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# Synthesis and kinetics of electronically altered photochromic dithizonatophenylmercury(II) complexes

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### ABSTRACT

A series of phenyl-substituted dithizones were synthesized, and preparation of the corresponding series of photochromic phenylmercury(II) complexes is for the first time reported. Adaption of previous methods enhanced synthesis convenience and product yields. A single crystal X-ray data collection of the *ortho*-S-methyl nitroformazan reaction intermediate was done. ADF computed molecular orbitals of the title compound show the HOMO and LUMO orbitals stretching along the entire ligand. The spontaneous back reaction kinetics of dithizonatophenylmercury(II) was studied at varied concentrations, temperatures and in different solvents. An exponential correlation was found between the rate of reverse isomerization and temperature, while increased solvent polarity and decreased molar mass facilitate higher return rates. The kinetic study of the series of twelve electronically altered complexes yielded a lowest rate of  $0.0002 \, \text{s}^{-1}$  for the *ortho*-methyl derivative, while the highest rate of  $0.0106 \, \text{s}^{-1}$  was measured for the *meta*-methoxy derivative.

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#### 1. Introduction

In 1878 already, Emil Fischer noticed formation of the  $\beta$ -phenyldithiocarbazic acid phenylhydrazine salt, **2**, during mixing of carbon disulphide and phenylhydrazine in organic solvents (see Scheme 1) [1]. After loss of hydrogen sulphide during heating, the thiocarbazide (H<sub>4</sub>Dz), **6**, was obtained. Addition of dilute alkali yielded the deep orange-red anion, HDz<sup>-</sup>, with the final black-green dithizone product (H<sub>2</sub>Dz), **7**, precipitating out on addition of dilute acid [2].

Billman and Cleland [3] introduced solvent free conditions based on the Fischer method, achieving an overall dithizone yield of 52–66%.

In 1943, Hubbard and Scott [4] published a method similar to an earlier method reported by Bamberger [5]. This method does away with initial preparation of **2**, but instead starts from the aryldiazonium chloride, **4**, the latter being prepared by diazotization of the arylamine with sodium nitrite. Addition of nitromethane precipitates the deep red nitroformazan, **5**. Bubbling ammonia and hydrogen sulphide gases through the nitroformazan solution yields the unstable dirty white thiocarbazide, **6**. Pelkis et al. [6] used a similar method to that of Bamberger [5] and Tarbell [7], while Mirkhalaf [8] employed ammonium sulphide instead of NH<sub>3</sub> and H<sub>2</sub>S gases during conversion of **5** to **6**. Although he obtained a pure

1010-6030/\$ - see front matter © 2012 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.jphotochem.2012.11.009 product, no data was provided on the success of the reaction in terms of yield. In the current study the reaction conditions of a series of eleven electronically altered phenyl-substituted dithizones and corresponding phenylmercury(II) complexes were examined, and characterization data and yields are reported.

Apart from dithizone being a very important colour development reagent in trace metal analyses, as may be noted from numerous related reports published annually, it also forms the basis of a marked photochromic reaction in some metal complexes (see Scheme 2). Photo-excitation by blue-green light results in colour changing isomerization around the -C=N- bond, while the spontaneous thermal back-reaction is unaffected by light.

Around 1950, Irving [9] and Webb [10] independently observed photochromic behaviour in the *bis*-dithizonatomercury(II) complex, Hg(HDz)<sub>2</sub>. Fifteen years later Meriwether et al. did a thorough investigation which led to the discovery of more photochromic metal dithizonates; Pt, Pd, Cd, Zn, Ag, Pb and Bi [11]. Failure to observe spectral changes in other metal dithizonates was ascribed to the possibility of very fast return rates. A kinetic study in benzene involving the back reaction of Hg(HDz)<sub>2</sub>, which was observed to have the longest half-life of all metal dithizonates, probed the effects of deuteration and water presence [12]. N-deuteration of the complex produced a threefold decrease in return rate, while the presence of water increased the return rate.

The initial photochromic reaction of dithizonatophenylmercury(II), DPM, in solution was recently investigated by femtosecond transient absorption spectroscopy [13]. Ultrafast excitation takes place within less than100 fs, followed by 180° photo-isomerization



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Scheme 1. Different approaches for the synthesis of dithizone, 7, as reported by various authors.

with a time constant of 1.5 ps. Excited-state absorption was observed for the orthogonally (90°) twisted intermediate state, from where bifurcation along pathways towards the ground states of the orange *cis* and blue *trans* configurations occurs below the funnel of the conical intersection. Faster than may be seen photochromism of DPM in a polar solvent like methanol was also for the first time observed by employing ultrafast laser spectroscopy.



**Scheme 2.** Photochromism of the 4-SCH<sub>3</sub> derivative of dithizonatophenylmercury(II), PhHg(4-SCH<sub>3</sub>)HDz.

The structure of the DPM orange resting state was solved by means of X-ray crystallography [14]. DFT calculations convincingly resolved ambiguity about the structure of the photo-induced blue form of DPM [15]. Whereas intra-molecular proton transfer was previously anticipated [16], geometry optimizations established the imine proton to stay intact during the photochromic reaction, with no geometry changes apart from mere isomerization around the -C=N- bond (Scheme 2).

