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SPIROCONJUGATION IN ORTHOTHIOCARBONATES[1]

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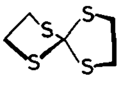
Abstract—The He(I) photoelectron (PE) spectra of the orthothiocarbonates **1**–**3** have been investigated. To understand the splitting pattern in the low energy region a comparison with chemically related molecules has been made. In addition, molecular orbital calculations based on a ZDO model and semiempirical calculations were carried out with variation of dihedral angles. The split of the first four orbitals, which depends very much on the geometry, is explicitly discussed. The splitting due to spiroconjugation amounts to 1.1 eV for **1**, 0.55 eV for **2**, and 0.45 eV for **3**.

The concept of spiroconjugation put forward by Simmons and Fukunaga[3] and Hoffmann, Imamura and Zeiss[4] has stimulated theoretical[5] and experimental interest.[6] In this paper we would like to report on the He(I) photoelectron (PE) spectra of the sulphur compounds **1**,[7] **2**,[7] and **3**[8] which are well suited for an investigation of spiroconjugation because of low ionization potentials of the 3p type lone pairs on the sulphur atoms.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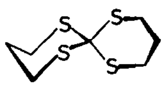
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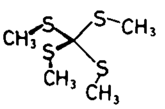
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The PE spectra of **1** to **3** are shown in Fig. 1 and the vertical ionization potentials, $I_{v,J}$, of the first bands are collected in Table 1. A comparison of the PE spectra shows that there are four bands below 10 eV. This view is supported by comparing the half band width of the first peak with the second peak in the PE spectra of **1** and **2** and by comparing the third peak (band ⑤) with the first two in the PE spectrum of **3**. Furthermore one notices by looking at Fig. 1 that bands ② to ④ become closer together on going from **1** to **3**. In contrast to this, band ⑤ remains relatively constant. These observations are summarized in Fig. 2.

DISCUSSION

Sulphur lone pair ionizations in alkyl sulphides

Substituting the hydrogen atoms of H_2S by alkyl groups we observe the following change in the first ionization potential (Table 2).

As anticipated the ionization potential decreases strongly when we replace the hydrogens in H_2S by alkyl groups due to both the inductive and hyperconjugative effect of these groups. This view is corroborated by the observation that in diethyl-sulphide and the 5- and

Table 1. Vertical ionization potentials for orthothiocarbonates, assignment and comparison with calculated values. All values in eV

Compound	Band	$I_{v,J}$	Assignment (D_{2d})	Koopmans values $-\epsilon_J$ ZDO	EH	MINDO/3
1	①	8.26	$a_2(\Psi_3)$	$-8.14(\Psi_3)$	$-11.91(\Psi_3)$	$-8.71(\Psi_3)$
	②	8.71	$e(\Psi_1, \Psi_2)$	$-8.72(\Psi_1)$	$-12.15(\Psi_1)$	$-8.90(\Psi_1)$
	③	9.01		$-8.97(\Psi_2)$	$-12.34(\Psi_2)$	$-9.18(\Psi_2)$
	④	9.36	$b_1(\Psi_4)$	$-9.36(\Psi_4)$	$-12.63(\Psi_4)$	$-10.20(\Psi_4)$
	⑤	10.77				
2	①	8.09	$a_2(\Psi_3)$	$-7.95(\Psi_3)$	$-11.75(\Psi_3)$	$-8.66(\Psi_3)$
	②	8.64	$b_1(\Psi_4)$	$-8.69(\Psi_4)$	$-12.02(\Psi_1)$	$-8.74(\Psi_1)$
	③ ④	8.85	$e(\Psi_1, \Psi_2)$	$-8.88(\Psi_1, \Psi_2)$	$-12.04(\Psi_2)$	$-8.75(\Psi_2)$
					$-12.30(\sigma)$	$-9.15(\sigma)$
	⑤	10.40				
3	①	8.29	$b_1(\Psi_3)$	—	$-11.33(\Psi_3)$	$-8.52(\Psi_1)$
	② ③ ④	8.69	$a_2(\Psi_4), e(\Psi_1, \Psi_2)$		$-11.92(\Psi_2)$	$-8.66(\Psi_2)$
					$-12.10(\Psi_1)$	$-8.79(\Psi_3)$
					$-12.22(\Psi_4)$	$-10.30(\Psi_4)$
	⑤	10.42				

