.726588000	8.214140000	-8.889547000
S	-0.206373000	11.907304000	-9.693244000
C	1.180454000	7.089776000	-9.577573000
C	1.406348000	5.902456000	-8.860796000
H	1.226278000	5.873877000	-7.784766000
C	1.415773000	7.117766000	-10.959040000
H	1.238328000	8.039196000	-11.507781000
C	1.870969000	5.969666000	-11.599201000
C	1.861475000	4.767648000	-9.522060000
C	2.104506000	4.774099000	-10.904567000
H	2.033335000	3.854750000	-8.949379000
H	2.050974000	6.004416000	-12.674785000
C	-0.833013000	11.196732000	-5.473354000
C	-0.572895000	10.054114000	-4.688659000
H	-0.141841000	9.174107000	-5.160110000
C	-1.375617000	12.334049000	-4.851187000
H	-1.566975000	13.214390000	-5.462942000
C	-1.663786000	12.328416000	-3.490595000
C	-0.861382000	10.063127000	-3.332917000
C	-1.417806000	11.194772000	-2.704532000

H	-0.652615000	9.174305000	-2.734756000
H	-2.087759000	13.220007000	-3.026798000
H	-0.607521000	12.499796000	-8.524102000
H	0.549031000	8.156149000	-7.883920000
C	2.593389000	3.537198000	-11.614916000
C	-1.752248000	11.172817000	-1.235812000
H	1.847391000	2.730323000	-11.573251000
H	-0.931919000	10.745415000	-0.644667000
H	3.514537000	3.149892000	-11.158369000
H	2.802401000	3.743521000	-12.670769000
H	-2.641959000	10.554132000	-1.045776000
H	-1.961169000	12.179553000	-0.856690000

α-naphtyldithizone (Symmetric form)

	x	y	z
H	-2.122844000	3.748878000	-4.261399000
C	-2.066073000	3.577741000	-3.186565000
C	-2.179524000	4.631433000	-2.301156000
C	-2.118072000	4.412896000	-0.916571000
C	-1.939072000	3.126915000	-0.421747000
C	-1.800002000	2.002686000	-1.306136000
C	-1.874730000	2.253224000	-2.716546000
C	-1.753268000	1.161221000	-3.615624000
C	-1.561592000	-0.121415000	-3.153994000
C	-1.479365000	-0.365057000	-1.766116000
C	-1.594706000	0.671342000	-0.862658000
H	-2.326679000	5.643797000	-2.673173000
H	-2.220033000	5.232753000	-0.210263000
H	-1.519010000	0.440795000	0.200030000
H	-1.321850000	-1.379514000	-1.402707000
H	-1.471178000	-0.949575000	-3.855509000
H	-1.815340000	1.360768000	-4.685654000
N	-1.908628000	2.891106000	0.945394000
N	-1.990865000	3.824377000	1.852324000
C	-2.002516000	3.314610000	3.116476000
N	-2.110415000	4.322506000	4.028022000
N	-2.171113000	3.876334000	5.251486000
S	-1.918461000	1.632578000	3.506562000
C	-2.255258000	4.688518000	6.374408000
C	-2.118199000	6.066824000	6.265157000
C	-2.175072000	6.871999000	7.413201000
C	-2.363187000	6.309122000	8.659915000
C	-2.518088000	4.907046000	8.806606000
C	-2.475507000	4.062207000	7.648408000
C	-2.666230000	2.667624000	7.816949000
C	-2.870608000	2.128380000	9.070469000
C	-2.895926000	2.956536000	10.213548000
C	-2.726424000	4.316092000	10.080543000
H	-1.955235000	6.497554000	5.280597000
H	-2.059186000	7.949684000	7.312555000
H	-2.397168000	6.935734000	9.550867000
H	-2.753137000	4.965372000	10.955897000

H	-3.056489000	2.517119000	11.196835000
H	-3.018985000	1.054934000	9.175667000
H	-2.667738000	1.996506000	6.957933000
H	-1.862861000	1.923436000	1.341443000
H	-2.125569000	2.832847000	5.321799000

α-naphtyldithizone (Enol form)

	x	y	z
H	-2.165313000	3.920912000	-4.207742000
C	-2.103349000	3.687898000	-3.145222000
C	-2.221370000	4.683121000	-2.197965000
C	-2.144537000	4.387277000	-0.825559000
C	-1.947229000	3.079588000	-0.405858000
C	-1.816775000	2.010435000	-1.356907000
C	-1.900401000	2.340223000	-2.750281000
C	-1.776836000	1.299545000	-3.708487000
C	-1.581683000	-0.007724000	-3.323305000
C	-1.498488000	-0.332162000	-1.952301000
C	-1.613139000	0.653666000	-0.994486000
H	-2.378946000	5.715201000	-2.507761000
H	-2.241434000	5.167960000	-0.075807000
H	-1.540015000	0.353838000	0.051869000
H	-1.343561000	-1.365563000	-1.646352000
H	-1.490265000	-0.793212000	-4.072225000
H	-1.840357000	1.559127000	-4.765542000
N	-1.875580000	2.765860000	0.948323000
N	-1.999118000	3.668839000	1.908345000
C	-1.953576000	3.218180000	3.143485000
N	-2.111509000	4.171995000	4.122279000
N	-2.123936000	3.705918000	5.313943000
S	-1.727265000	1.502921000	3.597856000
C	-2.239093000	4.624101000	6.360557000
C	-2.091622000	5.997451000	6.183770000
C	-2.176584000	6.871831000	7.277752000
C	-2.411187000	6.384544000	8.549523000
C	-2.575178000	4.995212000	8.775695000
C	-2.490256000	4.085625000	7.669651000
C	-2.678199000	2.702843000	7.912165000
C	-2.926170000	2.236352000	9.186206000
C	-3.001065000	3.129903000	10.278431000
C	-2.830414000	4.480488000	10.074575000
H	-1.896366000	6.371584000	5.181369000
H	-2.049750000	7.941854000	7.119658000
H	-2.472880000	7.064821000	9.399197000
H	-2.892220000	5.179175000	10.909561000
H	-3.198485000	2.747352000	11.279181000
H	-3.069618000	1.169283000	9.352538000
H	-2.633130000	2.009447000	7.075946000
H	-1.763320000	1.785563000	1.214633000
H	-1.849775000	2.012729000	4.908382000

α-naphtyldithizone (Keto form)

	x	y	z
H	-1.860534000	4.083557000	-4.125938000
C	-1.914609000	3.791493000	-3.077540000
C	-2.013259000	4.740819000	-2.086101000
C	-2.074525000	4.367498000	-0.727843000
C	-2.051542000	3.027753000	-0.365488000
C	-1.948737000	2.005667000	-1.372761000
C	-1.869804000	2.411086000	-2.744455000
C	-1.743875000	1.411109000	-3.743923000
C	-1.696740000	0.074227000	-3.414696000
C	-1.784328000	-0.322766000	-2.063449000
C	-1.912919000	0.621732000	-1.065961000
H	-2.032418000	5.798722000	-2.342374000
H	-2.110908000	5.143714000	0.034385000
H	-1.993771000	0.281308000	-0.034298000
H	-1.753509000	-1.380044000	-1.804711000
H	-1.595738000	-0.678853000	-4.195085000
H	-1.682259000	1.724959000	-4.786359000
N	-2.185933000	2.604298000	0.952724000
N	-2.180366000	3.482276000	2.000335000
C	-1.848875000	3.015291000	3.240779000
N	-2.152490000	4.019417000	4.179417000
N	-2.068478000	3.628586000	5.387556000
S	-1.188035000	1.493794000	3.461264000
C	-2.249087000	4.607691000	6.365501000
C	-2.105307000	5.975080000	6.133506000
C	-2.222988000	6.892144000	7.187384000
C	-2.498354000	6.452697000	8.470280000
C	-2.657977000	5.073857000	8.753131000
C	-2.520170000	4.121484000	7.691309000
C	-2.674065000	2.744112000	7.978435000
C	-2.957567000	2.326504000	9.262012000
C	-3.100761000	3.262452000	10.311958000
C	-2.949872000	4.608121000	10.062968000
H	-1.871080000	6.308591000	5.124361000
H	-2.087816000	7.955406000	6.994478000
H	-2.588693000	7.168237000	9.288035000
H	-3.055458000	5.337084000	10.866916000
H	-3.327147000	2.914520000	11.319072000
H	-3.071241000	1.263437000	9.471187000
H	-2.558680000	2.030343000	7.165686000
H	-1.730649000	1.736035000	1.292493000
H	-2.811181000	4.281628000	1.955406000

α-naphtyldithizone (Hydrogen bridge 1 form)

	x	y	z
H	-4.640688000	3.216270000	-3.537518000
C	-4.164339000	3.300576000	-2.560999000
C	-4.087994000	2.209314000	-1.720085000
C	-3.494354000	2.323019000	-0.454242000
C	-2.961973000	3.536463000	-0.035874000

C	-2.988730000	4.689580000	-0.889737000
C	-3.621719000	4.552117000	-2.171372000
C	-3.671761000	5.675812000	-3.036820000
C	-3.113223000	6.880688000	-2.673406000
C	-2.470195000	7.009059000	-1.423218000
C	-2.407416000	5.938615000	-0.553602000
H	-4.507398000	1.251435000	-2.023667000
H	-3.452344000	1.477490000	0.227158000
H	-1.875975000	6.065124000	0.389569000
H	-2.009717000	7.956682000	-1.148085000
H	-3.155344000	7.731017000	-3.352268000
H	-4.157904000	5.560600000	-4.006047000
N	-2.396392000	3.632776000	1.239036000
N	-2.134981000	2.554797000	1.938676000
C	-1.845842000	2.672353000	3.250325000
N	-2.147679000	3.886294000	3.843921000
N	-1.940498000	3.807828000	5.136534000
S	-1.230840000	1.317913000	4.117970000
C	-2.285999000	4.761388000	6.071193000
C	-2.544083000	6.080181000	5.706642000
C	-2.847664000	7.035774000	6.686350000
C	-2.909860000	6.682434000	8.021264000
C	-2.681214000	5.343223000	8.430221000
C	-2.360411000	4.347593000	7.450163000
C	-2.179568000	3.007862000	7.873537000
C	-2.292656000	2.668956000	9.206966000
C	-2.592837000	3.649469000	10.175789000
C	-2.783983000	4.958225000	9.792721000
H	-2.484866000	6.354349000	4.656585000
H	-3.029440000	8.066728000	6.387632000
H	-3.143112000	7.428966000	8.780221000
H	-3.029602000	5.720646000	10.531957000
H	-2.683844000	3.365399000	11.223223000
H	-2.159710000	1.631269000	9.509144000
H	-1.969755000	2.219502000	7.149423000
H	-2.337358000	4.544860000	1.704373000
H	-1.549510000	2.839745000	5.393044000

α-naphtyldithizone (Hydrogen bridge 2 form)

	x	y	z
H	-4.362672000	3.322611000	-3.624028000
C	-3.936661000	3.374067000	-2.623582000
C	-3.725012000	2.227204000	-1.887304000
C	-3.203031000	2.293622000	-0.584700000
C	-2.876740000	3.519564000	-0.020341000
C	-3.035899000	4.735370000	-0.767844000
C	-3.597178000	4.642203000	-2.086584000
C	-3.778519000	5.834119000	-2.837618000
C	-3.407140000	7.060519000	-2.333687000
C	-2.826603000	7.145859000	-1.048939000
C	-2.645534000	6.009718000	-0.285609000
H	-3.984946000	1.254746000	-2.302352000

H	-3.066703000	1.395243000	0.011380000
H	-2.165683000	6.105683000	0.687879000
H	-2.507180000	8.114043000	-0.663636000
H	-3.547480000	7.961728000	-2.926548000
H	-4.214142000	5.754968000	-3.834264000
N	-2.394941000	3.584508000	1.287418000
N	-2.002276000	2.483407000	1.917371000
C	-1.807523000	2.518145000	3.219973000
N	-2.099927000	3.641645000	3.953148000
N	-1.957999000	3.519740000	5.225776000
S	-1.200921000	1.009811000	3.949185000
C	-2.271814000	4.626642000	6.011283000
C	-2.438567000	5.917919000	5.510864000
C	-2.736586000	6.987581000	6.365187000
C	-2.881810000	6.780250000	7.725083000
C	-2.721798000	5.487913000	8.284290000
C	-2.400747000	4.384036000	7.426321000
C	-2.253384000	3.098571000	8.001289000
C	-2.411005000	2.909377000	9.357466000
C	-2.728134000	3.994845000	10.205315000
C	-2.879575000	5.256502000	9.678179000
H	-2.318406000	6.080092000	4.441254000
H	-2.853623000	7.988431000	5.953602000
H	-3.120251000	7.612557000	8.387672000
H	-3.127682000	6.100947000	10.321553000
H	-2.855459000	3.828349000	11.274211000
H	-2.293977000	1.911838000	9.781224000
H	-2.021152000	2.259195000	7.351034000
H	-2.532295000	4.430684000	1.842725000
H	-1.243214000	1.618280000	5.176842000

3,4-dimethyldithizone (Symmetric form)

	x	y	z
N	0.012865000	2.124930000	0.453029000
N	-0.371280000	1.868202000	-0.761819000
C	-1.429743000	2.622306000	-1.169088000
N	-1.711825000	2.307741000	-2.463915000
N	-2.684913000	3.006763000	-2.968417000
S	-2.247424000	3.804788000	-0.220086000
C	1.110628000	1.495934000	1.037790000
C	1.832987000	0.513159000	0.350710000
H	1.523163000	0.227717000	-0.650876000
C	1.494230000	1.875924000	2.331829000
H	0.921683000	2.643237000	2.856046000
C	2.601241000	1.296589000	2.951128000
C	2.932446000	-0.062917000	0.971455000
C	3.341313000	0.308451000	2.260214000
H	3.500351000	-0.826490000	0.438387000
C	-3.096309000	2.867409000	-4.292918000
C	-2.488093000	1.939264000	-5.145867000
H	-1.687633000	1.311349000	-4.764783000
C	-4.130527000	3.687640000	-4.766855000

H	-4.595950000	4.406963000	-4.090469000
C	-4.565386000	3.601299000	-6.089069000
C	-2.924441000	1.855975000	-6.460935000
C	-3.952241000	2.669017000	-6.958780000
H	-2.449947000	1.137471000	-7.130370000
H	-0.537325000	2.865360000	0.946594000
H	-3.115236000	3.704347000	-2.318156000
C	3.007388000	1.731017000	4.335609000
H	2.308238000	2.469522000	4.742370000
H	3.045087000	0.879061000	5.028310000
H	4.011062000	2.180267000	4.332671000
C	4.549965000	-0.333216000	2.888131000
H	4.291435000	-0.857524000	3.820233000
H	5.007482000	-1.059824000	2.207626000
H	5.313798000	0.414257000	3.148958000
C	-4.390135000	2.545261000	-8.394253000
H	-3.765675000	1.825463000	-8.935163000
H	-5.435506000	2.208549000	-8.468507000
H	-4.331405000	3.508769000	-8.920369000
C	-5.670354000	4.499251000	-6.582624000
H	-5.319780000	5.149882000	-7.396905000
H	-6.511324000	3.916047000	-6.983895000
H	-6.052423000	5.139000000	-5.780030000

3,4-dimethyldithizone (Enol form)

	x	y	z
N	-3.067533000	1.427039000	-4.638179000
N	-2.256186000	1.854196000	-5.522856000
C	-2.167381000	3.216540000	-5.683755000
N	-1.310589000	3.561915000	-6.612061000
N	-1.098105000	4.835203000	-6.885509000
S	-3.147022000	4.339212000	-4.692885000
C	-0.175387000	5.194062000	-7.878448000
C	0.489103000	4.212202000	-8.620653000
H	0.281871000	3.164615000	-8.423509000
C	0.083338000	6.549006000	-8.126747000
H	-0.436839000	7.313323000	-7.544666000
C	1.001267000	6.939796000	-9.103580000
C	1.399959000	4.606533000	-9.592848000
C	1.677638000	5.953275000	-9.855828000
H	1.916419000	3.838607000	-10.170466000
C	-3.096950000	0.020906000	-4.524567000
C	-2.254546000	-0.829667000	-5.259872000
H	-1.536698000	-0.392887000	-5.949373000
C	-4.020005000	-0.536334000	-3.628707000
H	-4.664569000	0.138338000	-3.064205000
C	-4.129752000	-1.918029000	-3.459790000
C	-2.356900000	-2.201064000	-5.090236000
C	-3.283770000	-2.771201000	-4.203449000
H	-1.700610000	-2.860268000	-5.660853000
H	-1.581183000	5.571951000	-6.365168000

H	-3.659052000	3.205219000	-4.077320000
C	-5.140276000	-2.493944000	-2.500378000
H	-5.857460000	-3.146178000	-3.019925000
H	-4.655732000	-3.110302000	-1.729226000
H	-5.705754000	-1.702916000	-1.996545000
C	-3.364082000	-4.268037000	-4.057545000
H	-3.166180000	-4.585421000	-3.022784000
H	-4.364261000	-4.645923000	-4.316519000
H	-2.636023000	-4.765332000	-4.708394000
C	1.269865000	8.403201000	-9.346158000
H	2.327772000	8.647924000	-9.173627000
H	1.047212000	8.683617000	-10.385477000
H	0.664604000	9.035411000	-8.687449000
C	2.680323000	6.329446000	-10.916556000
H	3.523091000	6.897537000	-10.495883000
H	3.088436000	5.435213000	-11.401429000
H	2.231638000	6.960920000	-11.697286000

3,4-dimethyldithizone (Keto form)

	x	y	z
N	2.728662000	8.485506000	-1.355090000
N	2.105895000	9.437824000	-0.794735000
C	1.230802000	9.029791000	0.238545000
N	0.706407000	10.161296000	0.787013000
N	0.017679000	10.092780000	1.972004000
S	0.839778000	7.503732000	0.794331000
C	3.589241000	8.866941000	-2.397449000
C	4.367358000	7.826784000	-2.930299000
H	4.235414000	6.831598000	-2.505191000
C	3.719062000	10.164926000	-2.921274000
H	3.108314000	10.968748000	-2.516633000
C	4.622895000	10.388977000	-3.948407000
C	5.284817000	8.048887000	-3.955489000
C	5.417086000	9.355739000	-4.477172000
H	4.727235000	11.392603000	-4.363434000
C	-1.092989000	10.938408000	2.167547000
C	-1.786016000	10.817372000	3.380968000
H	-1.457042000	10.069251000	4.104024000
C	-1.492472000	11.909108000	1.245059000
H	-0.993338000	11.998736000	0.281873000
C	-2.574070000	12.735492000	1.553282000
C	-2.874599000	11.633143000	3.680881000
C	-3.281120000	12.620851000	2.752697000
H	-2.886731000	13.484871000	0.824846000
H	-0.098696000	9.082508000	2.179929000
H	1.178968000	11.038696000	0.572425000
C	6.120150000	6.914429000	-4.490950000
H	7.193316000	7.101264000	-4.337013000
H	5.867333000	5.971146000	-3.995087000
H	5.973895000	6.781050000	-5.572578000
C	6.391944000	9.642870000	-5.586718000
H	7.418270000	9.375725000	-5.295363000

H	6.159319000	9.052974000	-6.485604000
H	6.381022000	10.702638000	-5.863260000
C	-3.602794000	11.462303000	4.989445000
H	-4.658288000	11.200286000	4.827638000
H	-3.147843000	10.672301000	5.596984000
H	-3.594382000	12.391332000	5.577012000
C	-4.451474000	13.523720000	3.046308000
H	-4.640508000	14.207655000	2.211161000
H	-5.371847000	12.948568000	3.225977000
H	-4.279280000	14.131478000	3.946964000

