GROUP IVB 1,3-DITHIOLANES AND CORRESPONDING OPEN-CHAIN COMPOUNDS: UV PES AND THEORETICAL STUDY OF THE ELECTRONIC AND CONFORMATIONAL PROPERTIES

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## Summary

The results of a UPS and theoretical study on two classes of compounds containing the $S-X(CH_3)_2-S$ group (X = C, Si and Sn), i.e. dithiolanes and the related open-chain species, are reported. The first few bands of the spectra are assigned to the corresponding MO's. It is found that the preferred conformations of the $(CH_3)_2X(SCH_3)_2$ species contain in all cases a planar $X{\stackrel{-SCH_3}{\raise2pt\hbox{}}\atop{-SCH_3}}$ moiety.

Furthermore it is found that d-orbital participation is significant only when X = Si, and the inductive effect operates in a detectable way only when X = Sn.

Introduction

Despite the fact that the nature of the S—X bond, where X is representing a Group IV B element, has been extensively studied [1—4], the mode of operation and the relative importance of the various electronic factors operating in the S—X containing molecules, and in particular their dependence on the molecular geometries, have not been completely assessed.

With the aim of elucidating some of these features, we report here the results of a combined UPS and theoretical study on two classes (I and II) of compounds containing the —S—X(CH₃)₂—S— group.

The theoretical study consisted of a perturbational orbital (PMO) analysis coupled with CNDO/2 computations. The main purpose is to identify the most
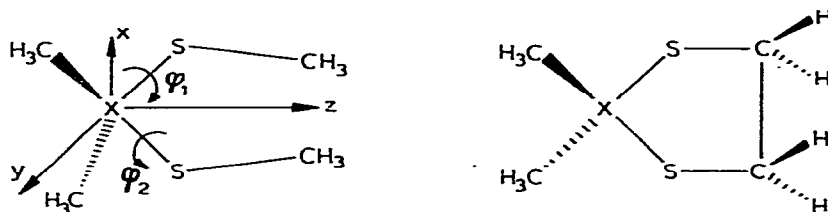
$$I_a, X = C;$$
$$I_b, X = S_i;$$
$$I_c, X = S_n$$

$$II_a, X = C;$$
$$II_b, X = S_i;$$
$$II_c, X = S_n$$

stable configuration of series I derivatives and to correlate the first few bands of the PE spectrum with the corresponding molecular orbitals (MO). In particular the importance of the electronic effects of the $X(CH_3)_2$ group is discussed, with special reference to the bonding and antibonding combination of the sulphur lone pairs.

Experimental and calculations

2,2-Dimethylthio-isopropane (Ia)

To a solution of acetone (1 g, 0.017 mol) and of methylmercaptan (1.65 g, 0.034 mol) in chloroform (50 ml), cooled to −20°C, 20 ml of 0.05 M BF$_3$-etherate in chloroform are added dropwise over a period of 15 min. After the addition, the reaction mixture is left to stand at room temperature for 15 h, washed three times with water, 10% aqueous KOH and water, and finally dried over K_2CO_3. Evaporation of the solvent affords a yellow oil which, after vacuum distillation, gives 2,2-Dimethylthio-isopropane (1.87 g, 80%) as a colourless oil, b.p. 155°C/760 mmHg. Found: C, 44.0; H, 8.81; S, 46.93. $C_5H_{12}S_2$ calcd.: C, 44.11; H, 8.82; S, 47.06%.

Di(methylthio)dimethylsilin (Ib)

To a solution of methylmercaptan (1.65 g, 0.034 mol) and triethylamine (3.47 g, 0.034 mol), in ether (50 ml) at 0°C, a solution of dichlordimethylsilane (2.20 g, 0.017 mol) in ether (20 ml), is added dropwise. After the addition, the reaction mixture is boiled under reflux for 18 h. The colourless precipitate of triethylammonium chloride is filtered off and the filtrate evaporated. The residual yellow oil is distilled to give di(methylthio)dimethylsilin, Ib (1.3 g, 50%) b.p. 72°C/20 mmHg. Found: C, 31.74; H, 8.00; S, 42.19. $C_4H_{12}S_2Si$ calcd.: C, 31.58; H, 7.88; S, 42.1%.