Comprehensive cyclic voltammetry studies of the redox pathways of both the free ligand [17] and the phenylmercury complex [18] were recently reported. The latter also revealed electrochromic behaviour, while dithizone itself is now known to be both solvatochromic and concentratochromic under certain conditions [19].

#### 2. Experimental methods

#### 2.1. General

Unless otherwise stated, dithizone, **7**, and all synthesis reagents and solvents (Sigma–Aldrich, Merck) were used without further purification. Reaction solutions were cooled on a KP250 cooling stirrer during syntheses. Water was doubly distilled. <sup>1</sup>H NMR spectra at 20 °C were recorded on Bruker Avance DPX 300 and Bruker Avance II 600 NMR spectrometers at 300 and 600 MHz respectively, with chemical shifts presented as  $\delta$  values referenced to SiMe<sub>4</sub> at 0.00 ppm. C<sub>6</sub>D<sub>6</sub> and CDCl<sub>3</sub> solvents were used. CDCl<sub>3</sub> was rid of acid by passing through basic alumina immediately before use. Melting points were determined on a Reichert Thermopan microscope with a Koffler hot-stage, and are uncorrected. UV–visible measurements were made on a Shimadzu UV-2550 spectrometer fitted with a Shimadzu CPS temperature controller, using an optical glass cuvette. Photo-excitation of the photochromic compounds was accomplished with a 400 W mercury–halide lamp.

ADF (Amsterdam Density Functional) calculations were carried out using DFT (Density Functional Theory) [20] with the PW91 (Perdew-Wang, 1991) exchange and correlation functional [21]. Optimized geometries were calculated for the neutral species and reported elsewhere [15]. Molecular orbital representations were processed and visualized with the Chemcraft software package, applied to the former output files [22].

#### 2.2. Synthesis

#### 2.2.1. General procedure

Formazans: The phenyl-substituted aniline (30 mmol) is added to a mixture of concentrated hydrochloric acid (15 mL) and water (25 mL) in a 100 mL beaker at 0 °C on a cooling stirrer. Sodium nitrite (3.1 g, 45 mmol) is slowly added while stirring, reacting with the aniline to form a clear solution (*ca* 30 min). The diazo solution is added to a mixture of sodium acetate (60 g), glacial acetic acid (35 mL) and water (20 mL) in a 500 mL beaker (stir the dry salt vigorously while adding the acid–water mixture). Nitromethane (8.6 mL, 150 mmol) is added after 10 min. After stirring for 2 h at room temperature the volume is increased with water to *ca* 300 mL. The red formazyl precipitate is filtered in a large Büchner funnel and washed with copious amounts of water. The nitroformazan may be dried overnight at 50 °C.

Dithizones: The nitroformazan (3 mmol) is suspended in absolute ethanol (60 mL) in a 150 mL lightly stoppered Erlen Meyer flask at 35 °C. While stirring, ammonium sulphide (20% aq, 6 mL, 17.6 mmol) is added. After 20 min (red colour fades, or precipitate forms) the mixture is poured onto crushed ice (100 mL) and a little water added to promote precipitation. The mostly dirty-white thiocarbazide is immediately filtered off in a sintered glass funnel and washed with water. Methanolic potassium hydroxide (2%) is intermittently poured onto the precipitate in the funnel (no suction), oxidizing it to the orange-red potassium salt, dissolving and washing it into a 250 mL flask. The solution is acidified with dilute HCl (2%) until full precipitation of the black dithizone product is effected, which then is gravity filtered through a filter paper and washed with copious amounts of water. For purification purposes the base–acid treatment is repeated.

Dithizonatophenylmercury(II) complexes: Triethylamine (0.2 mL, 1.4 mol) is added to a solution of the dithizone (0.8 mmol) and phenylmercury(II) chloride (0.2694 g, 0.82 mmol) in dichloromethane (50 mL). After stirring (15 min) and complete colour change from dark green to bright orange-red the solvent is removed under reduced pressure. The product is again dissolved in minimum dichloromethane and filtered through a small filter paper into a 25 mL Erlen Meyer flask. Ethanol (10 mL) is added to the filtrate and the product allowed to crystallize. (The 2-OCH<sub>3</sub>, 2-SCH<sub>3</sub> and 4-SCH<sub>3</sub> derivative products required addition of methanol instead of ethanol, as well as a few drops of water to aid crystallization.)

#### 2.2.2. Dithizone derivatives

2.2.2.1. 2-Methoxydithizone. Nitroformazan yield: 95%, dithizone yield: 76%, mp. 178–179 °C,  $\lambda_{max}$  (nm) (dichloromethane) 474 and 641, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  4.00 (s, 6H, OC<u>H<sub>3</sub></u>), 6.97–7.17 (m, 6H, 2 × C<sub>6</sub><u>H</u><sub>4</sub>), 7.95–8.02 (d, 2H, 2 × C<sub>6</sub><u>H</u><sub>4</sub>), 12.92 (s, 2H, 2 × N<u>H</u>).