3,4-dimethyldithizone (Hydrogen bridge 1 form)

	x	y	z
N	-3.117172000	10.751475000	-1.868611000
N	-2.446490000	11.868510000	-1.737468000
C	-2.749606000	12.749837000	-2.751125000
N	-2.094874000	13.938179000	-2.704885000
N	-1.389684000	14.203215000	-1.639656000
S	-3.859558000	12.406043000	-4.017535000
C	-2.959332000	9.642157000	-1.060020000
C	-3.722593000	8.498835000	-1.361591000
H	-4.395323000	8.525365000	-2.220416000
C	-2.083324000	9.623683000	0.035558000
H	-1.489141000	10.504416000	0.262894000
C	-1.996489000	8.471211000	0.805050000
C	-3.628514000	7.344069000	-0.592465000
C	-2.750494000	7.323149000	0.519055000
H	-1.318886000	8.454257000	1.659388000
C	-0.618836000	15.355895000	-1.503728000
C	-0.574771000	16.330341000	-2.511064000
H	-1.158627000	16.170605000	-3.415245000
C	0.120941000	15.526831000	-0.324807000
H	0.087657000	14.770240000	0.459183000
C	0.896329000	16.670367000	-0.173310000
C	0.199992000	17.476653000	-2.352461000
C	0.954342000	17.656936000	-1.165474000
H	1.474095000	16.802830000	0.741550000
H	-3.761132000	10.778081000	-2.721711000
H	-1.364915000	13.495677000	-0.892867000
C	-4.454785000	6.133294000	-0.942370000
H	-5.040071000	6.302301000	-1.852826000
H	-3.821840000	5.249759000	-1.103930000
H	-5.153395000	5.879022000	-0.132244000
C	-2.623055000	6.093223000	1.377266000
H	-3.592330000	5.796694000	1.804101000
H	-2.260700000	5.232384000	0.795577000
H	-1.924789000	6.258597000	2.205133000
C	0.231537000	18.515683000	-3.443505000
H	1.253468000	18.671264000	-3.817658000
H	-0.399316000	18.221287000	-4.288473000
H	-0.122517000	19.489635000	-3.076184000
C	1.804507000	18.884044000	-0.971662000

H	2.312469000	18.865006000	-0.001059000
H	2.572210000	18.969282000	-1.754621000
H	1.202395000	19.803225000	-1.021792000

3,4-dimethyldithizone (Hydrogen bridge 2 form)

	x	y	z
N	-0.628353000	11.309232000	-6.857289000
N	-0.163226000	10.275146000	-7.460999000
C	0.054661000	10.407361000	-8.808498000
N	0.506364000	9.387168000	-9.513338000
N	0.741400000	8.244392000	-8.889916000
S	-0.253096000	11.918172000	-9.701727000
C	1.191420000	7.107671000	-9.558112000
C	1.413684000	5.936889000	-8.820719000
H	1.240177000	5.924324000	-7.743897000
C	1.419247000	7.110595000	-10.941063000
H	1.241178000	8.029183000	-11.496529000
C	1.860369000	5.961006000	-11.594873000
C	1.855160000	4.791874000	-9.477563000
C	2.083820000	4.773477000	-10.858092000
H	2.025268000	3.882966000	-8.899578000
C	-0.849375000	11.173632000	-5.481358000
C	-0.521876000	10.043593000	-4.709957000
H	-0.048174000	9.188577000	-5.185481000
C	-1.448613000	12.276830000	-4.849358000
H	-1.692152000	13.143528000	-5.464432000
C	-1.740305000	12.277706000	-3.486987000
C	-0.804158000	10.042571000	-3.351724000
C	-1.413334000	11.138033000	-2.716922000
H	-0.547531000	9.167608000	-2.751957000
H	-0.667484000	12.497156000	-8.530123000
H	0.559134000	8.199906000	-7.884260000
C	-2.396961000	13.475525000	-2.848513000
H	-2.588508000	14.261228000	-3.587066000
H	-3.356085000	13.206513000	-2.382938000
H	-1.768557000	13.902482000	-2.053197000
C	-1.711572000	11.091973000	-1.242061000
H	-2.788880000	11.201752000	-1.047188000
H	-1.382760000	10.145045000	-0.799786000
H	-1.212271000	11.910947000	-0.703530000
C	2.095287000	5.995064000	-13.084119000
H	3.145019000	5.774761000	-13.328200000
H	1.485404000	5.242228000	-13.604239000
H	1.850366000	6.977978000	-13.500334000
C	2.547859000	3.513454000	-11.541934000
H	2.731901000	2.714338000	-10.815056000
H	1.799995000	3.146851000	-12.262064000
H	3.476032000	3.676068000	-12.109397000

β-fluorenedithizone (Symmetric form)

	x	y	z
C	1.274796000	2.563569000	2.349786000
C	0.311668000	1.865709000	3.112861000
C	1.950850000	3.646119000	2.883177000
H	2.697888000	4.193184000	2.305868000
C	0.030459000	2.267156000	4.425718000
C	1.661476000	4.039845000	4.203938000
H	-0.709568000	1.736239000	5.022990000
C	0.703208000	3.351317000	4.971453000
H	0.511113000	3.688432000	5.986467000
C	-0.900536000	-1.096905000	0.356001000
C	-1.525250000	-1.125475000	1.609177000
C	0.066557000	-0.128897000	0.063464000
H	-2.275622000	-1.886999000	1.818429000
H	0.548979000	-0.112941000	-0.914281000
C	-1.196221000	-0.190551000	2.590179000
C	0.398884000	0.805966000	1.036667000
H	-1.685557000	-0.218486000	3.563498000
C	-0.229514000	0.778829000	2.300692000
H	-1.170377000	-1.835592000	-0.397545000
C	1.396067000	1.940161000	0.979603000
N	2.355534000	5.126557000	4.719530000
N	2.190530000	5.587172000	5.926583000
C	2.991904000	6.656912000	6.195083000
N	2.773108000	7.084423000	7.471148000
N	3.514292000	8.106160000	7.791999000
S	4.115360000	7.360611000	5.089087000
C	4.346341000	9.820177000	9.239263000
C	3.484806000	8.725254000	9.034701000
C	4.336647000	10.451966000	10.469734000
C	2.627719000	8.277255000	10.057571000
C	3.479887000	10.009782000	11.502604000
H	1.979619000	7.428248000	9.857540000
C	2.626402000	8.918986000	11.288073000
H	1.962352000	8.568911000	12.077292000
H	5.003351000	10.150865000	8.433291000
C	5.057470000	12.762458000	13.311583000
C	4.668836000	11.822057000	12.364977000
C	4.458797000	12.737976000	14.576278000
H	4.753982000	13.469061000	15.327712000
C	3.685290000	10.857196000	12.674539000
C	3.483727000	11.781625000	14.885601000
H	3.029952000	11.778028000	15.875941000
C	3.089099000	10.835268000	13.940251000
H	2.329887000	10.093647000	14.187664000
H	5.816563000	13.509524000	13.077889000
C	5.150845000	11.631520000	10.945457000
H	3.069353000	5.643199000	4.151088000
H	4.154004000	8.435335000	7.029053000
H	1.155269000	2.658399000	0.182214000
H	2.416772000	1.579430000	0.785341000
H	4.973681000	12.524615000	10.328472000
H	6.230302000	11.424640000	10.903305000

β-fluorenedithizone (Enol form)

	x	y	z
C	1.250332000	2.554259000	2.358875000
C	0.343667000	1.908425000	3.227540000
C	1.987468000	3.646057000	2.786491000
H	2.689228000	4.150888000	2.119417000
C	0.184267000	2.371570000	4.538647000
C	1.817325000	4.104268000	4.105706000
H	-0.511708000	1.883997000	5.220400000
C	0.917886000	3.466722000	4.978450000
H	0.813141000	3.850142000	5.989721000
C	-1.174758000	-1.118300000	0.697389000
C	-1.688587000	-1.084274000	1.999148000
C	-0.211587000	-0.188500000	0.288391000
H	-2.438372000	-1.815285000	2.300170000
H	0.184504000	-0.219509000	-0.727389000
C	-1.251800000	-0.124840000	2.913267000
C	0.226975000	0.769841000	1.194243000
H	-1.657520000	-0.104163000	3.924655000
C	-0.289894000	0.805601000	2.507596000
H	-1.528131000	-1.874189000	-0.002651000
C	1.241904000	1.875477000	1.009207000
N	2.562382000	5.208512000	4.519435000
N	2.469090000	5.709480000	5.740171000
C	3.203634000	6.761113000	6.024178000
N	3.061333000	7.230064000	7.308681000
N	3.777133000	8.249865000	7.596724000
S	4.313354000	7.570469000	4.878763000
C	4.435312000	9.872392000	9.214673000
C	3.637182000	8.757666000	8.893735000
C	4.335722000	10.435018000	10.476402000
C	2.749822000	8.220291000	9.852816000
C	3.443432000	9.900596000	11.431669000
H	2.148538000	7.359422000	9.571305000
C	2.652234000	8.786559000	11.113412000
H	1.962539000	8.368545000	11.846134000
H	5.111137000	10.266748000	8.456165000
C	4.765939000	12.624709000	13.472965000
C	4.487142000	11.716690000	12.456954000
C	4.086910000	12.508606000	14.690796000
H	4.295049000	13.213659000	15.494549000
C	3.533987000	10.693330000	12.654355000
C	3.140278000	11.495055000	14.887287000
H	2.620856000	11.422637000	15.842185000
C	2.856543000	10.580528000	13.873578000
H	2.118388000	9.794513000	14.031902000
H	5.500360000	13.417598000	13.327733000
C	5.064854000	11.621389000	11.063552000
H	3.196764000	5.642684000	3.842599000
H	4.584762000	8.428789000	5.950981000
H	2.234174000	1.480580000	0.745214000
H	0.951097000	2.568496000	0.205967000

H	4.887948000	12.538869000	10.483177000
H	6.153292000	11.462584000	11.082248000

β-fluorenedithizone (Keto form)

	x	y	z
C	1.009674000	2.781207000	2.299861000
C	0.382767000	2.032295000	3.321012000
C	1.555640000	4.025452000	2.560082000
H	2.026283000	4.615702000	1.772650000
C	0.322113000	2.546549000	4.617146000
C	1.499094000	4.535595000	3.870725000
H	-0.142924000	1.979609000	5.422196000
C	0.883430000	3.792619000	4.891727000
H	0.875423000	4.175379000	5.910600000
C	-0.775031000	-1.427161000	1.181250000
C	-1.105553000	-1.401320000	2.541205000
C	-0.099477000	-0.351519000	0.593606000
H	-1.630390000	-2.247831000	2.982925000
H	0.156756000	-0.377499000	-0.466153000
C	-0.769467000	-0.304606000	3.336128000
C	0.238886000	0.743268000	1.380374000
H	-1.030039000	-0.292652000	4.394458000
C	-0.094474000	0.771664000	2.752173000
H	-1.045028000	-2.291951000	0.576341000
C	0.962575000	2.014867000	0.998458000
N	2.031527000	5.821407000	4.082159000
N	2.103922000	6.314493000	5.362180000
C	3.191099000	7.041769000	5.750583000
N	2.888297000	7.604619000	7.009925000
N	3.841645000	8.269908000	7.523922000
S	4.561623000	7.167611000	4.803783000
C	4.660913000	9.529728000	9.348086000
C	3.584344000	8.812683000	8.788132000
C	4.517640000	10.097041000	10.601743000
C	2.369734000	8.681318000	9.500400000
C	3.303683000	9.961798000	11.312854000
H	1.558151000	8.121466000	9.041402000
C	2.227066000	9.252260000	10.753732000
H	1.289782000	9.148242000	11.299774000
H	5.579831000	9.607916000	8.767878000
C	5.119549000	11.912448000	13.807571000
C	4.729355000	11.203581000	12.677130000
C	4.210270000	12.061854000	14.860014000
H	4.503327000	12.614458000	15.751864000
C	3.434350000	10.644891000	12.595672000
C	2.925573000	11.507984000	14.780566000
H	2.233195000	11.635794000	15.611830000
C	2.527401000	10.796586000	13.650157000
H	1.527363000	10.367462000	13.593196000
H	6.117435000	12.346602000	13.878342000
C	5.504733000	10.896802000	11.418079000
H	2.946194000	6.039687000	3.640365000

H	1.225386000	6.504500000	5.841588000
H	0.428840000	2.572532000	0.215047000
H	1.971989000	1.810992000	0.612130000
H	6.419432000	10.323722000	11.628673000
H	5.818221000	11.812713000	10.895986000

β-fluorenedithizone (Hydrogen bridge 1 form)

	x	y	z
C	1.460622000	2.435993000	2.660856000
C	0.337102000	2.038257000	3.424558000
C	2.242354000	3.503548000	3.054181000
H	3.109829000	3.821521000	2.474684000
C	0.004660000	2.733075000	4.596028000
C	1.902144000	4.198696000	4.235885000
H	-0.861531000	2.440035000	5.188014000
C	0.780812000	3.809432000	4.998986000
H	0.538454000	4.376352000	5.893557000
C	-1.080956000	-1.212683000	1.131169000
C	-1.809060000	-0.907323000	2.288439000
C	0.048917000	-0.464645000	0.781433000
H	-2.686508000	-1.500598000	2.542893000
H	0.609961000	-0.707077000	-0.121435000
C	-1.422785000	0.146712000	3.115348000
C	0.439271000	0.588048000	1.600716000
H	-1.994324000	0.379601000	4.013566000
C	-0.293012000	0.897239000	2.769184000
H	-1.398264000	-2.039740000	0.497373000
C	1.601678000	1.541974000	1.451600000
N	2.707507000	5.254350000	4.607008000
N	2.525797000	5.994991000	5.676126000
C	3.375319000	7.077285000	5.674904000
N	3.282018000	7.895194000	6.755283000
N	2.630814000	7.436374000	7.792216000
S	4.491826000	7.423609000	4.417072000
C	1.657263000	7.585864000	9.978302000
C	2.385033000	8.190289000	8.934121000
C	1.411183000	8.316808000	11.126302000
C	2.855777000	9.512224000	9.048388000
C	1.883536000	9.642499000	11.252901000
H	3.411218000	9.939539000	8.217547000
C	2.607250000	10.233355000	10.207154000
H	2.975127000	11.255013000	10.293238000
H	1.299419000	6.560141000	9.870841000
C	0.252423000	9.385843000	14.509660000
C	0.757546000	9.153891000	13.236240000
C	0.471259000	10.631608000	15.108365000
H	0.080282000	10.827383000	16.105876000
C	1.480656000	10.159244000	12.557272000
C	1.188995000	11.629559000	14.437435000
H	1.349120000	12.592875000	14.920288000
C	1.699382000	11.403085000	13.159704000
H	2.257317000	12.183641000	12.643120000
H	-0.306794000	8.613310000	15.038325000
C	0.663797000	7.914796000	12.375678000

H	3.493017000	5.636584000	3.993361000
H	2.230504000	6.490882000	7.721659000
H	2.567192000	1.015340000	1.443868000
H	1.544660000	2.114443000	0.514259000
H	1.123376000	7.042169000	12.862623000
H	-0.380119000	7.645094000	12.157484000

β-fluorenedithizone (Hydrogen bridge 2 form)

	x	y	z
C	1.619580000	4.124206000	1.126865000
C	0.537989000	3.479098000	1.767088000
C	2.338354000	5.109053000	1.780575000
H	3.176770000	5.623589000	1.311543000
C	0.182656000	3.832368000	3.078194000
C	1.990224000	5.462141000	3.101434000
H	-0.653802000	3.342584000	3.576374000
C	0.904473000	4.813717000	3.736560000
H	0.646450000	5.107549000	4.750957000
C	-0.717178000	0.805837000	-1.249720000
C	-1.442913000	0.771375000	-0.052200000
C	0.357924000	1.687595000	-1.408163000
H	-2.277167000	0.078224000	0.050762000
H	0.917008000	1.707729000	-2.344113000
C	-1.108014000	1.614252000	1.006382000
C	0.696872000	2.532012000	-0.356993000
H	-1.675991000	1.582553000	1.936001000
C	-0.033335000	2.497471000	0.851555000
H	-0.993444000	0.139259000	-2.065664000
C	1.795676000	3.565512000	-0.266389000
N	2.772259000	6.459069000	3.687440000
N	2.510425000	6.731418000	4.918561000
C	3.262382000	7.713949000	5.502285000
N	3.067682000	8.030820000	6.771178000
N	2.136690000	7.364639000	7.437033000
S	4.526863000	8.624142000	4.641134000
C	0.814571000	6.851049000	9.369600000
C	1.843399000	7.606647000	8.772766000
C	0.503462000	7.076377000	10.698779000
C	2.545827000	8.573354000	9.516710000
C	1.202756000	8.045121000	11.451762000
H	3.334338000	9.137242000	9.025233000
C	2.225492000	8.789365000	10.850836000
H	2.775073000	9.539401000	11.418891000
H	0.276809000	6.104283000	8.781724000
C	-1.072189000	6.924621000	14.081620000
C	-0.377122000	7.109935000	12.892605000
C	-0.728652000	7.698515000	15.196361000
H	-1.265259000	7.563722000	16.134615000
C	0.659965000	8.065398000	12.808032000
C	0.300109000	8.645036000	15.115291000
H	0.554876000	9.238539000	15.992748000
C	1.001475000	8.836048000	13.924250000
H	1.801206000	9.574840000	13.869410000

H	-1.874193000	6.188652000	14.150258000
C	-0.546180000	6.414094000	11.560683000
H	1.618882000	6.641985000	6.929847000
H	4.262603000	7.887418000	3.516445000
H	2.790990000	3.117840000	-0.403948000
H	1.689239000	4.344398000	-1.035744000
H	-1.557627000	6.552989000	11.150949000
H	-0.382021000	5.329350000	11.642254000

α-pyrenedithizone (Symmetric form)

	x	y	z
C	-0.118078000	-6.516366000	-10.788189000
C	0.744586000	-7.127459000	-9.827080000
C	0.346081000	-5.546073000	-11.633807000
C	2.117405000	-6.713196000	-9.773378000
C	1.701999000	-5.100564000	-11.598943000
C	2.589450000	-5.699147000	-10.656308000
H	-1.154168000	-6.838090000	-10.832891000
C	0.313508000	-8.103454000	-8.882701000
C	3.026315000	-7.285758000	-8.829932000
C	3.950449000	-5.264398000	-10.595215000
C	2.551522000	-8.267564000	-7.938150000
C	1.232188000	-8.654454000	-7.960368000
C	4.381385000	-6.842027000	-8.796835000
H	3.235982000	-8.711455000	-7.216557000
H	0.870322000	-9.401489000	-7.254238000
C	2.185044000	-4.090594000	-12.452642000
C	4.385488000	-4.250296000	-11.466408000
C	3.510643000	-3.671799000	-12.382893000
H	-0.330390000	-5.088879000	-12.355891000
C	4.829090000	-5.868894000	-9.642983000
H	5.054911000	-7.294687000	-8.069248000
H	5.422632000	-3.918586000	-11.412626000
H	3.866797000	-2.886082000	-13.047195000
H	5.865381000	-5.534068000	-9.601873000
H	1.503201000	-3.634372000	-13.170318000
N	-0.975725000	-8.563566000	-8.695151000
N	-2.062072000	-8.376349000	-9.404176000
C	-3.154974000	-8.886891000	-8.756741000
N	-4.305088000	-8.733876000	-9.482709000
N	-5.345400000	-9.126859000	-8.789615000
S	-3.093441000	-9.619648000	-7.184412000
C	-6.418180000	-9.061432000	-11.641224000
C	-7.211178000	-9.224763000	-10.464140000
C	-6.979964000	-9.145225000	-12.886354000
C	-8.620114000	-9.454531000	-10.610511000
C	-8.374223000	-9.390754000	-13.069236000
C	-9.195743000	-9.536922000	-11.911693000
H	-5.355049000	-8.869911000	-11.527889000
C	-6.677952000	-9.225933000	-9.143519000
C	-9.462589000	-9.631444000	-9.469546000
C	-10.594734000	-9.787873000	-12.067662000

C	-8.884517000	-9.598713000	-8.185331000
C	-7.530194000	-9.416484000	-8.031930000
C	-10.858672000	-9.860327000	-9.652101000
H	-9.517880000	-9.731443000	-7.309373000
H	-7.089092000	-9.407949000	-7.035489000
C	-8.958891000	-9.503042000	-14.345563000
C	-11.132324000	-9.892283000	-13.362825000
C	-10.320738000	-9.753924000	-14.486262000
H	-6.354741000	-9.028372000	-13.771351000
C	-11.406605000	-9.937324000	-10.900133000
H	-11.481437000	-9.983111000	-8.766100000
H	-12.198481000	-10.090010000	-13.476267000
H	-10.755634000	-9.844530000	-15.480325000
H	-12.473421000	-10.121892000	-11.025108000
H	-8.327421000	-9.396390000	-15.227667000
H	-1.170215000	-9.096650000	-7.805838000
H	-5.080961000	-9.438535000	-7.817637000

