STRUCTURES AND PROPERTIES OF 1,2-DITHIOLYLIUM-4-METHIDE, 1,2-DITHIOLYLIUM-4-OLATE AND 1,2-DITHIOLYLIUM-4-THIOLATE: AN MO STUDY AT THE HF AND POST-HF LEVELS

MATTHIAS MANN AND JÜRGEN FABIAN*

Institut für Organische Chemie der Technischen Universität Dresden, D-01062 Dresden, Germany

The molecular and electronic structures of the cyclic 1,2-dithiolium ylides (2) and their acyclic dithiocarbonyl valence isomers (4) were studied by *ab initio* methods. All molecular structures were fully optimized at the R(U)HF/6–31G* and R(U)MP2/6–31G* levels of theory. The results of the restricted and unrestricted Hartree–Fock (HF) calculations are less reliable since the RHF wavefunctions of the cyclic compounds proved to be singlet/triplet unstable. A marked ground-state energy depression occurs on passing from restricted to unrestricted HF methods. The title compounds are of diradicaloid nature and belong to the non-classical class of structures. The heterocycles are planar and display C_{2v} symmetry, while the cisoid open-chain dithiocarbonyl isomers are slightly distorted (C_2 symmetry). According to the calculated bond lengths and charge distributions, the title compounds are in fact more or less zwitterionic. The thiolate is the most polar compound of this series. According to RMP2 calculations, the thiolate (2, X = S) and olate (2, X = O) should exist in the single ground rather than in the triplet state. However, in these cases the isomeric acyclic compounds are predicted to be almost isoenergetic with the cyclic compounds. Since the cyclic ylides have higher dipole moments than the acyclic dithiocarbonyls, the ylides will gain stability in polar solvents. However, the continuum quantum chemical model used in estimating the solvent effect does not favour the ring compounds sufficiently to exclude valence isomerization between the ring-closed and ring-open compounds.

INTRODUCTION

In recent theoretical studies,[1,2] we examined the molecular and electronic structures of 1,2-dithiin (1) and derivatives and the stability of these compounds relative to their open-chain dithiocarbonyl valence isomers. These heterocycles are non-planar unsaturated disulphides consisting of a slightly distorted butadiene fragment and a disulphide bridge with one of the sulphur atoms positioned above and the other below the fictive plane (C_2 symmetry).

The molecular electronic structure of the cyclic disulphide is expected to alter greatly on passing from 1,2-dithiin (1) to the isomeric 4-methylene-1,2-dithiole (2a, X = CH$_2$). The cisoid butadiene C$_4$-subunit of 1 is now replaced by the cross-conjugated trimethylenemethane fragment. In contrast to 1, this

isomer cannot be satisfactorily written using a classical electrically neutral valence bond structure employing atoms in their normal valences. Moreover, if 2 (X = CH$_2$) is regarded as a derivative of trimethylenemethane [2-methylene-1,3-propanediyl (3, X = CH$_2$)],[3,4] this compound should be of diradical nature, such as indicated by formula 2a. The same problem occurs with the heteroanalogues of this series (2, X = S, O). These heterocycles contain substructures corresponding to the diradical oxyallyl [2-oxypropenyl (3, X = O)] and thiooxyallyl [2-thiopropenyl (3, X = S)], respectively. Both elusive diradical parent compounds have been extensively studied theoretically.[5–8]

These 'non-classical' molecules can alternatively be represented by a hypervalent structure or by a resonance hybrid of several dipolar structures. The latter representation is involved in the delocalized ylid structure 2b that is mostly used for convenience in organic chemistry. Zwitterionic formulae suggest that heteroatomic

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* Author for correspondence.

1

2 a b

3

(X = CH₂, S, O)

(X = CH_2, S, O)

