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# PHOTOELECTRON SPECTRA AND MOLECULAR PROPERTIES

## XXI*. DIMETHYL SULFIDE, METHYL SILYL SULFIDE, AND DISILYL SULFIDE

P. MOLLÈRE and H. BOCK**
*Institut für Anorganische Chemie II der Universität, 6 Frankfurt/Main 70, Theodor-Stern-Kai 7 (Germany)*
G. BECKER and G. FRITZ
*Institut für Anorganische Chemie der Universität, Karlsruhe (Germany)*
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## SUMMARY

The photoelectron spectra of methyl and silyl sulfides are assigned on the basis of modified CNDO-SCF-MO calculations. The orbital sequence ($2b_1$, $4a_1$, $3b_2$) is found to be independent of conformation. The static geometry of the sulfides is in keeping with a smaller charge shift to sulfur accompanying the carbon–silicon exchange. Comparison of the results with those of the analogous ethers lends support to the previous assignment of the latter.

In a previous paper[2], we presented the photoelectron (PE) spectra of dimethyl ether, methoxysilane and disiloxane, assigned on the basis of extensive molecular orbital calculations. In light of the fact that our somewhat surprising conclusions (concerning conformation-dependent orbital sequences) depended so heavily upon the calculations, it was suggested at that time that further supporting evidence could be forthcoming from the PE spectra of the three corresponding sulfides. Since then, Cradock and Whiteford[3] have assigned the spectra of $H_3COCH_3$, $H_3SiOSiH_3$, $H_3CSCH_3$, and $H_3SiSSiH_3$ by analogy with the parent substances, water and hydrogen sulfide. While according to our calculations, $H_2S$ can be expected to be a reasonable model for the derivatives $R_2S$, in which structural changes play a minor role (*vide infra*), the complex geometric perturbations involved in the methyl and silyl ethers[2] might seem to render a simplified $H_2O$ model uncertain at best. We now report the spectra of dimethyl sulfide, methyl silyl sulfide, and disilyl sulfide, together with orbital assignments based on modified CNDO-SCF MO calculations, which support our earlier conclusions concerning the orbital sequences in the methyl and silyl ethers.

## EXPERIMENTAL SECTION

All calculations were of the modified CNDO/2-type (including *d* orbitals in the

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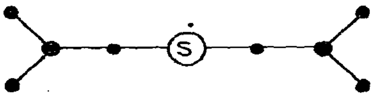
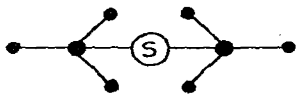
* For Part XIX see ref. 1, for Part XX see ref. 2.

** Address correspondence to this author.



"Singly Eclipsed"

(I)



(1)

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(II)

