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MO–LCAO Calculations on Polymethines: XXIII—The Origin of the Absorption Colour of Dithizone and Related Compounds

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SUMMARY

The two intense absorption bands of dithizone at about 440 and 620 nm give rise to the green colour observed in solution. In contrast to the view prevailing in the literature, the two colour bands are due to a single tautomer that has the diazatrimethinium thiolate rather than thiocarbazone or mercaptoformazan structure. This follows from quantum-chemically supported colour–structure relationships between dithizone and related compounds. Chromophorically dithizone belongs to the cyanine dyes. Internal substitution of CH of the trimethine chain by aza-type nitrogen atoms and additional meso-substitution by thiolate sulfur imparts to the trimethine cyanine a significant bathochromicity and brings about its unique chromophoric properties due to its two intense colour bands.

1 INTRODUCTION

As a versatile reagent in analytical chemistry dithizone has attracted permanent interest for more than 50 years.[1–3] Surprisingly, however, the

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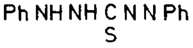
structure of this compound continues to be controversial and three tautomeric structures of general formulae **1**–**3** are still under discussion:

$\mathrm{PhNHN}\underset{\mathrm{S}}{\mathrm{C}}\mathrm{NNHPh}$

1



$\mathrm{PhNHNH}\underset{\mathrm{S}}{\mathrm{C}}\mathrm{NNPh}$

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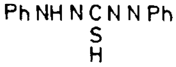


$\mathrm{PhNHN}\underset{\underset{\mathrm{H}}{\mathrm{S}}}{\mathrm{C}}\mathrm{NNPh}$

3

There are serious arguments in favour of **1**. According to the X-ray study of Laing[4] and a later analysis of these results by Kulpe and Seidel (cf. ref. 5) the molecule of dithizone is nearly C_{2v}-symmetrical in the crystal, i.e. the two hydrogen atoms of the chain are linked to the outer nitrogen atoms in accordance with formula **1**. Variable-temperature NMR studies of dithizone (down to $-90°C$) and its isotope-labelled analogues led Irving and Hutton[6,7] and Nöske[5] to the conclusion that the solid-state structure might be retained in solution. Additional arguments in favour of **1** have been postulated from IR[8] and Raman[9] spectroscopic studies and in investigations of the photochromic and thermochromic properties of dithizone in solution.[10]

In contrast, more recent studies[11–14] more or less adhere to the traditional view[2,3] that the two tautomers *N,N'*-diphenylthiocarbazone (**2**) and *C*-mercaptoformazan (**3**) are present in solutions of dithizone. According to ref. 13 a rapid equilibrium between **2** and **3** brings about the C_{2v}-averaged symmetry of the molecule suggested in the NMR spectrum. The most frequently presented arguments in favour of the two tautomers are based upon the two absorption bands in the visible region. This consideration goes back to early papers of Pel'kis and Dubenko.[15–18] The two bands differ in their relative intensity if the solvent is altered.[15,16] Moreover, replacement of the phenyl groups of dithizone by substituted phenyl groups weakens either one or the other of the two colour bands.[15–18] Constants of the tautomeric equilibrium have been calculated from the peak ratio of the two absorption bands.[17,18]

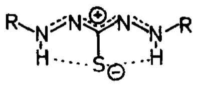
According to these studies the 610-nm absorption band is due to **2** and the 420-nm absorption band to **3**. In a slight modification, Uemura and Miyakawa[19] attributed two absorptions (at 440 and 620 nm) rather than one absorption to the 'ketonic' structure **2** and one absorption (at 465 nm) to the 'enolic' structure **3**. More recently Wagler and Koch[14] concluded, from a computer-assisted analysis of the spectra of dithizone in four different solvents, that both of the tautomers **2** and **3** absorb in both the 400- and the 600-nm region. According to their analysis, **2** absorbs more intensely at about 600 nm. The longest-wavelength absorption band of **2** is hypso- and hyper-chromically shifted relative to the corresponding absorption band of **3**. The tautomer **3** absorbs more intensely in the 400-nm region.