α-pyrenedithizone (Enol form)

	x	y	z
C	-0.235562000	-6.633276000	-10.727145000
C	0.693140000	-7.203150000	-9.802802000
C	0.148476000	-5.640474000	-11.587182000
C	2.045981000	-6.715575000	-9.793225000
C	1.477747000	-5.124248000	-11.600638000
C	2.428310000	-5.675534000	-10.682875000
H	-1.253854000	-7.005499000	-10.740481000
C	0.360502000	-8.256372000	-8.879962000
C	3.021431000	-7.250798000	-8.895817000
C	3.766864000	-5.157640000	-10.667233000
C	2.643727000	-8.299613000	-8.029211000
C	1.353384000	-8.782097000	-8.028677000
C	4.350165000	-6.717657000	-8.898445000
H	3.381133000	-8.728019000	-7.350460000
H	1.081581000	-9.591067000	-7.348135000
C	1.876802000	-4.089651000	-12.464671000
C	4.112567000	-4.129054000	-11.552358000
C	3.177457000	-3.599308000	-12.439374000
H	-0.579840000	-5.222883000	-12.286276000
C	4.708523000	-5.716058000	-9.743279000
H	5.076026000	-7.138472000	-8.199848000
H	5.132695000	-3.739239000	-11.535577000
H	3.467433000	-2.794308000	-13.109788000
H	5.724145000	-5.321612000	-9.733418000
H	1.148480000	-3.669875000	-13.158269000
N	-0.887795000	-8.830802000	-8.704460000
N	-2.044113000	-8.579520000	-9.314775000
C	-3.119776000	-9.059568000	-8.693765000
N	-4.320062000	-8.861007000	-9.341427000
N	-5.321429000	-9.223601000	-8.618410000
S	-3.136778000	-9.886033000	-7.073480000
C	-6.266627000	-9.196347000	-11.556793000
C	-7.113686000	-9.247857000	-10.408566000
C	-6.774979000	-9.278779000	-12.817660000

C	-8.532941000	-9.356377000	-10.617954000
C	-8.174011000	-9.412078000	-13.059840000
C	-9.059970000	-9.446384000	-11.933682000
H	-5.194465000	-9.085345000	-11.394196000
C	-6.628221000	-9.230059000	-9.066075000
C	-9.438959000	-9.393320000	-9.501608000
C	-10.463761000	-9.584274000	-12.147459000
C	-8.906252000	-9.361127000	-8.196412000
C	-7.546613000	-9.308442000	-7.992220000
C	-10.839823000	-9.491758000	-9.741247000
H	-9.571190000	-9.400389000	-7.344324000
H	-7.138243000	-9.294788000	-6.996497000
C	-8.713683000	-9.525213000	-14.357467000
C	-10.947418000	-9.696282000	-13.465695000
C	-10.072846000	-9.666440000	-14.552057000
H	-6.100388000	-9.249114000	-13.682835000
C	-11.335850000	-9.608131000	-11.019998000
H	-11.518208000	-9.503404000	-8.888455000
H	-12.018103000	-9.810085000	-13.626982000
H	-10.471418000	-9.759505000	-15.561879000
H	-12.395590000	-9.718908000	-11.178031000
H	-8.027594000	-9.503202000	-15.213053000
H	-0.990210000	-9.300649000	-7.775126000
H	-4.467679000	-9.711616000	-7.279950000

α-pyrenedithizone (Keto form)

	x	y	z
C	-0.121223000	-6.204542000	-10.161120000
C	0.765754000	-6.902069000	-9.274708000
C	0.333370000	-5.271227000	-11.046790000
C	2.167571000	-6.582762000	-9.344910000
C	1.718540000	-4.933825000	-11.139397000
C	2.635070000	-5.602535000	-10.272928000
H	-1.180053000	-6.440676000	-10.144544000
C	0.360269000	-7.915215000	-8.365778000
C	3.118902000	-7.254180000	-8.518743000
C	4.030264000	-5.293631000	-10.357312000
C	2.660650000	-8.244699000	-7.634785000
C	1.320452000	-8.559758000	-7.561598000
C	4.503835000	-6.918193000	-8.614939000
H	3.374702000	-8.766021000	-6.998262000
H	0.975870000	-9.317454000	-6.858606000
C	2.200740000	-3.984719000	-12.057929000
C	4.465193000	-4.336097000	-11.291567000
C	3.560529000	-3.692021000	-12.130446000
H	-0.368273000	-4.769705000	-11.713294000
C	4.945634000	-5.975713000	-9.495704000
H	5.206521000	-7.442181000	-7.966879000
H	5.529608000	-4.108162000	-11.353860000
H	3.919396000	-2.958079000	-12.850625000
H	6.006192000	-5.733103000	-9.563429000
H	1.494735000	-3.483129000	-12.719995000
N	-0.941672000	-8.399247000	-8.111420000
N	-2.099022000	-7.971211000	-8.748976000

C	-2.959127000	-8.940750000	-9.212952000
N	-4.265140000	-8.435013000	-9.278258000
N	-5.039241000	-9.059335000	-10.081528000
S	-2.484590000	-10.529606000	-9.425525000
C	-6.739660000	-9.801097000	-12.207168000
C	-7.248919000	-9.304059000	-10.970908000
C	-7.582913000	-10.239962000	-13.188877000
C	-8.661003000	-9.272522000	-10.768960000
C	-9.001771000	-10.237850000	-13.014068000
C	-9.535208000	-9.755372000	-11.783102000
H	-5.661390000	-9.823874000	-12.343966000
C	-6.395510000	-8.831678000	-9.927490000
C	-9.203052000	-8.780551000	-9.543538000
C	-10.945743000	-9.769463000	-11.567205000
C	-8.321707000	-8.295328000	-8.549282000
C	-6.957642000	-8.311656000	-8.738989000
C	-10.615987000	-8.811800000	-9.350175000
H	-8.738888000	-7.930121000	-7.610201000
H	-6.278426000	-7.978716000	-7.957636000
C	-9.884329000	-10.709327000	-14.002650000
C	-11.788540000	-10.260262000	-12.581300000
C	-11.260398000	-10.720768000	-13.784865000
H	-7.177313000	-10.614599000	-14.128716000
C	-11.453834000	-9.289867000	-10.319827000
H	-11.019288000	-8.450049000	-8.404646000
H	-12.865221000	-10.278534000	-12.412265000
H	-11.927475000	-11.094714000	-14.559847000
H	-12.530795000	-9.312433000	-10.153482000
H	-9.476665000	-11.073084000	-14.945717000
H	-0.986257000	-9.436834000	-8.125383000
H	-2.555108000	-7.174985000	-8.304366000

α-pyrenedithizone (Hydrogen bridge 1 form)

	x	y	z
C	-0.104034000	-6.431510000	-10.613646000
C	0.769987000	-7.074237000	-9.684890000
C	0.353911000	-5.486799000	-11.491306000
C	2.151832000	-6.691783000	-9.679994000
C	1.724523000	-5.099442000	-11.526132000
C	2.623610000	-5.710583000	-10.601967000
H	-1.153814000	-6.697435000	-10.597558000
C	0.346326000	-8.059573000	-8.737390000
C	3.072900000	-7.271667000	-8.754035000
C	3.999819000	-5.322227000	-10.602637000
C	2.597743000	-8.226338000	-7.828762000
C	1.276462000	-8.604554000	-7.820273000
C	4.439801000	-6.868649000	-8.777734000
H	3.292665000	-8.666010000	-7.114583000
H	0.922090000	-9.345419000	-7.104249000
C	2.208182000	-4.129705000	-12.425568000
C	4.436909000	-4.347983000	-11.519209000
C	3.549757000	-3.761049000	-12.419175000
H	-0.341814000	-5.004908000	-12.178167000
C	4.889758000	-5.932452000	-9.666088000

H	5.125490000	-7.324741000	-8.064007000
H	5.486842000	-4.054173000	-11.515169000
H	3.908082000	-3.008152000	-13.119367000
H	5.937471000	-5.632993000	-9.670128000
H	1.513212000	-3.667232000	-13.126630000
N	-0.927307000	-8.562619000	-8.619036000
N	-1.967401000	-8.293033000	-9.379652000
C	-3.133901000	-8.786836000	-8.848443000
N	-4.242233000	-8.561492000	-9.616101000
N	-3.991184000	-8.311110000	-10.880468000
S	-3.249567000	-9.604892000	-7.352821000
C	-6.935148000	-7.727725000	-10.421648000
C	-6.246930000	-7.564957000	-11.663054000
C	-8.261950000	-7.414180000	-10.304729000
C	-6.977982000	-7.072291000	-12.794862000
C	-9.018213000	-6.915634000	-11.406774000
C	-8.360062000	-6.748023000	-12.661019000
H	-6.384776000	-8.109480000	-9.568548000
C	-4.863806000	-7.858199000	-11.853070000
C	-6.345047000	-6.891301000	-14.063614000
C	-9.096370000	-6.248219000	-13.779403000
C	-4.977737000	-7.208309000	-14.194629000
C	-4.261265000	-7.677608000	-13.118799000
C	-7.102916000	-6.392609000	-15.163599000
H	-4.487658000	-7.074502000	-15.158010000
H	-3.202089000	-7.914127000	-13.230834000
C	-10.382227000	-6.584603000	-11.293563000
C	-10.456960000	-5.930750000	-13.618247000
C	-11.089803000	-6.097668000	-12.388203000
H	-8.763762000	-7.544957000	-9.346037000
C	-8.425809000	-6.081666000	-15.030380000
H	-6.598948000	-6.261684000	-16.121037000
H	-11.013473000	-5.547461000	-14.473490000
H	-12.143636000	-5.844680000	-12.283569000
H	-8.991656000	-5.698859000	-15.879368000
H	-10.878519000	-6.714459000	-10.331839000
H	-1.203149000	-9.159456000	-7.783820000
H	-2.996810000	-8.357378000	-11.150285000

α-pyrenedithizone (Hydrogen bridge 2 form)

	x	y	z
C	0.591742000	-8.512420000	-10.575429000
C	-0.114313000	-7.836245000	-11.620246000
C	1.934034000	-8.756219000	-10.666094000
C	0.626239000	-7.402818000	-12.771647000
C	2.697288000	-8.353180000	-11.802016000
C	2.026328000	-7.667545000	-12.859607000
H	0.039064000	-8.831468000	-9.699843000
C	-1.515596000	-7.571112000	-11.596961000
C	-0.014756000	-6.716407000	-13.849043000
C	2.768727000	-7.259110000	-14.012217000
C	-1.397156000	-6.463785000	-13.763134000
C	-2.122699000	-6.881311000	-12.669545000
C	0.750921000	-6.313144000	-14.984311000

H	-1.895757000	-5.936469000	-14.575530000
H	-3.194928000	-6.682903000	-12.621872000
C	4.075577000	-8.614524000	-11.912353000
C	4.143618000	-7.547334000	-14.079143000
C	4.786555000	-8.216669000	-13.040362000
H	2.444008000	-9.275590000	-9.854615000
C	2.088196000	-6.574356000	-15.067662000
H	0.238594000	-5.793238000	-15.793687000
H	4.703655000	-7.240059000	-14.962494000
H	5.851669000	-8.431403000	-13.112917000
H	2.659001000	-6.267324000	-15.943832000
H	4.579925000	-9.138750000	-11.100588000
N	-2.401454000	-7.947807000	-10.601401000
N	-2.121730000	-8.600241000	-9.478557000
C	-3.160098000	-9.012406000	-8.762698000
N	-4.425301000	-8.890140000	-9.265081000
N	-5.388227000	-9.252890000	-8.482341000
S	-2.802479000	-9.753751000	-7.188924000
C	-6.263827000	-9.323287000	-11.464177000
C	-7.136939000	-9.314127000	-10.332548000
C	-6.743678000	-9.377474000	-12.744616000
C	-8.548443000	-9.393911000	-10.578195000
C	-8.141462000	-9.430223000	-13.019041000
C	-9.044534000	-9.447259000	-11.915589000
H	-5.195116000	-9.300025000	-11.287911000
C	-6.684909000	-9.291080000	-8.967720000
C	-9.481690000	-9.430127000	-9.494994000
C	-10.449987000	-9.530385000	-12.164796000
C	-8.992963000	-9.417061000	-8.173126000
C	-7.640068000	-9.371023000	-7.926907000
C	-10.880051000	-9.501106000	-9.771840000
H	-9.700088000	-9.454329000	-7.345017000
H	-7.256580000	-9.373139000	-6.908717000
C	-8.648163000	-9.494565000	-14.331650000
C	-10.910174000	-9.595202000	-13.492099000
C	-10.017317000	-9.578749000	-14.562006000
H	-6.047550000	-9.395950000	-13.583595000
C	-11.349013000	-9.550536000	-11.053291000
H	-11.572332000	-9.523508000	-8.930365000
H	-11.982914000	-9.660810000	-13.675294000
H	-10.394092000	-9.633094000	-15.582036000
H	-12.419430000	-9.611694000	-11.248714000
H	-7.949385000	-9.484199000	-15.168342000
H	-3.396099000	-7.772174000	-10.780665000
H	-4.153104000	-9.920562000	-7.001168000

α-pyrenedithizone (Symmetric form)

	x	y	z
C	4.716315000	2.736419000	-10.975920000
C	4.752085000	3.176650000	-9.620396000
C	4.723602000	2.277514000	-8.540055000
C	4.812860000	4.593080000	-9.360006000

C	4.853008000	5.032264000	-8.033867000
C	4.829109000	4.141022000	-6.955151000
C	4.757985000	2.717333000	-7.213242000
C	4.733497000	3.639530000	-12.010212000
C	4.826969000	5.500228000	-10.460969000
H	4.898723000	6.102603000	-7.827544000
C	4.860999000	4.619970000	-5.615641000
C	4.707511000	1.845158000	-6.064432000
C	4.741566000	2.357619000	-4.777588000
C	4.820878000	3.745216000	-4.556099000
H	4.915120000	5.695165000	-5.448468000
H	4.702164000	1.659532000	-3.946503000
H	4.848147000	4.117154000	-3.533605000
C	4.787221000	5.037116000	-11.751070000
H	4.673913000	1.666090000	-11.177923000
H	4.665840000	1.213750000	-8.776181000
H	4.705445000	3.288302000	-13.040704000
H	4.869014000	6.570146000	-10.254099000
H	4.797033000	5.738816000	-12.584410000
N	4.602498000	0.466024000	-6.238885000
N	4.404563000	-0.327741000	-5.225069000
C	4.318879000	-1.649053000	-5.544703000
N	4.053816000	-2.329157000	-4.394738000
N	3.912713000	-3.615585000	-4.542790000
S	4.482925000	-2.328355000	-7.112816000
H	4.665778000	-0.006187000	-7.165245000
H	4.030843000	-3.965749000	-5.517183000
C	2.767897000	-5.982319000	-1.256199000
C	3.126618000	-6.640007000	-2.466099000
C	3.100094000	-8.036520000	-2.556032000
C	3.537200000	-5.863164000	-3.618430000
C	3.908935000	-6.538468000	-4.785363000
C	3.885200000	-7.941427000	-4.868901000
C	3.466667000	-8.711835000	-3.723498000
C	2.809697000	-4.611297000	-1.163072000
C	3.548567000	-4.427304000	-3.469293000
H	4.241790000	-5.989689000	-5.667357000
C	4.268922000	-8.639023000	-6.052103000
C	3.447761000	-10.135265000	-3.815294000
C	3.824561000	-10.768450000	-4.971957000
C	4.239940000	-10.011138000	-6.101828000
H	4.587602000	-8.061408000	-6.920204000
H	3.129007000	-10.709242000	-2.944420000
H	3.807560000	-11.856014000	-5.029858000
H	4.536958000	-10.529789000	-7.012247000
C	3.198356000	-3.831577000	-2.268197000
H	2.461079000	-6.589346000	-0.405228000
H	2.788519000	-8.611665000	-1.682770000
H	3.221858000	-2.747325000	-2.208062000
H	2.533207000	-4.113656000	-0.235200000

α-pyrenedithizone (Enol form)

	x	y	z
C	4.826176000	3.149342000	-10.997837000

C	4.805424000	3.445506000	-9.602642000
C	4.695022000	2.444404000	-8.623633000
C	4.895108000	4.824386000	-9.191363000
C	4.860062000	5.123542000	-7.826550000
C	4.744214000	4.130036000	-6.847501000
C	4.667956000	2.741973000	-7.256143000
C	4.933381000	4.151988000	-11.929790000
C	5.004798000	5.837512000	-10.189534000
H	4.917091000	6.165691000	-7.508661000
C	4.685364000	4.469937000	-5.465979000
C	4.551151000	1.753140000	-6.213412000
C	4.491792000	2.129804000	-4.883761000
C	4.555561000	3.489648000	-4.514810000
H	4.740770000	5.520598000	-5.183875000
H	4.398643000	1.352877000	-4.130647000
H	4.506760000	3.750290000	-3.458752000
C	5.022845000	5.512112000	-11.521672000
H	4.755558000	2.107966000	-11.314090000
H	4.614393000	1.415351000	-8.977802000
H	4.947341000	3.910481000	-12.991716000
H	5.072202000	6.877893000	-9.869632000
H	5.105976000	6.294941000	-12.274590000
N	4.487892000	0.393340000	-6.544930000
N	4.254962000	-0.494351000	-5.593508000
C	4.238085000	-1.779778000	-5.850799000
N	3.953690000	-2.525353000	-4.735019000
N	3.894226000	-3.795355000	-4.854689000
S	4.531013000	-2.532543000	-7.447962000
H	4.660770000	0.096795000	-7.506351000
H	4.319386000	-3.750373000	-6.829617000
C	2.862127000	-5.782887000	-1.255925000
C	3.206335000	-6.557907000	-2.396375000
C	3.208950000	-7.956958000	-2.334884000
C	3.562550000	-5.896492000	-3.635131000
C	3.901159000	-6.683435000	-4.739733000
C	3.902460000	-8.086500000	-4.675674000
C	3.547318000	-8.742387000	-3.439395000
C	2.862999000	-4.408505000	-1.313910000
C	3.555935000	-4.452724000	-3.653129000
H	4.173162000	-6.194909000	-5.673480000
C	4.246527000	-8.899987000	-5.796825000
C	3.553842000	-10.168248000	-3.383052000
C	3.891723000	-10.912728000	-4.483893000
C	4.240720000	-10.269720000	-5.704735000
H	4.515426000	-8.411628000	-6.733832000
H	3.284336000	-10.653496000	-2.444215000
H	3.893246000	-12.000832000	-4.428874000
H	4.506156000	-10.875611000	-6.570072000
C	3.207711000	-3.748477000	-2.506725000
H	2.596180000	-6.300858000	-0.334587000
H	2.940243000	-8.442241000	-1.395304000
H	3.207045000	-2.662572000	-2.557835000
H	2.595171000	-3.821272000	-0.436826000

α-pyrenedithizone (Keto form)

	x	y	z
C	4.467041000	3.570437000	-11.014885000
C	4.610530000	3.659715000	-9.598570000
C	4.495526000	2.537921000	-8.762283000
C	4.870395000	4.952147000	-9.012688000
C	5.000313000	5.051540000	-7.622947000
C	4.887161000	3.936578000	-6.785501000
C	4.634340000	2.639903000	-7.374587000
C	4.572353000	4.687431000	-11.805883000
C	4.971047000	6.088873000	-9.868152000
H	5.186462000	6.028495000	-7.174425000
C	4.991609000	4.061098000	-5.369083000
C	4.517959000	1.510585000	-6.487893000
C	4.628256000	1.680195000	-5.121602000
C	4.860956000	2.960428000	-4.563297000
H	5.175749000	5.046340000	-4.942644000
H	4.573446000	0.813506000	-4.465628000
H	4.951377000	3.054454000	-3.482441000
C	4.825180000	5.961607000	-11.226188000
H	4.273161000	2.594225000	-11.459987000
H	4.268599000	1.572454000	-9.214059000
H	4.461872000	4.603594000	-12.886215000
H	5.163346000	7.063636000	-9.418715000
H	4.901964000	6.838371000	-11.868246000
N	4.214635000	0.246815000	-7.057893000
N	3.837327000	-0.723889000	-6.166543000
C	4.293316000	-2.002788000	-6.216183000
N	3.673984000	-2.664385000	-5.133503000
N	3.998240000	-3.879597000	-4.957923000
S	5.409914000	-2.515158000	-7.347183000
H	4.912724000	-0.190255000	-7.688885000
H	3.054338000	-0.513467000	-5.551402000
C	2.796505000	-5.560439000	-1.277972000
C	3.141093000	-6.426511000	-2.351141000
C	3.117461000	-7.817767000	-2.193033000
C	3.526375000	-5.862224000	-3.626080000
C	3.859671000	-6.721172000	-4.674961000
C	3.831196000	-8.116503000	-4.514934000
C	3.451726000	-8.680525000	-3.240863000
C	2.821905000	-4.192131000	-1.432463000
C	3.532801000	-4.423265000	-3.752237000
H	4.152888000	-6.293078000	-5.632004000
C	4.166894000	-9.007413000	-5.577205000
C	3.430661000	-10.099336000	-3.090244000
C	3.761201000	-10.920921000	-4.137334000
C	4.131683000	-10.367779000	-5.394785000
H	4.452330000	-8.585471000	-6.540750000
H	3.145910000	-10.516779000	-2.123787000
H	3.741785000	-12.002709000	-4.010527000
H	4.389451000	-11.034663000	-6.216369000
C	3.188872000	-3.626609000	-2.666453000
H	2.522271000	-6.003155000	-0.320139000
H	2.828473000	-8.235065000	-1.227204000

