Polyhedron 179 (2020) 114386

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Synthesis, DFT and kinetic studies of chromic S-methyldithizone

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ARTICLE INFO

Article history: Received 18 November 2019 Accepted 19 January 2020 Available online 22 January 2020

Keywords: Photochromic Chronochromic Concentratochromic Isomerization Computational

ABSTRACT

Dithizone is one of the most well-known trace-metal analysis reagents, however, its S-alkylated derivatives received very little attention up to date. Synthesis, kinetic studies of its photo- and chronochromic reactions, as well as DFT and TDDFT results are presented here. For comparitive purposes the corresponding phenylmercury complex was also synthesized and included in this study. Blue-shifts in λ_{max} of the S-methylated compounds are in excess of 60 nm as compared to the metal complex. Relative geometry optimized energies, atomic charge distribution in conjunction with ¹H NMR, as well as TDDFTs all point to the pink *syn* geometry of S-methyldithizone as the prevalent isomer, with the yellow *anti* geometry only of slightly higher (3.8 kJ/mol) energy. B3LYP provides significantly better UV-visible spectrum approximation than LC-BLYP, OLYP and PW91. At 20 °C the rate of the chronochromic reaction is 0.0073 s⁻¹ in chloroform, and that of the photochromic return reaction is 0.0023 s⁻¹ in ethanol.

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1. Introduction

The (S-CH₃)HDz derivative of dithizone, H₂Dz, that is methylated on the sulphur position, was originally prepared by Irving *et al* [1]. This was accomplished in various ways; most conveniently by reacting dithizone in alkaline solution with $(CH_3)_2SO_4$ (see Scheme 1), otherwise by the reactions of CH₃I with Ag(HDz), or NaSCH₃ with 1,5-diphenyl-3-chloroformazan. Prior complexation with certain metals like Ag, Ni and Pd increases reactivity at the sulphur position, which then readily reacts with the alkyl group [2]. Methylation of ClHgHDz was also successful, however only in polar medium like ethanol, while refluxing for several hours.

Another more elaborate route by which S-alkylation is accomplished is to increase the nucleophilic nature of sulphur by first oxidizing H_2Dz to the cyclic dehydrodithizone compound, Dz (Scheme 1, *bottom left*) [3]. Reactions of the zwitter-ionic Dz with eg. I-CH₃ and Cl-CH₂COOH, even in non-polar chloroform, form RDz⁺X⁻ water-soluble salt products. Br-alkyls do not react with Dz, however, addition of 1,8-diazobicyclo-[5,4,0]undec-7-ene (DBU) had been shown to successfully catalyze the reaction [4]. Reduction of RDz⁺X⁻ by means of alkaline solutions of dextrose or ascorbic acid opens the tetrazolium ring again, to give the S-functionalized dithizone, (S-R)HDz [3].

As for (S-CH₃)HDz and its *ortho*-tolyl (with –CH₃ substituents on the phenyl rings) homologue in solution, immediately after

* Corresponding author. *E-mail address:* veschwkg@ufs.ac.za (K.G. von Eschwege). dissolution the colour in chloroform is reported to be pink [5]. Over time, however, partial isomerization from the pink to the yellow isomer was observed. Addition of trace amounts of acid or base to pink chloroform solutions was found to greatly accelerate isomerization to the yellow isomer (λ_{max} = 425 nm), while in turn, exposing yellow solutions to light, reverses the reaction to yield the original pink form (λ_{max} = 550 nm).

Solid state crystal structures of both the (S-CH₃)HDz and (S-CH₂COOH)HDz derivatives were published. The geometry of the carboxylic acid ligand corresponds to L1 (see Fig. 1 *syn* (*top*), and Table 1) [6]. Interestingly, different isomers for the methylated derivative were reported in two separate X-ray crystallography studies; the one geometry corresponding to the pink L1 isomer (Fig. 1, *syn*), [7] and the other to the yellow L2 isomer (*anti*) [8].