Until now quantum-chemical studies have tended to enhance the conflicts rather than produce a definitive answer to the problem. According to the first theoretical studies a single absorbing species is present in solutions of dithizone. This has been defined as **3** in one investigation[11] but as **1** in a second.[20,21] Based on experimental findings using IR spectroscopy[8] and X-ray diffraction,[4] the molecular structures of the all-*cis* configuration with intramolecular hydrogen bonds have been presupposed for the calculations. Spěváček and Spěváčková[11] carried out Pariser–Parr–Pople-type calculations of the π-electronic system and succeeded in defining two intense $\pi \rightarrow \pi^*$ transitions in the visible region (at about 410 and 800 nm). This result was obtained by a choice of parameters for sulfur, which in effect are relatable to the chelated SH substituent group. The presence of the tautomer **2** in solution was rejected because only a single $\pi \rightarrow \pi^*$ transition was calculated in the visible region (~435 nm). Tautomer **1** was not examined by these authors. Richter and Gdanitz,[20,21] on the other hand, derived the lowest-energy $\pi \rightarrow \pi^*$ transitions non-empirically using a more recently developed core potential method. Of the three tautomers under question they considered structure **1** only. They predicted the first two $\pi \rightarrow \pi^*$-type absorption bands in the near-infrared (~2600 nm) rather than in the visible region. These $\pi \rightarrow \pi^*$ transitions displayed extremely low transition probabilities. The three ensuing more intense shorter-wavelength $\pi \rightarrow \pi^*$ transitions were compared with the two colour bands of dithizone.

The aim of this present paper is to re-examine by quantum-chemical methods the tautomeric species that brings about the observed light absorption characteristics of dithizone. The tautomer **1** was of greatest interest because of the symmetric structure of dithizone in the solid state indicated by X-ray studies and also in solution as concluded from low-temperature NMR studies. Since numerical predictions may fail in π approximation because of the betainic electronic structure of **1** (*vide infra*) it appeared tenuous to draw firm conclusions from a few computations. Quantum-chemical considerations and calculations were thus used as a method to reveal or to substantiate colour–structure relationships between dithizone and related compounds. This approach simultaneously gives an interpretation of the nature of the chromophoric system of dithizone and shows why dithizone is green in solution.

2 QUALITATIVE THEORETICAL CONSIDERATIONS

The most attractive valence formula of the intramolecularly chelated tautomer **1** consists of two moieties, the *N*,*N*′-diphenyl diazatrimethinium chain and the thiolate (thioxide) sulfur in the meso-position. This composite molecule is represented by formula **4a**.



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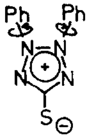

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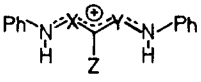

6

4	*R*
a	C_6H_5
b	p-$MeOC_6H_4$
c	p-$Me_2NC_6H_4$
d	p-$CH_3COC_6H_4$
e	$C_6H_4NO_2$
f	1-$C_{10}H_7$
g	2-$C_{10}H_7$
h	9-$C_{14}H_9$
i	H

6	*X*	*Y*	*Z*
a	N	N	SH
b	N	N	SMe
c	N	N	H
d	CH	N	H
e	CH	CH	H

The π-type interaction between the substituent and the chain is illustrated in Fig. 1. The appearance of two intense absorptions suggests that the orbital of the substituent is strongly involved in the two highest occupied molecular orbitals of **4a**. This is only to be expected if the substituent orbital is nearly isoenergetic with the HOMO of the trimethine chain. Efficient orbital splitting between the two localized occupied orbitals will then take place and produce two delocalized orbitals. As a result of this two electronic transitions from the two highest occupied MOs to the LUMO of the trimethinic chain should occur. This is illustrated in the upper panel of Fig. 1.