2.2.2.2. 3-Methoxydithizone. Nitroformazan yield: 73%, dithizone yield: 46%, mp. 148–149 °C,  $\lambda_{max}$  (nm) (dichloromethane) 453 and 625, <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz)  $\delta$  3.17 (s, 6H, 2 × OC<u>H</u><sub>3</sub>), 6.60–6.92 (m, 8H, 2 × C<sub>6</sub><u>H</u><sub>4</sub>), 13.03 (s, 2H, 2 × N<u>H</u>).

*2.2.2.3.* 4-*Methoxydithizone.* Nitroformazan yield: 59%. Dithizone synthesis failed, as the product decomposed during the last synthesis step.

*2.2.2.4. 2-Methyldithizone.* Nitroformazan yield: 75%, dithizone yield: 74%, mp. 162.8 °C,  $\lambda_{max}$  (nm)(dichloromethane) 457 and 623,

 $\label{eq:main_state} {}^{1}\text{H}\,\text{NMR}\,(\text{C}_{6}\text{D}_{6},300\,\text{MHz})(\text{ppm})\text{:}\,2.12\,(\text{s},6\text{H},2\times\text{C}_{\underline{H}3}),6.72-6.99\,(\text{m},6\text{H},2\times\text{C}_{6}\underline{H}_{4}),8.09-8.16\,(\text{d},2\text{H},2\times\text{C}_{6}\underline{H}_{4}),13.28\,(\text{s},2\text{H},2\times\text{N}\underline{H}).$ 

2.2.2.5. 3-*Methyldithizone*. Nitroformazan yield: 53%, dithizone yield: 23%, mp. 149–151 °C,  $\lambda_{max}$  (nm) (dichloromethane) 448 and 613, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) (ppm): 2.46, 2.48 (2 × s, 6H, 2 × CH<sub>3</sub>), 7.37–7.49 (m, 4H, 2 × C<sub>6</sub>H<sub>4</sub>), 7.70–7.85 (dd, 4H, 2 × C<sub>6</sub>H<sub>4</sub>).

2.2.2.6. 4-Methyldithizone. Nitroformazan yield: 88%, dithizone yield: 30%, mp. 98–103 °C,  $\lambda_{max}$  (nm) (dichloromethane) 452 and 622, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) (ppm): 2.43 (s, 6H, 2 × C<u>H<sub>3</sub></u>), 7.32–7.92 (m, 8H, 2 × C<sub>6</sub><u>H<sub>4</sub></u>).

2.2.2.7. 3,4-Dimethyldithizone. Nitroformazan yield: 78%, dithizone yield: 13%, mp. 129–131 °C,  $\lambda_{max}$  (nm) (dichloromethane) 453 and 623, <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz)  $\delta$  1.89–1.91 (2 × s, 12H, 4 × C<u>H</u><sub>3</sub>), 6.76 – 6.79 (d, 2H, 2 × C<sub>6</sub><u>H</u><sub>3</sub>), 7.11–7.19 (2 × s, 4H, 2 × C<sub>6</sub><u>H</u><sub>3</sub>), 13.04 (s, 2H, 2 × N<u>H</u>).

2.2.2.8. 2-Fluorodithizone. Nitroformazan yield: 32%, dithizone yield: 43%, mp. 114 °C,  $\lambda_{max}$  (nm) (dichloromethane) 450, 621, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.41–7.29 and 8.02–8.10 (2 × m, 8H, C<sub>6</sub><u>H</u><sub>4</sub>F).

2.2.2.9. 3-Fluorodithizone. Nitroformazan yield: 74%, dithizone yield: 25%, mp. 112 °C,  $\lambda_{max}$  (nm) (dichloromethane) 447, 611, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.03–7.16 and 7.35–7.63 (2 × m, 8H, C<sub>6</sub><u>H</u><sub>4</sub>F).

2.2.2.10. 4-Fluorodithizone. Nitroformazan yield: 80%, dithizone yield: 48%, mp. 174 °C,  $\lambda_{max}$  (nm) (dichloromethane) 446, 610, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.24 (m, 4H, o-C<sub>6</sub><u>H</u><sub>4</sub>F), 7.73 (m, 4H, m-C<sub>6</sub><u>H</u><sub>4</sub>F).

2.2.2.11. 2-S-methyldithizone. Nitroformazan yield: 93%, dithizone yield: 76%, mp. 118 °C,  $\lambda_{max}$  (nm) (dichloromethane) 477 and 643, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.45–2.61 (2 × s, 6H, 2 × SC<u>H<sub>3</sub></u>), 6.86–8.07 (m, 8H, 2 × C<sub>6</sub><u>H</u><sub>4</sub>), 13.37 (s, 2H, 2 × N<u>H</u>).

2.2.2.12. 4-S-methyldithizone. Nitroformazan yield: 87%, dithizone yield: 60%, mp. 85 °C,  $\lambda_{max}$  (nm) (dichloromethane) 486 and 667, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.54–2.58 (2 × s, 6H, 2 × SCH<sub>3</sub>), 7.29–7.38 (m, 4H, 2 × C<sub>6</sub>H<sub>4</sub>), 7.61–7.70 (m, 4H, 2 × C<sub>6</sub>H<sub>4</sub>), 12.53 (s, 2H, 2 × NH).

