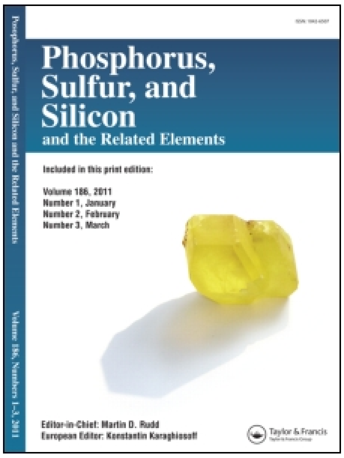

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SYNTHESIS AND ELECTRONIC STRUCTURE OF POTENTIALLY VALENCE ISOMERIC 1,2-DITHIOLYLIUM-4-OLATES†

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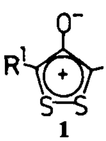
Methylthio substituted 1,2-dithiolylium-4-olates **1** are obtained by thiolation of 1,3-dichlorpropane-2-one or pyruvic thiomorpholide with sulfur and triethylamine in dimethylformamide and subsequent alklyation. Aminolysis yields the amino substituted derivatives. IR and UV/VIS spectra of the bis(methylthio), methylthio dimethylaminophenyl and bis(dimethylaminophenyl) compounds provide evidence in favour of the cyclic structure **1** whereas the spectra of the bis(amino) and amino methylthio compounds are rather compatible with non-cyclic valence isomeric structures **2**. Both **1** and **2** react with acids to form 4-hydroxy-1,2-dithiolylium salts. The colour-structure relationships of 1,2-dithiolylium-4-olates were examined by PPP-type calculations. The lowest excited states and the colour determining transitions are accounted for in terms of the dithiolylium and olate moieties. The negative solvatochromism of the colour bands of **1** is related to the marked amount of oxygen-to-dithiolylium charge transfer of the lowest-excited $\pi \rightarrow \pi^*$ transition. In larger molecules such as **1h** the colour is governed by the lowest electronic transition of polymethine-type subchromophores rather than that of the intramolecular charge transfer chromophores and, therefore are pertinent to cyanine dyes.

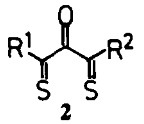
INTRODUCTION

Derivatives of 1,2-dithiolylium-4-olates (**1**) were first synthesized by Ohta *et al.*[1] and Schönberg *et al.*[2] and were later extensively studied by Barillier.[3] The cyclic structure of **1g** was confirmed by X-ray diffraction studies.[3,4] They belong to the mesomeric betaines.[5] Their meso-ionic electronic structure is in line with the exceedingly large CO bond lengths and extremely low CO vibration frequency (near 1500 cm^{-1}).[2,3] The dithio tricarbonyl compounds **2** are acyclic valence isomers of cyclic compounds **1**.



1

1	R^1	R^2
a	t-Bu	t-Bu
b	SMe	SMe
c	SMe	$N(CH_2)_4O$
d	SEt	C_6H_5
e	SMe	$C_6H_4NMe_2$
f	$N(CH_2)_4O$	$C_6H_4NMe_2$
g	C_6H_5	C_6H_5
h	$C_6H_4NMe_2$	$C_6H_4NMe_2$



2

2	R^1	R^2
a	$N(CH_2)_4O$	$N(CH_2)_4O$
b	SMe	SMe
c	SMe	$N(CH_2)_4O$
d	$N(CH_2)_4O$	$C_6H_4NMe_2$

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† MO-LCAO-Calculations on Sulfur-containing π-Electronic Systems, Part LI, Part L: W. Thiel, J. Fabian, B. Friebe, J. prakt Chem. in press.

The valence isomerism between α-dithiones and 1,2-dithietes has early attracted attention.[6] Experimental and theoretical studies of these isomeric compounds have brought to light that donor substituents favour the acyclic structure over the cyclic one while acceptor substituents (and to a lesser extent phenyl groups) favour the cyclic structure over the acyclic one. On the level of the simple one-electron approach the same should be true for **1** and **2**, resp. In other words, appropriate donor substitution might result in **2** rather than in **1**. In fact, X-ray study of the bis(morpholino) compound has corroborated the non-cyclic mesoxalic acid bis[thioamide] structure **2a**[7] and refuted former arguments in favour of the cyclic dithiolyium structure.[8] The molecular structure of **2a** is characterized by a severe distortion from planarity in the crystal.

At any rate, there should exist also borderline cases of comparable stability of **1** and **2**. A promising candidate might be the bis[methylthio] compound **1b** because of the weak donicity of its substituent groups. Its structure corresponds to **1b** according to our previous paper.[9] However, the peculiar behaviour in cycloaddition reactions found recently has been discussed in terms of the equilibrium between **1b** and **2b**.[10]

This paper is intended to meet two objectives mainly: i) to describe some new compounds of the series **1** and **2** and ii) to elucidate their molecular and electronic structures in solution by means of spectroscopic data.

Since the UV/VIS spectral data cannot be understood without quantum chemistry results of π-type calculations have been consulted.