This can also be described in terms of electronic configurations based on the localized frontier orbitals of the chain and the substituent orbital. Thus, the electronic states of the composite molecule are represented by the no-bond (NB) configuration, the locally excited (LE) configuration of the trimethine chain and the charge-transfer (CT) configuration that is caused by electron excitation from the substituent to the chain. As long as only the frontier orbitals of the chain are considered, the NB configuration will not be stabilized by mixing with the CT configuration. The LE configuration of the chain will, however, mix with the CT configuration, giving rise to two excited states. Consequently, two intense absorptions should emerge if these configurations are present to a similar extent. This will occur if both the LE and CT configurations have similar energy (lower panel of Fig. 1).

A larger difference in energy will lead to the predominance of either the

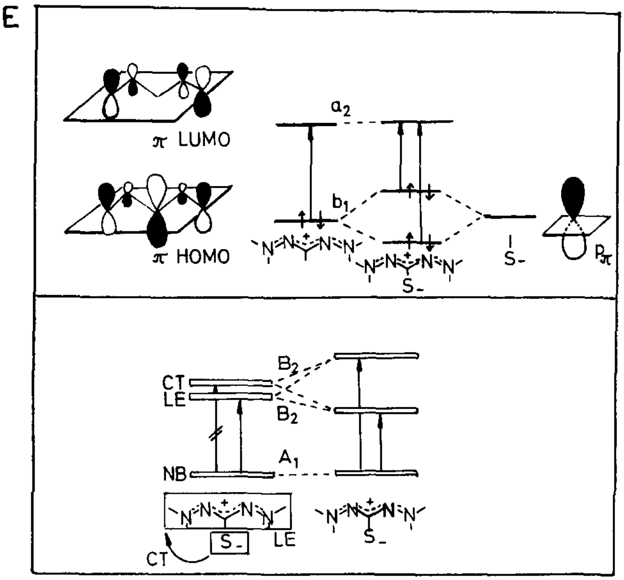

Fig. 1. The C_{2v} symmetric dithizone of molecular structure **1a** thought to be composed from diphenyl diazatrimethinium and thiolate sulfur. *Upper panel:* Frontier orbital interaction and electron excitation from the ultimate and penultimate occupied MOs of b_1-symmetry to the lowest unoccupied MO of a_2-symmetry. *Lower panel:* Configuration interaction in terms of the composite molecule approach (NB, no bond configuration; LE, locally excited configuration; CT, charge-transfer excited configuration) and electron excitation from the ground state of A_1 symmetry to the lowest-energy excited states of B_2 symmetry.

LE or the CT configuration in the excited state. Thus an intense LE band and a weak CT band will appear in place of two intense bands. The CT band is characterized by a strong change in the charge distribution on passing from the ground to the excited state. A pronounced solvent effect in terms of E_T solvent parameters will be the consequence. The relatively low effect of solvents on the position of the colour bands of dithizone is compatible with the concept that the LE and CT excitation are strongly mixed.

Additionally, structural modifications of the dithizone structure should disturb the above-mentioned balance between the LE- and CT-type excitations. The polymethinic chain may be enlarged or shortened, thus imparting to the longer or shorter wavelength absorption respectively more LE character. This effect is considered in the series **4**. A drastic effect should bring about cyclization of the chain at the terminal nitrogen atoms on passing from **4a** to **5**. Inspection of the frontier orbital depicted in Fig. 1 leads to the conclusion that the HOMO is stabilized whereas the LUMO is destabilized upon cyclization. Thus a short-wavelength absorption of the

LE type will result whilst a dominant CT transition remains at longer wavelengths. This band should display relatively low intensity and a pronounced solvent dependency. The *meso*-substituent itself can also be varied and used to lower the CT transition energy (series **6**). The CT excitation energy depends both upon the ionization potential of the

TABLE 1

Theoretical and Experimental Absorption Wavelengths λ (nm) and $\log \varepsilon$ Values (in Parentheses) in the Visible Region