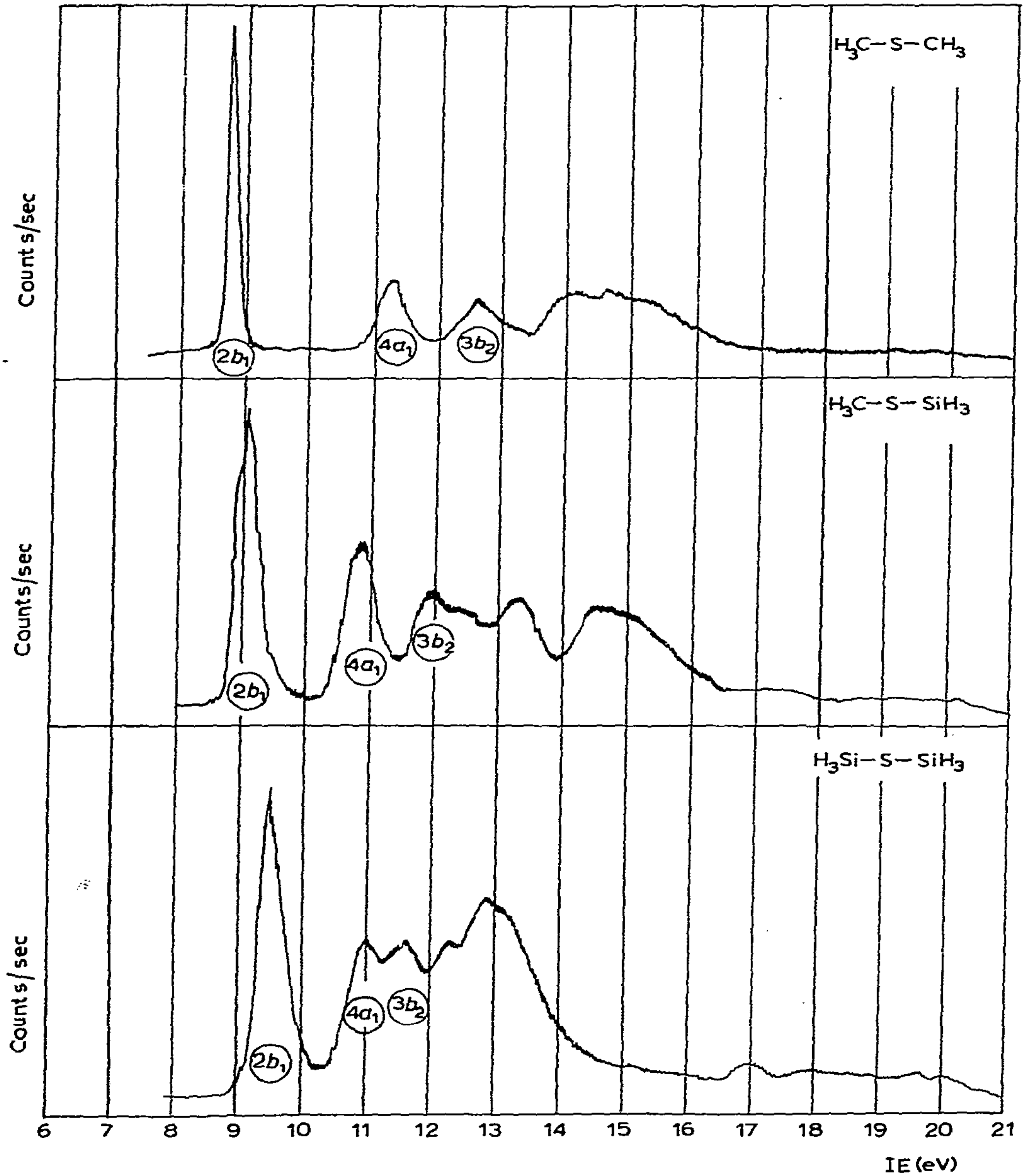

Fig. 1. Assigned photoelectron spectra.

basis set) as parametrized by Jaffé and Del Béné[4].

The PE spectra were measured with a Perkin–Elmer PS-16, employing at 127° electrostatic deflection-type analyzer.

*Dimethyl sulfide* of the highest commercial purity (*puriss*) was purchased from Fluka AG.

The synthesis of *methyl silyl sulfide* was directly analogous to that of methoxysilane[2]. Identity and purity of the product was determined by IR spectroscopy[5] and vapor pressure measurements (measured: $p(0°)$ 104 mmHg; lit.[6] $p(0°)$ 105 mmHg).

*Disilyl sulfide* was prepared by repeatedly passing $H_3SiI$ over red HgS at room temperature. The product was isolated and purified by fractional condensation. Purity was ascertained by molecular weight determination (found 93.5; calcd. 94.29) and NMR spectroscopy; the latter indicated the presence of approximately 2% benzene.

## RESULTS AND DISCUSSION

The photoelectron spectra and the assignments of the three highest occupied orbitals of the sulfides are presented in Fig. 1 and Table 1, together with results of the MO calculations.

For dimethyl sulfide and disilyl sulfide, the calculations were obtained using the structures determined by Pierce and Hayashi[7] and by Almenningen *et al.*[8], respectively. In the case of methyl silyl sulfide, a molecular geometry was constructed from appropriate components of the other two molecules and a central angle ($\angle$CSSi = 98.15°) assumed to be the mean of the known corresponding angles ($\angle$CSC = 98.9°; $\angle$SiSSi = 97.4°). In each case, two distinct conformations (I) and (II), were considered.