2,2-Dimethyl-1,3-dithiolane (IIa)

This has been prepared by reaction of 1,2-ethanedithiol, acetone and BF$_3$-etherate with the procedure previously outlined for Ia. After the usual work-up, evaporation of the solvent affords a yellow oil which when distilled under high vacuum gives 2,2-dimethyl 1,3-dithiolane (90% yield) b.p. 70°C/18 mmHg, in good agreement with the literature data [5].

TABLE 1

IONIZATION ENERGY VALUES (eV)

Compound	n_+	n_-	$\sigma^+(X—S)$	$\pi(C—X—C)$	$\sigma^-(X—S)$	$\sigma(S—CH_3)$
Ia	8.39	8.71	10.35			
Ib	8.72	8.98	10.15	10.7	11.1	11.9	12.55
Ic	8.45(sh)	8.61	9.57	9.94	10.25	11.8	12.25
IIa	8.62	8.84	10.53			
IIb		8.95	10.3	10.85		
IIc		8.71	9.8	10.13	10.5	11.7	11.9

2,2-Dimethyl-2-sila-1,3-dithiacyclopentane (IIb)

This compound was synthesized from ethanedithiol, triethylamine and dichlor-dimethylsilane in benzene by the procedure described for Ib. After the usual work-up, high vacuum distillation of the residual yellow oil gives 2,2-dimethyl-2-sila-1,3-dithiacyclopentane (30% yield) b.p. 92°C/18 mmHg. Found: C, 31.95; H, 6.66; S, 42.59. $C_4H_{10}S_2Si$ calcd.: C, 32.00; H, 6.66; S, 42.66%.
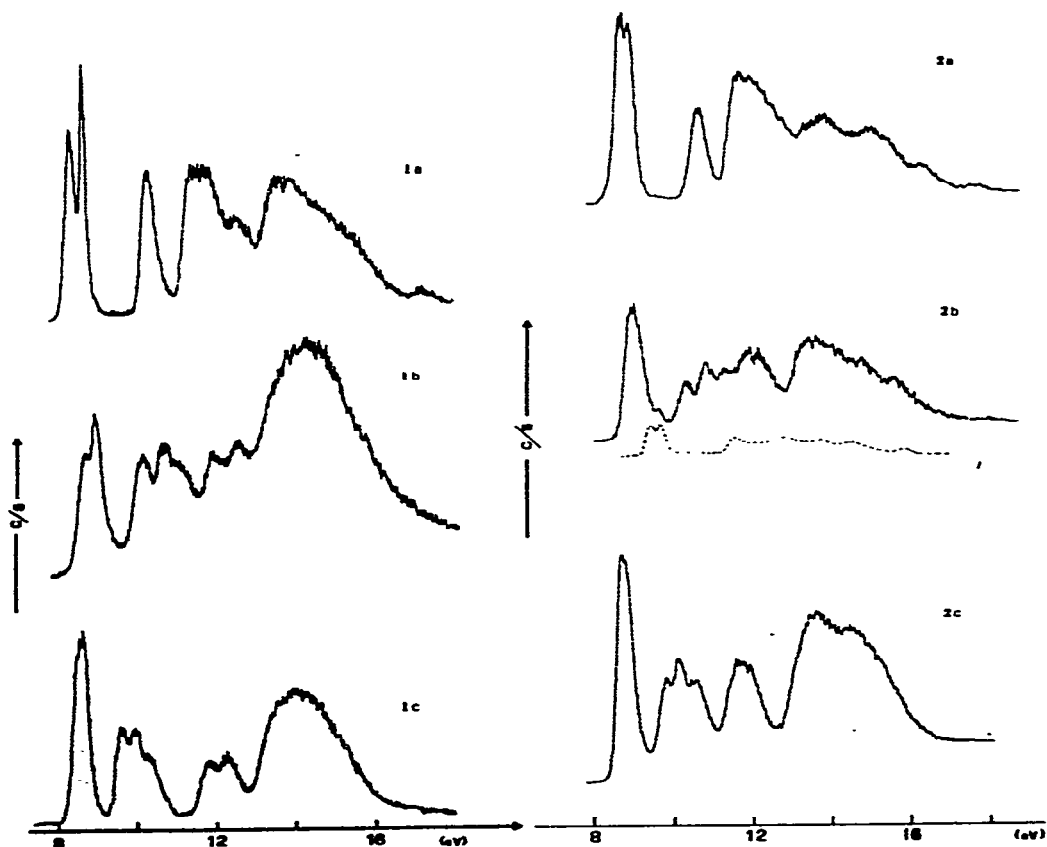