Hutton and Irving did ¹H, ¹³C and ¹⁵N NMR studies of S-methylated dithizone in solution. Differences in chemical shifts and coupling constants, and equilibria were explained in terms of four tautomers, where intra-molecular proton transfer between backbone nitrogens occur, as well as rotation around the nitrogen-carbon bonds, i.e. the carbon that is bonded to sulphur (see various tautomers in Table 1). Infra-red and resonance Raman studies of this compound in general agree with these findings [10,11], namely isomerization between ultimately the pink L1 and yellow L2 geometries. An equilibrium between symmetrical forms of the pink L1 isomer was also proposed, where the imine proton on the first backbone N is intramolecularly transferred to the last N, *via* the closed-ring L3 (see Table 1) intermediate.

In view of the natural affinity of the unsubstituted dithizone parent compound for a large number of metals, and its consequent









Scheme 1. Three synthesis pathways (*left*) of S-methyldithizone, (S-CH₃)HDz (*centre*), from dithizone, H₂Dz, which is then complexed with phenylmercury chloride in the presence of a strong base. Diluted acids demethylate the complex ligand (*right*).

extensive application in trace metal analyses, Loredo and Grote did an investigation into phenyl carboxy-substituted S-decyl dithizone as solvent extractant for precious metals [4]. Where-as the decyl substituent increased solubility in non-polar solvents, metal extraction ability was debilitated. From a multitude of analytical chemistry reports it may be seen that unsubstituted dithizone often complex a variety of metals without addition of base, while



Fig. 1. *Top*: Pink L1 and yellow L2 isomers of S-methyldithizone, (S-CH₃)HDz, as reported in two separate X-ray crystal studies [7,8]. *Bottom*: Corresponding photochromic complex blue (*left*) and orange (*right*) isomers, where instead of the CH₃ group, a metal is bonded to the ligand sulphur [9].

in other cases the presence of only a weak organic base is sufficient to singly deprotonate H_2Dz to its anionic form. The remaining backbone imine proton in (S-CH₃)HDz is however much less labile and requires a strong base to for instance complex mercury, as will be seen in the Experimental section here below.

The above-mentioned studies represent almost all the work that had up to date been done on this class of S-alkylated compounds. In the present study we resolved to do a proper DFT investigation of the chromic properties of S-methyldithizone, while also including its phenylmercury complex. The reaction rates of the chronochromic reaction, as well as photochromic back reaction of $(S-CH_3)HDz$ at various temperatures was experimentally determined.

Traditionally the photochromic behaviour of the dithizonato metal complexes received extensive attention, with the mercury complex having been at the centre of attention [9,12]. Here, colour change from orange to blue (see Fig. 1 *bottom*) occur only as a result of exposure to bright light, which then is instantaneously followed by the spontaneous thermal reaction, reverting to the orange resting state geometry. Of particular interest now is to also investigate properties of the reaction where the metal is replaced by an organic moiety, where addition of alkane substituents to the sulphur atom in the ligand represents the first step in a larger series of studies that may eventually develop into tri-dentate ligands, or ligands with more than one photochromic moiety, etc.

2. Experimental methods

2.1. General

Synthesis reagents (Sigma-Aldrich) and solvents (Merck, AR grade) were used without further purification. UV–visible spectra and reaction kinetics studied on a Shimadzu UV-2550 spectrophotometer fitted with a Shimadzu CPS temperature controller, using a quartz cuvette. Photochromic studies were performed using a 400 W mercury-halide lamp. ¹H NMR spectra were obtained on a 300 MHz Bruker Fourier NMR spectrometer at 25 °C.

Table 1

Structures and DFT computed energies of the six most probable isomers of $(S-CH_3)HDz$, and the two complex isomers of $C_6H_5Hg(S-Me)Dz$. Energies are indicated to be relative to the lowest energy isomers, L1 or C1.

Isomer	Structure	E (kJ/mol)				
		B3LYP	LC-BLYP	OLYP	PW91	
L1 pink	S N N H	0.0	0.0	0.0	0.0	
L2 yellow		3.8	5.4	3.4	4.6	
L3	S N N N H N O	13.6	15.8	15.0	12.3	
14		24.7	22.1	23.5	28.2	
L5	S H-N N=N	66.7	55.5	72.9	67.3	
L6		89.1	76.6	87.0	80.3	
C1		0.0	0.0	0.0	0.0	
C2		22.3	19.8	19.9	24.3	