4

5

(X = CH_2, S, O)
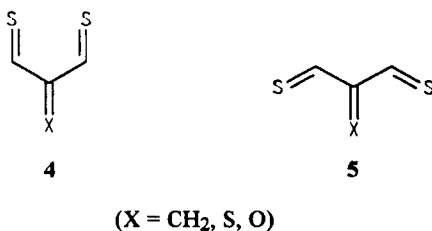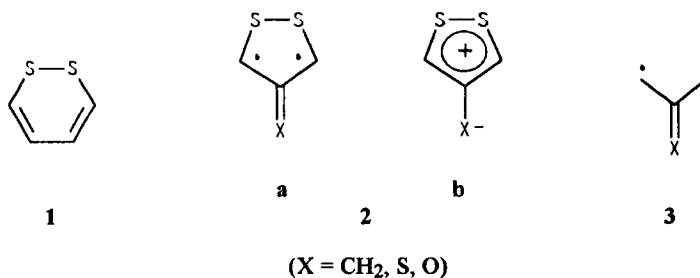
substitution of the exocyclic methylene group by more electronegative elements may stabilize the charge separated structure. The resulting compounds 1,2-dithiolylium-4-thiolate (**2**, X = S) and 1,2-dithiolylium-4-olate (**2**, X = O) belong, in principle, to the so-called mesoionic class of structures.[9] In contrast to compounds **2** with exocyclic CH_2 and S groups, various derivatives of **2** (X = O) are experimentally known and well characterized.[10,11] The cyclic structure of some 3,5-substituted derivatives has been confirmed by x-ray diffraction studies.[12,13] However, spectroscopic studies of 3,5-donor-substituted compounds suggest that these compounds exist either in the closed-ring (R = methylthio) or in the isomeric open-chain structure (R = morpholino).[10]

Attempts have been made to reveal the main structural features of these non-classical title compounds and their open-chain isomers at the semi-empirical PPP[14] and MNDO levels.[15] According to the MNDO calculations, the heterocyclic parent compound (**2**, X = CH_2) is less stable than the open-chain isomer, but the relative stability of the ring compound increased on passing from the methide to the olate and thiolate structures. In the case of the 1,2-dithiolylium-4-olate, the ring has virtually the same energy as the isomeric dithiocarbonyl compound. However, MNDO theory favours the triplet states of the ring structures as the molecular ground state in all three cases. A reliable estimate of the singlet/triplet (S/T) splitting, however, suffers from the fact that the heterocycles display diradicaloid behaviour. The SCF energies of the non-classical structures were appreciably lowered on passing from SCF to minimum CI calculations (2 × 2 or 3 × 3). A considerable decrease in energy was also observed on passing from restricted to unrestricted semi-empirical Hartree–Fock calculations. Without doubt, the semi-empirical approach is unable to cope with the diradicaloid electronic structure. In order to treat this problem more adequately, *ab initio* calculations appeared highly applicable. The rapid progress in computer techniques has it made possible to tackle this problem at the post-Hartree–Fock *ab initio* quantum chemical level.

The purpose of this work was to predict the molecu-

6

7

8

(X = S, O)

9 a b

(X = S, O)
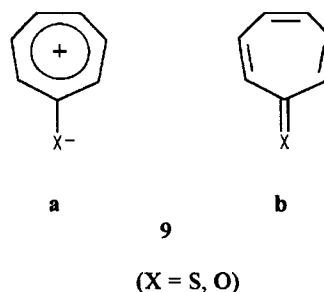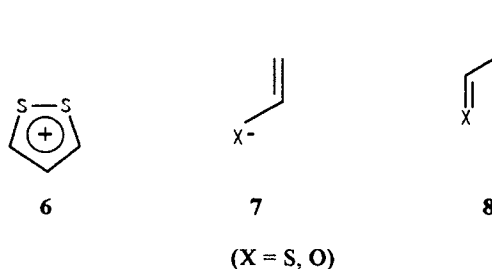
lar geometries and relative energies of the parent compounds 2 and 4 in their lowest energy singlet states and the S/T splitting energies of the cyclic compounds. In order to check the zwitterionic character, the charge distribution of the ring compounds are considered based on Mulliken's population analysis. In order to interpret the degree of the charge separation, some related compounds are also considered, namely 1,2-dithiolylium ion (6), thioenolate (7, X = S), enolate (7, X = O), thioacrolein (8, X = S) and acrolein (8, X = O). Further, the heterocycles 2 (X = O, S) are compared with the iso-π-electronic compounds thiotropone (9b, X = S) and tropone (9b, X = O), which might be considered as tropylium olate (9a, X = O) and tropylium thiolate (9a, X = S). The last-mentioned compounds are well known experimentally.

If 2 (X = O, S) is actually ylidic, the solvent effect will affect the isomerization energies. The solvatation energy is estimated for both the 1,2-dithiolylium-4-thiolate and the 1,2-dithiolylium-4-olate.