Fig. 1. Photoelectron He(I) spectra of compounds Ia—Ic and IIa—IIc.

Di(methylthio)dimethyltin (Ic) and 2,2-dimethyl-2-stanna-1,3-dithiacyclopentane (IIc)

These were prepared by the method of Abel and Brady [6].

Spectra were obtained using a Perkin—Elmer PS 18 photoelectron spectrometer. The error in the IE data is 0.05 or 0.01 eV, depending upon the number of decimal digits quoted in Table 1. IIb decomposes in part in the target chamber, probably producing ethanedithiol (see Fig. 1). CNDO/2 calculations [7], have been carried out on several configurations of Ia and Ib (see results and discussion), with and without the inclusion of the silicon and sulphur d orbitals.

Results and discussion

We begin our analysis by considering the carbon derivative Ia. Here, as well as in the other molecules investigated, the first two bands of the PE spectrum can be associated on energy grounds with the combination of the lone pairs * of the sulphur atoms denoted as n_+ and n_- (see later the reason for this symbolism). Their IE values (8.39 and 8.71 eV) are in fact very close to those reported [9,10] for 2,4-dithiapentane (8.66 and 8.91 eV) and to the first IE value of dimethyl-sulphide [10] (8.67 eV). The splitting of these two bands can be related to the extent of the interaction of n_+ and n_- with the other group orbitals of the molecule. However, the extent of such interaction and the type of group MO's involved in the interaction depend critically upon the conformation of the molecule. On the other hand, the conformation of Ia is unknown, and therefore the interpretation and the assignement of the PE spectrum must also involve the determination of the optimum conformation. To solve this problem we have found it useful to combine the information derived from the experimental data (PE spectrum) with the results of CNDO/2 computations. We have in fact carried out such computations for the following conformations defined here in terms of the two torsional angles φ_1 and φ_2 ($\varphi_1 = 0°$ and $\varphi_2 = 0°$ correspond to the *cis, cis* conformation; see Introduction): (i) $\varphi_1 = 0$, $\varphi_2 = 0$; (ii) $\varphi_1 = 0$, $\varphi_2 = 180$; (iii) $\varphi_1 = 0$, $\varphi_2 = 90$; (iv) $\varphi_1 = +20$, $\varphi_2 = -20$; (v) $\varphi_1 = 90$, $\varphi_2 = -90$; and (vi) $\varphi_1 = 180$, $\varphi_2 = 180$.

According to such computations, conformation (ii) is the most stable; conformation (vi) is less stable by ~1 Kcal/mol, while conformations (v) and (iii) are less stable by about 6 and 9 Kcal/mol, respectively. Conformations (iv) and (i) have a high and a very high energy, respectively, and therefore, on energy grounds, can be excluded. On the other hand, from the shape of the first two bands it can be inferred that only the second band, since it is very sharp, could correspond . to a combination of lone pairs having very slight interactions, both between themselves (through space) and with other MO's. The first band corresponds to the second combination which slightly interacts with the rest of the molecule. Furthermore the separation of these two bands is quite small (0.32 eV). Comparing this information with the results of the theoretical computations, we are able to exclude conformations (iii) and (v), not only by reason of their higher energy, but mainly because in such conformations both the lone pairs would