H	3.244457000	-2.547025000	-2.786445000
H	2.574144000	-3.541118000	-0.595273000

α-pyrenedithizone (Hydrogen bridge 1 form)

	x	y	z
C	4.392698000	-0.146245000	1.176123000
C	4.445015000	0.891579000	0.201148000
C	4.454010000	0.614495000	-1.173405000
C	4.485580000	2.262776000	0.642525000
C	4.527628000	3.278434000	-0.320002000
C	4.528197000	3.003217000	-1.694362000
C	4.493143000	1.627063000	-2.135156000
C	4.380317000	0.149960000	2.516366000
C	4.474451000	2.528908000	2.044257000
H	4.553949000	4.319126000	0.006128000
C	4.556865000	4.044981000	-2.665333000
C	4.483177000	1.383218000	-3.560885000
C	4.496807000	2.427472000	-4.471461000
C	4.540101000	3.758643000	-4.013081000
H	4.588409000	5.077741000	-2.319816000
H	4.477942000	2.195348000	-5.533655000
H	4.558328000	4.567060000	-4.741696000
C	4.422064000	1.502767000	2.954493000
H	4.362830000	-1.182320000	0.835551000
H	4.423925000	-0.439622000	-1.454269000
H	4.339932000	-0.651701000	3.252244000
H	4.506588000	3.565720000	2.379733000
H	4.412955000	1.719459000	4.021858000
N	4.458949000	0.064095000	-3.970564000
N	4.357433000	-0.353075000	-5.206620000
C	4.222897000	-1.711814000	-5.331640000
N	3.920259000	-2.357261000	-4.162971000
N	3.850571000	-3.663140000	-4.313326000
S	4.439407000	-2.490947000	-6.839046000
H	4.414840000	-0.677067000	-3.258115000
H	4.074005000	-3.954017000	-5.306008000
C	2.654507000	-6.225495000	-1.215411000
C	3.072705000	-6.799743000	-2.448119000
C	3.101214000	-8.188719000	-2.624518000
C	3.476464000	-5.941292000	-3.541092000
C	3.883053000	-6.524503000	-4.742096000
C	3.902488000	-7.918859000	-4.918463000
C	3.503447000	-8.775025000	-3.830022000
C	2.617352000	-4.858027000	-1.051184000
C	3.435618000	-4.511497000	-3.314171000
H	4.197536000	-5.908488000	-5.585582000
C	4.307215000	-8.518080000	-6.146188000
C	3.532126000	-10.189073000	-4.018807000
C	3.929863000	-10.728556000	-5.216213000
C	4.320191000	-9.883813000	-6.291551000
H	4.606479000	-7.870498000	-6.970494000
H	3.231206000	-10.832448000	-3.191569000
H	3.947629000	-11.809604000	-5.348898000
H	4.631156000	-10.328260000	-7.235939000

C	3.001855000	-3.999363000	-2.094457000
H	2.356254000	-6.889880000	-0.405135000
H	2.798037000	-8.829142000	-1.795231000
H	2.954555000	-2.920742000	-1.973020000
H	2.280456000	-4.429386000	-0.108759000

α-pyrenedithizone (Hydrogen bridge 2 form)

	x	y	z
C	3.802372000	0.732995000	0.661533000
C	3.838958000	1.588170000	-0.478413000
C	3.967701000	1.086928000	-1.782910000
C	3.739605000	3.012197000	-0.280669000
C	3.783365000	3.851949000	-1.399358000
C	3.912533000	3.354266000	-2.702647000
C	3.997918000	1.924209000	-2.902359000
C	3.669179000	1.250308000	1.926042000
C	3.605005000	3.511244000	1.049764000
H	3.716458000	4.931393000	-1.255898000
C	3.966653000	4.225488000	-3.828284000
C	4.110780000	1.442789000	-4.262037000
C	4.162392000	2.326710000	-5.325609000
C	4.095229000	3.717547000	-5.099594000
H	3.904147000	5.300141000	-3.661046000
H	4.243704000	1.926221000	-6.332799000
H	4.135718000	4.390735000	-5.954546000
C	3.568750000	2.655713000	2.122196000
H	3.880944000	-0.344354000	0.509866000
H	4.055072000	0.003606000	-1.882762000
H	3.640008000	0.585016000	2.788050000
H	3.530508000	4.588918000	1.197829000
H	3.463830000	3.050038000	3.132166000
N	4.154775000	0.073893000	-4.461642000
N	4.277184000	-0.484696000	-5.658970000
C	4.183321000	-1.806444000	-5.710624000
N	3.905733000	-2.508096000	-4.574519000
N	3.831172000	-3.792567000	-4.670281000
S	4.420801000	-2.554631000	-7.306701000
H	4.001230000	-0.563084000	-3.677961000
H	4.190939000	-3.781300000	-6.745757000
C	2.762151000	-5.911426000	-1.175903000
C	3.158390000	-6.633105000	-2.334887000
C	3.196170000	-8.033797000	-2.336167000
C	3.524948000	-5.909950000	-3.533466000
C	3.908560000	-6.634272000	-4.662644000
C	3.938937000	-8.037961000	-4.665567000
C	3.574808000	-8.759068000	-3.469670000
C	2.714547000	-4.534232000	-1.183218000
C	3.478458000	-4.462085000	-3.500732000
H	4.189662000	-6.094802000	-5.564746000
C	4.319844000	-8.785028000	-5.819914000
C	3.612377000	-10.185545000	-3.484581000
C	3.984500000	-10.866349000	-4.615741000
C	4.341446000	-10.157444000	-5.796511000
H	4.594080000	-8.243015000	-6.725245000

H	3.338421000	-10.724502000	-2.576920000
H	4.009037000	-11.955409000	-4.614894000
H	4.634020000	-10.713473000	-6.686333000
C	3.067577000	-3.814483000	-2.337685000
H	2.487189000	-6.470412000	-0.281725000
H	2.920008000	-8.569325000	-1.426628000
H	3.009142000	-2.728843000	-2.343039000
H	2.394240000	-3.994825000	-0.292566000

Coordinates for all optimized dithizonate derivatives studied in this research project

o-methoxydithizonatophenylmercury(II) – pink isomer

	x	y	z
N	0.154988000	2.169222000	0.292444000
N	-0.332492000	2.021299000	-0.918165000
C	-1.367640000	2.821424000	-1.215606000
N	-1.812733000	2.583699000	-2.483457000
N	-2.840997000	3.232328000	-2.908937000
S	-2.004013000	3.982516000	-0.050165000
C	1.195990000	1.402885000	0.797809000
C	1.811051000	0.371718000	0.081973000
H	1.458485000	0.160283000	-0.924815000
C	1.625209000	1.702710000	2.115049000
C	2.658159000	0.966370000	2.690673000
C	2.843909000	-0.358326000	0.666798000
C	3.265772000	-0.063870000	1.964403000
H	3.317751000	-1.162479000	0.107267000
H	2.991681000	1.189954000	3.701295000
H	4.070775000	-0.635044000	2.423530000
C	-3.193881000	2.957278000	-4.242411000
C	-2.311460000	2.364712000	-5.159938000
H	-1.321352000	2.094385000	-4.800702000
C	-4.492010000	3.322033000	-4.684887000
C	-4.866534000	3.098725000	-6.012303000
C	-2.689530000	2.145724000	-6.479150000
C	-3.967155000	2.514043000	-6.905110000
H	-1.986309000	1.695731000	-7.177898000
H	-5.862564000	3.371466000	-6.351247000
H	-4.272057000	2.350390000	-7.937529000
H	-0.275716000	2.879131000	0.906571000
O	-5.324663000	3.866466000	-3.741642000
O	0.949357000	2.732333000	2.718618000
C	-6.621508000	4.310542000	-4.165975000
C	1.329594000	3.079058000	4.051977000
H	-7.070295000	4.783731000	-3.288913000
H	1.178112000	2.234840000	4.738635000
H	0.676945000	3.906979000	4.339738000
H	2.377835000	3.405873000	4.091403000
H	-6.540209000	5.047820000	-4.975031000
H	-7.233008000	3.459619000	-4.494107000

Hg	-3.959165000	4.939148000	-1.494686000
C	-5.559734000	6.517283000	-1.267830000
C	-5.453441000	7.778946000	-1.878474000
C	-6.655114000	6.302804000	-0.411880000
H	-4.620414000	8.001488000	-2.548075000
H	-6.781651000	5.344422000	0.096251000
C	-6.395707000	8.785849000	-1.642058000
C	-7.603038000	7.304262000	-0.173130000
H	-6.282525000	9.758546000	-2.122632000
H	-8.438190000	7.110968000	0.501722000
C	-7.473171000	8.551711000	-0.785772000
H	-8.203584000	9.337919000	-0.592720000

o-methoxydithizonatophenylmercury(II) – purple isomer

	x	y	z
N	0.028484000	0.906455000	-2.101147000
N	-0.277005000	1.850268000	-1.236443000
C	-1.292117000	2.674234000	-1.536650000
N	-1.869505000	2.508622000	-2.761472000
N	-2.903512000	3.218692000	-3.076161000
S	-1.703582000	3.842059000	-0.284016000
C	1.072004000	0.016319000	-1.894034000
C	1.877573000	0.041555000	-0.750881000
H	1.677535000	0.799937000	0.002407000
C	1.301996000	-0.958026000	-2.897309000
C	2.327438000	-1.887435000	-2.737164000
C	2.898793000	-0.893027000	-0.600015000
C	3.124275000	-1.854095000	-1.587020000
H	3.519448000	-0.869601000	0.293952000
H	2.509877000	-2.639299000	-3.501314000
H	3.921258000	-2.586173000	-1.470629000
C	-3.357953000	3.040483000	-4.387890000
C	-2.557573000	2.516213000	-5.419669000
H	-1.533697000	2.242339000	-5.176106000
C	-4.687654000	3.441599000	-4.696506000
C	-5.172452000	3.302119000	-6.000756000
C	-3.045459000	2.385176000	-6.713076000
C	-4.355856000	2.776256000	-7.001908000
H	-2.403721000	1.994261000	-7.500889000
H	-6.191617000	3.596942000	-6.236416000
H	-4.747863000	2.680512000	-8.013388000
H	-0.522710000	0.829197000	-2.962050000
O	-5.428591000	3.924604000	-3.658201000
O	0.453063000	-0.888108000	-3.977612000
C	-6.753112000	4.398760000	-3.943829000
C	0.630901000	-1.862474000	-5.008837000
H	-7.120230000	4.821782000	-3.005746000
H	1.627306000	-1.778900000	-5.464594000
H	-0.134347000	-1.646267000	-5.758548000
H	0.486866000	-2.880018000	-4.620328000
H	-6.733116000	5.182548000	-4.711988000
H	-7.397817000	3.571159000	-4.268500000

Hg	-3.774400000	4.906413000	-1.370106000
C	-5.434875000	6.419814000	-1.152293000
C	-5.371159000	7.682247000	-1.767883000
C	-6.534238000	6.166127000	-0.312138000
H	-4.536469000	7.936076000	-2.424433000
H	-6.629138000	5.206421000	0.200175000
C	-6.357546000	8.650784000	-1.553305000
C	-7.526977000	7.128876000	-0.094819000
H	-6.275439000	9.625493000	-2.036358000
H	-8.363606000	6.906231000	0.568822000
C	-7.439088000	8.377094000	-0.713720000
H	-8.203598000	9.133927000	-0.536717000

m-methoxydithizonatophenylmercury(II) – orange isomer

	x	y	z
N	0.326753000	1.795768000	0.458351000
N	-0.138506000	1.619017000	-0.756018000
C	-1.146488000	2.424037000	-1.108912000
N	-1.534192000	2.193381000	-2.397105000
N	-2.448349000	2.935837000	-2.905186000
S	-1.816210000	3.613083000	0.023728000
C	1.405271000	1.087610000	0.985475000
C	2.060529000	0.073460000	0.268691000
H	1.724208000	-0.181760000	-0.732599000
C	1.817851000	1.437238000	2.273895000
C	2.898538000	0.776893000	2.863016000
C	3.131688000	-0.572154000	0.874573000
C	3.565688000	-0.237646000	2.163395000
H	3.652133000	-1.361141000	0.333229000
H	4.408742000	-0.763500000	2.604132000
C	-2.804284000	2.632441000	-4.239203000
C	-2.206836000	1.596365000	-4.984327000
H	-1.429847000	0.992150000	-4.524650000
C	-3.805556000	3.418826000	-4.814554000
C	-4.222950000	3.185921000	-6.129337000
C	-2.629738000	1.378059000	-6.286988000
C	-3.634058000	2.158945000	-6.876403000
H	-2.173449000	0.580422000	-6.872250000
H	-3.943068000	1.960492000	-7.899767000
H	-0.108100000	2.541138000	1.025216000
H	-4.282946000	4.224321000	-4.254667000
H	1.312488000	2.225780000	2.831365000
O	3.221485000	1.202186000	4.126213000
O	-5.211606000	4.018000000	-6.585359000
C	4.332057000	0.566523000	4.759642000
C	-5.668742000	3.810082000	-7.921464000
H	-4.857621000	3.955427000	-8.649341000
H	-6.446032000	4.559789000	-8.089072000
H	-6.096945000	2.805231000	-8.046256000
H	5.257961000	0.716890000	4.186690000
H	4.428463000	1.043640000	5.738260000
H	4.153873000	-0.509695000	4.893973000

Hg	-3.371884000	4.856892000	-1.623661000
C	-4.732507000	6.573828000	-2.108070000
C	-4.311169000	7.591209000	-2.981181000
C	-5.997230000	6.703449000	-1.510280000
H	-3.337021000	7.536289000	-3.470565000
H	-6.367983000	5.940616000	-0.823355000
C	-5.121053000	8.701089000	-3.244372000
C	-6.811839000	7.809842000	-1.773020000
H	-4.768829000	9.480726000	-3.921110000
H	-7.789365000	7.888703000	-1.295085000
C	-6.374053000	8.813468000	-2.638896000
H	-7.004957000	9.679746000	-2.839355000

m-methoxydithizonatophenylmercury(II) – blue isomer

	x	y	z
N	0.252353000	0.478340000	-1.930477000
N	-0.125595000	1.392157000	-1.065615000
C	-1.097101000	2.240314000	-1.425070000
N	-1.596953000	2.095579000	-2.687240000
N	-2.513075000	2.900373000	-3.101505000
S	-1.558137000	3.414349000	-0.185723000
C	1.285452000	-0.422151000	-1.682337000
C	2.011548000	-0.404437000	-0.480107000
H	1.765489000	0.328375000	0.283493000
C	1.581142000	-1.351322000	-2.685147000
C	2.610095000	-2.276866000	-2.494637000
C	3.030661000	-1.331758000	-0.313440000
C	3.345891000	-2.272697000	-1.302606000
H	3.605131000	-1.328594000	0.612052000
H	4.151812000	-2.982469000	-1.136538000
C	-2.960177000	2.687841000	-4.420261000
C	-2.439025000	1.695634000	-5.278871000
H	-1.645669000	1.043262000	-4.927413000
C	-3.980244000	3.531753000	-4.873816000
C	-4.485905000	3.398688000	-6.171797000
C	-2.948637000	1.575982000	-6.561249000
C	-3.970098000	2.416255000	-7.025922000
H	-2.549612000	0.814110000	-7.230053000
H	-4.347414000	2.297294000	-8.038642000
H	-0.226513000	0.458750000	-2.837147000
H	-4.395180000	4.305533000	-4.226740000
H	1.020474000	-1.370772000	-3.619969000
O	2.815692000	-3.144395000	-3.537773000
O	-5.480987000	4.276691000	-6.507858000
C	3.848920000	-4.116675000	-3.373498000
C	-6.005344000	4.184323000	-7.832800000
H	-5.224801000	4.368864000	-8.584825000
H	-6.770189000	4.961367000	-7.904119000
H	-6.463998000	3.201853000	-8.014688000
H	3.647158000	-4.772147000	-2.514545000
H	3.848278000	-4.709825000	-4.291407000
H	4.830978000	-3.639387000	-3.247619000

Hg	-3.231694000	4.784934000	-1.535710000
C	-4.628453000	6.473551000	-2.023114000
C	-4.188973000	7.541763000	-2.824118000
C	-5.928589000	6.545098000	-1.493992000
H	-3.187744000	7.534369000	-3.258412000
H	-6.316524000	5.742425000	-0.864526000
C	-5.012740000	8.642582000	-3.083335000
C	-6.757109000	7.642697000	-1.751799000
H	-4.644956000	9.460774000	-3.703869000
H	-7.760957000	7.676019000	-1.326553000
C	-6.299448000	8.696137000	-2.544791000
H	-6.941101000	9.555803000	-2.740230000

p-methoxydithizonatophenylmercury(II) – orange isomer

	x	y	z
N	0.591078000	1.826532000	0.360337000
N	0.133899000	1.674011000	-0.862436000
C	-0.950498000	2.401060000	-1.161065000
N	-1.360209000	2.204144000	-2.445756000
N	-2.403165000	2.832451000	-2.863933000
S	-1.685720000	3.472649000	0.051914000
C	1.684097000	1.143541000	0.885472000
C	2.392958000	0.172439000	0.171378000
H	2.090746000	-0.066487000	-0.845616000
C	2.068376000	1.456766000	2.202968000
C	3.136600000	0.808767000	2.794193000
C	3.470653000	-0.482250000	0.768741000
C	3.847500000	-0.170270000	2.083110000
H	4.008063000	-1.237830000	0.200409000
H	3.440779000	1.043291000	3.812529000
C	-2.760737000	2.613420000	-4.206349000
C	-2.024123000	1.807740000	-5.091733000
H	-1.128811000	1.312231000	-4.724214000
C	-3.918328000	3.255503000	-4.685605000
C	-4.328329000	3.103703000	-5.998056000
C	-2.428520000	1.651820000	-6.413088000
C	-3.585074000	2.301267000	-6.876773000
H	-1.837895000	1.026076000	-7.078736000
H	-5.222574000	3.601763000	-6.369185000
H	0.082769000	2.488811000	0.968176000
H	-4.504289000	3.886383000	-4.015209000
H	1.517531000	2.216130000	2.759140000
O	-4.065483000	2.219438000	-8.155524000
O	4.884502000	-0.757241000	2.762455000
C	-3.324023000	1.425993000	-9.085014000
C	5.610201000	-1.780593000	2.080803000
H	-3.281943000	0.374425000	-8.768404000
H	6.097465000	-1.391084000	1.175586000
H	4.955619000	-2.621937000	1.811760000
H	6.372874000	-2.123980000	2.784259000
H	-2.303232000	1.812471000	-9.213592000
H	-3.862429000	1.498568000	-10.033422000