Compound	*Theory*[a]	*Experiment*		*R*[b]	*Solvent*[c]	*Reference*
4a	610 (4·36), 436 (4·46)	617 (4·44),	447 (4·40)	1·09	H	
		622 (4·54),	453 (4·28)	1·80	B	
		607 (4·62),	445 (4·20)	2·59	C	
4b	638 (4·56), 463 (3·71)	646	476	2·96	B	17, 18
4c	720 (4·76), 491 (3·43)					
4d	625 (4·38), 439 (4·47)	650	455	0·79	A	17, 18
4e	643 (4·28), 433 (4·55)	—	550	—	A	17, 18
4f	668 (4·69), 487 (2·97)[d]	683	—		T	17, 18
4g	631 (4·69), 518 (2·62)	662	—			
4h	813 (4·72), 531 (2·87)					
4i	679 (3·56), 301 (4·59)[e]					
5	440 (3·54)	480 (3·03)			EA	31
6c	501 (4·73)	519 (4·47)			M/P	36–38
6d	469 (4·67)	450 (4·64)			C	42
6e	434 (4·62)	392 (4·63)			M	
7a	408 (4·63)					
7b	423 (4·52)	420 (4·25)			C	44
9a	408 (4·17)					
9b	368 (4·34)	394 (4·19)[f]			D	48
12	660 (4·18), 446 (4·41)					

[a] PPP calculations: up to 16 singly excited configurations (4 × 4). For parameters, except those of the intramolecularly chelated thiolate sulfur, see refs 23–25. $U_{S^-} = -20\,\text{eV}$ (average value of *U*-values of mercapto- and thiophenolato-type sulfur[26]), $\beta_{CS} = 0{\cdot}7\,\beta_{CC}$, $\gamma_{SS} = \gamma_{CC}$, $R_{CS} = 170\,\text{pm}$.

Theoretical $\log \varepsilon$ values are obtained from oscillator strengths by means of the equation $\log \varepsilon = \log f + 4{\cdot}5$. This equation is very crude because of the variable width of the absorption bands (the additive constant of the above equation used in the literature covers the range from 4 to 5). Oscillator strengths are transformed into ε-values only to facilitate the comparison between theory and experiment.

[b] $R = \varepsilon_{\max_1}/\varepsilon_{\max_2}$.

[c] A, acetone; B, benzene; C, chloroform; D, dioxane; EA, ethyl acetate; H, hexane; M, methanol; P, perchloric acid; T, carbon tetrachloride.

[d] There are additional weak absorptions at lower wavelengths in the visible region.

[e] Lowest energy $\pi \rightarrow \pi^*$ transitions according to CNDO/S all-valence electron calculations: 590 (3·28), 306 (4·46).

[f] Dimer.

substituent group and the electron affinity of the trimethine chain. PPP calculations[22] are used to pursue this general concept and to produce evidence in favour of the tautomer **1**. The results are shown in Table 1, together with relevant experimental data.

3 RESULTS AND DISCUSSION

3.1 Spectral absorptions of dithizones and related compounds

If the unsubstituted phenyl groups of dithizone are replaced by donor-substituted phenyl groups (e.g. on passing from **4a** to **4b**) the longer-wavelength absorption moves to red and increases in intensity (cf. Table 1). The first colour band is now significantly more intense relative to the second one. This is shown by the experimental peak ratio *R*: this ratio is larger for **4b** than for **4a**. *R* cannot, however, be defined for the naphthyl-substituted dithizones **4f** and **4g** because of the absence of the shorter-wavelength band in these compounds. The peak ratio is reduced on passing from **4a** to the acceptor-substituted dithizone **4d**.[17,18] Only a single short-wavelength colour band was observed for the nitro-substituted **4e**.