COMPUTATIONAL METHODS

Spectral data of **1** and **2** were calculated by the Pariser–Parr–Pople method[10] considering up to 16(4 × 4) singly excited configurations. Some uncertainty in parametrization of the betainic compounds renders reliable prediction of spectral data more difficult than in the case of the less polar covalent compounds. Satisfactory results have been achieved when the olate-type oxygen is treated as that in phenolates.[11] According to a most recent study on the related acyclic trimethinium olate (and thiolate) far too long wavelength absorptions are predicted with carbonyl (thiocarbonyl) parameter sets.[12]

The choice of the true olate-type oxygen is advantageous not only with respect to the UV/VIS spectral data. It brings about a charge distribution more akin to that of all valence electron (CNCO/2) calculations. As shown with **1b** in Fig. 1 the exocyclic oxygen bears a net atomic charge of −0.49 (definitely lower than in phenolate) while the π-population amounts to 1.77 (in the same order of magnitude as phenolate). Calculation on the π-level provides π-electron densities of 1.83 (with olate-type oxygen) and 1.63 (with carbonyl-type oxygen). Compared with the results of the CNDO/2 calculation the latter value is too low.

In order to make the results of PPP calculations with delocalized orbitals more transparent the calculated electronic wavefunctions of some representative structures have been analyzed by the Baba–Suzuki–Takemura technique (configuration analysis, CA) and the electronic transitions by the Ohta–Kuroda–Kunii technique. Merits and limitations of these methods were considered elsewhere.[13]

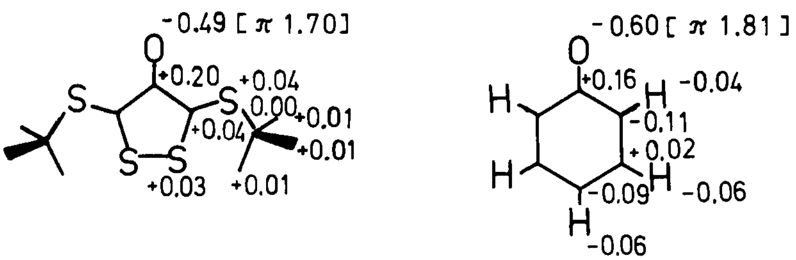


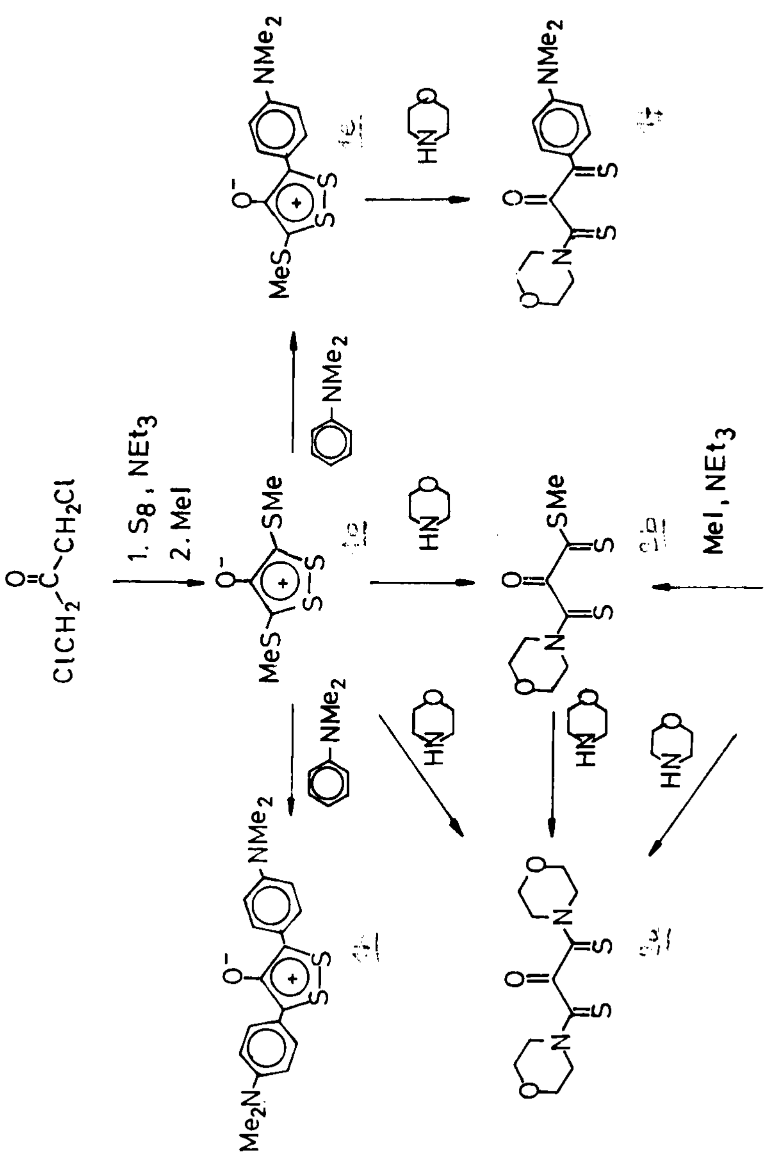
FIGURE 1 Charge distribution of bis[methylmercapto] 1,2-dithiolylium-4-olate (**1b**) and of phenolate according to CNDO/2 calculations with standard parameter sets (net atomic charges, π-electron density in parentheses).