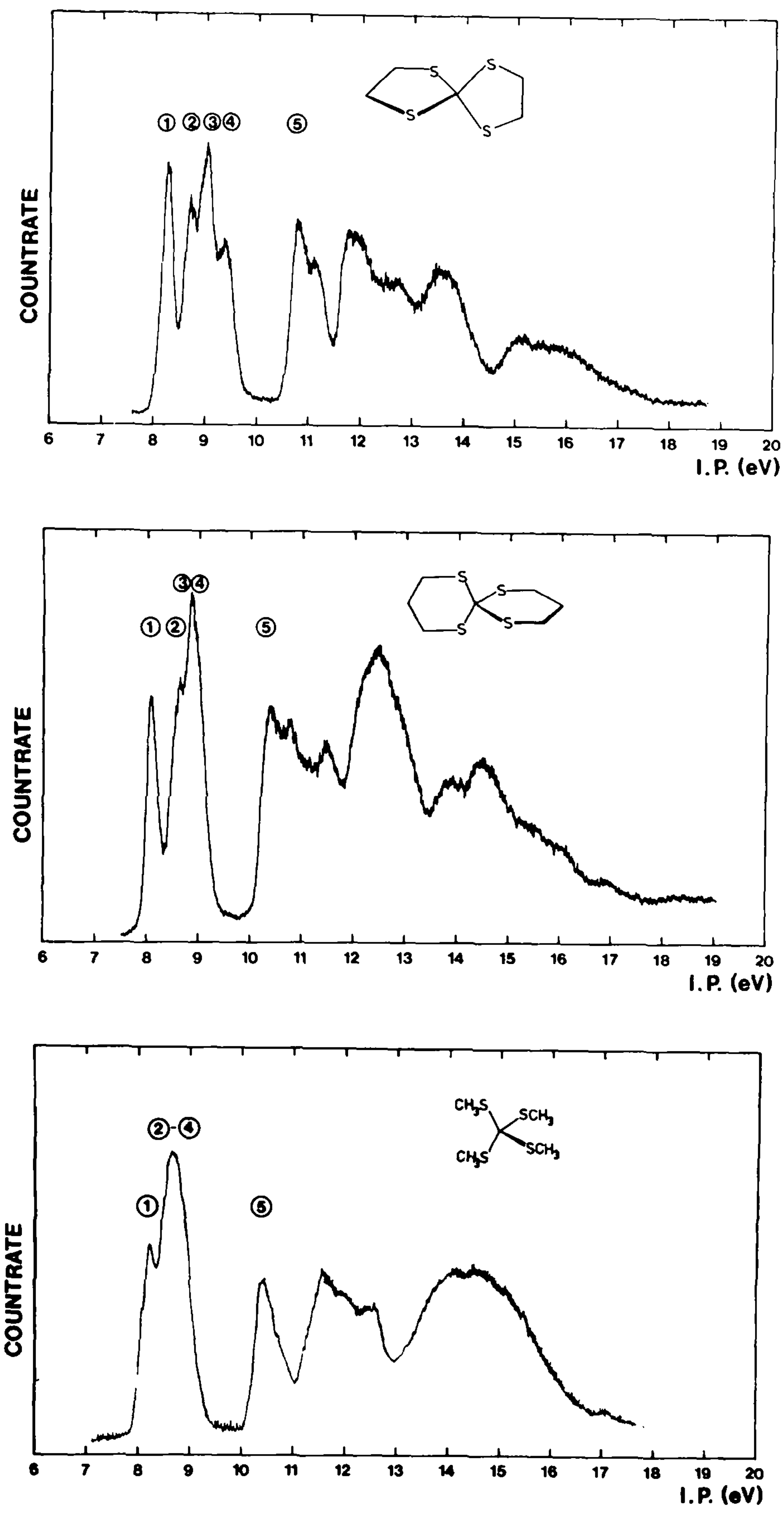


Fig. 1. PE spectra of 1, 2 and 3.