*2.2.3. Dithizonatophenylmercury complexes* 

2.2.3.1. Dithizonatophenylmercury(II). Yield: 81%, mp. 166 °C,  $\lambda_{max}$  (nm)(dichloromethane)470, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz) $\delta$ 7.60–8.00 (3 × m, 15 H, C<sub>6</sub><u>H</u><sub>5</sub>).

2.2.3.2. 2-Methoxydithizonatophenylmercury(II). Yield: 84%, mp. 212–213 °C,  $\lambda_{max}$  (nm) (dichloromethane) 498, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  3.68 and 4.03 (2 × s, 6H, 2 × CH<sub>3</sub>), 6.57–7.89 (m, 13H, 2 × C<sub>6</sub>H<sub>4</sub>, 1 × C<sub>6</sub>H<sub>5</sub>), 9.75 (s, 1H, 1 × NH).

2.2.3.3. 3-Methoxydithizonatophenylmercury(II). Yield: 63%, mp. 137–139 °C,  $\lambda_{max}$  (nm) (dichloromethane) 480, <sup>1</sup>H NMR (C<sub>6</sub>D<sub>6</sub>, 300 MHz)  $\delta$  3.21 and 3.34 (2 × s, 6H, 2 × C<u>H</u><sub>3</sub>), 6.67–7.87 (m, 13H, 2 × C<sub>6</sub><u>H</u><sub>4</sub>, 1 × C<sub>6</sub><u>H</u><sub>5</sub>), 9.52 (s, 1H, 1 × N<u>H</u>).

2.2.3.4. 2-Methyldithizonatophenylmercury(II). Yield: 63%, mp. 120–122 °C,  $\lambda_{max}$  (nm) (dichloromethane) 464, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.46 and 2.54 (2 × s, 6H, 2 × CH<sub>3</sub>), 6.98–7.82 (m, 13H, 2 × C<sub>6</sub>H<sub>4</sub>, 1 × C<sub>6</sub>H<sub>5</sub>), 9.20 (s, 1H, 1 × NH).

2.2.3.5. 3-*Methyldithizonatophenylmercury(II)*. Yield: 75%, mp. 170–173 °C,  $\lambda_{max}$  (nm) (dichloromethane) 476, <sup>1</sup>H NMR ( $C_6D_6$ , 300 MHz)  $\delta$  2.08 and 2.19 (2 × s, 6H, 2 × CH<sub>3</sub>), 6.76–8.04 (m, 13 H, 2 × C<sub>6</sub>H<sub>4</sub>, 1 × C<sub>6</sub>H<sub>5</sub>), 9.41 (s, 1H, 1 × NH).

2.2.3.6. 4-Methyldithizonatophenylmercury(II). Yield: 87%, mp. 146–148 °C,  $\lambda_{max}$  (nm) (dichloromethane) 482, <sup>1</sup>H NMR (3 C<sub>6</sub>D<sub>6</sub>, 300 MHz)  $\delta$  2.02 and 2.18 (2 × s, 6H, 2 × C<u>H</u><sub>3</sub>), 6.87–8.12 (m, 13H, 2 × C<sub>6</sub>H<sub>4</sub>, 1 × C<sub>6</sub>H<sub>5</sub>), 9.44 (s, 1H, 1 × N<u>H</u>).

2.2.3.7. 3,4-Dimethyldithizonatophenylmercury(II). Yield: 65%, mp. 180 °C,  $\lambda_{max}$  (nm) (dichloromethane) 485, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.21, 2.2988, 2.294 and 2.33 (4 × s, 12H, 4 × CH<sub>3</sub>), 7.12–7.80 (m, 11H, 1 × C<sub>6</sub>H<sub>5</sub>, 2 × C<sub>6</sub>H<sub>3</sub>), 9.15 (s, 1H, 1 × N<u>H</u>).

2.2.3.8. 2-Fluorodithizonatophenylmercury(II). Yield: 76%, mp. 163 °C,  $\lambda_{max}$  (nm) (dichloromethane) 468, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  6.99–7.88 (m, 13 H, 2 × C<sub>6</sub>H<sub>4</sub>F and 1 × C<sub>6</sub>H<sub>5</sub>).

2.2.3.9. 3-Fluorodithizonatophenylmercury(II). Yield: 64%, mp. 143 °C,  $\lambda_{max}$  (nm) (dichloromethane) 475, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  6.75–7.79 (m, 13 H, 2 × C<sub>6</sub>H<sub>4</sub>F and 1 × C<sub>6</sub>H<sub>5</sub>)

2.2.3.10. 4-Fluorodithizonatophenylmercury(II). Yield: 74%, mp. 208 °C,  $\lambda_{max}$  (nm) (dichloromethane) 471, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  7.06–7.99 (m, 13 H, 2 × C<sub>6</sub>H<sub>4</sub>F and 1 × C<sub>6</sub>H<sub>5</sub>)

2.2.3.11. 2-S-methyldithizonatophenylmercury(II). Yield: 73%, mp. 130 °C,  $\lambda_{max}$  (nm) (dichloromethane) 498, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.31 and 2.52(2 × s, 3H, 1 × SCH<sub>3</sub>), 6.99–7.84 (m, 13H, 1 × C<sub>6</sub>H<sub>5</sub> and 2 × C<sub>6</sub>H<sub>4</sub>), 10.29 (s, 1H, 1 × NH).