COMPUTATIONAL

The compounds were investigated by the *ab initio* electronic structure methodology[16] using the Gaussian 90 and Gaussian 92 series of programs.[17] Optimization of fully relaxed molecular geometries were first carried out at the closed- or open-shell R(U)HF/6–31G* level of theory [R(U)HF/6–31+G* for anions]. Although not required by the explicit imposition of symmetry in the calculation, all of the stationary points of the energy hypersurface display a higher symmetry (C_{2v} or C_2). In order to obtain information about the diradicaloid nature, the electronic system the RHF solutions was subjected to the RHF/UHF instability test. The test was positive for cyclic ylides. Since the UHF wavefunctions are strongly spin contaminated, the results of these calculations should be considered with caution. This outcome indicates the intrinsic deficiency of the single determinant approach in that case.

Electron correlation was considered via Møller–Plesset perturbation theory of the second order without constraints [R(U)MP2(full)]. Unless stated otherwise, relative energies of geometry-optimized structures quoted in the text refer to data obtained at this level and do not include vibrational zero-point energy correction. In order to evaluate additional effects of electron correlation, closed-shell quadratic single and double CI including triple contribution [RQCISD(T)] single-point calculations were also performed at the 6–31G* basis set level. The optimum geometries of the triplet molecules were calculated at the R(U)MP2/6–31G* level. S/T splitting energy were calculated based on R(U)MP2 energies after spin projection. Since the energies are calculated from total energies of the respective molecular species, the S/T splitting energies correspond to adiabatic energy gap.

The Hessian matrix was calculated to verify the optimum geometries as minima on the energy hypersurface. As indicated in the tables, in a few cases a small negative eigenvalue in the Hessian remained, in spite of presuming C_1 symmetry. Harmonic frequencies were obtained by diagonalization of the mass-weighed Cartesian force constants matrix, calculated from the analytical second derivative of the total energy. Unless stated otherwise, the frequencies are unscaled. They also served for calculating zero-point vibrational energies and thermodynamic data.

In order to elucidate the zwitterionic vs diradical character, attention was paid both to Mulliken net charges and to π-charges calculated therefrom. The π-population was extracted from the global population analysis assuming core changes of 1 and 2 for carbon and sulphur, respectively.

The solvent effect was estimated by the self-consistent reaction field (SCRF) method developed by Wong *et al.*[18] This continuum quantum mechanical solvent method defines a spherical cavity. The dielectric constant of acetonitrile was taken to simulate the effect of a polar solvent ($\varepsilon = 35.9$).

RESULTS AND DISCUSSION

Molecular geometry and electron distribution

Structural data for the heterocyclic disulphides and of ring-opened dithiocarbonyls are given in Tables 1–3. The C–S and S–S bond lengths of 2 (X = CH$_2$) (1.69 and 2.03 Å) are definitely shorter than those of 1,2-dithiete (1.76 and 2.11 Å) and 1,2-dithiin 1 (1.76 and 2.07 Å)[2] investigated in previous studies (RMP2/6–31G* level of theory). Another comparison offers the 1,2-dithiolylium ion 6 with corresponding of 1.68 Å (C–S) and 2.03 Å (S–S). This may be considered as an argument for the dithiolylium structure of 2. On the other hand, there is not much change in the C=C bond lengths when the corresponding bonds of 2 (X = CH$_2$) (1.35 Å) and of butadiene (1.34 Å) are compared. Thus, neither formula a nor b reflects the molecular geometry adequately.

The heteroanalogues of 2 (X = CH$_2$) are intriguing structures with exocyclic S and O rather than CH$_2$. Whereas the exocyclic bond of olate 2 (X = O, $R_{C=O} = 1.23$ Å) is comparable in length to the C=O bond in acrolein (1.23 Å), the thiolate 2 (X = S, $R_{C=S} = 1.68$ Å) exhibits a much longer bond than thioacrolein 8 (X = O) (1.63 Å) (cf. Table 4). The C=S bond in thiolate is even longer than in thiotropone 9 (X = S) (1.66 Å). The calculated molecular geometry suggests an extremely high zwitterionic nature of 2 (X = S). The zwitterionic character, however, is not always reflected in the bond length. As discussed by Lim *et al.*,[5] the strong polarization of the CO bond of 3 (X = O) keeps the bond short because of the Coulomb

Table 1. HF/6–31G* and MP2/6–31G* optimized geometry parameters (bond lengths in Å, angles in degrees), total energies E_{tot} (a.u.) and zero-point vibrational energies ZPE (a.u.) of 1,2-dithiolylium-4-methide and its valence isomers in the lowest energy singlet (s) and triplet (t) states; relative energies (ΔE, ΔH, ΔG) are referred to 2 and are given in kcal mol^{-1} and the dipole is given in debye