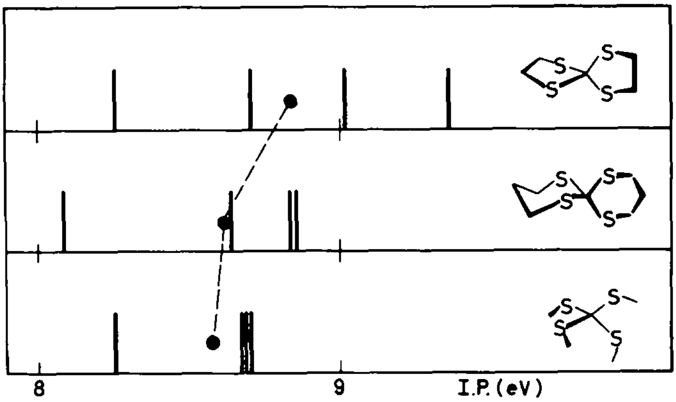
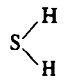
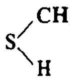
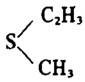
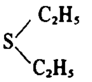
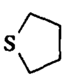
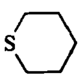


Fig. 2. PE spectroscopic splitting pattern for the lowest four ionization potentials of 1, 2 and 3. The center of gravity is indicated by a ●.

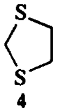
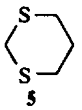
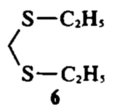
Table 2.

						
IP_1(eV)	10.47[9]	9.45[10]	8.67[10]	8.44[10]	8.42[11]	8.45[12]

6-membered sulphides the ionization potential remains constant since we expect similar hyperconjugative and inductive effects on the 3p lone pair of the sulphur center in all three species.

In the 1,3-disulphides **4** to **6** shown in Table 3 we observe that the center of gravity, $\overline{IP}_{1,2}$, in case of **4** and **6** is raised with respect to that of **5**. This we attribute to the fact that in **4** and **6** C–C hyperconjugation, as found in the sulphides, is not possible but only C–H hyperconjugation which exerts a smaller effect. The centers of gravity for the first two bands obtained for **4**, **5** and **6** are close to those values we derive when we assume that the first four bands of **1**, **2** and **3** are due to the ejection of an electron out of an orbital which is essentially a linear combination of the sulphur 3p orbitals (see Fig. 3). The centres of gravity are for **1**: 8.84 eV, for **2**: 8.64 eV and for **3**: 8.58 eV (Table 1).

Table 3.

	 **4**	 **5**	 **6**
IP_1(eV)	8.77	8.33	8.66
IP_2(eV)	9.12	8.76	8.91
$\overline{IP}_{1,2}$(eV)	8.95	8.55	8.79

Basis orbitals

For the interpretation of the PE spectra we assume the validity of Koopmans' theorem $(-\epsilon_J = I_{v,J})$[15] which allows us to correlate the energies of the molecular orbitals, ϵ_J, with the observed vertical ionization potentials, $I_{v,J}$.

In a first approach to construct a MO-model, we consider only the 3p orbitals on the sulphur centers 1 to 4 as shown in Fig. 3. These four basis orbitals give rise to the four linear combinations (1) to (4).

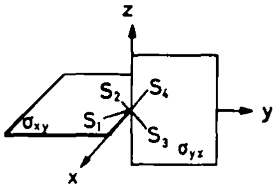


Fig. 3.

$$\Psi_1(S, A) = \frac{1}{\sqrt{2}}(p_{z,1} + p_{z,2}) \quad (1)$$

$$\Psi_2(A, S) = \frac{1}{\sqrt{2}}(-p_{x,3} - p_{x,4}) \quad (2)$$

$$\Psi_3(A, A) = \frac{1}{\sqrt{2}}(p_{z,1} - p_{z,2}) \quad (3)$$

$$\Psi_4(A, A) = \frac{1}{\sqrt{2}}(-p_{x,3} + p_{x,4}). \quad (4)$$

The symbols S and A mean symmetric and antisymmetric, respectively, with respect to the planes σ_{yz} and σ_{xy} specified in Fig. 3. For reasons of symmetry Ψ_3 and Ψ_4 can interact with each other giving rise to the following symmetry adapted linear combinations corresponding to the irreducible representations A_2 and B_1 in D_{2d}:

$$\Psi_3'(A_2) = \frac{1}{2}(p_{z,1} - p_{z,2} + p_{x,3} - p_{x,4}) \quad (5)$$

$$\Psi_4'(B_1) = \frac{1}{2}(p_{z,1} - p_{z,2} - p_{x,3} + p_{x,4}). \quad (6)$$

The orbitals Ψ_1 and Ψ_2 are already in the symmetry-adapted form. In D_{2d} symmetry they belong to the irreducible representation E.