2.2.3.12. 4-S-methyldithizonatophenylmercury(II). Yield: 72%, mp. 176 °C,  $\lambda_{max}$  (nm) (dichloromethane) 509, <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz)  $\delta$  2.53 (s, 6H, 2 × SCH<sub>3</sub>), 7.10–7.95 (m, 13H, 1 × C<sub>6</sub>H<sub>5</sub> and 2 × C<sub>6</sub>H<sub>4</sub>), 9.20 (1H, s, 1 × NH).

#### 3. Results and discussion

#### 3.1. Synthesis

Syntheses of the dithizone ligands were done according to an adapted method by Mirkhalaf, Whittaker and Schiffrin [8]. This method conveniently allows the use of a series of phenylsubstituted anilines as starting reagents, from which the intended electronically altered series of photochromic mercury complexes could for the first time be synthesized.

Low yields of some intermediary nitroformazan and dithizone derivatives necessitated revising certain reaction conditions. It was consequently found that increasing the sodium nitrite, nitromethane and ammonium sulphide excess quantities significantly improved product yields, see Scheme 1 (bottom path) and the general synthesis description in Section 2.2. A slightly higher solution temperature (35 °C) during addition of  $(NH_4)_2S$  also gave increased reaction rates and higher thiocarbazide yields. An additional increase in the reaction rate at even higher temperatures (>40 °C) was observed, but it simultaneously lowered the yields of the relatively unstable thiocarbazides. The main advantage of using  $(NH_4)_2S$  lies in the abolition of the inconvenient use of noxious NH<sub>3</sub> and H<sub>2</sub>S gasses, traditionally employed in the substitution reaction of NO<sub>2</sub> with S.

Highest nitroformazan yields, in excess of 90%, were achieved for the two electron donating species, OCH<sub>3</sub> and SCH<sub>3</sub>, both being in the *ortho* positions. This is reflected in corresponding highest dithizone yields of 76% each. The lowest yield of 13% was found for 3,4-dimethyldithizone. Regardless implemented improvements, the 4-methoxy and 2,4,6-trimethyl derivatives could not be synthesized. Of the 2,4,6-trimethyl species only small amounts of the typical brick-red formazan product formed, and only at elevated temperatures of up to 35°C. Heating to 40°C caused blackening of the product. Although the 4-methoxy derivative gave a 59% nitroformazan yield, both this and the trimethyl compounds decomposed during the last step where the thiocarbazide (6) is oxidized to the orange-red K<sup>+</sup>HDz<sup>-</sup> salt. During the last step the otherwise typical intense orange-red colour disappeared. This finding indicates the boundary at which even stronger electron donating substituents may no longer be employed. At the opposite end, *i.e.* the 'electron-withdrawing boundary', it was found that the transition from one to more fluoro-substituents on each phenyl ring results in gradual loss of product colour, and consequently also its application in photochromic reactions [23].

Complexation was accomplished by a convenient procedure whereby triethylamine was employed to deprotonate dithizone before reacting with the mercury salt [15]. Reactions with all the ligand derivatives take place instantaneously. Recrystallization from dichloromethane and ethanol allows the product to precipitate out, while keeping the small excess of PhHgCl and the (CH<sub>3</sub>CH<sub>2</sub>)<sub>3</sub>NH<sup>+</sup>Cl<sup>-</sup> byproduct dissolved in the remaining ethanol. Although the photochromic dithizonatomercury complex was discovered more than 60 years ago [9], derivatization of this class of photochromic metal complexes is for the first time explored.

#### 3.2. Structure

Towards supplementary characterization, attempts were made to grow crystals of all the derivatives of nitroformazan, dithizone and the dithizonatophenylmercury complexes. Sizeable nitroformazan crystals were readily produced, while dithizone crystals large enough for single crystal X-ray crystallography were not obtained. The relative ease by which crystals of especially the ortho nitroformazan derivatives are produced is not only illustrated by the recent publication of crystal structures of the ortho-methyl [24], ortho-methoxy [25] and ortho-S-methyl [26] nitroformazans, but also by the fact that two different polymorphs of the latter compound were obtained from different solvent systems. Acetone overlaid with hexane yielded the latter monoclinic crystal system in the  $P2_1/c$  space group (Z=4), while the structure that is reported here,<sup>1</sup> was found to be a triclinic crystal in the P-1space group (Z=2), grown from a tetrahydrofuran-methanol solution (see Fig. 1). Performing the data collection at both 298 K and 200 K without observing any significant change eliminated the possibility of the observed polymorphism being a temperature effect.