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* It has previously been shown [8] that the HOMO of the SCH_3 group is mainly sulphur lone pair in nature.

interact. Therefore the most stable conformer must have conformation (ii) or

(vi) with a planar C$\underset{\text{SCH}_3}{\overset{\text{SCH}_3}{<}}$ moiety, in agreement with the conclusions reached [9]

for the similar 2,4-dithiapentane. Here two kinds of interactions are present: a "through space" interaction between the two sulphur lone pairs, causing a small splitting between the antibonding combination (n_-) and the bonding combina-

tion (n_+), and also the interaction of n_+ with the π and π^* MO's of the $\underset{\text{H}_3\text{C}}{\overset{\text{H}_3\text{C}}{>}}$C

fragment. The latter interaction is shown in Fig. 2: the destabilizing interaction 1 predominates over the stabilizing interaction 2, raising the energy of n_+ above that of n_- (according to CNDO/2 calculations), and therefore the first band can be associated with n_+ and the second band with n_-. The third band in the spectrum (10.35 eV), can be associated with one or both of the two $\sigma((\text{CH}_3)_2\text{C—S})$ MO's by comparison with the assignment [1] of the spectrum of $\text{CH}_3\text{SC}(\text{CH}_3)_3$. From the intensity of the band it can also be inferred that only one MO is involved. The CNDO/2 computations show that in conformation (iv) these two MO's are therefore nearly degenerate while in conformation (ii) there is a significant separation. Thus we suggest that the most stable conformer corresponds to conformation (ii), and that the third peak can be associated with the bonding combination of the two $\sigma((\text{CH}_3)_2\text{C—S})$ bonds. This conformational preference can be rationalized in terms of "non bonded" attraction [11] between the —SCH$_3$ cis moiety and the adjacent sulphur lone pair.

Again according to the CNDO/2 computations the next MO's correspond to combination between the $\sigma(\text{C—S})$ and the $\sigma(\text{S—CH}_3)$ bonds, and to the MO of

the $\underset{\text{H}_3\text{C}}{\overset{\text{H}_3\text{C}}{>}}$C moiety. However the corresponding peaks in the spectrum are not

easily identified, since they lie very close in energy and only a very broad band is observed.

The same assignement of the first three bands holds also for the carbon derivative IIa. The conformation of this molecule, according to Dreiding models, must contain a non planar cycle. Therefore also n_- can now slightly interact with other MO's. Accordingly the second band is less sharp than the corresponding band, of Ia and the separation between the first and second bands is also reduced.

The assignment of the optimum conformation of Ib (X = Si) proceeds on the same lines. Calculations have provided results very similar to those already described for the carbon derivative i.e. conformation (ii) is found to be the most stable; however conformation (vi) is less stable by only 0.2 Kcal/mol. Again the other conformations can be excluded because the sharp second band again indicates an association with only slightly interacting combination of the sulphur lone pairs (n_-). Furthermore the intensity of the third band again suggests that it can be associated with only one MO, and therefore it seems reasonable to conclude that the most stable conformer corresponds to conformation (ii), by analogy with Ia. The assignment follows readily: the first two peaks (8.72 and 8.98 eV), are therefore associated with n_+ and n_-, while the third band (10.15 eV), to a bonding combination of the $\sigma(\text{Si—S})$ bonds (see $\sigma(\text{Si—S})$ = 10.1 eV in CH$_3$SSi-(CH$_3$)$_3$ [1]). According to the CNDO/2 results, the fourth peak (10.7 eV) should be associated with an antibonding combination of the $\sigma(\text{Si—S})$ bonds and the