There is no necessity to explain these results in terms of the equilibrium between the 'enolic' and 'ketonic' tautomers as in refs 17 and 18. According to the PPP calculations this spectral behaviour is compatible with the presence of a single tautomer that has the diazatrimethinium thiolate structure. In the case of the donor-substituted phenyl or naphthyl derivatives of dithizone, the longest-wavelength transition is calculated to be more intense than the following $\pi \rightarrow \pi^*$ transition at higher energies (cf. Table 1). Thus the calculation reflects the higher peak ratio found experimentally with donor substitution. The lowest energy transition is then mainly localized on the chain. According to the alteration of the charge distribution upon excitation the first transition is of the LE type (trimethine chain) rather than of the CT type.† The CT contribution is stronger, however, in the case of the higher-energy transition and the

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† The effective charge transfer can be simply evaluated by the amount of electronic charge transferred from the substituent group to the chain. Within the approach depicted in Fig. 1, CT is inherent in the wavefunctions and is defined quantitatively if the delocalized wavefunctions are projected on to the wavefunctions of the fragmented molecule. This is carried out by configuration analysis[27,28] of the electronic states that are involved in the electronic transition of interest. Each electronic state is then defined in terms of NB, LE and CT configurations. Similarly, delocalized systems of different chromophores can be compared and analysed in terms of relatedness. The ensuing discussion refers to theoretical quantities obtained along these lines. For brevity, numerical results are not listed in this paper.

intensity of the latter is low. In the case of the naphthyl-substituted derivatives **4f** and **4g** this is one of several weak transitions. This may explain the experimental finding that the second absorption maximum band is not apparent in these compounds. The weak absorption is evidently submerged beneath the additional weak absorption bands. In the case of compounds **4** with terminal 9-anthryl residues (**4h**) the first intense colour band is expected to be shifted to the IR region (cf. Table 1).

The calculated two lowest-energy transitions of acceptor-substituted **4** are distinguished from those of the donor-substituted **4** by their inverse relative intensity (cf. Table 1). This result agrees with the relatively low peak ratio found experimentally for **4d**. The single colour band of the nitro-substituted dithizone in the 500-nm region is not satisfactorily compatible with formula **4e**. According to the calculations the colour bands of **4e** should not differ dramatically from those of **4d**. This striking discrepancy may indicate the presence of the mercaptoformazan tautomer due to the effect of the strongly electron-withdrawing NO_2 group on the NH acidity.

If H stands for R in **4**, two colour bands are anticipated (cf. Table 1). However, the CT excitation energy from S^- to the chain is now significantly lower than the excitation energy of the chain fragment. As a consequence, the longest-wavelength absorption of **4i** is predicted to be weak and the shorter-wavelength absorption to be intense.

The absorption feature of the mesoionic dehydrodithizone (**5**) is satisfactorily related to that of **4a**. The expected blue shift is corroborated theoretically. The blue shift is enhanced owing to the departure of the phenyl groups from the plane (about 45°).[29,30] The longest-wavelength absorption of **5** is correctly predicted to be of relatively low intensity. The electronic transition exhibits strong CT character.

The zwitterionic electron distribution is reduced upon excitation. This is fully in line with the negative solvatochromism of **5** and the correlation between the absorption wavelength and E_T solvent parameters.[31] The second $\pi \rightarrow \pi^*$ transition of **5** falls in the near-ultraviolet and does not contribute to the colour. It is mainly localized in the heterocyclic residue. In spite of the peculiarities of the two lowest excited states of **5**, these states are still clearly related to those of the dithizone molecule (see footnote †).

The colour band of **5** will undergo an extreme blue shift if the negative charge on the sulfur atom is completely removed by protonation or methylation. The resulting compounds are white salts.[31] These compounds only show $\pi \rightarrow \pi^*$ absorption bands in the UV region. Remarkably, even the dramatic blue shift on passing from dithizone (**4a**) to the hypsochromic derivatives of dehydrodithizone (**5**) does not cause the presumed IR absorption bands of dithizone[19] to enter the visible region.