The orbitals Ψ_1, Ψ_2, Ψ_3' and Ψ_4' are shown in Fig. 4, which displays a qualitative interaction diagram for the

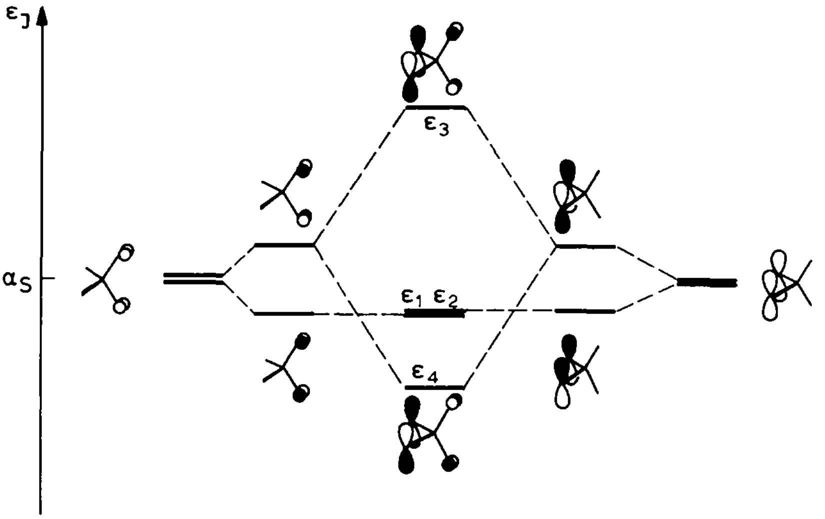
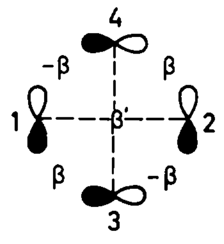


Fig. 4. Qualitative model for the spiroconjugation between the sulphur lone pairs in orthothiocarbonates.

interaction of the four lone pair orbitals on sulphur. It is assumed that through space interaction between S_1-S_2 and S_3-S_4, respectively, dominates. This assumption is based on semiempirical calculations assuming nonplanar structures for **4** and **5**.

Model calculations

In Fig. 4 we assumed two different interactions: the through space interaction between S_1-S_2 and S_3-S_4 described by the parameter β' and the spiroconjugation described by β.



The above choice of relative phases of the basis 3p atomic orbitals makes the value of the through space interaction term negative ($+\beta'$). The two resonance integrals are defined as follows:

$$\beta = -\langle p_{z,1}|H|p_{x,4}\rangle = \langle p_{z,1}|H|p_{x,3}\rangle = \langle p_{z,2}|H|p_{x,4}\rangle = -\langle p_{z,2}|H|p_{x,3}\rangle \quad (7)$$

$$\beta' = \langle p_{z,1}|H|p_{z,2}\rangle = \langle p_{x,3}|H|p_{x,4}\rangle. \quad (8)$$

In order to derive the interaction matrix one must first specify the following resonance integrals:

$$H_{3,3} = \langle\Psi_3|H|\Psi_3\rangle = \langle\Psi_4|H|\Psi_4| = H_{4,4} = A_S - \beta'. \quad (9)$$

A_S is the Coulomb integral of a sulphur 3p orbital.

For the off-diagonal element we obtain

$$H_{3,4} = \langle\Psi_3|H'|\Psi_4\rangle = H_{4,3} = 2\beta. \quad (10)$$

This leads to the following secular determinant:

$$\begin{vmatrix} A_S-\beta'-\epsilon & 2\beta \\ 2\beta & A_S-\beta'-\epsilon \end{vmatrix} = 0. \quad (11)$$

To solve this equation numerically we have to estimate A_S, β' and β.

The basis orbital energy (A_S) of sulphur in **1** and **2** should incorporate the inductive and hyperconjugative effects of the methylene chains but not the hyperconjugative effect of the central C–S bonds. We therefore expect different basis orbital energies of sulphur in **1** and **2**.

Varying the basis orbital energies of sulphur between −8.8 eV and −9.3 eV we obtain quite a good fit with experiment by adopting a value of −9.3 eV in case of **1** and −9.1 eV in case of **2**.

For our planar model we adopt an intermediate value of

$$A_S = -9.2\,\text{eV}. \quad (12)$$

To evaluate β' we make use of the following assumption:

$$\beta_{S\ S} = \frac{\beta_{C-C}}{S_{C-C}} \cdot S_{S\cdot\cdot S} \simeq \frac{-3.0}{0.27}$$

$$= S_{S\ S} = -11.1\, S_{S\cdot\cdot S}\,[\text{eV}]. \quad (13)$$

In (13) S_{C-C} is the π-overlap integral for two carbon atoms separated by 1.34 Å and β_{C-C} is the corresponding resonance integral.