RESULTS AND DISCUSSION

Syntheses

Thiolation of 1,3-dichlorpropane-2-one with sulfur in dimethylformamide in the presence of triethylamine at 0° and consecutive alkylation with methyl iodide affords the mesoionic 3,5-bis(methylthio)-1,2-dithiolylium-4-olate (**1b**).[9] This compound reacts with N,N-dimethylaniline in boiling mixture of glacial acetic acid and pyridine to form 3-(p-dimethylaminophenyl)-5-methylthio-1,2-dithiolylium-4-olat (**1e**) and 3,5-bis(p-dimethylaminophenyl-1,2-dithiolylium-4-olat (**1h**). The reaction of **1e** with morpholine in ethanol at room temperature results in 3-(p-dimethylaminophenyl)-5-morpholino-1,2-dithiolylium-4-olate (**1f**) or its valence isomeric 1-(p-dimethylaminophenyl)-3-morpholino propane-1,3-dithio-trione (**2f**) (vide infra). 1-Methylthio-3-morpholino-1,3-dithio-trione (**2c**) which is a derivative of the mesoxalic acid, has been obtained by alkylation of 4-hydroxy-5-morpholino-1,2-dithiole-3-thione (**3**) which is available by thiolation of pyruvic thiomorpholide. Compound **1b** combines easily with morpholine to produce 1,3-dithiomesoxalic acid morpholide **2a**.[14] As borne out by spectroscopic data (vide infra) the intermediate **2c** is also formed when **1b** is subjected to aminolysis. The reactions mentioned above are assembled in Scheme 1.

The 1,2-dithiolylium-4-olate structure of the newly synthesized compounds is corroborated by spectroscopic data which parallel those found by Barillier.[3] Thus the carbonyl stretching vibration frequency (or a related coupled frequency) of **1b**, **1d** and **1h** appears near 1480 cm^{-1} rather than at about 1700 cm^{-1} as usual. On the other hand, compounds of the series **2** display this frequency at 1660 cm^{-1} such as demonstrated with **2a**.[7] The presence of an absorption of 1650 cm^{-1} (in KBr) in the case of **1f** cast some doubt on its cyclic structure in solid state. The structure of these compounds requires additional consideration (vide infra), ^{13}C chemical shifts have been attained only in part because of the low solubility of the compounds. The NMR values of **1b** compare very favourably with former experimental values. As to be expected, ^{13}C of the CO group of **1b** (165.2 ppm) is low field shifted with respect to **1a** (172.4 ppm) and **1d** (167.7 ppm).[3] Unfortunately, the ^{13}C chemical shifts of non-cyclic carbonyl compounds have

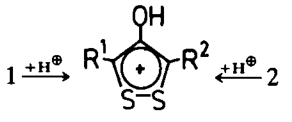


SCHEME 1 Synthesis of 3,5-donor-substituted 1,2-dithiolylium-4-olates.

been recorded in the same region (e.g. **2a:** 166.4 ppm) preventing any reliable discrimination between the valence isomeric structures.

The UV/VIS spectra are juxtaposed and discussed in more detail below.

Both the cyclic compounds **1** and the acyclic compounds **2** undergo protonation in 60% perchloric acid. The resulting 4-hydroxy-1,2-dithiolylium (**3**) perchlorates have been identified spectroscopically (vide infra).



4

4	R^1	R^2
a	$N(CH_2)_4O$	$N(CH_2)_4O$
b	SMe	SMe
c	SMe	$N(CH_2)_4O$

In order to study the course of deprotonation the chloride of **4c** has been isolated.

UV/VIS spectral data

Spectral data in the ultraviolet and visible region of the compounds studied in this paper are collected in Table I. For the sake of comparison some data of the literature[3] were enclosed in the compilation. All compounds of the series **1** exhibit more or less intense absorptions in the visible region ranging from 450 up to about 650 nm. These colour bands cause the orange, red, violet or blue colour of the compounds in solution. Except for **1f** the compounds suffer a hypsochromic shift on passing from dioxane to ethanol (negative solvatochromism). This is displayed in Fig. 2 (panel A) for **1b**. An additional hypsochromic shift is observed when ethanol is replaced by perchloric acid. In the latter case protonation of **1** will bring about the ionic **4**. The solvent effect found agrees with that reported formerly for 1,2-dithiolylium-4-olates.[2,3]

The more detailed inspection of the spectra revealed that the position of the colour band of bis(methylthio) compounds **1b** is fully compatible with those of the 1,2-dithiolylium-4-olates known. A steady bathochromic shift is observed if the SMe groups of **1b** are replaced step by step by Ph groups on going from **1b** (516 nm) via **1d** (545 nm) to **1g** (579 nm).

Considering the 1,2-dithiolylium-4-olates as substituted dithiolylium ions the effect of the olate-type oxygen is remarkably large in some cases. In the alkyl substituted compounds the shift of the first intense absorption amounts to nearly 200 nm on passing from **5a** to **1a**. While the colour band of **1a**, **1b** and **1g** is of moderate intensity in dioxane a pronounced increase in intensity is observed on introducing extended donor substituents such as dimethylaminophenyl groups into the 1,2-dithiolylium-4-olate ring system (cf. Fig. 1, panel C). If the position of the colour band is related again to those of the dithiolylium ion the O^- substituent appears to be no longer operative. The compound **1h** absorbs in the same wavelength region and with nearly the same intensity than the parent 1,2-dithiolylium ion **5c**.