2.2. Synthesis

a. S-Methyldithizone (adapted dimethylsulfate method) [5]: A solution of dithizone (5.0 g, 19.5 mmol) in aqueous sodium hydroxide (0.5 M, 100 mL) was shaken well with dimethylsulfate (1.9 mL, 2.6 g, 20.6 mmol) in a glass stoppered flask. The initial orange colour of the solution rapidly disappeared and a black solid separated almost immediately. A further portion of the NaOH solution (15 mL) was added, and the mixture was heated gently on a water bath for 30 min to destroy any excess dimethylsulfate. On cooling, the mixture was extracted with chloroform and the organic extract was washed several times with dilute aqueous ammonia (to remove unmethylated dithizone) and with water,

and finally the organic extract was dried over sodiumsulfate. The resulting S-methylated dithizone was purified by chromatography on 100 g silica, using chloroform as eluent. The dark brown product band, running ahead, was followed by narrower light brown, light green, and pink bands. Recrystallization from warm ethanol (700 mL) gave 3.48 g black S-methylated dithizone needles with a bronze reflex (66%).

Mp 118–120 °C, λ_{max} /nm (dichloromethane) 542, ¹H NMR (300 MHz, CDCl₃) (two isomers): δ 2.41 & 2.55 (3 H, 2 × s, CH₃), 7.05 – 7.97 (10 H, 3 × m, C₆H₅), 9.53 & 10.27 (1 H, 2 × s, NH).

b. S-Methyldithizone (methyliodide method) [13]: Methyliodide (0.05 g, 0.34 mmol) was added to potassium dithizonate (0.05 g, 0.17 mmol) dissolved in acetone (40 mL). While stirring the solution at room temperature for 1 h, the orange colour changed to deep purple. The reaction mixture was filtered and the solvent removed under reduced pressure. The residue was dissolved in dichloromethane (100 mL), leaving potassium iodide and any unreacted potassium dithizonate behind. After a second filtration the solvent was removed under reduced pressure, and recrystallization done from ethanol (100 mL). The black S-methylated dithizone crystals were washed with 1 M aqueous ammonia (to remove unmethylated dithizone), followed by water, and a small amount of ice cold ethanol to give 0.0269 g (64%) pure product.

Characterization data agreed with that of published method (a) here above.

c. S-Methyldithizonatophenylmercury(II): Phenylmercury(II) chloride (0.58 g, 1.85 mmol) and S-methyldithizone (0.5 g, 1.85 mmol) was dissolved in dichloromethane (100 mL) in a separating funnel. An aqueous solution of sodium hydroxide (0.2 M, 100 mL) was added, and the funnel shaken well. The organic layer was washed several times with distilled water and dried by filtration through sodium sulphate. The solvent was removed under reduced pressure and recrystallization done from dichloromethane and ethanol, yielding 0.95 g (94%) pure product.

Mp 143 °C, λ_{max} /nm (dichloromethane) 442 & 600, ¹H NMR (300 MHz, CDCl₃): δ 2.53 (3 H, s, CH₃), 7.02 – 7.980 (15 H, m, $3 \times C_6H_5$).

2.3. Quantum computational methods

Density functional theory (DFT) calculations were performed utilizing the Gaussian 09 calculation package [14]. Full geometry optimization and TDDFT as implemented in Gaussian 09 were done. The triple- ζ basis set 6-311G(d,p) [15,16] in combination with a variety of functionals were used: B3LYP [17,18,19], BLYP [20,21], OLYP [22], and PW91 [23]. For calculations involving Hg, the triple- ζ 6-311G(d, p) basis set was used for lighter atoms (C, H, N, S), the Stuttgart/Dresden (SDD) pseudopotential for describing the Hg metal electronic core, and the def2-TZVPP basis set for the metal valence electrons [24]. Calculations were conducted in gas, as well as in the ethanol solvent phase. For the solvent calculations the solvation model density (SMD) [25] polarizable continuum model (PCM) was used, with an integral equation formalism variant (IEF-PCM) [26]. TDDFT calculations to generate UV-visible spectra were carried out on the optimized geometries in both gas phase and ethanol as solvent. All structures were confirmed to be true minimum structures by a frequency analysis, i.e. no imaginary frequencies. Input coordinates for the compounds were constructed using Chemcraft [27]. Optimized coordinates of the DFT/B3LYP gas phase calculations are provided in the Supporting Information.