Protonation and methylation of **4a** gives other well-known derivatives of the dithizone chromophore. The spectra of the corresponding ions **6a** and

6b exhibit the expected blue shift with respect to **4a**. In solution they are red in colour, **6a** absorbing at 520 nm[32] and **6b** at 530 nm.[5] The absorbing species belong, however, not necessarily to planar molecules. Thus, according to X-ray diffraction the SMe group of **6b** is tilted out of the plane.[33] The protonated dithizone, on the other hand, is assumed to be the *N*-protonated tautomer **2** in the di-*cis* configuration[32] rather than the *S*-protonated tautomer **1** (in the all-*cis* configuration). Various *meso*-substituted formazanium ions **6** (X = Y = N, Z = SO_3H,[34] CH, NO_2,[35] etc.) absorb between 520 and 570 nm but the molecular configurations have not been previously studied.

If the substituent in the *meso*-position is replaced by hydrogen on passing from **4a** to **6c**, a single intense absorption band emerges in the 500-nm region according to experimental[36–38] and theoretical studies (cf. Table 1). As expected from the qualitative considerations (Fig. 1) the absorption band of this parent chain molecule occurs at wavelengths between the two colour bands of dithizone. In accordance with polymethine colour rules[39–41] the aza nitrogen atoms are responsible for the marked red shift of about 100 nm when comparing the diphenyl trimethinium ion **6e** and the monoaza-substituted **6d** with **6c** (cf. Table 1).

Thus, the colour–structure relationships confirm that dithizone belongs chromophorically to the series **4**–**6**. The PPP calculations lead to the conclusion that the two strong absorptions of dithizone encompass two intense $\pi \rightarrow \pi^*$ transitions (Fig. 2). As expected by qualitative MO theory

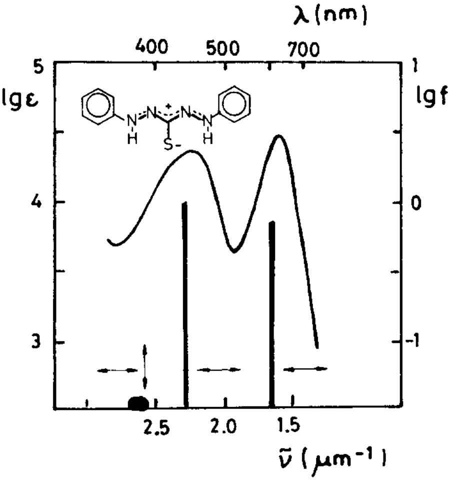


Fig. 2. Visible absorption spectrum of dithizone in cyclohexane and calculated $\pi \rightarrow \pi^*$ transitions. Vertical lines indicate the position and intensity of the calculated transitions. The height of the lines corresponds to the logarithm of the oscillator strength. Double-headed arrows illustrate the direction of the transition oscillators with respect to the molecular frame of the formula given.

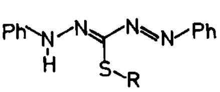
(Fig. 1), they are polarized perpendicular to the twofold axis. Dichroic measurements are necessary to support this point. In terms of the composite trimethinium thiolate structure both the LE and CT transitions participate in the two lowest-energy transitions. The charge on the sulfur atom is reduced upon excitation in both cases. The lowest-energy transition has a slightly larger CT contribution. Experimental results confirm that the first colour band is in fact slightly more sensitive to the solvent than the second band.[43]

It is thus not necessary to assign the first $\pi \rightarrow \pi^*$ absorption band of dithizone to considerably lower or considerably longer wavelengths than 600 nm. Thus a previous empirical assignment of the first intense absorption of dithizone to the $\pi \rightarrow \pi^*$ transition[5] and the second band to the lowest-energy transition is not substantiated by the results of this present investigation. Also, dithizone is definitely not an IR chromophore of the $\pi \rightarrow \pi^*$ type as claimed recently.[20,21]