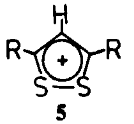
The absorption feature of **1h** even strongly reminds to that of polymethine dyes. In fact, the longest-wavelength absorption of **1h** approaches to less than 100 nm to that of vinylogous diphenylmethane dye **6c**. The 1,2-dithiolylium-4-olates absorb generally at shorter wavelengths than the corresponding open-chain

TABLE I

Absorption Maxima (in nm) and lg ε values of molar absorption coefficients (in $l/mol^{-1}\,cm^{-1}$) of **1** and **2**

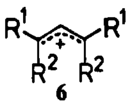
Compound	Dioxane	Solvent ethanol	60% Perchloric acid[a]
1a	463 (3.73)[b]	426 (4.00)[b]	
1b	509 (3.82)	462 (4.26)	394 (4.37)
	338 (3.84)	332 (3.82)	337 (3.89)
	307 (3.88)	279 (3.80)	256 (3.23)
1d	545 (4.42)[b]	482 (4.28)	—
	577[d]	541 (4.54)	397 (4.32)
	425	411 (3.75)	324 (3.93)
	331	316 (3.84)	268 (3.60)
	268	255 (4.04)	
1c	—	418 (4.08)[c]	367 (4.26)
		286 (3.70)	318 (3.87)
		230 sh (3.79)	235 (3.33)
1f/2h	480 (4.58)	483[d]	372 (4.12)
		380	291 (3.90)
	286 (4.15)	283	249 sh (3.79)
	238 (4.11)	235	
1g	579 (3.76)[b]	498 (4.45)[b]	—
1h	648[d]	606 (4.68)	604 (4.70)
	467	470 (3.86)	508 (4.03)
	411	391 (3.71)	
	352	349 (3.75)	
	301	290 (4.16)	295 (4.21)
2a	377 sh (3.25)	376 sh (3.21)	350 (4.17)
	314 (3.94)	312 (4.01)	
	272 (4.21)	271 (4.24)	261 (3.35)
2c	—	433 sh (3.10)	367 (4.26)
		340 (3.78)	318 (3.87)
		287 (4.07)	235 (3.33)
		228 (3.90)	

[a] Monoprotonation of **1** and **2**, resp., resulting in **4**; **1h** in glacial acetic acid.
[b] Taken from Reference 3.
[c] Quickly measured after dissolving the hydrochloride of **1c** in water.
[d] lg ε values have not been determined because of low solubility.



5

a	R = H	287 nm (3.45)[15]
b	$R = C_6H_5$	381 nm (4.24)[16]
c	$R = C_6H_4NMe_2$	588 nm



6

a	$R^1 = R^1 = Me$	305 nm (4.02)[17]
b	$R^1 = C_6H_5, R^2 = H$	498 nm (4.00)
c	$R^1 = C_6H_4NMe_2, R^2 = H$	693 nm
d	$R^1 = SMe, R^2 = H$	407 nm[18]

polymethine dyes because the S–S donor group shifts more strongly hypsochromic than the O^- group bathochromic.

Theoretical and experimental data are entered in Table II. Since maximum absorption coefficients could not be recorded in dioxane in each case, data in chloroform are listed in addition. Due to the fact that the olate-type oxygen parameters were defined in polar solvents experimental data in dioxane are not

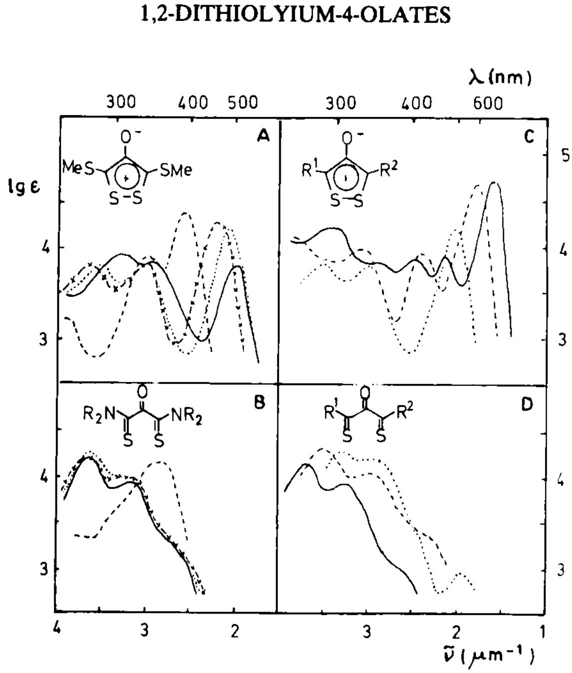


FIGURE 2 Compilation of absorption spectra of **1b** (panel *A*) and **2a** (R = morpholino, panel *B*) in dioxane (——), chloroform (----), ethanol (–×–×–) and perchloric acid (----) and the effect of structural modifications of **1** (panel *C*) exemplified with **1b** ($R^1 = R^2 = SMe$:----), **1e** ($R^1 = SMe$, $R^2 = C_6H_4NMe_2$:---) and **1h** ($R^1 = R^2 = C_6H_4NMe_2$;——) in chloroform and of **2** (panel *D*) exemplified with **2a** ($R^1 = R^2 =$ morpholino:——), **2c** ($R^1 = SMe_2$, $R^2 =$ morpholino:---) and **2b** ($R^1 = R^2 = SMe$:---, tentative assignment cf. text) in cyclohexane (qualitative measurements for **2b** and **2c**).

necessarily the best reference data. Nevertheless, the overall agreement between theory and experiment is quite satisfactory. The theoretical absorption wavelengths are only slightly too low. This error must appear reinforced at longer wavelengths in the λ-scale. Reparametrization of oxygen parameters may lower the numerical differences but will not result in any new conclusion.