Hg	-3.663384000	4.335577000	-1.354616000
C	-5.522073000	5.583535000	-1.503680000
C	-5.450217000	6.963240000	-1.760700000
C	-6.790157000	5.025601000	-1.268460000
H	-4.488461000	7.443750000	-1.947816000
H	-6.898516000	3.959001000	-1.062764000
C	-6.600981000	7.757847000	-1.777810000
C	-7.944109000	5.816139000	-1.283935000
H	-6.518316000	8.827447000	-1.975578000
H	-8.916570000	5.360019000	-1.093133000
C	-7.851478000	7.185790000	-1.535841000
H	-8.748947000	7.804967000	-1.541963000

p-methoxydithizonatophenylmercury(II) – blue isomer

	x	y	z
N	0.597820000	0.637218000	-2.071635000
N	0.147283000	1.478116000	-1.164975000
C	-0.936964000	2.206503000	-1.457890000
N	-1.439717000	2.088365000	-2.717860000
N	-2.489338000	2.767271000	-3.050580000
S	-1.516004000	3.224295000	-0.130402000
C	1.762272000	-0.103627000	-1.891252000
C	2.550241000	0.032423000	-0.742019000
H	2.244132000	0.738131000	0.026104000
C	2.147959000	-1.011272000	-2.895203000
C	3.299823000	-1.765845000	-2.749807000
C	3.706912000	-0.727613000	-0.595542000
C	4.091471000	-1.630815000	-1.598015000
H	4.304997000	-0.605393000	0.304539000
H	3.608604000	-2.471376000	-3.518616000
C	-2.899800000	2.642361000	-4.383160000
C	-2.205284000	1.898647000	-5.356086000
H	-1.288532000	1.387861000	-5.073856000
C	-4.075786000	3.318222000	-4.769888000
C	-4.542577000	3.248919000	-6.069289000
C	-2.667431000	1.823299000	-6.662985000
C	-3.843400000	2.499190000	-7.030196000
H	-2.107398000	1.244883000	-7.394237000
H	-5.449705000	3.770859000	-6.369414000
H	0.084728000	0.574042000	-2.957205000
H	-4.623638000	3.904566000	-4.031324000
H	1.535661000	-1.123293000	-3.791115000
O	-4.377139000	2.491571000	-8.287915000
O	5.213094000	-2.418047000	-1.547938000
C	-3.686249000	1.740034000	-9.289596000
C	6.041670000	-2.288473000	-0.391606000
H	-3.641752000	0.673682000	-9.027623000
H	5.496525000	-2.560183000	0.523516000
H	6.433421000	-1.265928000	-0.294037000
H	6.872007000	-2.983259000	-0.539661000
H	-2.668261000	2.123940000	-9.444599000
H	-4.265493000	1.865193000	-10.207692000

Hg	-3.547649000	4.243328000	-1.275904000
C	-5.385865000	5.526558000	-1.415823000
C	-5.286167000	6.903041000	-1.684430000
C	-6.661778000	5.009220000	-1.130978000
H	-4.317920000	7.354995000	-1.907391000
H	-6.793702000	3.948114000	-0.910578000
C	-6.412479000	7.731807000	-1.664199000
C	-7.792311000	5.833151000	-1.109413000
H	-6.305485000	8.797729000	-1.869376000
H	-8.769818000	5.407747000	-0.878121000
C	-7.669517000	7.199023000	-1.372446000
H	-8.547201000	7.845219000	-1.345196000

o-methyldithizonatophenylmercury(II) – orange isomer

	x	y	z
N	0.439988000	1.788242000	0.380692000
N	-0.023534000	1.639215000	-0.839495000
C	-1.082183000	2.391134000	-1.153418000
N	-1.498245000	2.145020000	-2.432509000
N	-2.550984000	2.740704000	-2.864347000
S	-1.795744000	3.519417000	0.012511000
C	1.523039000	1.066103000	0.884665000
C	2.182466000	0.110617000	0.098323000
H	1.837453000	-0.057262000	-0.919156000
C	1.924878000	1.325333000	2.215251000
C	3.002055000	0.593185000	2.719520000
C	3.251249000	-0.599047000	0.634053000
C	3.665730000	-0.361553000	1.947525000
H	3.761806000	-1.342935000	0.023802000
H	3.323389000	0.779939000	3.744899000
H	4.500721000	-0.917355000	2.370260000
C	-2.853152000	2.482728000	-4.226342000
C	-1.825160000	2.311426000	-5.167575000
H	-0.795628000	2.348837000	-4.817657000
C	-4.207818000	2.438604000	-4.626592000
C	-4.479166000	2.230806000	-5.983177000
C	-2.125289000	2.121143000	-6.510712000
C	-3.459368000	2.082509000	-6.923310000
H	-1.320989000	2.009251000	-7.236564000
H	-5.520250000	2.174139000	-6.303903000
H	-3.706900000	1.933650000	-7.973450000
H	-0.038850000	2.475340000	0.981805000
C	1.214780000	2.352573000	3.060137000
C	-5.341286000	2.554006000	-3.639329000
H	-5.144114000	1.978978000	-2.726654000
H	0.151323000	2.105861000	3.199625000
H	1.260321000	3.356428000	2.611570000
H	1.670867000	2.414584000	4.053595000
H	-5.522798000	3.601645000	-3.349878000
H	-6.271595000	2.181050000	-4.083596000
Hg	-3.453073000	4.691543000	-1.596891000
C	-4.835503000	6.413535000	-2.000463000

C	-4.336895000	7.598452000	-2.567792000
C	-6.194411000	6.375846000	-1.647106000
H	-3.287941000	7.677486000	-2.858562000
H	-6.628568000	5.479700000	-1.199694000
C	-5.164422000	8.706588000	-2.772965000
C	-7.025919000	7.482423000	-1.850269000
H	-4.752975000	9.615730000	-3.213299000
H	-8.076935000	7.430744000	-1.563859000
C	-6.511569000	8.651733000	-2.412305000
H	-7.156663000	9.516722000	-2.567083000

o-methyldithizonatophenylmercury(II) – blue isomer

	x	y	z
N	0.435291000	0.622163000	-2.019202000
N	0.038729000	1.515734000	-1.137711000
C	-1.017232000	2.279143000	-1.444665000
N	-1.548295000	2.110625000	-2.692267000
N	-2.625504000	2.738998000	-3.017893000
S	-1.550700000	3.382489000	-0.171144000
C	1.526855000	-0.219046000	-1.805393000
C	2.248336000	-0.170052000	-0.602715000
H	1.945850000	0.545065000	0.158600000
C	1.876738000	-1.128558000	-2.831418000
C	2.961575000	-1.977284000	-2.602066000
C	3.320829000	-1.032210000	-0.409383000
C	3.683245000	-1.941032000	-1.407543000
H	3.876476000	-0.994541000	0.526812000
H	3.243026000	-2.684481000	-3.383261000
H	4.522612000	-2.617757000	-1.258437000
C	-3.007217000	2.577324000	-4.367903000
C	-2.042037000	2.486469000	-5.388119000
H	-0.990745000	2.542505000	-5.111140000
C	-4.386771000	2.550538000	-4.682782000
C	-4.744264000	2.420020000	-6.028525000
C	-2.429093000	2.379348000	-6.717917000
C	-3.787920000	2.341935000	-7.041272000
H	-1.675175000	2.337889000	-7.503274000
H	-5.803577000	2.373517000	-6.283909000
H	-4.103304000	2.256751000	-8.080216000
H	-0.090680000	0.564731000	-2.897311000
C	1.107081000	-1.183571000	-4.127298000
C	-5.448504000	2.611232000	-3.616365000
H	-5.210185000	1.957675000	-2.768799000
H	1.129698000	-0.221374000	-4.661686000
H	0.050317000	-1.446686000	-3.970014000
H	1.535546000	-1.938423000	-4.795069000
H	-5.564361000	3.635458000	-3.229144000
H	-6.418374000	2.306859000	-4.025693000
Hg	-3.323781000	4.677316000	-1.472220000
C	-4.783647000	6.319760000	-1.933277000
C	-4.328768000	7.511707000	-2.523978000
C	-6.149760000	6.228108000	-1.616347000
H	-3.276453000	7.634361000	-2.786873000
H	-6.553092000	5.326467000	-1.150876000

C	-5.201821000	8.571069000	-2.788201000
C	-7.028152000	7.285410000	-1.878521000
H	-4.822012000	9.485440000	-3.245213000
H	-8.083583000	7.191381000	-1.619560000
C	-6.555372000	8.460931000	-2.464395000
H	-7.237172000	9.287489000	-2.665653000

m-methyldithizonatophenylmercury(II) – orange isomer

	x	y	z
N	0.437140000	1.645550000	0.329588000
N	-0.018937000	1.498432000	-0.892297000
C	-1.073472000	2.261161000	-1.205899000
N	-1.456057000	2.074125000	-2.501983000
N	-2.426240000	2.775605000	-2.965560000
S	-1.799513000	3.356361000	-0.013648000
C	1.541076000	0.966369000	0.840146000
C	2.237645000	-0.000790000	0.106055000
H	1.916116000	-0.244008000	-0.903713000
C	1.942156000	1.296742000	2.145355000
H	1.385822000	2.058469000	2.696363000
C	3.038469000	0.674143000	2.738455000
C	3.332898000	-0.622422000	0.701151000
C	3.734431000	-0.294722000	1.997691000
H	3.885442000	-1.376132000	0.141917000
H	4.597854000	-0.792613000	2.440707000
C	-2.766777000	2.533371000	-4.315156000
C	-2.119815000	1.575994000	-5.117433000
H	-1.315209000	0.983451000	-4.689241000
C	-3.804468000	3.304922000	-4.859351000
H	-4.302348000	4.048709000	-4.232084000
C	-4.214624000	3.148775000	-6.185701000
C	-2.522096000	1.418159000	-6.437389000
C	-3.556331000	2.194640000	-6.971778000
H	-2.022952000	0.682328000	-7.066488000
H	-3.854058000	2.058828000	-8.012533000
H	-0.042685000	2.336639000	0.928686000
C	3.455965000	1.029482000	4.143117000
C	-5.352299000	3.970043000	-6.738627000
H	2.913886000	1.908035000	4.510542000
H	-5.388986000	4.965213000	-6.279497000
H	-5.265126000	4.092282000	-7.824329000
H	-6.317730000	3.483742000	-6.537880000
H	4.530594000	1.245722000	4.195123000
H	3.256403000	0.199257000	4.834565000
Hg	-3.549849000	4.472489000	-1.549541000
C	-5.167640000	6.009483000	-1.790114000
C	-4.879979000	7.287319000	-2.300377000
C	-6.480717000	5.755764000	-1.359141000
H	-3.874119000	7.534962000	-2.644549000
H	-6.753223000	4.780395000	-0.952275000
C	-5.865760000	8.276885000	-2.373726000
C	-7.470050000	6.741718000	-1.431451000

H	-5.615660000	9.262868000	-2.767336000
H	-8.480787000	6.521666000	-1.085988000
C	-7.163523000	8.007125000	-1.936493000
H	-7.931357000	8.779511000	-1.985357000

m-methyldithizonatophenylmercury(II) – blue isomer

	x	y	z
N	0.428495000	0.504267000	-1.982980000
N	-0.036229000	1.352311000	-1.093398000
C	-1.054064000	2.149018000	-1.443028000
N	-1.518021000	2.027023000	-2.720440000
N	-2.488093000	2.777646000	-3.117060000
S	-1.616415000	3.233804000	-0.165453000
C	1.498441000	-0.350965000	-1.728634000
C	2.173123000	-0.346581000	-0.500688000
H	1.857878000	0.341929000	0.279105000
C	1.888291000	-1.231197000	-2.752462000
H	1.348004000	-1.221720000	-3.702186000
C	2.950106000	-2.115616000	-2.569742000
C	3.231744000	-1.231239000	-0.321248000
C	3.621244000	-2.107744000	-1.336739000
H	3.763955000	-1.237117000	0.629274000
H	4.453380000	-2.792994000	-1.173004000
C	-2.898053000	2.594481000	-4.450873000
C	-2.318215000	1.657939000	-5.329502000
H	-1.506141000	1.027433000	-4.978329000
C	-3.946032000	3.409694000	-4.908907000
H	-4.389426000	4.135574000	-4.223558000
C	-4.427688000	3.313983000	-6.217255000
C	-2.789844000	1.560076000	-6.630394000
C	-3.833479000	2.379353000	-7.075802000
H	-2.341345000	0.840003000	-7.314275000
H	-4.188038000	2.291943000	-8.103574000
H	-0.019030000	0.492081000	-2.905534000
C	3.373918000	-3.051478000	-3.673556000
C	-5.574342000	4.175759000	-6.681235000
H	2.675380000	-3.020862000	-4.517250000
H	-5.584461000	5.142974000	-6.165669000
H	-5.523395000	4.356705000	-7.761082000
H	-6.536276000	3.685464000	-6.474366000
H	3.428816000	-4.087243000	-3.314598000
H	4.370664000	-2.785716000	-4.052715000
Hg	-3.453711000	4.447553000	-1.447633000
C	-5.100164000	5.941554000	-1.771396000
C	-4.823033000	7.221421000	-2.284215000
C	-6.423984000	5.666340000	-1.387284000
H	-3.810214000	7.487719000	-2.592078000
H	-6.691875000	4.689820000	-0.979509000
C	-5.825197000	8.189809000	-2.403329000
C	-7.430696000	6.630292000	-1.506282000
H	-5.580963000	9.178344000	-2.794311000
H	-8.448877000	6.392799000	-1.193925000

C	-7.132752000	7.896743000	-2.011194000
H	-7.913947000	8.653109000	-2.092858000

p-methyldithizonatophenylmercury(II) – orange isomer

	x	y	z
N	0.609288000	1.752638000	0.364967000
N	0.153798000	1.645222000	-0.861259000
C	-0.930396000	2.377660000	-1.142918000
N	-1.320211000	2.206454000	-2.438536000
N	-2.352236000	2.841396000	-2.865545000
S	-1.684337000	3.411837000	0.083922000
C	1.716381000	1.053920000	0.843419000
C	2.422815000	0.135307000	0.054037000
H	2.102215000	-0.042643000	-0.969593000
C	2.115426000	1.288222000	2.167457000
H	1.563573000	2.001581000	2.780780000
C	3.209902000	0.610056000	2.692398000
C	3.512776000	-0.532268000	0.600367000
C	3.932184000	-0.311993000	1.923459000
H	4.054302000	-1.250279000	-0.017654000
H	3.507551000	0.800729000	3.723805000
C	-2.687448000	2.617005000	-4.217731000
C	-1.968027000	1.748370000	-5.061022000
H	-1.111419000	1.215927000	-4.655255000
C	-3.796576000	3.299801000	-4.737367000
H	-4.371805000	3.968322000	-4.094328000
C	-4.175871000	3.126791000	-6.065243000
C	-2.358849000	1.584941000	-6.381258000
C	-3.466050000	2.270255000	-6.915259000
H	-1.793482000	0.906326000	-7.022661000
H	-5.042922000	3.666563000	-6.447064000
H	0.102120000	2.387957000	1.001624000
C	-3.860431000	2.091332000	-8.358163000
C	5.130710000	-1.029567000	2.489059000
H	-3.939458000	1.028028000	-8.620995000
H	6.066872000	-0.605047000	2.097875000
H	5.163332000	-0.950401000	3.581899000
H	5.122324000	-2.094541000	2.223835000
H	-4.823045000	2.568738000	-8.573032000
H	-3.109738000	2.533459000	-9.029185000
Hg	-3.661152000	4.283123000	-1.338857000
C	-5.532596000	5.519381000	-1.421725000
C	-5.625384000	6.677402000	-2.211586000
C	-6.634626000	5.185467000	-0.615347000
H	-4.796019000	6.980587000	-2.853383000
H	-6.610098000	4.296597000	0.017583000
C	-6.773923000	7.477097000	-2.192751000
C	-7.785202000	5.979079000	-0.595441000
H	-6.819201000	8.375653000	-2.808973000
H	-8.625641000	5.699005000	0.041287000
C	-7.856168000	7.130510000	-1.382341000
H	-8.749481000	7.755378000	-1.361224000

p-methyldithizonatophenylmercury(II) – blue isomer

	x	y	z
N	0.567465000	0.574033000	-1.966600000
N	0.094313000	1.396014000	-1.056663000
C	-0.952952000	2.167188000	-1.373602000
N	-1.427401000	2.071606000	-2.648834000
N	-2.446478000	2.782815000	-2.998047000
S	-1.531409000	3.197801000	-0.056500000
C	1.665390000	-0.251797000	-1.737166000
C	2.356960000	-0.239430000	-0.516208000
H	2.030091000	0.436834000	0.269872000
C	2.080647000	-1.112821000	-2.764459000
H	1.546884000	-1.120836000	-3.715878000
C	3.172234000	-1.951841000	-2.566575000
C	3.442678000	-1.086435000	-0.341562000
C	3.874577000	-1.960536000	-1.354083000
H	3.976426000	-1.067564000	0.610146000
H	3.486165000	-2.613861000	-3.374170000
C	-2.855888000	2.656297000	-4.335072000
C	-2.195691000	1.859498000	-5.293476000
H	-1.310477000	1.301936000	-4.999005000
C	-3.993981000	3.379234000	-4.731389000
H	-4.520233000	3.995908000	-4.001286000
C	-4.458561000	3.305725000	-6.040167000
C	-2.670076000	1.795809000	-6.593324000
C	-3.809926000	2.516201000	-6.998122000
H	-2.147433000	1.173724000	-7.322600000
H	-5.345840000	3.873059000	-6.323032000
H	0.104024000	0.559399000	-2.881343000
C	-4.298164000	2.441954000	-8.420526000
C	5.041442000	-2.887126000	-1.130395000
H	-4.424694000	1.399639000	-8.743110000
H	4.751809000	-3.742428000	-0.502287000
H	5.423001000	-3.286509000	-2.077091000
H	5.865999000	-2.374916000	-0.618143000
H	-5.257377000	2.956614000	-8.543575000
H	-3.576512000	2.905504000	-9.109179000
Hg	-3.540945000	4.242748000	-1.222664000
C	-5.405104000	5.478015000	-1.420522000
C	-5.470446000	6.609589000	-2.251727000
C	-6.541209000	5.167293000	-0.651981000
H	-4.614882000	6.897215000	-2.865937000
H	-6.540622000	4.300793000	0.012127000
C	-6.621978000	7.402569000	-2.310444000
C	-7.695785000	5.954040000	-0.708843000
H	-6.644478000	8.280616000	-2.957324000
H	-8.561535000	5.691203000	-0.099619000
C	-7.737932000	7.077051000	-1.536954000
H	-8.633990000	7.696866000	-1.576294000

α-nathpthyldithizonatophenylmercury(II) – orange isomer

	x	y	z
H	-1.912235000	4.432535000	-4.566263000
C	-1.876832000	4.204969000	-3.501341000
C	-1.969793000	5.212101000	-2.563430000
C	-1.935759000	4.923382000	-1.187960000
C	-1.803631000	3.610722000	-0.757895000
C	-1.687344000	2.530716000	-1.700308000
C	-1.734540000	2.852557000	-3.096417000
C	-1.634265000	1.801814000	-4.046208000
C	-1.488100000	0.491913000	-3.648334000
C	-1.431219000	0.176661000	-2.273808000
C	-1.527625000	1.172155000	-1.323599000
H	-2.080389000	6.246457000	-2.884661000
H	-2.024991000	5.711734000	-0.444663000
H	-1.468348000	0.881816000	-0.274353000
H	-1.307572000	-0.858115000	-1.958457000
H	-1.412775000	-0.302705000	-4.389107000
H	-1.675143000	2.055146000	-5.105328000
N	-1.794843000	3.285765000	0.591666000
N	-1.848226000	4.161759000	1.573681000
C	-1.892454000	3.625792000	2.799954000
N	-1.967320000	4.587428000	3.769223000
N	-2.095309000	4.213947000	4.993045000
S	-1.859686000	1.867110000	3.027302000
C	-2.155308000	5.207747000	5.990512000
C	-2.780058000	4.794430000	7.166096000
C	-2.930631000	5.641801000	8.272583000
C	-2.415643000	6.917840000	8.228826000
C	-1.732426000	7.382210000	7.076347000
C	-1.598049000	6.539475000	5.915465000
C	-0.881127000	7.053389000	4.804709000
C	-0.323577000	8.317405000	4.838894000
C	-0.464376000	9.142673000	5.972315000
C	-1.159149000	8.679904000	7.066947000
H	-3.185913000	3.783583000	7.213107000
H	-3.448316000	5.280201000	9.158562000
H	-2.513361000	7.586364000	9.084164000
H	-1.272208000	9.300925000	7.956141000
H	-0.022766000	10.138418000	5.982736000
H	0.229804000	8.680374000	3.973573000
H	-0.787321000	6.443577000	3.912807000
H	-1.793525000	2.294136000	0.871134000
Hg	-1.992592000	1.796068000	5.604072000
C	-1.989681000	0.538512000	7.459854000
C	-3.067717000	-0.309814000	7.764038000
C	-0.869966000	0.509919000	8.308126000
H	-3.957482000	-0.326542000	7.131947000
H	-0.007970000	1.149807000	8.112809000
C	-3.029016000	-1.158181000	8.875359000
C	-0.825521000	-0.340133000	9.417871000
H	-3.876894000	-1.810026000	9.089397000
H	0.058220000	-0.349929000	10.057212000
C	-1.905204000	-1.177857000	9.703194000