Assuming a tetrahedral S–C–S angle and a S–C bond length of 1.80 Å we obtain the following overlap integrals:

$$S_{\text{spiro}}: \quad \langle 3p_{z,1}|3p_{y,3}\rangle = 0.037$$

$$S_{\text{through space}}: \quad \langle 3p_{z,1}|3p_{z,2}\rangle = +0.024. \quad (14)$$

From (13) and (14) we obtain

$$\beta = -0.41 \quad \text{and} \quad \beta' = -0.26\,\text{eV} \quad (15)$$

which, if substituted together with (13) in (11), yield

$$\epsilon_3 = -8.12\,\text{eV and } \epsilon_4 = -9.76\,\text{eV}. \quad (16)$$

The degenerate eigenvalues amount to $\epsilon_1 = \epsilon_2 = -9.46$; the corresponding wave functions Ψ_3' and Ψ_4' are given in (5) and (6).

The result obtained does, however, not correlate with the experimental splitting pattern (Fig. 2).

Semiempirical calculations of the EH[16] and MINDO/3[17] type suggest that in addition to through space interaction and spiroconjugation also through bond interaction[18] between e(Ψ) and e(σ) has to be taken into account. This through bond interaction is illustrated in Fig. 5 for one possible linear combination.

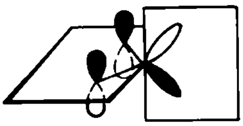


Fig. 5.

In addition, the non-planar structure 1 of the orthothiocarbonates investigated, has to be incorporated into the model.

Deviation from D_{2d} symmetry

A consideration of molecular models for 1 and 2 shows that the assumed planarity for the rings in 1 and 2 is not valid, and that the degree of nonplanarity is larger in 2 than in 1. We express the nonplanarity by the deviation of the 3p orbital on the sulphur centers from its original position, i.e. perpendicular to the plane defined by C_1, S_1 and S_2 (x–y plane) and C_1, S_3 and S_4 (y–z plane) respectively. The original position of the 3p orbital of S_1 or S_2 is parallel to the z axis. Its deviation from this direction can be described by two angles θ and ϕ defined in Fig. 6 for S_2.

Analogously, each 3p orbital on the centers S_1, S_2, S_3 and S_4 can be expressed in terms of p_x, p_y and p_z as a function of the angles θ and ϕ (for details see Appendix).

As a consequence of a non-planar structure, the four 3p orbitals on the sulphur centers are arranged as shown in Fig. 6. There are three different spiro resonance integrals β_2, β_3 and β_4 and one non-spiro resonance integral β_1. These resonance integrals can be evaluated as shown in the Appendix and thus our ZDO model can be extended to the non planar case.

The best fit between the recorded PE spectra and our model calculations is found when we choose $\theta = 5°$ and $\phi = 30°$ for 1 and $\theta = 24°$ and $\phi = 45°$ for 2. The numerical values are listed with those of other semiempirical calculations in Table 1. Comparison with the observed PE spectroscopic ionization potentials (Fig. 7) demonstrates, that our modified model now incorporates all essential features of conjugation in orthothiocarbonates.

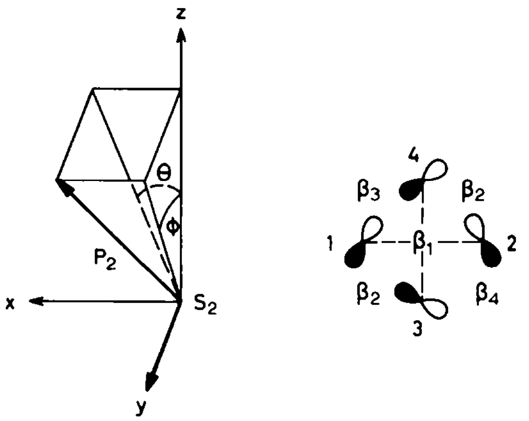


Fig. 6.