3. Results and discussion

3.1. Synthesis

H₂Dz reactions with metals often require the presence of base to singly deprotonate the ligand backbone. Using the ready deprotonated potassium salt, K⁺HDz⁻ instead (see Scheme 1) [28,29], is a convenient alternative that does not require possibly interfering bases during such reactions. The negative charge in K⁺HDz⁻ is located on the sulphur atom, which, during methylation with methyliodide, makes it ideal for nucleophilic attack on the δ + methyl carbon in CH₃I, yielding (S-CH₃)HDz. In par. 2.2*b* above, this method is reported, illustrating similar yield as in the traditional reaction done with dimethylsulphate (par. 2.2*a*), namely *ca* 65% [5]. As opposed to the newly reported KHDz route, the latter method however requires additional product purification by column chromatography.

During product characterization clear evidence for solution equilibrium between the two structural isomers of $(S-CH_3)HDz$ was observed in the ¹H NMR spectrum obtained in deuterated chloroform. Fig. 2 shows two methyl singulets at 2.41 and 2.55 ppm, of which the sum of the integration values add up to the required total of 3 for the three methyl protons. The same is true for the imine proton signals at 9.53 and 10.27 ppm, adding up to 1, and the *para*-phenyl protons at *ca* 7.9 and 7.1 ppm, adding up to 2. The integration ratio's of all three these sets of protons being 2 : 1 are indicative of a 2 :1 concentration ratio between the L1 and L2 isomers in CDCl₃ at room temperature in this particular solution.

Assignment of these signals is supported by DFT-computed atomic charge distributions, where all the backbone nitrogens in both isomers are partially negatively charged, as opposed to the δ -positive sulphur moiety. With the imine H in L1 close to the third backbone N (with which hydrogen bonding is expected) this



Fig. 2. ¹H NMR of (S-Me)HDz in CDCl₃. Relative integral values and chemical shifts at *ca* 2.50 and above 9.50, are indicative of two structural isomers.

proton will be significantly more shielded than in the case of the L2 isomer where it is close to the δ -positive S atom. The more prevalent L1 signal at 9.53 ppm is therefore in perfect agreement with the tautomer of lowest computed energy being that of the L1 isomer, as will be seen in the next section. The chemical shift between the methyl signals of the two isomers is as expected less pronounced, as it does not experience such a large change in chemical environment. A similar chemical shift was reported by Romero *et al*; in the *E*/*Z* isomerization of a nitro-substitued hydrazone, where the *Z* isomer shields the imine proton in the intramolecular N–H…N bond [30].

The reaction of $(S-CH_3)HDz$ with metals, eg. C_6H_5HgCl in this case, requires a strong base like sodium hydroxide to remove the imine proton, which then allows for complexation with the $(S-CH_3)Dz^-$ anion. The green $C_6H_5Hg(S-CH_3)Dz$ complex yield is almost quantitative and do not require additional purification. Care must however be taken, as the labile methyl substituent is readily removed by the presence of weak acid, giving the orange C_6H_5HgHDz complex, see Scheme 1. Even the minute amounts of HCl often present in deuterated chloroform may re-protonate the ligand, as signalled by a color change from yellow-green to orange. Efforts to grow sizeable single crystals of the methylated complex that are suitable for X-ray crystallography were unsuccesful. It was consequently decided to include a theoretical structure optimization of also the phenylmercury complex in the present study.