	2 (X=CH₂, s)				2 (X=CH₂, t)		4 (X=CH₂, s)		5 (X=CH₂, s)	
	RHF[a]	UHF[b]	RMP2[c]	UMP2	UHF	UMP2	RHF	RMP2	RHF	RMP2[d]
C_2C_1	1·360	1·333	1·354	1·368	1·411	1·405	1·334	1·354	1·335	1·349
C_3C_2	1·436	1·460	1·463	1·438	1·413	1·402	1·480	1·472	1·477	1·478
S_4C_3	1·679	1·739	1·687	1·711	1·753	1·730	1·604	1·624	1·612	1·624
H_7C_3	1·073	1·072	1·086	1·083	1·072	1·082	1·080	1·095	1·080	1·094
H_9C_1	1·073	1·074	1·082	1·084	1·073	1·082	1·075	1·086	1·073	1·085
$C_3S_4C_1$	126·7	124·0	126·2	124·2	122·6	122·5	117·4	117·7	121·9	122·1
$S_4C_3C_2$	121·5	118·5	120·4	119·2	117·8	118·1	129·0	127·6	128·4	127·5
$C_5C_3C_1$	106·5	112·0	107·7	111·7	114·9	115·0	125·2	124·6	116·2	115·7
$H_7C_3C_2$	123·1	124·0	123·9	124·2	124·9	125·0	112·4	113·5	113·8	114·3
$H_9C_1C_2$	120·9	121·4	121·1	121·1	121·0	121·1	121·8	121·6	120·8	120·6
$S_4C_3C_2C_1$	180·0	179·9	180·0	180·0	179·9	180·0	153·6	155·0	-0·5	-0·4
$H_7C_3C_2C_1$	0·0	0·0	0·0	0·0	-0·1	0·0	-21·8	-21·6	179·4	179·5
$H_9C_1C_2C_3$	0·0	0·0	-0·1	0·0	0·0	0·0	4·0	3·3	0·0	0·1
CSSC	0·0	0·0	0·0	0·0	0·0	0·0	—	—	—	—
SS	1·997	2·086	2·027	2·083	2·093	2·099	3·566	3·454	5·544	5·548
E_{tot} (HF/6–31G*)	-948·658988	-948·725133	-948·656680	-948·722093	-948·760285	-948·759237	-948·749625	-948·747502	-948·756392	-948·755330
E_{tot} (MP2/6–31G*)			-949·493284	-949·481767		-949·491247		-949·542544		-949·545238
ZPE	0·06983	0·07040	0·06540	0·06878	0·06758	0·06545	0·07208	0·06746	0·07199	0·06750
$\langle S \rangle^2$	0·0	1·0	0·0	1·0	2·2	2·2	0·0	0·0	0·0	0·0
ΔE_{tot} (HF and MP2, resp.)	0·0	-41·5	0·0	+7·2	-63·6	+1·3	-56·9	-30·9	-61·1	-32·6
ΔZPE	0·0	+0·4	0·0	+2·1	-1·4	0·0	+1·4	+1·3	+1·4	+1·3
$\Delta H_{298.15}$	0·0	+0·2	0·0	+3·1	-1·2	+0·9	+1·7	+2·3	+1·7	+1·9
$\Delta G_{298.15}$	0·0	+0·5	0·0	+0·8	-2·1	-1·5	+0·5	-0·5	+0·1	+0·1
μ	3·7	1·5	3·4	1·2	2·4	2·3	5·0	5·1	0·3	0·3

[a] RHF → UHF instability.
[b] One imaginary frequency: -48·4 cm^{-1}.
[c] Two imaginary frequencies: -132·3, -56·7 cm^{-1}.
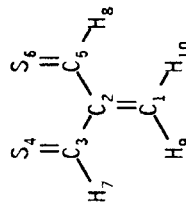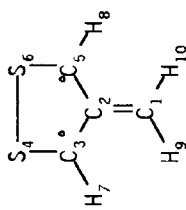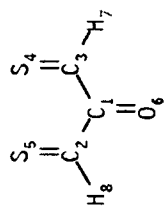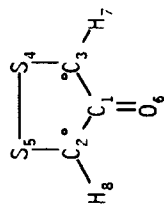[d] One imaginary frequency: -24·3 cm^{-1}.
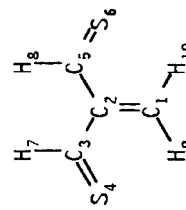
Table 2. HF/6–31G* and MP2/6–31G* optimized geometry parameters (bond lengths in Å, angles in degrees), total energies E_{tot} (a.u.) and zero-point vibrational energies ZPE (a.u.) of 1,2-dithiolylium-4-olate and its valence isomer in the lowest energy singlet (s) and triplet (t) states; relative energies (ΔE, ΔH, ΔG) are referred to **2** and are given in kcal mol⁻¹ and the dipole is given in debye