Structure approximation for $C(SCH_3)_4$

The structure of 3 is unknown. To interprete its PE spectrum (Fig. 1) we adopt a similar conformation (Fig. 8a) of the methyl-groups as it was calculated for trimethylphosphate.[19] EH calculations on 3 are in good agreement with experiment for a rotational angle $\omega \sim 50$–$60°$ (Fig. 9). The angle ω is defined in (Fig. 8a).

In such a conformation the arrangement of the 3p orbitals on the sulphur centers is the same as in 2 (Figs. 8b, 8c). This explains the close similarity of the PE spectra of 2 and 3.

Summary and concluding remarks

Assuming the validity of Koopmans' theorem, for 1 a good agreement between calculations (ZDO and EH) and experiment (Table 1) is obtained only if we allow the five membered rings in 1 to be nonplanar. The splitting, $\epsilon_3 - \epsilon_4$,

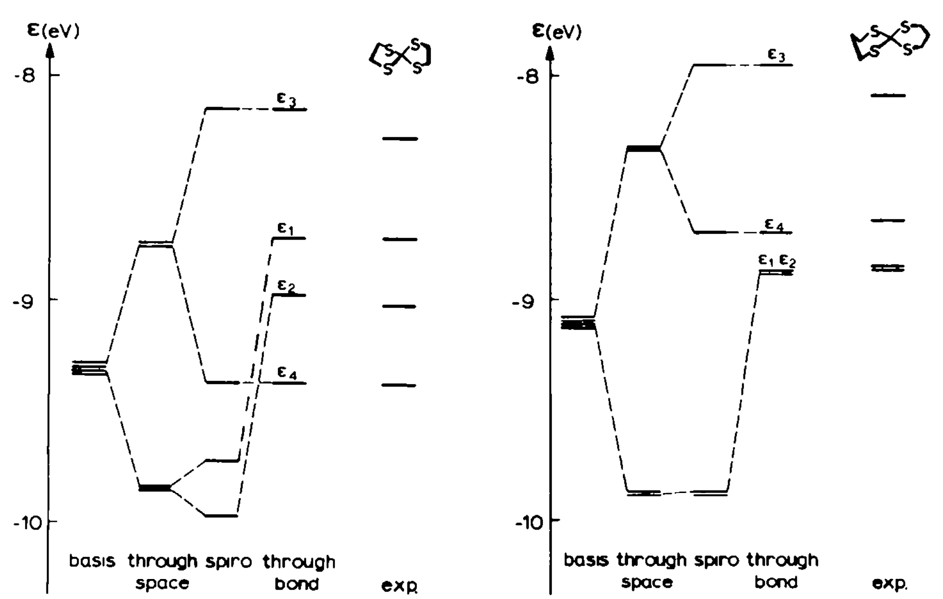


Fig. 7. Comparison between the calculated and observed splitting patterns for the cyclic orthothiocarbonates 1 and 2.

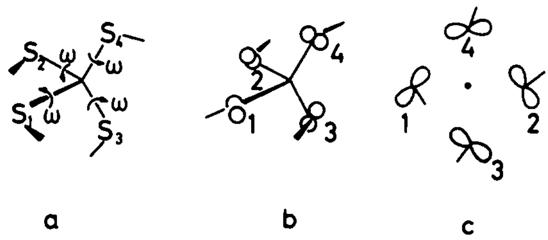


Fig. 8.

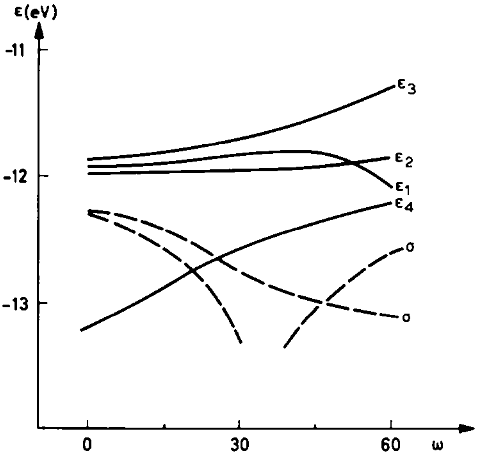


Fig. 9. EH eigenvalues for orthothiocarbonate 3 as a function of the rotational angle ω.

due to spiroconjugation amounts to 1.1 eV. Although MINDO/3 predicts for 1 some σ levels between 3p lone pair levels we consider this prediction to be an artefact as experienced in similar cases.[16]

For 2 the results of a ZDO model and of semiempirical calculations differ (see Table 1). The ZDO model predicts, analogous to 1, that the first four ionization potentials should arise from the 3p lone pair orbitals Ψ_1 to Ψ_4 if we adopt nonplanar six membered rings in 2. The splitting due to the spiroconjugation then amounts to 0.55 eV. The observation that the center of gravity for bands ① to ④ in 2 is about the same as for 5, is in line with the assignment.