The similar conformation of all reported nitroformazan structures is ascribed to the intramolecular H-bond interaction between the single imine proton, (N11)H, and N13 which is distanced at 1.976 Å, and to a lessor degree N14, which is situated 2.566 Å from the hydrogen atom. The *bent* conformation differs from the *linear* conformation of dithizone, where the two imine protons are each bound to a nitrogen bordering a phenyl ring, and thus sterically preventing a similar *bent* conformation (see Scheme 1 (**5** and **7**) [19]). The nitroformazan molecule is otherwise largely planar, with the NO<sub>2</sub> and S(12) groups being coplanar to the molecular formazan

<sup>&</sup>lt;sup>1</sup> Crystallographic data for the structure reported in this article had been deposited with the Cambridge Crystallographic Data Centre with deposition number, CCDC 896693, and may be obtained free of charge from the Director, CCDC, 12 Union Road, Cambridge CB21EZ, UK [fax: +44 1223 336 033; deposit@ccdc.cam.ac.uk or www.ccd.cam.ac.uk].



**Fig. 1.** The molecular structure of the *ortho*-S-methylnitroformazan, *i.e.* (*E*)-1-[2-(methylsulfanyl)phenyl]-2-( $\{(E)$ -2-[2-(methylsulfanyl)phenyl]hydrazinylidene $\}$  (nitro)methyl)diazene, with anisotropic displacement ellipsoids drawn at 50% probability level. Intramolecular H-bonds are depicted by dotted lines.

backbone. The second, S(11)— $CH_3$ , substituent is twisted out of the plane by  $58.73^{\circ}$ .

ADF computed molecular orbitals of the title compound reveals orbitals extending over the entire ligand, including both phenyl rings and the sulphur atom (only HOMO) (see Fig. 2). This computed result corresponds to the experimental observation that the photochromic property is characteristic of dithizonates with phenyl end groups, as opposed to aliphatic groups. The large degree of electron delocalization resulting from  $\pi$ -orbital overlapping is typical of sp<sup>2</sup> hybridization of nitrogen atoms along the linear and planar backbone of the molecule. The -C=N- double bond character in the HOMO is made manifest by the higher depicted electron density between the carbon and nitrogen atoms, as opposed to decreased electron density in the LUMO (see arrows). Photo-induced excitation of the DPM HOMO results in the electron promoted to the LUMO, where the -C=N- double bond is reduced to a single bond, which is a prerequisite for subsequent rotation around this axis. Apart from the blue isomer and its orbitals having a bent geometry (not shown), respective orbitals of the two isomers are essentially alike.



**Fig. 3.** The photochromic back-reaction of the blue-grey photo-induced isomer, **9**, of a  $6 \times 10^{-5}$  M solution of PhHg(4-SCH<sub>3</sub>)HDz in DCM, reverting to the red ground state, **8**, with isosbestic points at 563, 429, 372 and 281 nm. Spectra were recorded at 0.1, 1, 3, 5, 7, 10, 15, 30 and 60 min after exposure to white light from a 400 W mercury-halide lamp.

#### 3.3. Kinetics

Since discovery of the photochromic behaviour of  $Hg(HDz)_2$ in 1950 [9] no comprehensive kinetic study of the radiationless thermal back reaction of metal dithizonates had been reported. The photochromic property, as measured by the return rate in solution, is found to be very sensitive to temperature, the metal, impurities, acids and bases, and the polarity of solvents. Addition of a few drops of ethanol, acetic acid or triethylamine reduces the return reaction half-life profoundly. Hydroxylic solvents and organic acids and bases are generally the poorest media for observing photochromism. The strongest photochromic effect is observed in dry non-polar solvents, such as the halogenated solvents and toluene.

In an attempt to quantify these observations, the rates of return were measured at different concentrations, temperatures and in different solvents. In addition, return rates of a series of twelve electronically altered complexes in dichloromethane were also measured. In view of the many factors possibly affecting the rate of return, where applicable, care was taken to maintain similar conditions during all measurements, *e.g.* similar washing procedures, solvents from similar batches, and the same cuvette and instrument were used right through. Complex stability in dichloromethane proved to be of no concern, as *e.g.* a sealed solution of 2-methoxydithizonatophenylmercury(II), having been stored in the dark for two years, showed undiminished and repeated photochromic behaviour in sunlight.

Scheme 2 represents the photochromic reaction of PhHg(4-SCH<sub>3</sub>)HDz, where the absorption of green light results in a reversible colour change from red, **8**, to blue-grey, **9**. By the overlay of consecutive spectra, Fig. 3 illustrates the corresponding spontaneous radiationless back reaction in dichloromethane. The absorbance maxima at 617, 407 and 291 nm disappear over a



Fig. 2. (a) ADF calculated HOMO and (b) LUMO of the orange isomer of DPM. Bonding and anti-bonding orbitals are differentiated by colour. Arrows indicate axis of rotation.

#### Table 1

Absorbance maxima of the dithizone free ligand ( $\lambda_1$  and  $\lambda_2$ ) and corresponding dithizonatophenylmercury(II) complexes ( $\lambda$  – resting state isomer,  $\lambda^*$  – photo-induced isomer) in DCM, arranged in increasing order of complex  $\lambda$ .