	2 (X = O, s)				2 (X = O, t)		4 (X = O, s)	
	RHF[a]	UHF	RMP2[b]	UMP2	UHF	UMP2[c]	RHF	RMP2
C_1C_2	1·430	1·463	1·464	1·445	1·427	1·455	1·506	1·497
S_4C_3	1·680	1·718	1·678	1·678	1·743	1·707	1·595	1·621
O_6C_1	1·226	1·199	1·234	1·250	1·257	1·219	1·190	1·233
H_7C_3	1·073	1·072	1·086	1·084	1·071	1·081	1·078	1·092
$C_3C_1C_2$	107·6	110·7	107·9	108·9	115·5	112·9	122·3	122·0
$S_4C_3C_1$	121·2	119·2	120·5	120·5	117·2	118·6	125·1	124·5
$O_6C_1C_3$	126·2	124·7	126·1	125·5	122·2	123·5	118·9	119·0
$H_7C_3C_1$	121·9	122·2	122·3	122·3	123·6	122·2	112·7	113·4
$S_4C_3C_1C_2$	0·0	0·0	0·0	0·0	0·0	0·0	-42·5	-37·9
$O_6C_1C_3S_4$	180·0	180·0	180·0	180·0	180·0	180·0	137·5	142·1
$H_7C_3C_1C_2$	180·0	180·0	180·0	180·0	180·0	180·0	144·4	149·4
CSSC	0·0	0·0	0·0	0·0	0·0	0·0	51·6	47·2
SS	2·013	2·080	2·041	2·055	2·108	2·134	3·755	3·599
E_{tot} (HF/6–31G*)	-984·549655	-984·581271	-984·546931	-984·575034	-984·589462	-948·586254	-984·58235	-984·577377
E_{tot} (MP2/6–31G*)			-985·421617	-985·391229		-985·358075		-985·420575
ZPE	0·04714	0·04507	0·04418	0·04482	0·04361	0·04178	0·04639	0·04284
$\langle S \rangle^2$	0·0	0·9	0·0	0·8	2·2	2·2	0·0	0·0
E_{tot} (QCISD/6–31G*)			-985·405363					-985·422390
E_{tot} (SCRF)	-984·556433		-985·426505				-984·582339	-985·420583
ΔE_{tot} (HF and MP2, resp.)	0·0	-19·8	0·0	+19·1	-25·0	+39·9	-20·5	+0·7
ΔE_{tot} (QCISD)	0·0		0·0					-10·7
ΔE_{tot} (SCRF)	0·0		0·0				-16·3	+3·7
ΔZPE	0·0	-1·3	0·0	+0·4	-2·2	-1·5	-0·5	-0·8
$\Delta H_{298·15}$	0·0	-0·9	0·0	+0·4	-1·7	-1·6	+0·4	-0·1
$\Delta G_{298·15}$	0·0	-1·7	0·0	+0·5	-3·5	-2·1	-2·3	-2·6
μ	5·6	2·6	5·6	3·5	0·5	0·8	0·1	0·1

[a] RHF → UHF instability.
[b] The corresponding first three bond lengths of 3,5-diphenyl-1,2-dithiolylium-4-olate are 1·448, 1·698 and 1·250 Å.[12]
[c] One imaginary frequency: -26·1 cm⁻¹.