The results of EH and MINDO/3 for 2 (Table 1), however, suggest that two σ or three σ orbitals are placed above Ψ_4. These orbitals are schematically sketched out in Fig. 10.

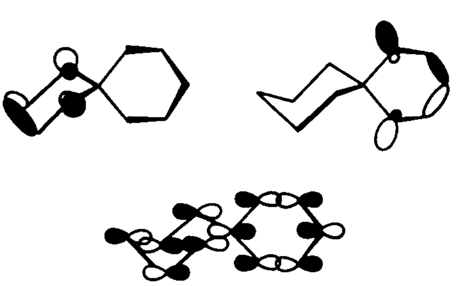


Fig. 10.

They represent linear combinations between the sp^2 lone pairs or 3p orbitals on sulphur and the 2p orbitals on carbon, forming high lying "ribbon orbitals".[20] A final answer is not possible at the present stage due to the complexity of the interrelation between geometry (which is unknown) and orbital interactions.

The PE spectrum of 3 is very similar to that of 2. In contrast to the case of 2, EH calculations predict the first four ionization potentials of 3 to arise from the 3p lone pair orbitals. Their calculated splitting pattern compares well with the observed one.

Summarizing, a comparison between calculation and experimental result indicates a good agreement if the through bond interaction is taken into account. It is interesting to note that in 1 the splitting due to spiroconjugation is nearly twice as large as in 2 and 3. On the other hand, the splitting due to through space interaction is larger for 2 and 3 than for 1. This can be rationalized by adopting different dihedral angles.

EXPERIMENTAL

The preparation of compounds 1, 2 and 3 has been described in the literature.[7,8] All compounds used were analytically pure. The PE spectra were recorded on a PS 18 photoelectron spectrometer (Perkin Elmer Ltd, Beaconsfield, England). The recording conditions were 1: 90°C, 2: 90°C, 3: 25°C.

For the EH and MINDO/3 calculations standard bond lengths and angles[21] were used. As basis set only s and p orbitals were taken.

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APPENDIX

The deviation of the $3p_z$ orbital of S_1 and S_2 and the $3p_x$ orbital of S_3 and S_4 from its colinearity with the z- and x-axis respectively is defined in Fig. 6. The 3p orbitals can be treated as vectors and thus the 3p orbital on each sulphur center can be expressed in terms of p_x, p_y and p_z components as follows:

$$\begin{aligned} p_1 &= A(\mathrm{tg}\theta p_{x,1} - \mathrm{tg}\phi p_{y,1} + p_{z,1}) \\ p_2 &= A(\mathrm{tg}\theta p_{x,2} + \mathrm{tg}\phi p_{y,2} + p_{z,2}) \\ p_3 &= A(\mathrm{tg}\theta p_{x,3} - p_{y,3} - \mathrm{tg}\phi p_{z,3}) \qquad \text{(A1)} \\ p_4 &= A(\mathrm{tg}\theta p_{x,4} - p_{y,4} + \mathrm{tg}\phi p_{z,4}) \\ A &= 1/\sqrt{(\mathrm{tg}^2\theta + \mathrm{tg}^2\theta + 1)}. \end{aligned}$$

The overlap integrals between the $p_n (n = 1 \text{ to } 4)$ are expressed in terms of the six component overlaps shown below.

If we place on each sulphur center a $3p_x$, $3p_y$ and $3p_z$ atomic orbital we can derive six kinds of overlap integrals between them. They are evaluated as follows when the S_1–C–S_2 angle is assumed to be tetrahedral and the C–S distance is taken as 1.8 Å:

$$\begin{aligned} &S_{1z,2z} = 0.024; \quad S_{1z,3x} = -0.053; \quad S_{1z,3y} = -0.037; \\ &S_{1z,3z} = -0.013; \quad S_{1y,2y} = -0.125; \quad S_{1x,3x} = -0.051 \qquad \text{(A2)} \end{aligned}$$

where $S_{1n,3m}$ is defined as $\int p_{1_n} p_{3_m} d\tau$.