fifth peak (11.1 eV) to the π MO of the $\underset{\text{H}_3\text{C}}{\overset{\text{H}_3\text{C}}{>}}$Si moiety. However an inversion of
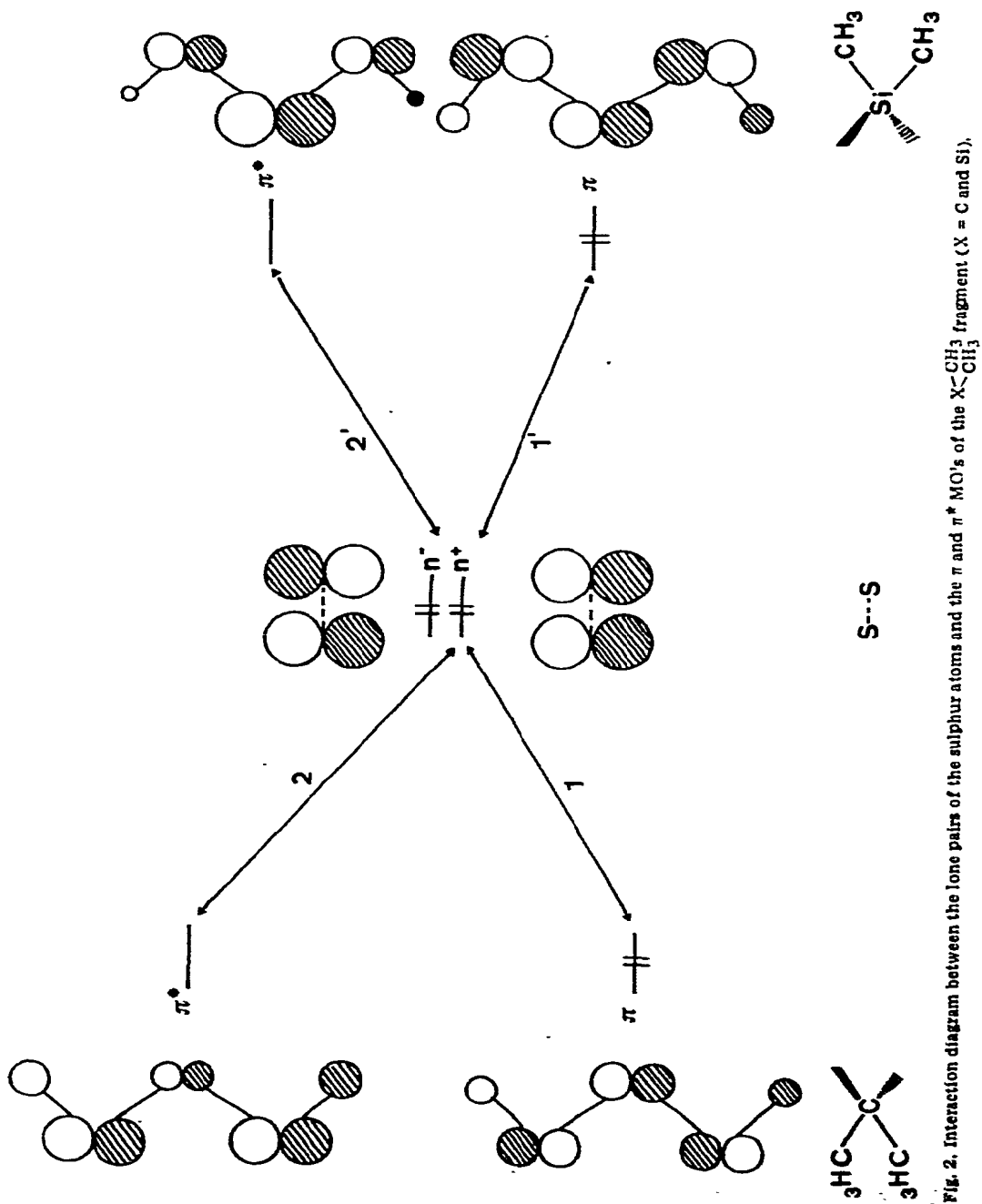
Fig. 2. Interaction diagram between the lone pairs of the sulphur atoms and the π and π^* MO's of the $X\!-\!CH_3$ fragment ($X = C$ and Si).