TABLE 1

ASSIGNED IONIZATION ENERGIES AND RELATED CALCULATED DATA

| *Orbital assignment* | *Ionization energies of the compounds (eV) for conformation (I) and (II)* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | *$H_3CSCH_3$* | | | *$H_3CSSiH_3$* | | | *$H_3SiSSiH_3$* | | |
| | *Calcd.* | | *Measured* | *Calcd.* | | *Measured* | *Calcd.* | | *Measured* |
| *Conformation* | *(I)* | *(II)* | | *(I)* | *(II)* | | *(I)* | *(II)* | |
| $2b_1$ | 11.63 | 11.68 | 8.67 | 12.04 | 12.07 | 9.10 | 12.61 | 12.65 | 9.59 |
| $4a_1$ | 13.29 | 13.27 | 11.17 | 12.89 | 12.89 | 10.85 | 13.49 | 13.44 | 10.98 |
| $3b_2$ | 13.82 | 13.94 | 12.57 | 14.21 | 14.27 | 11.94 | 13.76 | 13.90 | 11.68 |
| Calculated total energy (eV) | 482.29 | 483.13 | | 504.42 | 505.10 | | 524.99 | 525.70 | |
| Electron density in the sulfur "lone pair" orbital ($3p_x$) | 1.9978 | 1.9970 | | 1.9910 | 1.9207 | | 1.8329 | 1.8516 | |

The data in Table 1 indicate that the trends in orbital behavior within the series of three sulfides should not be complicated by the perturbations which accompany significant changes in geometry[2,9]: the differences in the angle at sulfur are minor, and the calculated total energies (consistent with the available evidence for $H_3Si-S-SiH_3$) suggest that all three molecules prefer the same "doubly eclipsed" conformations; moreover, the calculations imply that the higher occupied orbitals in the sulfides, unlike those of the oxygen analogues, do not exhibit any considerable sensitivity to conformation.

The elimination of geometry as a factor greatly simplifies the problem of understanding the behavior of the orbitals in question, in that it only remains to consider the effects of substituting silicon for carbon. Furthermore, it may be reasonable to assume here, that the same arguments concerning counteracting $\sigma$-donor and $\pi$-acceptor effects applied to the orbitals of the ether system[2], will be equally valid here: the smaller valence state ionization potentials of the silicon atomic orbitals effect an inductive destabilization which, in turn, may be countermanded by symmetry-correct $p \rightarrow d\pi$ back-donation. Thus in the $2b_1$ molecular orbital (Fig. 2), where both symmetry and energy considerations allow maximized delocalization of the sulfur "lone pair" into vacant silicon $3d$ orbitals, this effect can be expected to dominate. Indeed, both the calculations and the spectra (the first PE bond is shifted to higher ionization energies and broadened) clearly reflect the delocalization and concomitant stabilization of the "lone pair" as silicon atoms are introduced. In the $4a_1$ molecular orbital (Fig. 2) there is the possibility of a similar stabilizing effect involving an in-plane sulfur $3p$ orbital; however, poor overlap due to the small angle Si–S–Si constrains the $p\pi$–$d\pi$ interaction and establishes a more delicate balance. The inductive factor is obviously dominant at first, but the extra measure of delocalization gained from a second silicon

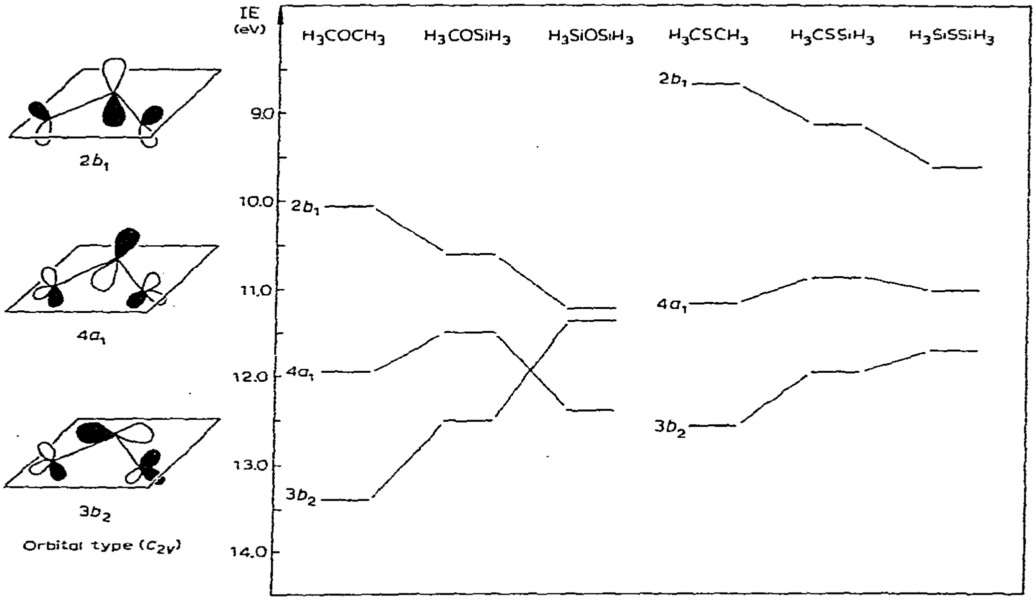

Fig. 2. Correlation of the three highest occupied orbitals in ROR' and RSR'.