According to Table II the lowest energy oxygen-to-dithiolylium CT-state dominates to about 64% the lowest energy state of **1a** (the completeness of the description amount to about 85% according to the BST-analysis). The reference to the intramolecular CT state is significantly deteriorated, however, for the structures **1b–1h** while the reference the lowest-energy locally excited state (of the dithiolylium ion) is improved. The same conclusion can be drawn from analyses that refer to electronic transitions (OKK-analysis) rather than from electronic states (BST-analysis) (cf. Table II). In complete agreement with the analysis the negative charge at the oxygen atom (amounting to −0.70 to −0.85 in the serie **1**) is more or less reduced upon excitation. Thus, the first electronic transition of **1** can be referred to as an intramolecular CT transition. The charge transferred is largest for the compound **1a**.

The experimentally observed negative solvatochromism is in line with this assignment. The oxygen-to-dithiolylium charge transfer upon excitation reduces the capability of polar solvent molecules to stabilize the molecule in the excited state and the energy gap between ground and first excited state will increase on

TABLE II

Theoretical and experimental spectral data of the colour band of 1,2-dithiolylium-4-olates, change of the π-electron density at the oxygen atom and results of the Baba–Suzuki–Takemura (BST) and Ohta–Kuroda–Kunii (OKK) analysis of the lowest-energy locally excited and charge transferred states (LE_1 and CT_1, resp.) and LE- and CT-transition, respectively

	$\lambda_{ber.}(\lg \varepsilon)$[a]	$\lambda_{exp.}(\lg \varepsilon)$ dioxane chloroform	q_0	BST-analysis % CT_1	BST-analysis % LE_1	OKK-analysis % CT	OKK-analysis % LE
1a	457 (3.79)	463 (3.77)[c] —	0·63	64	23	54	46
1b	472 (4.08)	509 (3.82) 489 (4.20)	0.42	43	39	37	63
1c	433 (4.10)	418[b]	0.40	40	35	33	66
1d	487 (4.28)	543 (4.52)[c]	0.37	38	34	35	64
1e	525 (4.48)	577 565 (4.67)	0.26	27	51	22	77
1f	500 (4.47)	480 (4.58) 488 (4.55)	0.24	21	51	14	85
1g	522 (4.41)	575 (3.76)[c,d]	0.35	36	42	35	65
1h	588 (4.62)	632 (4.71) 648	0.22	23	52	14	52

[a] In order to facilitate the comparison between theoretical and experimental absorption intensities the theoretical $\lg f$ values have been transformed into $\lg \varepsilon$ values by the following approximate relationship: $\lg \varepsilon = 4.5 - \lg f$

[b] In ethanol.

[c] Reference 3.

[d] The experimental $\lg \varepsilon$ value appears to be too low, $\lg \varepsilon$ in benzene: 4.23,[2] $\lg \varepsilon$ in dioxane of p,p′-bis[methyl]substituted **1g**: 4.67[3].

going from non-polar to polar solvents. Although the full elucidation of the solvent effects goes beyond the scope of this paper the main spectroscopic effect of protic solvents on **1** can easily be modelled. The solvent molecules will form hydrogen bonds to the strongly charged oxygen atoms of **1**. This effect can be simulated in PPP calculations by imparting the oxygen atom a higher ionization energy. The results of these calculations are as follows: 1) The first band should suffer a hypsochromic and hyperchromic shift 2) the second band should nearly hold its position and intensity and 3) the third band should undergo a bathochromic and hyperchromic shift.

The experimental solvent effect on **1b** really reflects this theoretical prediction (cf. Fig. 1, panel A).

The results of the PPP calculations enables one to give more detailed interpretation of the whole spectral curve recorded if the wavefunctions are subjected to the BST-projection. The spectrum of **1b** will illustrate this point. The calculated spectrum of **1b** is depicted in Fig. 3. Three π–π^* transitions are obviously responsible for the three absorption bands observed experimentally. According to the analysis of the correlation between the excited state these transitions are related to three transitions of the 1,2-dithiolylium-4-olate parent structure. The strong shift the higher energy transitions on passing from the unsubstituted to the substituted 1,2-dithiolylium-4-olates **2a** is due to the strong