3.2 The presence of isomers

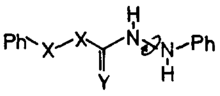
Although the calculated spectral data of **4a** match quite well the spectral features of dithizone it should also be considered that tautomers of **4a** are involved in its light absorption. The 'enolic' **2** should absorb in the 400-nm region and this is confirmed by the longest-wavelength absorptions of *S*-alkylmercaptoformazans (of all-*trans* configuration) such as **7**, which absorb near 400 nm[44] (cf. Table 1). Similarly, the disulfide which results from oxidation of dithizone absorbs at 410 nm.[45] Because of the distortion around the S—S bond the compounds should contain this chromophoric system twice. The long-wavelength absorptions of **7b** are well reproduced theoretically (cf. Table 1). Thus the absorption at 400 nm calculated for the colour band of the **3**-type tautomer **7a** should be reliable.

To predict the spectral feature of the 'ketonic' tautomers is more difficult due to a lack of structures containing this chromophore. The theoretical calculation presupposed non-coplanarity of the tautomer **2** because of distortion about the hydrazinic N—N bond structure (cf. **8**). This assumption is confirmed by results of X-ray studies on diphenylthiocarbazide (**8b**)[46] and diphenylcarbazone (**8c**).[47] Diazenecarbothioic acid amide (**9a**) thus contains the chromophoric system under consideration. It is predicted to absorb at about 400 nm (cf. Table 1). If the amino group of **9a** is replaced by the phenyl group, a strong absorption band at about 400 nm has been found both theoretically[48] and experimentally. Thus tautomers of the type **2** cannot be responsible for the 600 nm absorption of dithizone. This will also not be the case if **8a** would exist in the planar di-*cis* configuration **10**. According to the PPP calculation of **10** the absorption



7

7	*R*
a	H
b	Me



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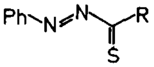
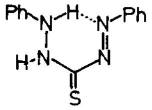
8	*X*	*Y*
a	N	S
b	NH	S
c	N	O



9

9	*R*
a	NH_2
b	Ph



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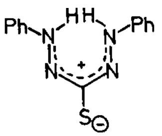
maximum of the 'ketonic' **3**-type tautomers should appear at wavelengths no longer than 500 nm.

The spectral characteristics do not exclude the presence of portions of tautomers of the general formulae **2** and **3** in the solution because their absorptions may be buried beneath the second intense absorption band of **4a**. Until now, however, variable-temperature UV/VIS[49] and NMR spectroscopy[5–7] of dithizone in solution have not indicated any species in equilibrium with **4a**. The two resolved dithizone spectra isomers presented in ref. 14 cannot be due to **2**- and **3**-type tautomers because the first absorptions appear at more than 600 nm in each case. The similarity between the spectra rather suggests two chromophores of the same tautomer such as **4a** and one of its configurational isomers. Whereas the di-*cis* configuration **11** can be discarded from the ensuing considerations, **4a** might equilibrate with the mono-*cis* configuration **12**.

According to the PPP calculation the isomer **12** should display the same spectral pattern as **4a**, but the colour bands are shifted to longer



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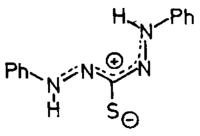

12

wavelengths (cf. Table 1). The appearance of a longer-wavelength absorption of lower intensity for one component in the resolved spectrum of dithizone might fit well the spectral characteristics of **12**. There are, however, two serious arguments against such an interpretation. Polar solvents should contain a larger amount of **12** in the solution than saturated hydrocarbons, for the calculated π-component of the dipole moment is higher for **12** than that of **4a**. The species with the more bathochromic first colour band predominates, however, in cyclohexane rather than in polar solvents according to ref. 14. Likewise, the isomerization rate between **4a** and **12** is expected to be relatively slow and **12** should be detectable by low-temperature NMR spectroscopy.

4 CONCLUSIONS

This study has led to the conclusion that dithizone in solution exists as a single tautomeric species best represented as the diazatrimethinium thiolate (**4a**). The two intense absorption bands in the visible region are compatible with this structure and give rise to the green colour of dithizone in organic solvents.

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