H	-1.869448000	-1.845097000	10.564392000

α-nathpthyldithizonatophenylmercury(II) – blue isomer

	x	y	z
H	-1.510419000	8.509986000	-2.858373000
C	-1.613817000	7.935042000	-1.939039000
C	-1.535607000	6.557175000	-1.956620000
C	-1.661446000	5.812213000	-0.772610000
C	-1.874407000	6.458454000	0.437588000
C	-1.966207000	7.892417000	0.504074000
C	-1.827048000	8.628169000	-0.719855000
C	-1.903855000	10.045009000	-0.679742000
C	-2.107246000	10.717298000	0.504760000
C	-2.245346000	9.993427000	1.708642000
C	-2.177486000	8.615023000	1.706571000
H	-1.370509000	6.031332000	-2.895640000
H	-1.594047000	4.727312000	-0.779419000
H	-2.291429000	8.101942000	2.661391000
H	-2.408937000	10.521628000	2.647000000
H	-2.163099000	11.804863000	0.515989000
H	-1.796015000	10.594955000	-1.614572000
N	-1.996503000	5.737998000	1.618632000
N	-1.885238000	4.424425000	1.678050000
C	-1.926559000	3.855730000	2.891205000
N	-1.986969000	4.711147000	3.954022000
N	-2.075196000	4.243548000	5.152643000
S	-1.872573000	2.090830000	2.901982000
C	-2.088316000	5.177577000	6.198144000
C	-2.707316000	4.727222000	7.364496000
C	-2.898408000	5.566007000	8.471123000
C	-2.443936000	6.866673000	8.435073000
C	-1.738956000	7.356634000	7.305451000
C	-1.528188000	6.512084000	6.160277000
C	-0.728428000	7.022637000	5.105178000
C	-0.209275000	8.302327000	5.149152000
C	-0.470592000	9.147750000	6.246539000
C	-1.212949000	8.675579000	7.305702000
H	-3.086021000	3.705763000	7.388859000
H	-3.417263000	5.185150000	9.348546000
H	-2.601548000	7.533775000	9.282477000
H	-1.395014000	9.304835000	8.177026000
H	-0.066756000	10.159176000	6.264552000
H	0.410640000	8.656315000	4.326336000
H	-0.505522000	6.386335000	4.255388000
H	-2.134031000	6.227906000	2.507112000
Hg	-1.981474000	1.693238000	5.419266000
C	-2.000805000	0.568546000	7.359819000
C	-3.073770000	-0.266114000	7.716647000
C	-0.898394000	0.624468000	8.230298000
H	-3.950699000	-0.348512000	7.072470000
H	-0.038973000	1.255826000	7.998299000
C	-3.047480000	-1.017730000	8.896145000

C	-0.865590000	-0.127862000	9.409500000
H	-3.891453000	-1.660777000	9.148289000
H	0.005254000	-0.072622000	10.064187000
C	-1.940629000	-0.952977000	9.744357000
H	-1.914028000	-1.544662000	10.659568000

3,4-dimethyldithizonatophenylmercury(II) – orange isomer

	x	y	z
N	0.574672000	1.749674000	0.392888000
N	0.114992000	1.638406000	-0.830940000
C	-0.975544000	2.360965000	-1.111691000
N	-1.352143000	2.198196000	-2.411467000
N	-2.371000000	2.845463000	-2.850951000
S	-1.748423000	3.379195000	0.117794000
C	1.698635000	1.069425000	0.859121000
C	2.401543000	0.150974000	0.072821000
H	2.071221000	-0.051000000	-0.942643000
C	2.118859000	1.334853000	2.171183000
H	1.563292000	2.057339000	2.772770000
C	3.232192000	0.700262000	2.716489000
C	3.511433000	-0.482513000	0.622329000
C	3.948129000	-0.231237000	1.930484000
H	4.061954000	-1.201960000	0.014472000
C	-2.689814000	2.623403000	-4.207318000
C	-2.002724000	1.711656000	-5.024784000
H	-1.180955000	1.138855000	-4.603932000
C	-3.750896000	3.360154000	-4.753712000
H	-4.292325000	4.065177000	-4.118831000
C	-4.138403000	3.218468000	-6.085813000
C	-2.389876000	1.562800000	-6.348844000
C	-3.446877000	2.299354000	-6.905739000
H	-1.856842000	0.850599000	-6.981159000
H	0.071580000	2.386294000	1.030878000
C	-3.831370000	2.110262000	-8.349342000
C	5.157015000	-0.938083000	2.485645000
H	-3.213914000	1.340926000	-8.826283000
H	5.946099000	-0.225411000	2.769063000
H	4.910421000	-1.509756000	3.392394000
H	5.579664000	-1.633933000	1.752560000
H	-4.885217000	1.811508000	-8.450528000
H	-3.714095000	3.042553000	-8.922013000
Hg	-3.683977000	4.291740000	-1.338552000
C	-5.546917000	5.543097000	-1.439759000
C	-5.646101000	6.674163000	-2.267743000
C	-6.642078000	5.240342000	-0.612176000
H	-4.821406000	6.954714000	-2.926227000
H	-6.613227000	4.374158000	0.051354000
C	-6.792669000	7.476290000	-2.265517000
C	-7.792130000	6.036038000	-0.609427000
H	-6.842087000	8.354263000	-2.910734000
H	-8.626715000	5.779465000	0.043963000
C	-7.868774000	7.159210000	-1.434537000
H	-8.761068000	7.785636000	-1.427168000

C	3.659830000	1.013253000	4.127357000
H	3.003627000	1.762755000	4.583392000
H	3.640371000	0.115023000	4.760927000
H	4.688534000	1.399706000	4.157415000
C	-5.279765000	4.037225000	-6.633260000
H	-4.957147000	4.654030000	-7.484703000
H	-6.093980000	3.394882000	-6.999599000
H	-5.694275000	4.702821000	-5.868243000

3,4-dimethyldithizonatophenylmercury(II) – blue isomer

	x	y	z
N	0.596372000	0.620794000	-1.960614000
N	0.102294000	1.425509000	-1.045912000
C	-0.948221000	2.189950000	-1.369684000
N	-1.416373000	2.087565000	-2.646527000
N	-2.428899000	2.800988000	-3.009144000
S	-1.544352000	3.215679000	-0.056986000
C	1.679110000	-0.221170000	-1.720178000
C	2.358508000	-0.226777000	-0.496020000
H	2.042500000	0.448155000	0.295208000
C	2.082529000	-1.088280000	-2.747609000
H	1.545075000	-1.077398000	-3.698903000
C	3.148542000	-1.968570000	-2.574519000
C	3.423229000	-1.104256000	-0.329580000
C	3.838196000	-1.983024000	-1.340728000
H	3.954807000	-1.110894000	0.623036000
C	-2.842736000	2.646860000	-4.342176000
C	-2.267241000	1.740521000	-5.251121000
H	-1.452960000	1.098945000	-4.926067000
C	-3.900893000	3.461102000	-4.781085000
H	-4.357659000	4.157113000	-4.074954000
C	-4.384498000	3.404305000	-6.087144000
C	-2.749785000	1.674953000	-6.549264000
C	-3.800019000	2.493061000	-6.996336000
H	-2.302523000	0.967240000	-7.249080000
H	0.146039000	0.616359000	-2.881864000
C	-4.286072000	2.397883000	-8.417722000
C	4.991192000	-2.924782000	-1.110749000
H	-3.764201000	1.603370000	-8.963085000
H	4.679237000	-3.975412000	-1.204751000
H	5.795770000	-2.768705000	-1.844248000
H	5.416664000	-2.789364000	-0.110340000
H	-5.365412000	2.190870000	-8.462843000
H	-4.125928000	3.342354000	-8.959574000
Hg	-3.549259000	4.247194000	-1.243855000
C	-5.418596000	5.483684000	-1.411217000
C	-5.494671000	6.630737000	-2.219784000
C	-6.546343000	5.157057000	-0.637818000
H	-4.644234000	6.933525000	-2.834238000
H	-6.537781000	4.279072000	0.010691000
C	-6.648702000	7.422730000	-2.253112000
C	-7.703505000	5.942631000	-0.668640000

H	-6.678947000	8.313543000	-2.882120000
H	-8.562558000	5.667065000	-0.055480000
C	-7.756416000	7.080250000	-1.475584000
H	-8.653885000	7.699050000	-1.494639000
C	3.548314000	-2.896566000	-3.693114000
H	2.920879000	-2.745700000	-4.578815000
H	4.595325000	-2.741683000	-3.988802000
H	3.457908000	-3.949324000	-3.389917000
C	-5.514593000	4.304978000	-6.516018000
H	-5.214877000	4.949291000	-7.354933000
H	-6.382237000	3.722651000	-6.858931000
H	-5.844255000	4.947231000	-5.692527000

α-pyrenedithizonatophenylmercury(II) – orange isomer

	x	y	z
C	-0.123494000	-7.213763000	-11.410589000
C	0.779611000	-7.649442000	-10.390070000
C	0.330997000	-6.571619000	-12.528060000
C	2.184300000	-7.416423000	-10.572988000
C	1.719717000	-6.310165000	-12.735435000
C	2.647773000	-6.748838000	-11.744227000
H	-1.182705000	-7.409838000	-11.282294000
C	0.368509000	-8.278425000	-9.181540000
C	3.136613000	-7.828644000	-9.590423000
C	4.044705000	-6.501682000	-11.929715000
C	2.673881000	-8.459330000	-8.421930000
C	1.327526000	-8.667740000	-8.222841000
C	4.525966000	-7.584367000	-9.807405000
H	3.390354000	-8.781846000	-7.667926000
H	0.983392000	-9.155472000	-7.310322000
C	2.196703000	-5.635215000	-13.874412000
C	4.472842000	-5.823142000	-13.083797000
C	3.557238000	-5.394135000	-14.041841000
H	-0.376339000	-6.245140000	-13.290480000
C	4.966057000	-6.946186000	-10.929917000
H	5.232715000	-7.916305000	-9.047080000
H	5.537352000	-5.631832000	-13.217619000
H	3.909513000	-4.865839000	-14.926224000
H	6.029069000	-6.760019000	-11.080249000
H	1.483174000	-5.298942000	-14.626580000
N	-0.938010000	-8.540474000	-8.788402000
N	-2.046352000	-8.499245000	-9.500988000
C	-3.156028000	-8.824968000	-8.817798000
N	-4.258249000	-8.898382000	-9.625023000
N	-5.345963000	-9.339550000	-9.088722000
S	-3.085437000	-9.174473000	-7.077262000
C	-6.158070000	-7.555931000	-11.459787000
C	-6.909155000	-8.673103000	-10.974752000
C	-6.640236000	-6.754171000	-12.455965000
C	-8.183357000	-8.945866000	-11.577173000
C	-7.905383000	-6.996754000	-13.072692000
C	-8.673213000	-8.111883000	-12.625518000

H	-5.182092000	-7.361996000	-11.026841000
C	-6.497923000	-9.488193000	-9.876882000
C	-8.989229000	-10.038611000	-11.131292000
C	-9.944744000	-8.375361000	-13.224526000
C	-8.533005000	-10.823526000	-10.058527000
C	-7.337561000	-10.530921000	-9.437878000
C	-10.244625000	-10.293987000	-11.762294000
H	-9.139409000	-11.658614000	-9.710757000
C	-8.417154000	-6.172231000	-14.091702000
C	-10.414094000	-7.524561000	-14.240118000
C	-9.658523000	-6.434342000	-14.664810000
H	-6.052104000	-5.902966000	-12.799489000
C	-10.706950000	-9.496258000	-12.767283000
H	-10.835006000	-11.140962000	-11.412490000
H	-11.385407000	-7.728679000	-14.691440000
H	-10.042004000	-5.783747000	-15.449045000
H	-11.671314000	-9.696774000	-13.233514000
H	-7.828078000	-5.318206000	-14.426548000
H	-1.060076000	-8.843591000	-7.806093000
Hg	-5.627028000	-9.307575000	-6.608625000
C	-7.392208000	-9.196707000	-5.233356000
C	-7.809400000	-7.942990000	-4.754897000
C	-8.114166000	-10.330252000	-4.827060000
H	-7.280292000	-7.032712000	-5.042655000
H	-7.827405000	-11.325699000	-5.170467000
C	-8.910750000	-7.824472000	-3.901999000
C	-9.216183000	-10.215785000	-3.972400000
H	-9.215960000	-6.839835000	-3.545847000
H	-9.762324000	-11.109921000	-3.668847000
C	-9.617111000	-8.961774000	-3.508328000
H	-10.476132000	-8.871032000	-2.843151000
H	-6.995419000	-11.142410000	-8.603482000

α-pyrenedithizonatophenylmercury(II) – blue isomer

	x	y	z
C	0.398546000	-8.914462000	-11.209073000
C	-0.301948000	-8.413552000	-12.351352000
C	1.725708000	-9.237442000	-11.278904000
C	0.426858000	-8.234320000	-13.575844000
C	2.476127000	-9.084054000	-12.482289000
C	1.811235000	-8.570602000	-13.635344000
H	-0.143795000	-9.032422000	-10.277197000
C	-1.696813000	-8.118731000	-12.366576000
C	-0.215972000	-7.742978000	-14.754459000
C	2.541317000	-8.412918000	-14.855779000
C	-1.592827000	-7.453083000	-14.705480000
C	-2.311109000	-7.648390000	-13.547473000
C	0.540229000	-7.576649000	-15.952986000
H	-2.093149000	-7.079983000	-15.598132000
H	-3.380397000	-7.433385000	-13.528217000
C	3.838059000	-9.430079000	-12.567897000
C	3.900112000	-8.775129000	-14.892932000
C	4.537317000	-9.278796000	-13.761243000

H	2.233867000	-9.626432000	-10.396452000
C	1.865652000	-7.898557000	-16.005650000
H	0.029718000	-7.191936000	-16.835927000
H	4.450342000	-8.659158000	-15.826524000
H	5.588709000	-9.557353000	-13.812148000
H	2.429226000	-7.774500000	-16.930199000
H	4.338756000	-9.825110000	-11.684013000
N	-2.580461000	-8.293063000	-11.313421000
N	-2.298555000	-8.535219000	-10.047461000
C	-3.345131000	-8.798348000	-9.240942000
N	-4.559447000	-8.906445000	-9.847166000
N	-5.576661000	-9.303354000	-9.151916000
S	-2.958915000	-9.006246000	-7.528661000
C	-6.632677000	-7.459023000	-11.344045000
C	-7.278382000	-8.654665000	-10.895055000
C	-7.170438000	-6.682274000	-12.331608000
C	-8.531645000	-9.007487000	-11.492491000
C	-8.395251000	-7.033682000	-12.977493000
C	-9.074604000	-8.210425000	-12.543354000
H	-5.707596000	-7.153396000	-10.865012000
C	-6.790029000	-9.465318000	-9.823373000
C	-9.261295000	-10.149971000	-11.039086000
C	-10.314450000	-8.572480000	-13.155882000
C	-8.764256000	-10.884172000	-9.946316000
C	-7.577891000	-10.527956000	-9.340409000
C	-10.486195000	-10.500765000	-11.682835000
H	-9.325700000	-11.743697000	-9.582484000
C	-8.962195000	-6.245499000	-13.996059000
C	-10.837305000	-7.759445000	-14.176747000
C	-10.169579000	-6.607325000	-14.586374000
H	-6.670440000	-5.761519000	-12.632044000
C	-10.992104000	-9.748222000	-12.702376000
H	-11.017300000	-11.386296000	-11.333584000
H	-11.782385000	-8.040022000	-14.641636000
H	-10.597220000	-5.984683000	-15.370442000
H	-11.931258000	-10.026074000	-13.180952000
H	-8.445524000	-5.339887000	-14.313600000
H	-3.582285000	-8.304206000	-11.549732000
Hg	-5.349858000	-9.201482000	-6.621544000
C	-7.161689000	-9.143764000	-5.298736000
C	-7.638885000	-7.900641000	-4.848224000
C	-7.894515000	-10.290201000	-4.949943000
H	-7.106811000	-6.979615000	-5.092822000
H	-7.566013000	-11.280180000	-5.272853000
C	-8.804391000	-7.803780000	-4.082046000
C	-9.060768000	-10.199280000	-4.181844000
H	-9.154342000	-6.825417000	-3.749225000
H	-9.613523000	-11.103872000	-3.924359000
C	-9.519854000	-8.954538000	-3.747089000
H	-10.430298000	-8.881244000	-3.151704000
H	-7.192386000	-11.108167000	-8.503957000

α-anthracenedithizonatophenylmercury(II) – orange isomer

	x	y	z
C	6.785921000	-0.279801000	-12.405945000
C	7.083087000	0.509924000	-11.256471000
C	6.771767000	0.081826000	-9.956762000
C	7.716207000	1.791809000	-11.443610000
C	7.999378000	2.572932000	-10.318504000
C	7.684083000	2.152486000	-9.020750000
C	7.053236000	0.863517000	-8.831268000
C	7.093940000	0.167911000	-13.666187000
C	8.021622000	2.220780000	-12.769644000
H	8.473625000	3.546316000	-10.452649000
C	7.959159000	2.976956000	-7.891750000
C	6.734310000	0.471584000	-7.478350000
C	7.010261000	1.309167000	-6.412896000
C	7.623729000	2.562135000	-6.626453000
H	8.433483000	3.944058000	-8.055027000
H	6.742656000	0.981208000	-5.412021000
H	7.830332000	3.199884000	-5.768647000
C	7.718751000	1.432512000	-13.850453000
H	6.306508000	-1.248508000	-12.265008000
H	6.285066000	-0.889818000	-9.862294000
H	6.859513000	-0.445518000	-14.535046000
H	8.499087000	3.191323000	-12.906567000
H	7.954868000	1.772162000	-14.857893000
N	6.129507000	-0.764484000	-7.265123000
N	5.720816000	-1.143865000	-6.070641000
C	5.156006000	-2.344790000	-5.973138000
N	4.734922000	-2.576106000	-4.687939000
N	4.085080000	-3.657498000	-4.448713000
S	4.997073000	-3.424991000	-7.377783000
H	5.992897000	-1.419964000	-8.043701000
C	2.598822000	-4.676460000	-0.624814000
C	3.743398000	-3.830567000	-0.653172000
C	4.353250000	-3.429869000	0.542233000
C	4.300598000	-3.399972000	-1.922668000
C	5.436319000	-2.585510000	-1.902470000
C	6.056621000	-2.204411000	-0.700930000
C	5.504521000	-2.635456000	0.557255000
C	2.034690000	-5.136524000	-1.789029000
C	3.672241000	-3.903961000	-3.129842000
H	5.848390000	-2.227669000	-2.840702000
C	7.235636000	-1.402077000	-0.691499000
C	6.157164000	-2.250074000	1.765203000
C	7.294848000	-1.483400000	1.733140000
C	7.839891000	-1.053775000	0.491164000
H	7.651314000	-1.077077000	-1.645461000
H	5.737376000	-2.581543000	2.715633000
H	7.788343000	-1.200092000	2.662049000
H	8.744193000	-0.446661000	0.484471000
C	2.589743000	-4.768243000	-3.028963000
H	2.189888000	-4.965864000	0.343210000
H	3.925802000	-3.768494000	1.487429000
H	2.146037000	-5.149687000	-3.947652000

H	1.168130000	-5.794035000	-1.765064000
Hg	4.154312000	-5.519162000	-6.126003000
C	3.645812000	-7.618602000	-5.522089000
C	4.657425000	-8.457505000	-5.024800000
C	2.322518000	-8.086858000	-5.475924000
H	5.701110000	-8.139126000	-5.037218000
H	1.501511000	-7.474806000	-5.854426000
C	4.357946000	-9.714649000	-4.490242000
C	2.018517000	-9.344166000	-4.943189000
H	5.160416000	-10.343231000	-4.102527000
H	0.982912000	-9.685677000	-4.915362000
C	3.036200000	-10.159471000	-4.444418000
H	2.800214000	-11.135991000	-4.020844000