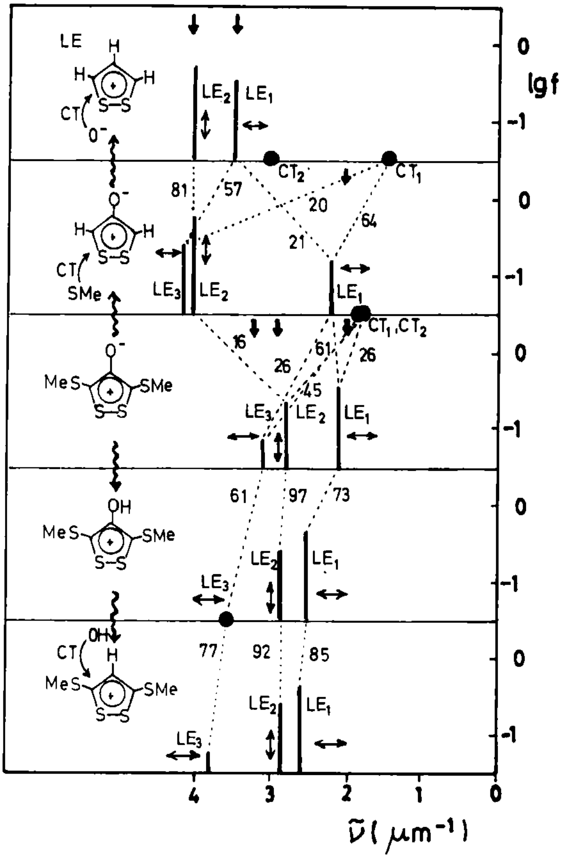


FIGURE 3 Correlations between the ground and three lowest energy excited states of 1,2-dithiolylium-4-olates and 1,2-dithiolylium ions (and residual fragments) according to PPP-CA calculations. The vertical lines indicate the transition energies and their heights the oscillator strengths calculated (given in terms of lg *f*). The double-headed arrow indicate the direction of transition moments with respect to the molecular framework. Numbers along the dotted lines are the contributions of the most important reference state (≥15%) to the ground and excited state, resp., of the π-system under consideration. Experimental excitation energies are marked by vertical arrow.

mixing of the locally excited state with the substituent (SMe)-to-dithiolylium CT (26 and 45%, resp).

The appearance of the three π–π^* transitions of the 1,2-dithiolylium-4-olate itself can easily be understood in terms of the dithiolylium and olate subunits. It is originated in an effective mixing of the lowest energy CT state (discussed above) and lowest energy locally excited state. The resulting splitting of the term level brings about two transition polarized perpendicular to the two-fold molecular axis ($A_1 \rightarrow B_2$ transitions). Due to the large amount of the CT configuration (64%) the intensity of the first electron transition is rather low. The $A_1 \rightarrow A_1$ transition of the dithiolylium ion (polarized along the axis) remains nearly unaffected upon substitution by 0^-.

This approach can also easily be used to rationalize the spectral characteristics of the remaining compounds of the series **1**. The bathochromicity of the colour band is controlled by three effects: 1) the energy of the CT transition which is determined by the electron affinity of the dithiolylium ion 2) the energy of the LE transition of the dithiolylium ion 3) the energy of the interaction between the CT and LE states which can be estimated by the overlap of the relevant occupied orbitals of the dithiolylium and olate subunits. It needs not to be detailed that the nature of the colour band in series **1** alters significantly on passing from **1a** to **1h** owing to relative energy of the charge transferred and locally excited states. The solvatochromic effect of protic solvent and of protonation on the colour band is straightforward as well because the donicity of the oxygen is reduced with respect to the unperturbed olate-type oxygen.

As shown in Fig. 2 (panel B) the acyclic **2a** displays an absorption spectrum less structured than **1b** but likewise consisting of three absorption bands. The intensity of absorption bands steadily decreases on passing from the near UV towards the visible region. In contrast to the cyclic structure the solvent effect is negligibly small. The absorption is dramatically changed only if **2a** is dissolved in perchloric acid. Under these conditions the compound is protonated.

The experimental spectrum of **2a** could not be satisfactorily reproduced by PPP calculation. Albeit the emergence of an absorption band of moderate intensity at long wavelengths is correctly predicted the position of the band is grossly overestimated in wavelengths. Because of the strong departure of **2a** from the planarity any calculation on the π-level must be viewed with suspicion. Unfortunately, calculations by the all-valence electron CNDO/S method also failed in the case of **2** (such as in series **1**). The weakness of this approach renders more difficult to identify valence isomeric non-cyclic congeners of **1** UV/VIS spectroscopically.

The spectral data of the morpholino dimethylaminophenyl compound **1f**/**2d** are contradictory. The $\tilde{\nu}_{CO}$ frequency in solid state is in favour with the non-cyclic structure **2d** and also the solvent effect on the UV/VIS spectrum (positive solvatochromism) is exceptional. PPP calculations suggest that the spectrum of the cyclic **1f** should be closely similar to **1e** apart from some blue shift of the absorption band. This is not observed. On the other hand, the very intense colour band in dioxane, chloroform and dimethylformamide with lg ε values of more than 4.5 at the maximum absorption (cf. Table II) is compatible with the 1,2-dithiolylium-4-olate rather than with the non-cyclic carbonyl structure. If the solvents above mentioned are replaced by cyclohexane the situation becomes more intricate. The colour band has now considerably lost intensity and is placed at 465 nm. The appearance of a medium intensity long wavelength absorption may suggest the prevalence of the non-cyclic compound **2d**, but this assignment could not be supported by recording any weak $n \rightarrow \pi^*$ absorption in the 550 nm region (as found for p-dimethylaminothiobenzophenone).[19] Any more serious study of the morpholino dimethylaminophenyl compound **1f**/**2d** is hampered by its poor solubility in cyclohexane.