Substituent	Ligand		Complex	
	$\lambda_1$	λ2	λ	$\lambda^*$
2-CH <sub>3</sub>	457	623	464	580
2-F	450	621	468	590
Н	443	609	470	590
4-F	446	620	471	590
3-F	447	610	475	591
3-CH <sub>3</sub>	448	613	476	591
3-0CH <sub>3</sub>	453	625	480	597
4-CH <sub>3</sub>	452	622	482	597
3,4-(CH <sub>3</sub> ) <sub>2</sub>	453	623	485	602
2-SCH <sub>3</sub>	477	643	488	594
2-OCH <sub>3</sub>	474	641	498	610
4-SCH <sub>3</sub>	486	667	509	617

60 min time period, while the resting state peaks appear at 509, 388 and 280 nm. The small peak observed at *ca* 407 nm is unique to the two S-methyl derivatives. In the other complexes this peak appears as a blue-shifted shoulder (*ca* 360 nm) to the right of the high-energy absorption band (*ca* 280 nm). The S-methyl substituent is thus observed to have a significant influence on the two lower energy absorption bands, but leaves the high-energy absorption at *ca* 280 nm relatively unaffected.

In the current series the longest wavelength absorbance maxima are observed for the former PhHg(4-SCH<sub>3</sub>)HDz derivative ( $\lambda = 509 \text{ nm}$  and  $\lambda^* = 617 \text{ nm}$ ) (see Table 1). The orthomethyl derivative yielded shortest  $\lambda_{max}$  values ( $\lambda = 464 \text{ nm}$  and  $\lambda^* = 580 \text{ nm}$ ). These values correspond to overall wavelength shifts of 45 and 37 nm respectively. Considering the earlier mentioned boundaries within which the dithizone ligand may be synthesized (Section 3.1) the above wavelengths give the maximum shifts in absorbance maxima, to date, that may be achieved by electronically altering the ligand.

In general, complexes associated with electron withdrawing fluorine substituents absorb at higher energies, while the electron donating substituents have the opposite effect. This trend is roughly reflected in corresponding free ligand data (Table 1). Molar absorptivity coefficients at  $\lambda_{max}$  of the resting state complex isomers vary from *ca* 14 000 to 20 000 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> in DCM, with the exception of the *meta*-fluoro derivative being only 4800 dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup>. No particular trend was observed.

During all the kinetic studies reported here the series of dithizonatophenylmercury(II) complexes were photo-excited under illumination with white light from a 400 W metal-halide lamp, and the spontaneous back reaction spectrophotometrically followed at  $\lambda_{max}$  of the photo-induced isomers. Application of first order kinetic models [27] to spectroscopic data established the regeneration of the ground states to all be first order processes.

At the outset, a concentration study done in dichloromethane solutions at 20 °C, with concentrations varying from 1.5 to  $7.5 \times 10^{-5}$  M, yielded no significant trend or difference in rate constants. The result was expected, as the reaction is merely an isomerization which is not dependent on reactant concentrations *per se.* Although much increased proximity of analyte molecules may in fact alter the environment and possibly the reaction rate, higher concentrations from Beer's law. Furthermore, photochemical conversion of the bulk of high concentration solutions to the blue isomeric form becomes increasingly difficult as applied light is blocked out by outer dye molecules.

Secondly, a temperature study was performed by following the back reaction at 0, 10, 20 and 30 °C in dichloromethane. Fig. 4 (top) illustrates the exponential decline curves ( $R^2 > 0.99$ ) obtained



**Fig. 4.** *Top*: Disappearance of the photo-induced blue isomer of photochromic DPM  $(3 \times 10^{-5} \text{ M})$  in DCM, at 0 ( $\bullet$ ), 10 ( $\blacktriangle$ ), 20 ( $\blacksquare$ ) and 30 °C ( $\bullet$ ), measured at 590 nm. *Middle*: First order kinetics, illustrated by linear plots of  $\ln[A_0/A_t]$  versus time. *Bottom*: A trend line through the plot of rate constant versus temperature fits an exponential correlation with  $R^2 > 0.98$ .

for the blue photo-induced isomer of unsubstituted DPM. The exponential increase in rate constants (Fig. 4, middle and bottom) confirms early claims of a thermal radiationless back reaction [11,16]. The relative small overall temperature increase on going from  $0 \circ C$  ( $k = 0.0005 \text{ s}^{-1}$ ) to  $30 \circ C$  ( $k = 0.0052 \text{ s}^{-1}$ ) resulted in a roughly ten times increase in reaction rate. Similarly, a decrease in temperature significantly slows down the reaction, with the consequence that DPM may be frozen almost indefinitely in the blue photo-induced state at very low temperatures, an observation that was experimentally observed. Under similar conditions extrapolation of the exponential curve ( $y = 0.0004e^{0.0814x}$ ) predicts a blue isomer half life [where  $A(t_{V_2}) = 0.11$ ] of 1 s at 91 °C, while for  $t_{V_2}$  to be equal to 1 day the temperature has to be lowered to  $-48 \circ C$ . Accordingly, Meriwether *et al.* observed photochromism of Cd and Pb dithizonate complexes only as low as  $-80 \circ C$ , while the longer lived



**Fig. 5.** *Top*: First order kinetics, illustrated by linear plots of  $\ln[A_0/A_t]$  versus time, representing disappearance of the blue photo-induced isomer of photochromic DPM  $(3 \times 10^{-5} \text{ M})$  in different solvents, measured at  $\lambda_{max}$  in each solvent, at  $10^{\circ}$ C. *Bottom*: Rate dependence on solvent molar mass ( $\bullet$ ) and dielectric constant ( $\blacksquare$ ) as indicated by trend lines.

complexes of Hg, Pt, Pd, Ag and Bi were seen to be photochromic at room temperature [11].