3.2. Spectroscopy and kinetics

The UV-visible electronic spectra of intensely colored dithizone, its derivatives and complexes, are highly sensitive to chemical changes, eg. an acetone solution of the H₂Dz starting material has a typical blue-green colour (H₂Dz: λ_{max} = 444 & 612 nm), which changes to orange-red when stripped of one proton (KHDz: λ_{max} = 502 nm). Methylation changes the colour to purple ((S-CH₃)HDz: λ_{max} = 542 nm), while consequent complexation with phenylmercury(II) results in a deep green colour (C₆H₅Hg(S-CH₃) Dz: λ_{max} = 442 & 600 nm). Demethylation of C₆H₅Hg(S-CH₃)Dz, or direct complexation of Hg with H₂Dz, gives the familiar orange photochromic complex that changes colour to blue in the presence of bright light (C₆H₅HgHDz: $\lambda_{max} = 470 \leftrightarrow 590$ nm, in DCM) [9]. Interestingly, the two absorption bands observed in the visible spectra of both the methylated complex and unsubstituted dithizone overlaps almost perfectly. The molar absorptivities (ε) are different though, where for H₂Dz, $\epsilon_{(612 nm)} > \epsilon_{(444 nm)}$, while for $C_6H_5Hg(S-CH_3)Dz$, $\varepsilon_{(600 nm)} < \varepsilon_{(442 nm)}$, see Fig. 3 (left- and rightmost absorbance peaks of both compounds).



Fig. 3. UV/vis spectra (λ_{max} , from *left* to *right*) of C₆H₅Hg(S-CH₃Dz), K⁺HDz⁻, (S-CH₃) HDz (L1 pink isomer) and H₂Dz, in acetone (concentrations not similar). Line colors correspond to solution colors.



Fig. 4. Photochromic reaction of 3.24×10^{-5} M S-methylated dithizone in ethanol at 20 °C, in a 1 cm cuvette, during 5 s exposure to bright light. Line colors correspond to solution colors. (The chronochromic reaction in chloroform is opposite to the indicated direction.)

As previously reported [5,31], (S-CH₃)HDz auto-isomerizes from the freshly dissolved pink solution to yellow over time, and thus undergoes a form of chronochromism. The spectra of the two isomers, with λ_{max} at 540 and 410 nm and isosbestic points at 350 and 474 nm are shown in Fig. 4. This chronochromic colour change in non-polar chloroform ($\varepsilon = 4.8$ [32]) proceeds in the same pinkto-yellow direction as observed for the photochromic reverse reaction of the same compound in ethanol (ε = 25.3). The polar reaction medium where-in photochromism of this purely organic compound is visible is different to metal dithizonates, where photochromism is visible only in mostly non-polar solvents. In polar medium like methanol (ε = 33.0) the reaction of metal dithizonates is so fast that it may be observed only by femtosecond laser spectroscopy [33,34]. In non-polar solvents the back reaction of the mercury complex is slowed down to several minutes in selected cases [35,36]. This is vastly different to (S-CH₃)HDz where polar solvents instead stabilize the photo-induced pink isomer more so than non-polar solvents. Even in very polar DMSO (ε = 47.2) we observed (S-CH₃)HDz to be photochromic.

The effect of replacing the Hg metal on the ligand sulphur with an organic methyl group resulted in a blue-shift of 61 nm in acetone, i.e. from 471 (orange) [35] to 410 nm (yellow), and 63 nm for the corresponding photo-generated isomers, i.e. from 603 (blue) to 540 nm (pink). This shift is significantly more pronounced than the 37 nm that is reported for when phenyl substituents on the ligand are varied from strongly electron donating to strongly electron withdrawing [34]. Exposure of an ethanolic (S-CH₃)HDz solution to direct sunlight results in a color change from yellow to pink, which spontaneously reverses in shade, i.e. the peak at 540 nm disappears while the peak at 410 nm re-appears. The absorbance peak shift of 130 nm between these two ground state isomers is comparable to the 120 nm corresponding shift seen between the blue and orange isomers of PhHgHDz.

Kinetic data of the photochromic back reaction of $(S-CH_3)HDz$ in ethanol (pink \rightarrow yellow) is shown in Fig. 5. Photo-excitation of dilute solutions in a quartz cuvette was accomplished with a 400 W mercury-halide lamp, which closely simulates daylight. After apparent full color conversion in the bright light, solution absorbance was monitored at constant temperature in a UV-visible spectrometer at the absorbance maximum of the yellow isomer, namely 410 nm. This reaction is, as for the dithizonato metal complexes, also temperature dependant, see Fig. 5 (*bottom*). The plot of $\ln(k/T)$ where k is the reation rate, vs 1/T with T being the absolute temperature, shows the expected almost perfect linear relationship (R² = 1.00). From the Eyring equation (see insert