The same is true for bis[dimethylthio] compound **1a**. The intensity ratio between the ε-values of the first two absorption bands decrease from 2.78 in ethanol to 0.07 in cyclohexane. Thus its spectrum is getting similar to the spectra of the non-cyclic structure if the compound is dissolved in cyclohexane. This is shown in Fig. 2 (panel D). For the sake of comparison the qualitatively recorded spectrum has been juxtaposed to the spectra of **2a** and **2b** in Fig. 1 (panel D). In the case of the non-cyclic structure **2b** the weak absorption band at 526 nm should be due to the $n \rightarrow \pi^*$ transition of thiocarbonyl group which has been found for esters of the α-oxodithiocarbonic acids between 450 and 500 nm. It should also be mentioned that the weak absorption band in cyclohexane (and hexane) is non-symmetric in shape and seems to consist of two distinct absorption bands (an inflexion in the 500 nm region in addition to the 526 nm absorption maximum).

Although **1b** and **1f** may be candidates to demonstrate valence isomerism under certain conditions, more proper compounds can be designed by weakening the electron releasing capacity if the nitrogen containing group in **2a** and enhancing the electron donating capacity of the sulfur-containing group in **1b**.

The question of the presence of isomeric species in perchloric acid is out of discussion since both the cyclic structure **1** and non-cyclic structure **2** are transformed into the cyclic 4-hdroxy-1,2-dithiolylium ions (**4**). The spectra of **4a** and **4b** differ markedly from those of the corresponding 1,2-dithiolylium-4-olate (Figure 2, panel A and B). They are compared in Figure 4 with the results of the PPP calculations. Two intense $\pi \rightarrow \pi^*$ absorptions account for the long-wavelength absorptions found. The spectral feature of 4-hydroxy-1,2-dithiolylium ions is closely similar to the 3-hydroxy-1,2-dithiolylium ions which were examined in one of our former papers.[20] As shown in Figure 3 a clear-cut relationship exists between the lowest-energy transition of **4b** to those of **1b** and to those of the bis[methylthio] substituted 1,2-dithiolylium ions. In contrast to O$^-$the OH group

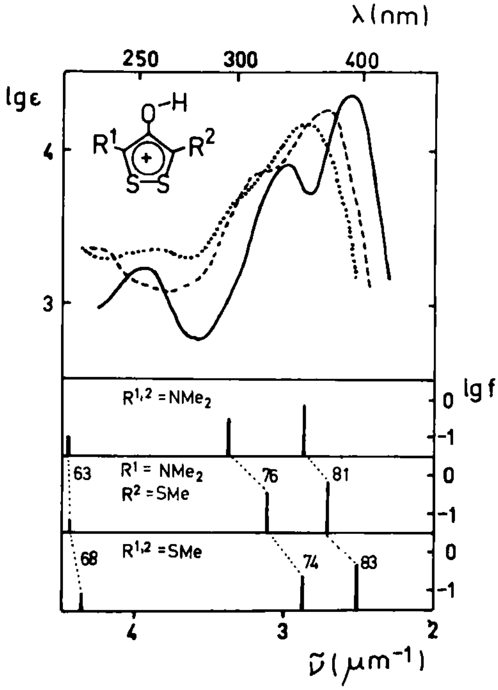


FIGURE 4 Absorption spectra of the 4-hydroxy-1,2-dithiolylium ions **4a** (····), **4b** (——) and **4c** (---) in perchloric acid and results of the PPP calculations (cf. caption to Figure 3).

exerts only a weak effect on the long wavelength absorption of the 1,2-dithiolylium heterocycle.

If the acidity of the solution is lowered the non-protonated compound will be regained. Deprotonation of 4-hydroxy-3-methylthio-5-morpholino-1,2-dithiolylium ion (**4c**) by introducing the salt into icy water brings about a sharp absorption maximum at about 410 nm. It vanishes after a few minutes and the spectrum of the non-cyclic structure emerges. The position of the transient absorptions is in agreement with the formation of the cyclic 3-methylthio-5-morpholinol,2-dithiolylium-4-olate (**1c**) which undergoes rapid isomerization to the corresponding non-cyclic derivative of the mesoxalic acid (**2c**).

EXPERIMENTAL

3,5-Bis(methylthio)-1,2-dithiolylium-4-olat (**1b**)

1b was prepared according to Reference 9 (80% yield). Recrystallization from water resulted in the dihydrate. The water-free specimen was obtained by solving the dihydrate in chloroform and removing water by water separation. Orange plates, m.p. 146–148°C, IR (KBr), $\tilde{\nu}$ (cm^{-1}) 1450 (CO), ^{1}H-NMR (CD$_3$CN), δ (ppm): 2.79 (S, 6H); ^{13}C-NMR (DMSO-D$_6$) δ (ppm): 165.2 (CO), 156.5 (CS), 15.1 (CH$_3$S); MS: m/e = 210 (M).