the assignment of the last two peaks is in better agreement with previous results (see σ(Si—S) from CH$_3$SSi(CH$_3$)$_3$ at 10.7 eV [1]). The next two peaks (11.9 and 12.55 eV) can be associated with combinations of the σ(S—CH$_3$) bonds according to the calculations and in agreement with the I.E. value (12.2 eV [1]) of the corresponding band in the spectrum of CH$_3$SSi(CH$_3$)$_3$.

By comparison with the I.E.s of the corresponding carbon derivative, it can be seen that both n_+ and n_- are significantly stabilized in the silicon derivative. It is informative to discuss the origin of such effects, since various factors such as extent of the interaction between the two lone pairs, the silicon $3d$ orbitals, inductive effects and hyperconjugation could be invoked to such purpose. For the silicon derivative Ib with conformation (ii) we have carried out CNDO/2 computations with and without $3d$ orbitals. The computations without $3d$ orbitals show that (a) the interaction between the two lone pairs and the inductive effect does not differ significantly from the situaiton in the carbon compound since n has almost exactly the same orbital energy in the carbon and in the silicon derivative; (b) the hyperconjugative effect would tend to destabilize n_+ even more because of the larger interaction 1' (in contrast with the experimental findings); (c) hyperconjugative effects alone, even if in principle they can be invoked to explain the stabilization of n_+ through interaction 2', cannot explain the stabilization of n_-. Therefore the stabilization can be associated with silicon d orbital participation. However such participation is different with n_+ than with n_-. In the former case in fact, the silicon d orbital involved in the interaction is the $3d_{yz}$, which mixes with the π^* MO of the $\overset{H_3C}{\underset{H_3C}{>}}$Si group, thus producing an empty orbital at a very low energy which stabilizes n_+ through interaction 2', while the smaller stabilization of n_- arises from interaction with the empty silicon $3d_{xy}$ orbital.

The assignment for the silicon derivative IIb follows that for Ib, and is given in Table 1. Again, because of the non planarity of the cycle in IIb, n_- can now also interact, and the related band then overlaps significantly with that associated with n_+.

The discussion for Ic follows by analogy with those of Ia and Ib. The optimum conformer must again correspond to a conformation with a planar Sn$\overset{SCH_3}{\underset{SCH_3}{<}}$ moiety, and the assignment of the various peaks (based on that of the corresponding CH$_3$SSn(CH$_3$)$_3$ derivative [1]) is the same as in Ib and is given in the table. The most interesting features of this spectrum are that the first two (sharp) bands now overlap significantly, and are destabilized with respect to those in Ia and Ib. These observations can be rationalized by assuming that both hyperconjugative interactions and interaction with the tin d orbitals are negligible, and that mainly the inductive effect operates.

The spectrum of the IIc derivative is also assigned on the same basis as for IIa and IIb and is given in Table 1.

Conclusions

We have attempted to use PES and theoretical information not only for understanding the electronic structure of the classes of molecules under examina-

tion, but also for determining their optimum conformations. The most impoɪtant conclusions are as follows:

(i) the most stable conformer of the derivatives Ia—Ic corresponds to a conformation with a planr $X{<}{SCH_3 \atop SCH_3}$ moiety; (ii) the n_+/n_- splitting decreases in the order Ia > Ib > Ic. This trend can be rationalized in terms of a larger 2′ interaction (compared to 2) in Ib and in terms of a reduced interaction between the two sulphur lone pairs and reduced hyperconjugative interactions in Ic because of the longer S—Sn bond [12]. Metal d orbital participation in bonding is significant only when X = Si; (iii) the inductive effect, which should destabilize the sulphur lone pair combinations by an increasing extent on going from C to Si to Sn, becomes significant only when X = Sn, since in the other cases it is masked by other effects mentioned above.

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