α-anthracenedithizonatophenylmercury(II) – blue isomer

	x	y	z
C	1.090294000	2.886276000	-3.896470000
C	2.397205000	3.076430000	-4.431548000
C	3.169446000	2.005008000	-4.907832000
C	2.932688000	4.413000000	-4.495756000
C	4.203257000	4.604243000	-5.052070000
C	4.968843000	3.539005000	-5.542712000
C	4.444313000	2.194732000	-5.446868000
C	0.353308000	3.952395000	-3.444114000
C	2.138177000	5.493843000	-4.010125000
H	4.605265000	5.615972000	-5.122549000
C	6.232837000	3.754383000	-6.164288000
C	5.261803000	1.118606000	-5.957710000
C	6.474718000	1.376599000	-6.570870000
C	6.950596000	2.700768000	-6.678700000
H	6.614269000	4.772884000	-6.231256000
H	7.055169000	0.539299000	-6.950484000
H	7.911732000	2.877817000	-7.158930000
C	0.884153000	5.270525000	-3.499416000
H	0.686031000	1.874519000	-3.851990000
H	2.721042000	1.011838000	-4.870053000
H	-0.644520000	3.792623000	-3.037869000
H	2.546112000	6.503786000	-4.056760000
H	0.286917000	6.104192000	-3.133319000
N	4.785841000	-0.179924000	-5.831299000
N	5.283071000	-1.193607000	-6.525171000
C	4.896687000	-2.420247000	-6.152442000
N	4.296778000	-2.530921000	-4.926071000
N	3.761282000	-3.661291000	-4.599554000
S	5.273709000	-3.709427000	-7.302749000
H	4.134188000	-0.411127000	-5.073593000
C	2.382590000	-4.503485000	-0.701887000
C	3.559182000	-3.709158000	-0.803953000
C	4.261688000	-3.327987000	0.347289000
C	4.064641000	-3.326921000	-2.108515000
C	5.247140000	-2.584631000	-2.168775000
C	5.964148000	-2.230493000	-1.014385000
C	5.460103000	-2.609688000	0.280433000
C	1.754235000	-4.981339000	-1.826904000

C	3.363236000	-3.839618000	-3.271297000
H	5.638556000	-2.277823000	-3.134891000
C	7.195324000	-1.515492000	-1.087351000
C	6.212718000	-2.261709000	1.441287000
C	7.399932000	-1.582051000	1.329383000
C	7.895839000	-1.203393000	0.051237000
H	7.573888000	-1.227098000	-2.068394000
H	5.830461000	-2.554479000	2.419491000
H	7.970959000	-1.329865000	2.221970000
H	8.839346000	-0.663688000	-0.019753000
C	2.267939000	-4.680050000	-3.101180000
H	2.007985000	-4.752569000	0.290780000
H	3.875835000	-3.632645000	1.321305000
H	1.790382000	-5.087283000	-3.990894000
H	0.870644000	-5.610771000	-1.741523000
Hg	4.295656000	-5.696206000	-6.028039000
C	3.689796000	-7.715891000	-5.270881000
C	4.639398000	-8.563853000	-4.676194000
C	2.346463000	-8.126425000	-5.256632000
H	5.695809000	-8.290486000	-4.661770000
H	1.571049000	-7.505961000	-5.710733000
C	4.261157000	-9.772162000	-4.080749000
C	1.962617000	-9.334056000	-4.663505000
H	5.017211000	-10.409251000	-3.619965000
H	0.912475000	-9.629550000	-4.663635000
C	2.920273000	-10.158292000	-4.069962000
H	2.623106000	-11.096460000	-3.600621000

β-fluorenedithizonatophenylmercury(II) – orange isomer

	x	y	z
C	0.170780000	2.335215000	2.505129000
C	-0.715653000	1.762615000	3.443363000
C	0.999856000	3.384694000	2.861578000
H	1.688863000	3.832552000	2.142824000
C	-0.764786000	2.258611000	4.751757000
C	0.944381000	3.873862000	4.179924000
H	-1.444661000	1.826810000	5.485608000
C	0.062329000	3.311662000	5.120838000
H	0.048947000	3.717609000	6.128883000
C	-2.545694000	-1.235203000	1.093542000
C	-2.973741000	-1.144027000	2.423533000
C	-1.565155000	-0.367248000	0.599768000
H	-3.737966000	-1.827872000	2.790021000
H	-1.236164000	-0.443474000	-0.437227000
C	-2.432127000	-0.187478000	3.282466000
C	-1.021651000	0.588379000	1.450739000
H	-2.769897000	-0.122502000	4.316753000
C	-1.452059000	0.681657000	2.792233000
H	-2.980183000	-1.988265000	0.438084000
C	0.036197000	1.632597000	1.174631000
N	1.789782000	4.926843000	4.522495000
N	1.812406000	5.454972000	5.725187000
C	2.681229000	6.448287000	5.928729000
N	2.606651000	6.897807000	7.214484000

N	3.389671000	7.844335000	7.591318000
S	3.750679000	7.027212000	4.635353000
C	2.258084000	7.712057000	9.788071000
C	3.249790000	8.240133000	8.934022000
C	2.203651000	8.150004000	11.096593000
C	4.156720000	9.200888000	9.420762000
C	3.120898000	9.110266000	11.587159000
H	4.926533000	9.592098000	8.755379000
C	4.100359000	9.637773000	10.739350000
H	4.817995000	10.374155000	11.097957000
H	1.566281000	6.971722000	9.392061000
C	1.238475000	8.608270000	14.676272000
C	1.725852000	8.562639000	13.375130000
C	1.856471000	9.455433000	15.602389000
H	1.485412000	9.499535000	16.625153000
C	2.826889000	9.361873000	12.995407000
C	2.949477000	10.246848000	15.227989000
H	3.418396000	10.898535000	15.964234000
C	3.442469000	10.207681000	13.924203000
H	4.293834000	10.825457000	13.638414000
H	0.388783000	7.994051000	14.976322000
C	1.252815000	7.741390000	12.198466000
H	2.437434000	5.309723000	3.817734000
Hg	4.980621000	8.861862000	5.975246000
C	6.434557000	10.546607000	6.279977000
C	6.073745000	11.673517000	7.038819000
C	7.724812000	10.518052000	5.723320000
H	5.081483000	11.747018000	7.488663000
H	8.051146000	9.666920000	5.123699000
C	6.966338000	12.733118000	7.235313000
C	8.622257000	11.572475000	5.920259000
H	6.660163000	13.598591000	7.823981000
H	9.618677000	11.525722000	5.479503000
C	8.244152000	12.684112000	6.676954000
H	8.941887000	13.508079000	6.828898000
H	1.307682000	6.662014000	12.402719000
H	0.207606000	7.962057000	11.936199000
H	-0.271075000	2.325908000	0.377855000
H	0.986000000	1.179950000	0.854086000

β-fluorenedithizonatophenylmercury(II) – blue isomer

	x	y	z
C	-1.099438000	2.022489000	8.627370000
C	-1.531333000	1.414291000	7.428311000
C	-0.209938000	3.081091000	8.603395000
H	0.130313000	3.555729000	9.526092000
C	-1.056158000	1.883675000	6.196379000
C	0.260696000	3.547342000	7.359393000
H	-1.382033000	1.424542000	5.263649000
C	-0.164574000	2.947683000	6.159039000
H	0.218662000	3.335517000	5.218616000
C	-4.151795000	-1.540721000	8.932567000
C	-4.011779000	-1.487903000	7.540405000
C	-3.447632000	-0.652006000	9.752370000

H	-4.568254000	-2.186962000	6.918001000
H	-3.560841000	-0.697528000	10.836325000
C	-3.169431000	-0.550151000	6.943194000
C	-2.607477000	0.284905000	9.163434000
H	-3.066428000	-0.514899000	5.858907000
C	-2.464710000	0.340354000	7.759763000
H	-4.814908000	-2.279218000	9.380508000
C	-1.749225000	1.346945000	9.811814000
N	1.156152000	4.608565000	7.368061000
N	1.679940000	5.129060000	6.277424000
C	2.479914000	6.195466000	6.424921000
N	2.577871000	6.716149000	7.680809000
N	3.382104000	7.705238000	7.896119000
S	3.257448000	6.755900000	4.937423000
C	2.331770000	7.974082000	10.124331000
C	3.351505000	8.248650000	9.184244000
C	2.387942000	8.572918000	11.367419000
C	4.396516000	9.133647000	9.525298000
C	3.447244000	9.448686000	11.709867000
H	5.175431000	9.335993000	8.790415000
C	4.453818000	9.727034000	10.778114000
H	5.274667000	10.400278000	11.021174000
H	1.510739000	7.319116000	9.839720000
C	1.607902000	9.652369000	14.857661000
C	2.044949000	9.357593000	13.571572000
C	2.366083000	10.522344000	15.647914000
H	2.034805000	10.761291000	16.657459000
C	3.235680000	9.928971000	13.071440000
C	3.547928000	11.089532000	15.154264000
H	4.125036000	11.763606000	15.785750000
C	3.991646000	10.799318000	13.864583000
H	4.912003000	11.242903000	13.485172000
H	0.689026000	9.215400000	15.249440000
C	1.422700000	8.461623000	12.525851000
H	1.406032000	5.049928000	8.260673000
Hg	4.693226000	8.619006000	5.925752000
C	6.172987000	10.295333000	6.135830000
C	5.870086000	11.430701000	6.907504000
C	7.430047000	10.251110000	5.507523000
H	4.905730000	11.518133000	7.412129000
H	7.711718000	9.394691000	4.892913000
C	6.785916000	12.479270000	7.050463000
C	8.350327000	11.294576000	5.649165000
H	6.523675000	13.350949000	7.651412000
H	9.319283000	11.233671000	5.152270000
C	8.030549000	12.412072000	6.421868000
H	8.745951000	13.227674000	6.531553000
H	0.413342000	8.797901000	12.246274000
H	1.326127000	7.424664000	12.879580000
H	-1.003240000	0.911463000	10.493025000
H	-2.349451000	2.052509000	10.405207000

Crystallographic data for the crystals discussed in this research project.

o-methoxydehydrodithizone

Atomic coordinates

	x	y	z
S1	0.94113 (4)	0.35569 (6)	0.39602 (6)
N1	0.92670 (12)	0.20582 (17)	0.25103 (17)
N2	0.90050 (11)	0.20201 (16)	0.16004 (17)
N3	0.87217 (12)	0.29604 (17)	0.13628 (18)
N4	0.87976 (12)	0.36420 (17)	0.21135 (18)
C3	0.91500 (14)	0.3082 (2)	0.2832 (2)
C11	0.83626 (14)	0.3154 (2)	0.0438 (2)
C12	0.77732 (14)	0.2548 (2)	0.0246 (2)
C13	0.74450 (15)	0.2681 (2)	−0.0670 (2)
H13	0.7052	0.2265	−0.0828
C14	0.76917 (17)	0.3422 (2)	−0.1354 (2)
H14	0.7464	0.3511	−0.198
C15	0.82674 (16)	0.4038 (2)	−0.1141 (2)
H15	0.8424	0.4553	−0.1613
C16	0.86101 (15)	0.3897 (2)	−0.0240 (2)
H16	0.9008	0.4303	−0.0089
O1	0.84463 (11)	0.01383 (15)	0.21656 (16)
C1	0.81522 (18)	−0.0853 (2)	0.2495 (3)
H1A	0.7779	−0.1056	0.204
H1B	0.7972	−0.0769	0.318
H1C	0.8505	−0.141	0.2491
C21	0.90302 (14)	0.1126 (2)	0.0934 (2)
C22	0.87405 (15)	0.0159 (2)	0.1243 (2)
C23	0.87648 (16)	−0.0689 (2)	0.0568 (2)
H23	0.8586	−0.1364	0.076
C24	0.90459 (16)	−0.0560 (2)	−0.0376 (3
H24	0.9045	−0.1145	−0.0831
C25	0.93295 (16)	0.0403 (3)	−0.0676 (2)
H25	0.9524	0.0478	−0.1329
C26	0.93252 (15)	0.1258 (2)	−0.0009 (2)
H26	0.9522	0.1923	−0.0195
O2	0.75650 (10)	0.18958 (15)	0.10072 (14)
C2	0.71273 (16)	0.1018 (2)	0.0731 (3)
H2A	0.6689	0.1295	0.0483
H2B	0.7047	0.0565	0.1321
H2C	0.7348	0.0596	0.0201
C01	0.96482 (19)	0.3561 (3)	0.6608 (3)
H02A	0.9476	0.299	0.6172
H02B	0.9974	0.4004	0.6231
H02C	0.9264	0.4004	0.6835
H02D	0.9694	0.3499	0.5868
H02E	0.9167	0.3784	0.672
O01 1	0.2112 (4)	0.75	0.084 (2)
C02 1	0.3083 (5)	0.75	0.0332 (14)

Cl1	0.9637 (7)	0.2275 (7)	0.6975 (8)
Cl2	1.0037 (4)	0.4567 (5)	0.6826 (5)

Bond lengths [Å]

S1—C3	1.690 (3)	C21—C26	1.387 (4)
N1—N2	1.313 (3)	C21—C22	1.398 (4)
N1—C3	1.371 (3)	C22—C23	1.391 (4)
N2—N3	1.339 (3)	C23—C24	1.377 (5)
N2—C21	1.428 (3)	C23—H23	0.95
N3—N4	1.321 (3)	C24—C25	1.386 (5)
N3—C11	1.434 (4)	C24—H24	0.95
N4—C3	1.369 (3)	C25—C26	1.390 (4)
C11—C16	1.382 (4)	C25—H25	0.95
C11—C12	1.401 (4)	C26—H26	0.95
C12—O2	1.361 (3)	O2—C2	1.439 (3)
C12—C13	1.385 (4)	C2—H2A	0.98
C13—C14	1.385 (4)	C2—H2B	0.98
C13—H13	0.95	C2—H2C	0.98
C14—C15	1.392 (4)	C01—C02	1.494 (4)
C14—H14	0.95	C01—Cl2	1.499 (7)
C15—C16	1.382 (4)	C01—Cl1	1.683 (8)
C15—H15	0.95	C01—H02A	0.98
C16—H16	0.95	C01—H02B	0.98
O1—C22	1.353 (3)	C01—H02C	0.98
O1—C1	1.436 (3)	C01—H02D	0.99
C1—H1A	0.98	C01—H02E	0.99
C1—H1B	0.98	O01—C02	1.216 (8)
C1—H1C	0.98	C02—C01i	1.494 (4)

Bond angels [°]

N2—N1—C3	104.8 (2)	C23—C24—H24	119.2
N1—N2—N3	110.2 (2)	C25—C24—H24	119.2
N1—N2—C21	125.9 (2)	C24—C25—C26	119.0 (3)
N3—N2—C21	123.9 (2)	C24—C25—H25	120.5
N4—N3—N2	110.2 (2)	C26—C25—H25	120.5
N4—N3—C11	126.3 (2)	C21—C26—C25	119.1 (3)
N2—N3—C11	123.5 (2)	C21—C26—H26	120.4
N3—N4—C3	104.6 (2)	C25—C26—H26	120.4
N4—C3—N1	110.2 (2)	C12—O2—C2	116.5 (2)
N4—C3—S1	126.1 (2)	O2—C2—H2A	109.5
N1—C3—S1	123.7 (2)	O2—C2—H2B	109.5
C16—C11—C12	122.2 (3)	H2A—C2—H2B	109.5
C16—C11—N3	120.1 (2)	O2—C2—H2C	109.5
C12—C11—N3	117.7 (2)	H2A—C2—H2C	109.5
O2—C12—C13	125.9 (3)	H2B—C2—H2C	109.5
O2—C12—C11	115.8 (2)	C02—C01—Cl2	87.2 (4)
C13—C12—C11	118.3 (3)	C02—C01—Cl1	52.7 (4)
C12—C13—C14	119.7 (3)	Cl2—C01—Cl1	139.1 (5)
C12—C13—H13	120.1	C02—C01—H02A	109.5
C14—C13—H13	120.1	Cl2—C01—H02A	154.4
C13—C14—C15	121.2 (3)	Cl1—C01—H02A	57.8
C13—C14—H14	119.4	C02—C01—H02B	109.5

C15—C14—H14	119.4	Cl2—C01—H02B	45.2
C16—C15—C14	119.7 (3)	Cl1—C01—H02B	134.2
C16—C15—H15	120.2	H02A—C01—H02B	109.5
C14—C15—H15	120.2	C02—C01—H02C	109.5
C15—C16—C11	118.8 (3)	Cl2—C01—H02C	81.5
C15—C16—H16	120.6	Cl1—C01—H02C	116.2
C11—C16—H16	120.6	H02A—C01—H02C	109.5
C22—O1—C1	117.5 (2)	H02B—C01—H02C	109.5
O1—C1—H1A	109.5	C02—C01—H02D	135.6
O1—C1—H1B	109.5	Cl2—C01—H02D	102.3
H1A—C1—H1B	109.5	Cl1—C01—H02D	102.3
O1—C1—H1C	109.5	H02A—C01—H02D	52.1
H1A—C1—H1C	109.5	H02B—C01—H02D	58.7
H1B—C1—H1C	109.5	H02C—C01—H02D	114.8
C26—C21—C22	122.4 (3)	C02—C01—H02E	115.4
C26—C21—N2	118.7 (2)	Cl2—C01—H02E	102.3
C22—C21—N2	118.9 (3)	Cl1—C01—H02E	102.3
O1—C22—C23	125.7 (3)	H02A—C01—H02E	88.3
O1—C22—C21	117.0 (2)	H02B—C01—H02E	122.1
C23—C22—C21	117.3 (3)	H02C—C01—H02E	21.5
C24—C23—C22	120.7 (3)	H02D—C01—H02E	104.9
C24—C23—H23	119.7	O01—C02—C01i	113.6 (3)
C22—C23—H23	119.7	O01—C02—C01	113.6 (3)
C23—C24—C25	121.5 (3)	C01i—C02—C01	132.8 (6)

Torsion angles [°]