3-(p-Dimethylaminophenyl)-5-methylthio-1,2-dithiolylium-4-olat (**1e**)

2,10 g (0.01 mol) **1b** were dissolved in 25 ml glacid acetic acid. After addition of 0.5 ml pyridine 2.42 g (0.02 mol) N,N-dimethylaniline dissolved a small amount of glacid acetic acid was added dropwise at boiling temperature. The solution was refluxed as long as any **1b** could be detected by thin-layer chromatography on SILOFOL (ca. 0.5 h). At room temperature about 100 ml diethyl ether were added, the precipitate was removed by filtration and recrystallized from isopropanol (0.65 g, 23% yield).

Green-black sparkling needles. m.p.: 210–212°C (dec.); IR (KBr): $\tilde{\nu}$ (cm^{-1}: 1475 (CO); ^{1}H-NMR (DMSO-D$_6$) δ (ppm): 8.08, 7.98, 6.83, 6.73 (arom.), 3.06 (S, 6H), 2.92 (S, 3H).

3,5-Bis-(p-dimethylaminophenyl)-1,2-dithiolylium-4-olat (**1h**)

1h was prepared according to **1e**. Reactions of **1b** with 6.05 g (0.05 mol) N,N-dimethylaniline afforded 0.64 g **1h** (18% yield). Green-black sparkling needles, m.p. 243–246°C (dec.); Ir (KBr) $\tilde{\nu}$ (cm^{-1}): 1475 (CO); ^{1}H-NMR (DMSO-D$_6$) δ (ppm): 8.44, 8.34, 8.86, 6.76 (arom.), 3.04 (S, 12H).

3-(p-Dimethylaminophenyl)-5-morpholino-1,2-dithiolylium-4-olat (**1f**)

2.83 g (0.01 mol) **1e** were suspended in 50 ml ethanol and 1.74 g morpholine dissolved in a small amount of ethanol was added dropwise with stirring at room temperature. During additional stirring of 2–3 h **1e** was slowly dissolved and **1f** began to precipitate. Cooling of the solution completed the crystallization of 1.32 g **1f** (41% yield).

Red plates (from ethanol). m.p. 230–232°C (dec.); IR (KBr) $\tilde{\nu}\,(\mathrm{cm}^{-1})$: 1660 (CO); ^{1}H-NMR ($CDCL_3$) δ (ppm): 8.22, 8.12, 6.74, 6.64 (arom.), 4.40 – 3.70 (m, 8H), 3.17 (S, 6H).

4-Hydroxy-5-morpholino-1,2-dithiol-3-thione (**3**)

17.3 (0.1 mol) pyruvic thiomorpholide were dissolved in 50 ml dimethylformamide and within 1/2 h to a mixture of 19.2 g (0.6 mol) sulfur and 60.6 g (0.6 mol) triethylamine in 100 ml dimethylformamide was dropwise added at 60–70°C with stirring. Stirring was continued for 2 h at this temperature. The cooled reaction mixture was poured into icy water and the pH value of the solution reduced to 8–9 by diluted HCl. The brownish deposit tending to decomposition was extracted with cold acetone, filtered and the solution concentrated by rotatory evaporation. Upon cooling yellow needles precipitated. 6.35 g (27% yield); m.p. 113–114°C (from cyclohexane); IR (KBr) $\tilde{\nu}\,(\mathrm{cm}^{-1})$: 3170 (OH), 1530 (CN); ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.85 (2, 1H), 3.83 (t, 4H, —H_2COCH_2—), 2.22 (t, 4H, —CH_2—N—CH_2—); ^{13}C-NMR ($CDCl_3$) δ (ppm): 185.5 (CS), 159.5 (COH), 139.3 (CH), 65.9 (—CH_2OCH_2—), 50.1 (—CH_2NCH_2—).

1,1,3-Trithiomesoxalic acid monomethylester morpholid (**2c**)

The solution of 2.35 g (0.01 mol) **3** was treated at 0°C with a slight excess of methyl iodide in 100 ml chloroform and 1.01 g (0.01 mol) triethylamine. After washing the solution with water and drying with $MgSO_4$ the solvent was removed resulting in 2.37 g of a red oil (95% yield).

IR (KBr) $\tilde{\nu}\,(\mathrm{cm}^{-1})$: 1660 (CO), 1505 (CN); ^{1}H-NMR ($CDCl_3$) δ (ppm) 4.10–3.91 (m, 8H), 2.77 (s, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 227.9 ($CSSCH_3$), 193.6 (CSN), 173.3 (CO), 66.5, 66.1 ($O(CH)_2$), 52.5, 47.5 (—$N(CH_2)_2$), 19.0 (—SMe); MS: m/e = 249 (M).

4-Hydroxy-3-methylthio-5-morpholino-1,2-dithiolium chloride (**4c**)

A solution of 2.49 (0.01 mol) **2b** in a little ethanol was mixed with concentrated HCl with a slight excess. After addition of diethyl ether **4c** 2.63 g yellow needles precipitated (92% yield). m.p. 166–167°C, IR (KBr) $\tilde{\nu}\,(\mathrm{cm}^{-1})$: 1530 (CN); ^{1}H-NMR (DCl) δ (ppm): 4.08 – 3.98 (m, 8H), 2.75 (s, 3H).

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