Rate measurements of the return reaction of DPM were made in the five solvents; dichloromethane, toluene, tetrahydrofuran, diethyl ether and acetone (see Fig. 5 (top)). In order to make standard UV/visible measurements, *i.e.* without the use of specialized equipment, fast reactions in the more polar solvents had to be slowed down by cooling all solutions to 10 °C.

A rough correlation was found between the observed rates and corresponding solvent dielectric constants and molar masses (Fig. 5, bottom). This observation corresponds to earlier results from measurements done in benzene and tetrahydrofuran [12]. As return of the photochromic reaction merely involves free rotation of the –NN(H)Ph moiety of DPM in solution, resistance against this motion is expected to increase as the molar mass of the surrounding solvent increases, *i.e.* a reflection of inertia in solvent molecules. Accordingly it was found that the highest return rate occurs in acetone (k=0.0939 s<sup>-1</sup>), which has the smallest molar mass and highest dielectric constant. The lowest rates are consequently observed in dichloromethane (k=0.0008 s<sup>-1</sup>) and toluene (k=0.0083 s<sup>-1</sup>) (see Table 2).

Lastly, a kinetic study involving the series of twelve electronically altered dithizonatophenylmercury(II) complexes was done. Observed rates for the spontaneous back reactions in dichloromethane at 20 °C are listed in Table 3. The highest rate in the series was found for the *meta*-methoxy compound, with k being  $0.0106 \, \text{s}^{-1}$ , which is 53 times faster than the lowest rate of  $0.0002 \, \text{s}^{-1}$  of the *ortho*-methyl compound. Apart from the *ortho*-methyl complex also absorbing the highest energy photons, *i.e.* 

#### Table 2

Rates of the spontaneous reverse reaction of DPM in five solvents at 10 °C, arranged in ascending order, related to solvent molar mass (MM), dielectric constant ( $\varepsilon$ ) and  $\lambda^*$  of the photo-induced blue isomer.

Solvent	Rate (s <sup>-1</sup> )	$MM (g mol^{-1})$	ε	$\lambda^* (nm)$
DCM	0.0008	84.93	8.9	590
Toluene	0.0083	92.14	2.4	603
THF	0.0250	72.11	7.6	600
Ether	0.0309	74.12	4.3	598
Acetone	0.0939	58.08	20.7	602

#### Table 3

Reaction rates of the spontaneous reverse reaction of DPM and eleven electronically altered derivatives  $(3 \times 10^{-5} \text{ M})$  in DCM at 20 °C, arranged in increasing order.

Substituent	Rate
2-CH <sub>3</sub>	0.0002
4-F	0.0003
2-OCH <sub>3</sub>	0.0003
2-SCH <sub>3</sub>	0.0004
2-F	0.0006
4-CH <sub>3</sub>	0.0012
3,4-(CH <sub>3</sub> ) <sub>2</sub>	0.0013
4-SCH <sub>3</sub>	0.0017
3-CH <sub>3</sub>	0.0020
Н	0.0024
3-F	0.0038
3-OCH <sub>3</sub>	0.0106

Trend line fits gave  $R^2 > 0.98$ .

having the smallest  $\lambda_{max}$  values (see Table 1, 2-CH<sub>3</sub> –  $\lambda$  and  $\lambda^*$ ), no other correlations between reaction rate and absorbance maxima are seen. Also, no correlation is found with the well-known Hammett constants [28] and relative group electronegativities [29]. Together with altered electronic influences obtained by the systematic phenyl substitution pattern in the current photochromic series, steric effects, hydrogen bonding and non-bonding interactions, etc., are all expected to influence the back-isomerization of the photoinduced state. Thus, no simple explanation may be given for the observed trend. Nevertheless, a general internal trend is observed which may be seen in the ortho-substituted photo-induced isomers being most stable (with the exception of 4-F), as is reflected by corresponding lowest reaction rates. These are followed by the para-substituted species, while the meta derivatives (including the unsubstituted DPM, H) gave the highest rates. Only the meta-fluoro and meta-methoxy compounds have faster rates than the parent DPM compound, while all other substituents slowed down the reverse reaction.

#### 4. Conclusion

Modification of earlier methods simplified the synthetic procedure and brought about increased yields for the series of twelve photochromic dithizonatophenylmercury(II) complexes, *via* the nitroformazan intermediate and dithizone free ligand. Computed molecular orbitals correspond to the observed isomerization reaction by revealing a single C–N bond in the LUMO, which allows free rotation around this axis, as opposed to the HOMO C=N double bond. A comprehensive kinetic study of the spontaneous radiationless thermal back reaction of the photochromic mercury complexes illustrates rate constants dependent on temperature, solvent and phenyl substituent.

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