C3—N1—N2—N3	−1.4 (3)	C12—C11—C16—C15	−0.6 (4)
C3—N1—N2—C21	176.8 (2)	N3—C11—C16—C15	177.6 (2)
N1—N2—N3—N4	0.5 (3)	N1—N2—C21—C26	−122.6 (3)
C21—N2—N3—N4	−177.7 (2)	N3—N2—C21—C26	55.4 (4)
N1—N2—N3—C11	−176.7 (2)	N1—N2—C21—C22	59.1 (4)
C21—N2—N3—C	11 5.1 (4)	N3—N2—C21—C22	−122.9 (3)
N2—N3—N4—C3	0.6 (3)	C1—O1—C22—C23	2.2 (4)
C11—N3—N4—C3	177.7 (2)	C1—O1—C22—C21	−179.5 (3)
N3—N4—C3—N1	−1.5 (3)	C26—C21—C22—O1	−177.7 (3)
N3—N4—C3—S1	178.6 (2)	N2—C21—C22—O1	0.5 (4)
N2—N1—C3—N4	1.8 (3)	C26—C21—C22—C23	0.8 (4)
N2—N1—C3—S1	−178.2 (2)	N2—C21—C22—C23	179.0 (2)
N4—N3—C11—C16	66.4 (4)	O1—C22—C23—C24	176.4 (3)
N2—N3—C11—C16	−116.8 (3)	C21—C22—C23—C24	−1.9 (4)
N4—N3—C11—C12	−115.2 (3)	C22—C23—C24—C25	1.8 (5)
N2—N3—C11—C12	61.6 (3)	C23—C24—C25—C26	−0.4 (4)
C16—C11—C12—O2	−176.0 (2)	C22—C21—C26—C25	0.6 (4)
N3—C11—C12—O2	5.6 (4)	N2—C21—C26—C25	−177.7 (2)
C16—C11—C12—C13	2.1 (4)	C24—C25—C26—C21	−0.8 (4)
N3—C11—C12—C13	−176.2 (2)	C13—C12—O2—C2 22	9.0 (4)
O2—C12—C13—C14	176.1 (3)	C11—C12—O2—C2	−159.1 (3)
C11—C12—C13—C14	−1.9 (4)	Cl2—C01—C02—O01	−160.1 (3)
C12—C13—C14—C15	0.2 (4)	Cl1—C01—C02—O01	11.4 (6)
C13—C14—C15—C16	1.3 (5)	Cl2—C01—C02—C01i	19.9 (3)
C14—C15—C16—C11	−1.1 (4)	Cl1—C01—C02—C01i	−168.6 (6)

o-fluorodisulphide-dithizone

Atomic coordinates

	x	y	z
S	9.673997000	9.628310000	2.472945000
S	11.076970000	8.117560000	2.770625000
F	9.930569000	5.336114000	-0.937695000
F	13.398250000	11.262797000	5.459624000
N	11.618520000	7.224864000	-0.024441000
H	10.967326000	6.937891000	0.493524000
F	8.665108000	6.511975000	5.924789000
F	12.107942000	12.980373000	0.475976000
N	13.173728000	10.163784000	3.013784000
N	12.467284000	8.138119000	0.398736000
C	12.338466000	8.623093000	1.610923000
N	9.468238000	10.287090000	5.183564000
N	10.452617000	11.846703000	3.903536000
C	10.908758000	5.758758000	-1.789845000
N	13.263183000	9.633139000	1.858312000
C	14.726114000	11.919307000	2.148002000
H	14.725579000	11.544840000	1.273761000
N	10.930044000	12.266847000	2.758405000
H	10.907775000	11.745947000	2.050864000
N	9.023216000	9.114101000	5.259237000
C	11.782352000	6.726167000	-1.319980000
C	14.025935000	11.286038000	3.179075000
C	10.992437000	5.214605000	-3.045118000
H	10.367080000	4.562406000	-3.334026000
C	12.909437000	6.602920000	-3.437900000
H	13.610787000	6.886100000	-4.012425000
C	12.798323000	7.156144000	-2.171817000
H	13.410705000	7.824281000	-1.886357000
C	15.420762000	13.088898000	2.400248000
H	15.892007000	13.519005000	1.695214000
C	11.486682000	13.574170000	2.666594000
C	9.914980000	10.655018000	3.934087000
C	12.008584000	5.638021000	-3.881602000
H	12.091325000	5.272227000	-4.755060000
C	14.068833000	11.855880000	4.439832000
C	15.433309000	13.637359000	3.670875000
H	15.907298000	14.445333000	3.830683000
C	7.550316000	7.960576000	9.036964000
H	7.206390000	7.687044000	9.878304000
C	8.530905000	8.774687000	6.567310000
C	12.650344000	15.146152000	1.262794000
H	13.060712000	15.347016000	0.429287000
C	14.761683000	13.019967000	4.711191000
H	14.776815000	13.385213000	5.587000000
C	8.329821000	7.446759000	6.848226000
C	12.068296000	13.925762000	1.483704000
C	7.756053000	9.296436000	8.780018000

H	7.565810000	9.939020000	9.452150000
C	12.043629000	15.752739000	3.493833000
H	12.035733000	16.390831000	4.197300000
C	7.843626000	7.016801000	8.070285000
H	7.712958000	6.091465000	8.241059000
C	8.238786000	9.716401000	7.543859000
H	8.368419000	10.640857000	7.369951000
C	11.470962000	14.497544000	3.689676000
H	11.071579000	14.279007000	4.524749000
C	12.623325000	16.073805000	2.279609000
H	13.003458000	16.934056000	2.148002000
C	9.480262000	14.596357000	7.188209000
H	9.522491000	13.978005000	6.417372000
H	8.980206000	14.144192000	7.913610000
C	10.903834000	14.895956000	7.670766000
H	11.381353000	15.404222000	6.968865000
H	10.856697000	15.466897000	8.479204000
C	8.733334000	15.853358000	6.779290000
H	7.832002000	15.613966000	6.476909000
H	9.215130000	16.296959000	6.049188000
H	8.669956000	16.460731000	7.545426000
C	13.116081000	13.949069000	8.479204000
H	13.073852000	14.567421000	9.250041000
H	13.616137000	14.401234000	7.753803000
C	11.692509000	13.649470000	7.996648000
H	11.214990000	13.141204000	8.698548000
H	11.739646000	13.078529000	7.188209000
C	13.863009000	12.692069000	8.888124000
H	14.764341000	12.931460000	9.190505000
H	13.381213000	12.248467000	9.618225000
H	13.926387000	12.084695000	8.121987000

Bond lengths [Å]

S1	S2	2.083(1)
S1	C23	1.802(4)
S2	C8	1.787(3)
F1	C11	1.364(3)
F2	C25	1.357(4)
N3	H3	0.880(2)
N3	N7	1.317(4)
N3	C16	1.398(4)
F4	C31	1.356(4)
F5	C32	1.382(4)
N6	N12	1.275(4)
N6	C17	1.419(5)
N7	C8	1.312(4)
C8	N12	1.392(5)
N9	N15	1.257(4)
N9	C23	1.377(4)
N10	N14	1.310(3)
N10	C23	1.308(5)
C11	C16	1.386(6)
C11	C18	1.371(4)

C13	H13	0.951(3)
C13	C17	1.398(4)
C13	C21	1.384(6)
N14	H14	0.879(3)
N14	C22	1.424(5)
N15	C28	1.438(4)
C16	C20	1.394(4)
C17	C25	1.384(5)
C18	H18	0.949(4)
C18	C24	1.383(4)
C19	H19	0.950(3)
C19	C20	1.386(5)
C19	C24	1.393(6)
C20	H20	0.950(4)
C21	H21	0.951(3)
C21	C26	1.384(5)
C22	C32	1.364(4)
C22	C39	1.378(5)
C24	H24	0.951(3)
C25	C30	1.382(6)
C26	H26	0.950(4)
C26	C30	1.384(4)
C27	H27	0.949(3)
C27	C34	1.376(5)
C27	C36	1.382(5)
C28	C31	1.372(5)
C28	C38	1.388(5)
C29	H29	0.951(3)
C29	C32	1.370(6)
C29	C40	1.377(6)
C30	H30	0.949(4)
C31	C36	1.384(4)
C34	H34	0.949(4)
C34	C38	1.392(4)
C35	H35	0.950(5)
C35	C39	1.393(6)
C35	C40	1.383(6)
C36	H36	0.950(4)
C38	H38	0.950(4)
C39	H39	0.951(3)
C40	H40	0.950(4)
C1	H1A	0.989(4)
C1	H1B	0.990(3)
C1	C2	1.533(6)
C1	C3	1.518(5)
C2	H2A	0.989(3)
C2	H2B	0.991(4)
C2	C2	1.511(5)
C3	H3A	0.980(4)
C3	H3B	0.981(3)
C3	H3C	0.980(4)
C1	H1A	0.989(4)
C1	H1B	0.990(3)
C1	C2	1.533(6)
C1	C3	1.518(5)

C2	H2A	0.989(3)
C2	H2B	0.991(4)
C3	H3A	0.980(4)
C3	H3B	0.981(3)
C3	H3C	0.980(4)

Bond angels [°]

S2	S1	C23	102.0(1)
S1	S2	C8	100.2(1)
H3	N3	N7	120.9(3)
H3	N3	C16	121.1(3)
N7	N3	C16	118.0(2)
N12	N6	C17	113.1(2)
N3	N7	C8	119.3(3)
S2	C8	N7	124.4(2)
S2	C8	N12	124.0(2)
N7	C8	N12	111.6(3)
N15	N9	C23	114.8(3)
N14	N10	C23	117.6(3)
F1	C11	C16	117.2(3)
F1	C11	C18	119.5(3)
C16	C11	C18	123.3(3)
N6	N12	C8	114.6(2)
H13	C13	C17	120.0(3)
H13	C13	C21	120.0(3)
C17	C13	C21	120.0(3)
N10	N14	H14	120.3(3)
N10	N14	C22	119.6(2)
H14	N14	C22	120.1(3)
N9	N15	C28	113.3(2)
N3	C16	C11	119.3(3)
N3	C16	C20	122.8(3)
C11	C16	C20	117.9(3)
N6	C17	C13	125.0(3)
N6	C17	C25	116.8(3)
C13	C17	C25	118.0(3)
C11	C18	H18	120.8(3)
C11	C18	C24	118.5(3)
H18	C18	C24	120.7(3)
H19	C19	C20	119.5(3)
H19	C19	C24	119.4(3)
C20	C19	C24	121.0(3)
C16	C20	C19	119.6(3)
C16	C20	H20	120.2(3)
C19	C20	H20	120.2(3)
C13	C21	H21	119.7(3)
C13	C21	C26	120.5(3)
H21	C21	C26	119.8(3)
N14	C22	C32	117.3(3)
N14	C22	C39	124.3(3)
C32	C22	C39	118.4(3)
S1	C23	N9	122.7(2)
S1	C23	N10	123.7(2)

N9	C23	N10	113.5(3)
C18	C24	C19	119.7(3)
C18	C24	H24	120.1(3)
C19	C24	H24	120.2(3)
F2	C25	C17	119.3(3)
F2	C25	C30	117.9(3)
C17	C25	C30	122.8(3)
C21	C26	H26	119.7(3)
C21	C26	C30	120.6(3)
H26	C26	C30	119.7(3)
H27	C27	C34	120.0(3)
H27	C27	C36	120.0(3)
C34	C27	C36	120.0(3)
N15	C28	C31	117.7(3)
N15	C28	C38	123.5(3)
C31	C28	C38	118.8(3)
H29	C29	C32	120.9(4)
H29	C29	C40	120.9(4)
C32	C29	C40	118.2(3)
C25	C30	C26	118.1(3)
C25	C30	H30	120.9(3)
C26	C30	H30	121.0(3)
F4	C31	C28	119.4(3)
F4	C31	C36	118.3(3)
C28	C31	C36	122.2(3)
F5	C32	C22	117.9(3)
F5	C32	C29	118.7(3)
C22	C32	C29	123.4(3)
C27	C34	H34	119.7(3)
C27	C34	C38	120.7(3)
H34	C34	C38	119.6(4)
H35	C35	C39	119.8(4)
H35	C35	C40	119.8(4)
C39	C35	C40	120.3(4)
C27	C36	C31	118.7(3)
C27	C36	H36	120.7(3)
C31	C36	H36	120.6(3)
C28	C38	C34	119.6(3)
C28	C38	H38	120.2(3)
C34	C38	H38	120.2(4)
C22	C39	C35	119.6(3)
C22	C39	H39	120.2(3)
C35	C39	H39	120.2(3)
C29	C40	C35	120.0(4)
C29	C40	H40	120.0(4)
C35	C40	H40	120.0(4)
H1A	C1	H1B	107.9(3)
H1A	C1	C2	109.1(3)
H1A	C1	C3	109.2(3)
H1B	C1	C2	109.1(3)
H1B	C1	C3	109.1(3)
C2	C1	C3	112.3(3)
C1	C2	H2A	109.0(3)
C1	C2	H2B	109.0(3)
C1	C2	C2	113.1(3)

H2A	C2	H2B	107.8(3)
H2A	C2	C2	109.0(3)
H2B	C2	C2	108.9(3)
C1	C3	H3A	109.5(3)
C1	C3	H3B	109.5(3)
C1	C3	H3C	109.5(3)
H3A	C3	H3B	109.4(3)
H3A	C3	H3C	109.5(3)
H3B	C3	H3C	109.5(3)
H1A	C1	H1B	107.9(3)
H1A	C1	C2	109.1(3)
H1A	C1	C3	109.2(3)
H1B	C1	C2	109.1(3)
H1B	C1	C3	109.1(3)
C2	C1	C3	112.3(3)
C2	C2	C1	113.1(3)
C2	C2	H2A	109.0(3)
C2	C2	H2B	108.9(3)
C1	C2	H2A	109.0(3)
C1	C2	H2B	109.0(3)
H2A	C2	H2B	107.8(3)
C1	C3	H3A	109.5(3)
C1	C3	H3B	109.5(3)
C1	C3	H3C	109.5(3)
H3A	C3	H3B	109.4(3)
H3A	C3	H3C	109.5(3)
H3B	C3	H3C	109.5(3)

Torsion angles [°]

C23	S1	S2	C8	-104.1(2)
S2	S1	C23	N9	-74.7(3)
S2	S1	C23	N10	109.5(3)
S1	S2	C8	N7	-97.2(3)
S1	S2	C8	N12	79.2(3)
H3	N3	N7	C8	0.1(4)
C16	N3	N7	C8	-179.9(3)
H3	N3	C16	C11	-0.4(5)
H3	N3	C16	C20	179.9(3)
N7	N3	C16	C11	179.6(3)
N7	N3	C16	C20	-0.1(4)
C17	N6	N12	C8	-173.3(3)
N12	N6	C17	C13	10.8(4)
N12	N6	C17	C25	-175.0(3)
N3	N7	C8	S2	0.6(4)
N3	N7	C8	N12	-176.2(2)
S2	C8	N12	N6	2.0(4)
N7	C8	N12	N6	178.8(3)
C23	N9	N15	C28	-178.4(3)
N15	N9	C23	S1	8.1(4)
N15	N9	C23	N10	-175.8(3)
C23	N10	N14	H14	-2.0(4)
C23	N10	N14	C22	178.0(3)
N14	N10	C23	S1	-5.3(4)
N14	N10	C23	N9	178.6(2)

F1	C11	C16	N3	-0.6(4)
F1	C11	C16	C20	179.2(3)
C18	C11	C16	N3	179.9(3)
C18	C11	C16	C20	-0.3(5)
F1	C11	C18	H18	1.4(5)
F1	C11	C18	C24	-178.7(3)
C16	C11	C18	H18	-179.1(3)
C16	C11	C18	C24	0.8(5)
H13	C13	C17	N6	-6.7(5)
H13	C13	C17	C25	179.1(3)
C21	C13	C17	N6	173.4(3)
C21	C13	C17	C25	-0.8(5)
H13	C13	C21	H21	0.4(6)
H13	C13	C21	C26	-179.6(3)
C17	C13	C21	H21	-179.7(3)
C17	C13	C21	C26	0.3(5)
N10	N14	C22	C32	174.8(3)
N10	N14	C22	C39	-5.3(5)
H14	N14	C22	C32	-5.2(4)
H14	N14	C22	C39	174.7(3)
N9	N15	C28	C31	-164.5(3)
N9	N15	C28	C38	16.2(4)
N3	C16	C20	C19	179.1(3)
N3	C16	C20	H20	-0.9(5)
C11	C16	C20	C19	-0.6(5)
C11	C16	C20	H20	179.4(3)
N6	C17	C25	F2	5.4(4)
N6	C17	C25	C30	-174.1(3)
C13	C17	C25	F2	180.0(3)
C13	C17	C25	C30	0.5(5)
C11	C18	C24	C19	-0.4(5)
C11	C18	C24	H24	179.6(3)
H18	C18	C24	C19	179.6(3)
H18	C18	C24	H24	-0.4(5)
H19	C19	C20	C16	-179.0(3)
H19	C19	C20	H20	1.0(5)
C24	C19	C20	C16	1.0(5)
C24	C19	C20	H20	-179.0(3)
H19	C19	C24	C18	179.5(3)
H19	C19	C24	H24	-0.5(5)
C20	C19	C24	C18	-0.5(5)
C20	C19	C24	H24	179.5(3)
C13	C21	C26	H26	-179.4(3)
C13	C21	C26	C30	0.5(5)
H21	C21	C26	H26	0.5(6)
H21	C21	C26	C30	-179.5(3)
N14	C22	C32	F5	-1.7(5)
N14	C22	C32	C29	-179.5(3)
C39	C22	C32	F5	178.4(3)
C39	C22	C32	C29	0.7(5)
N14	C22	C39	C35	-179.9(3)
N14	C22	C39	H39	0.1(5)
C32	C22	C39	C35	-0.0(5)
C32	C22	C39	H39	180.0(3)
F2	C25	C30	C26	-179.2(3)

F2	C25	C30	H30	0.8(5)
C17	C25	C30	C26	0.3(5)
C17	C25	C30	H30	-179.7(3)
C21	C26	C30	C25	-0.8(5)
C21	C26	C30	H30	179.2(3)
H26	C26	C30	C25	179.2(3)
H26	C26	C30	H30	-0.9(6)
H27	C27	C34	H34	1.0(6)
H27	C27	C34	C38	-178.9(3)
C36	C27	C34	H34	-179.0(3)
C36	C27	C34	C38	1.0(5)
H27	C27	C36	C31	179.3(3)
H27	C27	C36	H36	-0.6(6)
C34	C27	C36	C31	-0.7(5)
C34	C27	C36	H36	179.4(3)
N15	C28	C31	F4	3.5(5)
N15	C28	C31	C36	-179.2(3)
C38	C28	C31	F4	-177.2(3)
C38	C28	C31	C36	0.1(5)
N15	C28	C38	C34	179.5(3)
N15	C28	C38	H38	-0.6(6)
C31	C28	C38	C34	0.2(5)
C31	C28	C38	H38	-179.8(3)
H29	C29	C32	F5	1.0(5)
H29	C29	C32	C22	178.8(3)
C40	C29	C32	F5	-179.0(3)
C40	C29	C32	C22	-1.3(5)
H29	C29	C40	C35	-178.8(4)
H29	C29	C40	H40	1.2(6)
C32	C29	C40	C35	1.3(6)
C32	C29	C40	H40	-178.8(4)
F4	C31	C36	C27	177.4(3)
F4	C31	C36	H36	-2.7(5)
C28	C31	C36	C27	0.1(5)
C28	C31	C36	H36	-180.0(3)
C27	C34	C38	C28	-0.8(5)
C27	C34	C38	H38	179.3(3)
H34	C34	C38	C28	179.3(3)
H34	C34	C38	H38	-0.7(6)
H35	C35	C39	C22	-179.9(4)
H35	C35	C39	H39	0.1(6)
C40	C35	C39	C22	0.1(6)
C40	C35	C39	H39	-179.9(4)
H35	C35	C40	C29	179.3(4)
H35	C35	C40	H40	-0.7(7)
C39	C35	C40	C29	-0.8(6)
C39	C35	C40	H40	179.3(4)
H1A	C1	C2	H2A	66.3(4)
H1A	C1	C2	H2B	-176.3(3)
H1A	C1	C2	C2	-55.0(4)
H1B	C1	C2	H2A	-176.0(3)
H1B	C1	C2	H2B	-58.6(4)
H1B	C1	C2	C2	62.6(4)
C3	C1	C2	H2A	-54.9(4)
C3	C1	C2	H2B	62.5(4)

C3	C1	C2	C2	-176.3(3)
H1A	C1	C3	H3A	58.6(4)
H1A	C1	C3	H3B	-61.3(4)
H1A	C1	C3	H3C	178.7(3)
H1B	C1	C3	H3A	-59.0(4)
H1B	C1	C3	H3B	-178.9(3)
H1B	C1	C3	H3C	61.0(4)
C2	C1	C3	H3A	179.9(3)
C2	C1	C3	H3B	59.9(4)
C2	C1	C3	H3C	-60.1(4)
C1	C2	C2	C1	180.0(3)
C1	C2	C2	H2A	-58.7(4)
C1	C2	C2	H2B	58.7(4)
H2A	C2	C2	C1	58.7(4)
H2A	C2	C2	H2A	-180.0(3)
H2A	C2	C2	H2B	-62.6(4)
H2B	C2	C2	C1	-58.7(4)
H2B	C2	C2	H2A	62.6(4)
H2B	C2	C2	H2B	180.0(3)
H1A	C1	C2	C2	55.0(4)
H1A	C1	C2	H2A	-66.3(4)
H1A	C1	C2	H2B	176.3(3)
H1B	C1	C2	C2	-62.6(4)
H1B	C1	C2	H2A	176.0(3)
H1B	C1	C2	H2B	58.6(4)
C3	C1	C2	C2	176.3(3)
C3	C1	C2	H2A	54.9(4)
C3	C1	C2	H2B	-62.5(4)
H1A	C1	C3	H3A	-58.6(4)
H1A	C1	C3	H3B	61.3(4)
H1A	C1	C3	H3C	-178.7(3)
H1B	C1	C3	H3A	59.0(4)
H1B	C1	C3	H3B	178.9(3)
H1B	C1	C3	H3C	-61.0(4)
C2	C1	C3	H3A	-179.9(3)
C2	C1	C3	H3B	-59.9(4)
C2	C1	C3	H3C	60.1(4)