Table 3. HF/6–31G* and MP2/6–31G* optimized geometry parameters (bond lengths in Å, angles in degrees), total energies E_{tot} (a.u.) and zero-point vibrational energies ZPE (a.u.) of 1,2-dithiolylium-4-thiolate and its valence isomer in the lowest energy singlet (s) and triplet (t) states; relative energies (ΔE, ΔH, ΔG) are referred to 2 and are given in kcal mol⁻¹ and the dipole is given in debye

	2 (X = S, s)				2 (X = S, t)		4 (X = S, s)	
	RHF[a]	UHF[b]	RMP2	UMP2	UHF	UMP2	RHF	RMP2
C_1C_2	1·397	1·427	1·430	1·406	1·406	1·395	1·488	1·477
S_4C_3	1·688	1·715	1·685	1·678	1·751	1·726	1·601	1·627
S_6C_1	1·728	1·666	1·678	1·711	1·716	1·708	1·616	1·644
H_7C_3	1·073	1·072	1·086	1·086	1·071	1·082	1·077	1·092
$C_3C_1C_2$	109·7	111·2	108·9	109·6	116·0	116·1	121·7	121·6
$S_4C_3C_1$	120·7	119·5	120·4	120·5	117·3	117·6	125·3	125·1
$S_6C_1C_1$	125·2	124·4	125·5	125·2	122·0	122·0	119·2	119·2
$H_7C_3C_1$	122·6	122·8	123·0	123·2	124·6	124·6	113·5	114·2
$S_4C_3C_1C_2$	0·0	0·0	0·0	-0·1	0·0	-0·1	-40·6	-35·2
$S_6C_1C_3S_4$	180·0	180·0	180·0	-180·1	180·0	180·0	139·4	144·8
$H_7C_3C_1C_2$	180·0	180·0	180·0	180·0	180·0	179·9	145·7	150·7
CSSC	0·0	0·0	0·0	0·0	0·0	0·0	—	—
SS	2·020	2·062	2·026	2·025	2·097	2·107	3·666	3·508
E_{tot} (HF/6–31G*)	-1307·21483	-1307·22817	-1307·21195	-1307·22462	-1307·25226	-1307·25117	-1307·22079	-1307·21821
E_{tot} (MP2/6–31G*)			-1308·02576	-1308·00493		-1307·98757		-1308·02202
ZPE	0·04543	0·04203	0·04251	0·04369	0·04245	0·04134	0·04413	0·04107
$\langle S \rangle^2$	0·0	0·8	0·0	0·6	2·2	2·2	0·0	0·0
E_{tot} (QCISD/6–31G*)	-1307·23008		-1308·01471					-1308·02228
E_{tot} (SCRF)			-1308·03755				-1307·22096	-1308·02215
ΔE_{tot} (HF and MP2, resp.)	0·0	-8·4	0·0	+13·1	-23·5	+24·0	-3·7	+2·3
ΔE_{tot} (QCISD)	0·0		0·0					-4·8
ΔE_{int} (SCRF)	0·0		0·0				+5·7	+9·7
ΔZPE	0·0	-2·1	0·0	+0·7	-1·9	-0·7	-0·8	-0·9
$\Delta H_{298·15}$	0·0	-2·2	0·0	+0·7	-1·5	-0·5	-0·1	-0·2
$\Delta G_{298·15}$	0·0	-2·2	0·0	+0·8	-3·0	-1·5	-2·5	-2·7
μ	8·5	4·6	8·1	5·8	0·2	0·1	1·0	1·0

[a] RHF → UHF instability.
[b] One imaginary frequency: -130·4 cm⁻¹.

Table 4. Bond lengths r_{CX} (Å), force constants f_{CX} (mdyn Å^{-1}) and scaled stretching frequencies v_{CX} (cm^{-1})[a] of CO and CS bonds and total (q_X) and π-charges (q_X^π) of the exocyclic oxygen and sulphur atom, respectively, calculated for the singlet molecules at the MP2/6–31G* geometry

Parameter	X = O					X = S			
	2	7	7[b]	8	9	2	7[c]	8[c]	9[c]
r_{CX}	1·234	1·275	1·284	1·226	1·245	1·678	1·732	1·628[d]	1·664[e]
v_{CX}	1679·3	1652·0	1553	1685·8	1581·8 1632·4	908·5 1310·0	723	1076	1112
q_X[f]	−0·70	−0·81	−0·81	−0·52	−0·62	−0·42	−0·87	−0·12	−0·26
q_X^π	−0·64	−0·69	−0·69	−0·37	−0·45	−0·78	−0·86	−0·30	−0·47

[a] In order to take into account the anharmonicity of the vibration, calculated frequencies are scaled by 0·95 at the MP2/6–31G* level.
[b] 6–31+G* basis set.
[c] Ref. 23.
[d] Microwave study, 1·62 Å.[24]
[e] X-ray diffraction study, 1·675 Å.[25]
[f] SCF densities, calculated at MP2/6–31G* optimum geometries.

attraction between carbon and oxygen. At any rate, pure enolate structures of the anions **7** exhibit considerably longer C–S and C–O bonds than the cyclic thiolate and olate structures (see Table 4).