Fig. 5. *Top*: Linear correlation plots of $\ln[A_0/A_t]$ vs time shows first order kinetics in the spontaneous photochromic back reaction of (S-Me)HDz at different temperatures in ethanol. (**X** – 10, **=** – 20, **•** – 30, **•** – 40, **•** – 50) °C. The *insert* give measured absorbance vs time for the appearance of the peak at 417 nm at 20 °C. *Bottom*: The trend line through the Eyring plot shows a linear correlation with $R^2 = 1.00$. *Insert*: Eyring-Polanyi equation.

in Fig. 5, bottom) the enthalpy of activation, ΔH^* , may be derived from the slope term, $\Delta H^*/RT$, while the entropy, ΔS^* , is obtained from the intercept term, $\Delta S^*/R + \ln(k_B/h)$. These values are found to be 27 kJ/mol and -191 J/K/mol respectively.

Kinetic data of the chronochromic reaction (pink \rightarrow yellow) of a freshly prepared pink (S-CH₃)HDz solution in CHCl₃ is shown in Fig. 6. The chronochromic reaction is comparable to the above photochromic return reaction in that both represent pink L1 to yellow L2 isomerization. At 20 °C a rate of 0.0073 s⁻¹ is found for the chronochromic reaction, which is more than three times faster than the photochromic return reaction rate (k = 0.0023 s⁻¹) at the same temperature. This difference is attributed to the different solvents, i.e. chronochromism for this purely organic compound is observed in mainly non-polar solvents and photochromism in polar solvents. The faster chronochromic rate in non-polar chloroform (pink \rightarrow yellow) is therefore consistent with the observation that the photo-excited pink L1 isomer is better stabilized by polar solvents.

3.3. DFT studies

For the first time Density Functional Theory was involved in the study of S-alkylated dithizones. Geometry optimizations using four different basis sets had been done on the six most likely isomers of (S-CH₃)HDz. Results from the four sets were consistent in establishing the *syn* L1 isomer to be of lowest energy, and thus the



Fig. 6. The chronochromic auto-isomerization reaction of (S-Me)HDz at 20 °C in chloroform shows first order kinetics, as illustrated by the linear plot of $\ln[A_0/A_t]$ vs time. *Insert*: Measured absorbance vs time for the appearance of the peak at 417 nm.

preferred geometry, see Table 1. The geometry optimization energy of the linear *anti* L2 isomer is only slightly higher, namely 3.8 kJ/mol (B3LYP). These lowest and relative close energies are consistent with the two different isomers found in the X-ray single crystal studies mentioned earlier.

Relative to the energies of the former two isomers, a significant increase in geometry-optimized energy is seen for the remaining four isomers, varying from 13.6 kJ/mol for the L3 isomer to 89.1 kJ/mol for L6. The large energy difference between L3 and those



Fig. 7. B3LYP TDDFT (ethanol as solvent) computed oscillators (*bars*) overlaid with experimental UV-visible spectra (also in ethanol) of the pink L1 isomer (*top*) and the yellow L2 isomer of (S-CH₃)HDz [31]. The L1 shoulder at 420 nm (*top*) and L2 shoulder at 540 nm (*bottom*) are due to partial L1 \leftrightarrow L2 isomerization.

of the L1 and L2 experimentally found geometries therefore excludes L3 from room temperature equilibria, which finding is contrary to a previous proposal in this regard (see Introduction). The L3 configuration is however similar to the nitroformazan synthesis precursor of dithizone, which consistently crystallizes in the L3-type geometry [37–39]. Instead of the S moiety in (S-Me)HDz a NO₂ group is bonded to the backbone carbon in nitroformazan. The latter strongly electron-withdrawing substituent thus promotes the closed ring structure that is maintained by the N–H…N hydrogen bond in this configuration.

The various isomers of $(S-CH_3)HDz$ are different to those of H_2Dz . Apart from isomerization around bonds, H_2Dz tautomers are also formed by intramolecular proton transfer reactions. The first dithizone proton (that is otherwise readily substituted by a methyl group in $(S-CH_3)HDz$) is significantly more labile than the remaining imine proton in S-methylated dithizone, and thus readily transfers to neighboring N or S atoms, resulting in the various tautomers of H_2Dz [31].