This yields

$$\begin{aligned} S_{1,2} &= \int p_1 p_2 d\tau = S_{3,4} \\ &= B(\mathrm{tg}^2\theta S_{1x,2x} - \mathrm{tg}^2\phi S_{1y,2y} + S_{1z,2z}) \qquad \text{(A3)} \\ S_{1,3} &= S_{2,4} = B(\mathrm{tg}^2\theta S_{1x,3x} - 2\mathrm{tg}\theta\mathrm{tg}\phi S_{1z,3x} \\ &\quad + \mathrm{tg}^2\phi S_{1z,3y} - S_{1z,3y}) \\ S_{1,4} &= B(\mathrm{tg}^2\theta S_{1x,3x} + 2(\mathrm{tg}\theta\mathrm{tg}\phi + \mathrm{tg}\theta)S_{1z,3x} \\ &\quad + 2\mathrm{tg}\phi S_{1z,3z} + \mathrm{tg}^2\phi S_{1z,3y} + S_{1z,3y}) \\ S_{2,3} &= B(\mathrm{tg}^2\theta S_{1x,3x} 2(\mathrm{tg}\theta g\phi - \mathrm{tg}\theta)S_{1z,3x} \\ &\quad - 2\mathrm{tg}\phi S_{1z,3z} + \mathrm{tg}^2\phi S_{1z,3y} + S_{1z,3y}) \\ B &= 1 : (\mathrm{tg}^2\theta + \mathrm{tg}^2\phi + 1). \end{aligned}$$

The best fit between the recorded PE spectra and our model calculations is found when we choose $\theta = 5°$ and $\phi = 30°$ for **1** and $\theta = 25°$ and $\phi = 45°$ for **2**. With these angles, the overlap integrals given in eqns A(1) to A(3) we obtain the following values for β_1 to β_4:

	β_1(eV)	β_2(eV)	β_3(eV)	β_4(eV)
1	−0.546	−0.246	0.415	0.320
2	−0.773	−0.192	0.061	0.296

(A4)

With these values we can set up the following secular determinants:

Interaction $\Psi(p_1 + p_4) - \Psi(p_2 + p_3)$

$$\begin{vmatrix} A_s + \beta_3 - \epsilon & \beta_1 + \beta_2 \\ \beta_1 + \beta_2 & A_s + \beta_4 - \epsilon \end{vmatrix} = 0$$

Interaction $\Psi(p_1 - p_4) - \Psi(p_2 - p_3)$

$$\begin{vmatrix} A_s - \beta_3 - \epsilon & \beta_1 - \beta_2 \\ \beta_1 - \beta_2 & A_s - \beta_4 - \epsilon \end{vmatrix} = 0 \qquad \text{(A5)}$$

and obtain the eigenvalues and eigenvectors (see also Fig. 2) for **1** ($A_S = -9.3$ eV)

$$\begin{aligned} &\epsilon_1 = -9.72\ \text{eV} \quad \Psi_1 = 0.48(p_1 + p_4) + 0.51(p_2 + p_3) \\ &\epsilon_2 = -9.97\ \text{eV} \quad \Psi_2 = 0.54(p_1 - p_4) + 0.46(p_2 - p_3) \\ &\epsilon_3 = -8.14\ \text{eV} \quad \Psi_3 = 0.51(p_1 + p_4) - 0.48(p_2 + p_3) \\ &\epsilon_4 = -9.36\ \text{eV} \quad \Psi_4 = 0.46(p_1 - p_4) + 0.54(p_3 - p_2) \qquad \text{(A6)} \end{aligned}$$

and for **2** ($A_S = -9.1$ eV)

$$\begin{aligned} &\epsilon_1 = -9.87\ \text{eV} \quad \Psi_1 = 0.45(p_1 - p_4) + 0.55(p_2 - p_3) \\ &\epsilon_2 = -9.89\ \text{eV} \quad \Psi_2 = 0.53(p_1 + p_4) + 0.47(p_2 + p_3) \\ &\epsilon_3 = -7.95\ \text{eV} \quad \Psi_3 = 0.47(p_1 + p_4) - 0.53(p_2 + p_3) \\ &\epsilon_4 = -8.69\ \text{eV} \quad \Psi_4 = 0.55(p_1 - p_4) + 0.45(p_3 - p_2). \qquad \text{(A7)} \end{aligned}$$

In contrast to the planar case, in the nonplanar case for **1** the energy levels ϵ_1 and ϵ_2 are split by 0.25 eV.