The ylidic structure in the thiolate and olate structures is supported by the electron distribution and the dipole moments. According to the data in Table 4, electron charge is shifted from the ring to the exocyclic group or atoms. Within the π-electron system, the intramolecular electron transfer in the thiolate structure **2** amounts to −0·78e (cf. thiotropone, −0·47e) and in the olate structure −0·64e (cf. tropone, −0·45e). Thus, the ylidic formula of **2** (X = S) appears as to be a fairly good representation of the actual electron distribution. The total charge at the heteroatom is mainly determined by the electronegativity, which is larger for oxygen than for sulphur. Mesomeric formulae of conjugated compounds represent the π-electron distribution rather than the total electron distribution. Although dipole moments are defined by the whole electron system, the calculated dipole moments support the greater zwitterionic character of the thiolate (cf. Tables 2 and 3). The dipole moment of 8·1 D of the thiolate greatly exceeds that of the olate (5·6 D).

The geometries of the isomeric compounds of classical structure in series **4** are more conventional. The only peculiarity is the slight distortion of the s-cis,s-cis structures (C_2 symmetry) while the s-trans,s-trans structures are planar (C_{2h} symmetry). The C=C bond length in **4** (X = CH$_2$, 1·35 Å) corresponds closely to that of butadiene (1·36 Å), and the same holds for the C=S bonds (1·62 Å) when compared with the corresponding bonds of trans-dithioglyoxal (1·63 Å) and thioacrolein (1·63 Å).

Vibrational frequencies

In order to ensure that geometry-optimized structures have actually been calculated, the Hessian was checked

for the presence of exclusively positive eigenvalues. At the RMP2 level, this condition was fulfilled in all cases except for **2** and **5** (X = CH$_2$). Knowledge of the vibrational spectra may be of use for the experimental detection of the title compounds (or their isomers) by means of the matrix isolation technique. For this purpose, line spectra of **2** (X = O, S) are depicted in Figure 1. The most intense absorptions expected in the infrared absorption spectrum belong to out-of-plane vibrational modes. We refrain from discussing normal modes in detail and restrict ourselves rather to the consideration of the exocyclic CS and CO stretching vibrations of the thiolate and olate (see Table 4). The CO stretch of the 1,2-dithiolylium-4-olate is higher than that of the pure enolate of **7** (X = O) and it appears at similar wavenumbers to those calculated for acrolein (**8**, X = O). Tropone is less suited for comparison.

Experimental[19] and theoretical[20] vibrational analysis of the spectrum of tropone revealed that the CO bond is involved in coupled vibrations. The same problem occurs with thione and thiolate compounds. Whereas the calculated CS stretch of thiotropone is unequivocally positioned at 1112 cm^{-1} (scaled by 0·95; experimental[21] 1087 cm^{-1}), the unknown thiolate should exhibit two frequencies rather than one.

Valence isomerization and singlet/triplet splitting

Introduction of the disulphide bridge into the dimethylenemethane parent structure (**3**, X = CH$_2$) stabilizes the singlet state relative to the triplet state. In the case of the 1,2-dithiolylium methide (**2**, X = CH$_2$), the singlet and triplet states are nearly degenerate. The singlet molecule is favoured by only 1·3 kcal mol^{-1} (1 kcal = 4·184 kJ) over the triplet molecule at the MP2 level of theory (cf. Table 1). The small S/T gap raises the question of whether higher levels of theory might reverse the favoured state. Fortunately, from the chemical point of view this question is minor interest: the
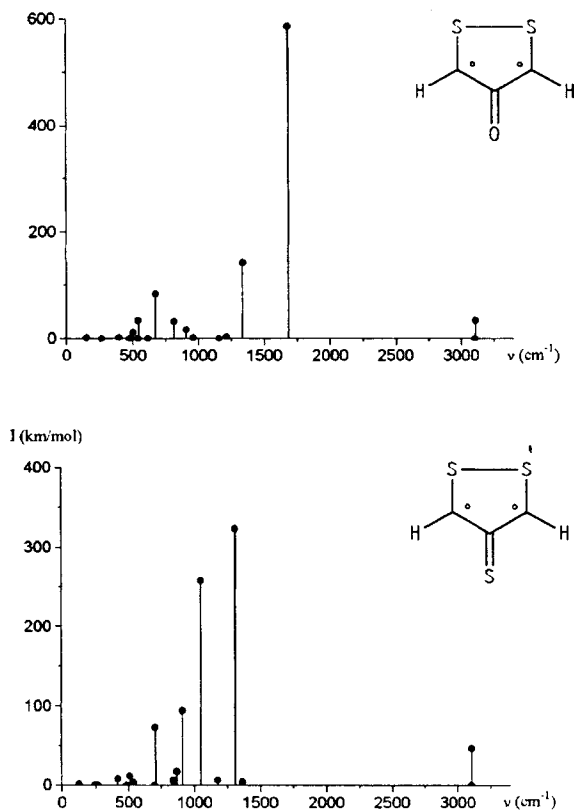
Figure 1. RMP2/6-31G* normal-mode vibrational frequencies ν (cm^{-1}) and intensities (km mol^{-1}) of the title compounds presented as line spectra (top, 2, X = O; bottom, 2, X = S)