Apart from computed relative energies, and ¹H NMR in combination with computed atomic charge distribution, also time dependant DFT/B3LYP-computed electronic oscillators give clear confirmation of the structural isomers responsible for particular colors in solution. From the (ethanol) TDDFTs of all six isomers unambiguous assignments could be made: the L1 oscillators correspond almost exactly to the UV-vis spectrum of the pink solution, with eg. the computed main oscillator being at 549 nm while experimental $\lambda_{max} = 542$ nm, see Fig. 7 (*top*). The higher energy oscillators below 400 nm correspond well to the overlap of absorbance bands seen in this region. The same is true for the L2 oscillators where the computed maximum is at 425 nm, also only 7 nm higher than the experimental absorbance maximum at 418 nm (Fig. 7, *bottom*).

None of the four highest energy isomer TDDFTs (L3 – L6) resemble the experimentally observed spectra of the pink or yellow solutions (see Supporting Information). Also, and as opposed to the above solvent calculations, gas phase did not give good resemblances; electronic transitions were blue-shifted, eg. peak maxima were computed to be at 512 nm for L1 and 402 nm for the L2 isomer. Lastly, TDDFTs computed with the PW91 and OLYP functionals resulted in large red-shifts, often more than 100 nm higher than

Table 2

B3LYP gas phase molecular orbital (MO) renderings of (S-CH₃)HDz L1 & L2 (*top*), $C_{6}H_{5}HgHDz$ c1 (*middle*) and $C_{6}H_{5}Hg(S-Me)Dz$ C1 & C2 (*bottom*). C-N axes of rotation are indicated by red arrows. (MOs obtained with other functionals or in solvent phase are similar to gasphase MOs.)



experimentally observed maxima, while LC-BLYP computed the same transitions more than 100 nm too low. B3LYP was therefore the only functional that realistically resembled experimental spectra.

As for solutions of the metal complex, $C_6H_5Hg(S-CH_3)Dz$, two absorbance bands were experimentally observed in the visible region, peaking at 442 and 600 nm, see Fig. 2. As opposed to unsubstituted dithizone, H₂Dz, where both visible region absorbance bands are definitely associated with a single H₂Dz isomer (see spectrum in Fig. 2 and Ref. [40] for H₂Dz discussion), it is here proposed that the two bands of the $C_6H_5Hg(S-CH_3)Dz$ complex are representative of different isomers existing simultaneously in solution. Also, as opposed to unsubstituted C₆H₅HgHDz where the HOMO backbone C=N double bond requires photo-excitation to the LUMO C-N single bond before rotation may occur (see Ref. [9] for discussion), free rotation around the $C_6H_5Hg(S-CH_3)Dz$ HOMO C-N single bond (see Table 2) may readily occur in solution. TDDFT ethanol medium calculations of the C1 (see Table 1 and Supporting Information for TDDFTs) C₆H₅Hg(S-CH₃)Dz isomer reveals longest wavelength electronic oscillators at 435 and 448 nm (shoulder), which corresponds almost perfectly with the observed main experimental peak at 442 nm. Absence of lower energy (longer wavelength) oscillators confirms the C1 isomer as origin of this absorbance band. The TDDFT spectrum of C2 shows the expected red-shift, namely to 509 nm. Although this shift is less than seen experimentally (600 nm), it needs to be pointed out that this much lower intensity band is very wide, which may be indicative of a torsion angle that is not fixed, but enjoys greater rotational degrees of freedom. Such would be expected in view of the C-N bond being single, around which rotation may occur freely. What is therefore experimentally observed, is a solution mixture where C1 is the prevalent isomer.

Orbital renderings of $(S-CH_3)HDz$ clearly show simularity between the two photochromic compounds, with this ligand and the traditionally well-known photochromic C_6H_5HgHDz complex having similar electron distribution patterns along its photo-active backbones. In all cases significant electron density is, apart from along the backbone, also located on the protruding sulphur atom in the HOMOs. This is however not the case for any of the LUMOs, which is indicative of limited but directional intramolecular charge transfer away from the sulphur atom upon excitation of the HOMO.