isomeric open-chain dithiocarbonyls 4 and 5 (X = CH$_2$) are more than 30 kcal mol^{-1} lower in energy and thus clearly more stable than the cyclic 1,2-dithiolylium-4-methide structure (2, X = CH$_2$).

According to the relative energies given in the lower parts of Tables 2 and 3, the cyclic structures are stabilized on passing from the methide to the thiolate or olate structure. The heterocycles in the latter cases are now nearly isoenergetic with the dithiocarbonyls. Dithiocarbonyls should exist in rotamers. As demonstrated with 4 (X = CH$_2$) and 5 (X = CH$_2$) the last-mentioned compound is more stable by 4 kcal mol^{-1}. Isomerizations of rotamers should occur at room temperature.

In order to check the reliability of the small difference in energy between the ring-closed and ring-opened isomers, the energies of the isolated molecules were recalculated at a higher level of theory [RQCISD(T)/6-31G*//RMP2/6-31G* calculations]. In addition, ZPE and thermodynamic corrections were performed to define heats of isomerization, and the self-consistent

reaction field was employed to simulate the solvent effect (both at the MP2/6-31G* level).

At the higher level of theory, surprisingly, the dithiocarbonyls are stabilized by 5 and 10 kcal mol^{-1} relative to the (diradicaloid) thiolate and olate compounds, respectively. However, as expected, zwitterionic structures are stabilized in polar solvents. The gain in energy amounts to about 7 kcal mol^{-1} for thiolate and about 3 kcal mol^{-1} for olate in acetonitrile as solvent. Finally, ZPE and thermodynamic correction favour slightly the open-chain structure by about 3 kcal mol^{-1} at room temperature. In total, 1,2-dithiolylium-4-olate is predicted to be slightly favoured as an open-chain isomer whereas in the case of the sulphur compounds both the ring-closed and the ring-opened isomers may equilibrate in case of a low barrier of isomerization.

Both the thiolate and olate singlet molecules are diradicaloid, as indicated by the RHF/UHF instability of the RHF solution. Accordingly, the S/T gap is small, about 20 kcal mol^{-1}. The energy of the RHF/6-31G* calculation at optimum geometry is depressed by 8·4 kcal mol^{-1} for the thiolate and 20 kcal mol^{-1} for the olate by geometry optimization within the UHF/6-31G* procedure (cf. Tables 2 and 3). The diradical character may be of significance in the chemical reactivity at the ring carbon atoms. It is known that the 3,5-substituted compounds 2 undergo thermal [4 + 3]cycloaddition reactions with 2,3-dimethylbuta-1,3-diene,[22] as is known for many reactive 1,3-dipoles.

CONCLUSION

Although the title compounds are closely related in their topology and their diradicaloid nature, they differ in their molecular structures and their electronic properties. 1,2-Dithiolylium-4-thiolate and 1,2-dithiolylium-4-olate are clearly related to the iso-π-electronic compounds thiotropone (tropylium thiolate) and tropone (tropylium olate), respectively. The first-mentioned compound approaches the zwitterionic structure most.

The heterocycles differ from the related troponoid compounds in that the S—S bond may open, resulting in dithiocarbonyls. Owing to energetically favoured ring opening, 1,2-dithiolylium-4-methide should be preferred as the open-chain valence isomer. In the case of the heteroanalogues, the valence isomers are, however, nearly equal in energy. Owing to the pronounced solvent effect expected for the strongly polar 1,2-dithiolylium-4-thiolate, this heterocycle may display both isomers in equilibrium in solution.

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