Bond distances in (S-CH₃)HDz are theoretically simulated with a large degree of accuracy, differing from available experimental bond lengths by at most 0.04 Å, in some cases as little as 0.004 Å, see Table 3. Where as in general N–N and C–N single bond distances are *ca* 1.41 and 1.45 Å and the respective double bonds are 1.23 and 1.28 Å [41], the bond distances along the N and C backbone of the (S-CH₃)HDz ligand, both free and complexed, all lie in between these values. This is indicative of π -electron delocalization, which also includes the aromatic phenyl rings at opposite ends, as may also be seen for unsubstituted H_2Dz [42] and its mercury complex, see Table 3. This high degree of unsaturation lies at the basis of the high molar absorptivities, reflected in the intense colors of dithizone, its derivatives and complexes.

Bond strengths around the Hg atom undergo a complete change as a result of the S-methylation, with the Hg–S bond distance increasing by *ca* 0.5 Å. The concomitant shortening of the Hg–N bond shows a change from the weaker dative covalent bond in C_6H_5HgHDz to a direct covalent bond in the S-methylated complex. The S–C bond distance of 1.77 Å nevertheless stays largely unaffected whether methylated or not.

Lastly it should be noted that a clear change in N–C–S–CH₃ rotational angle between the L1 and L2 isomers are seen in the respective crystal structures (see Fig. 8 A & C). The L1 ground state isomer is almost perfectly planar, with the methyl group being rotated by only 5.72° out of the flat plain formed by the rest of the molecule. This orientation appears to be sterically favored, but may also be due to crystal packing effects, since this co-planar orientation is not supported by DFT single molecule calculations (Fig. 8 B). In the L2 photo-induced linear structure (C), however, the methyl



Fig. 8. Experimental (A & C) and computed (B & D) (S-CH₃)HDz geometries of the pink L1 (*top*) and linear yellow L2 (*bottom*) isomers. The backbone imine protons (H) are indicated.

Table 3

Selected X-ray single crystal and B3LYP-calculated bond lengths (Å) of the two isomers of $(S-CH_3)HDz$ and $C_6H_5Hg(S-CH_3)Dz$. For comparison purposes bond lengths of the photochromic C_6H_5HgHDz are also included. Nitrogens are numbered along the ligand backbone, with N1 carrying the imine proton.

	X-ray			DFT					
	(S-CH ₃)HDz		H ₂ Dz [28]	(S-CH ₃)HDz		PhHgHDz		PhHg(S-CH ₃)Dz	
Bond	L1 [7]	L2 [8]		L1	L2	c1	c2	C1	C2
Hg-S	-	-	-			2.399	2.380	2.908	2.950
Hg-N1	-	-	-			2.677	2.739	2.146	2.136
S-CH ₃	1.790	1.859	-	1.833	1.836	-	-	1.833	1.830
S-C	1.758	1.762	1.712	1.786	1.808	1.778	1.779	1.803	1.793
N1-N2	1.344	1.337	1.295	1.319	1.315	1.316	1.317	1.263	1.262
N2-C	1.300	1.368	1.345	1.308	1.302	1.312	1.315	1.383	1.397
C-N3	1.391	1.328	1.334	1.389	1.387	1.378	1.376	1.304	1.295
N3-N4	1.266	1.300	1.299	1.262	1.260	1.261	1.265	1.306	1.313

group is rotated by 85.21° out of the plain, which is in agreement with *ab initio* DFT approximation (D).

4. Conclusion

(S-CH₃)HDz was obtained as pure product by reaction of the KHDz dithizonate salt with CH₃I. Instead of metalation at the sulphur position, methylation also yields a photochromic product, however with different solvent behavior; the photochromic back reaction in the metal complex is slowed down in non-polar solvents, while in the methylated compound it is slowed down in polar solvents. DFT clarified the geometries of both (S-CH₃)HDz and PhHg(S-CH₃)Dz unambigiously, eg. by determining geometries of isomers in solution and thereby also the origins of its observed chromisms. The colors of these compounds, as seen in its photo-, chrono- as well as concentratochromisms, are readily corroborated by time-dependant DFT calculations, and are very sensitive to synthetic and physical alterations.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work is based upon research supported by the South African National Research Foundation (Grants 113327 and 96111) and the University of the Free State. The CHPC of South Africa and the High Performance Computing facility of the UFS are acknowledged for computer time.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.poly.2020.114386.

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