atom overrides the simultaneous increase in inductive effect, thus rationalising the irregular behavior of the $4a_1$ orbital. Finally, the symmetry of the $3b_2$ orbital (Fig. 2) rules out any $p \rightarrow d\pi$ interactions, so that the substitution of silicon for carbon merely furnishes an unmitigated destabilizing inductive effect.

These trends in the ionization energies of the $2b_1$, $4a_1$ and $3b_2$ orbitals of the sulfides are illustrated in Fig. 2, where the first three ionization energies of the ethers are presented as well; the orbital assignments of the sulfur compounds are corroborated both by our calculations and by the qualitative arguments of Cradock and Whiteford[3], while the assignments of the ethers are according to our earlier calculations[2]. The remarkable parallelism in the behavior pattern of the corresponding orbitals of the sulfur derivatives and their oxygen analogues* is felt to strongly support our previously reported assignment of the latter compounds.

There is one final point which may warrant brief consideration: namely, why this series of methyl and silyl sulfides should fail to undergo the significant geometric changes exhibited by the valence isoelectronic ethers. One explanation may be furnished by the data in Table 2, where the calculated charge distributions indicate that concentration of localized charge in the sulfides is far less critical than in the oxygen derivatives. This condition should not only reduce the impetus to alter structure in order to redistribute charge, but should also lessen the sensitivity of the electronic states of the RSR' system to geometric perturbations. In turn, the correlation of orbitals within the series of sulfides is simplified, and the reliability of the assignments made for the above spectra is enhanced.

TABLE 2

CALCULATED CHARGE DISTRIBUTIONS FOR MOLECULES $R_2X$ WITH "DOUBLY ECLIPSED" CONFORMATION (II)

While modified CNDO/2 calculations were used to obtain the data in Table 1 and to assign the spectra, the data for the sulfides in Table 2 were calculated with the normal CNDO/2 program in order to provide a proper comparison with the ether data calculated earlier by the same method[10].

| *Compound* | *Atom* | *Charge per atom* | *Compound* | *Atom* | *Charge per atom* |
|---|---|---|---|---|---|
| $H_3COCH_3$ | O | −0.2070 | $H_3CSCH_3$ | S | −0.0754 |
| | C | +0.1370 | | C | −0.0607 |
| | H | −0.0051 | | H | +0.0353 |
| | H | −0.0142 | | H | +0.0316 |
| | H | −0.0142 | | H | +0.0316 |
| $H_3SiOSiH_3$ | O | −0.2200 | $H_3SiSSiH_3$ | S | +0.0047 |
| | Si | +0.5459 | | Si | +0.3699 |
| | H | −0.1417 | | H | −0.1177 |
| | H | −0.1471 | | H | −0.1273 |
| | H | −0·1471 | | H | −0.1273 |

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* The orbital crossing ($4a_1$–$3b_2$) in the ethers can be rationalized in terms of non-bonded interactions involved in changing conformation[2].

## REFERENCES

1 G. Wagner, H. Bock, R. Budenz and F. Seel, *Chem. Ber.*, 106 (1973) 1285.
2 H. Bock, P. Mollère, G. Becker and G. Fritz, *J. Organometal. Chem.*, 61 (1973) 113.
3 S. Cradock and R. Whiteford, *J. Chem. Soc., Faraday Trans., II*, (1972) 281.
4 H. Jaffé and J. Del Béné, *J. Chem. Phys.*, 48 (1969) 1307.
5 B. Sternbach and A. G. MacDiarmid, *J. Inorg. Nucl. Chem.* 23 (1961) 225.
6 H. J. Emelèus, A. G. MacDiarmid and A. D. Maddock, *J. Inorg. Nucl. Chem.*, 1 (1955) 194.
7 L. Pierce and M. Hayashi, *J. Chem. Phys.*, 35 (1961) 479.
8 A. Almenningen, K. Hedberg and R. Seip, *Acta Chem. Scand.*, 17 (1963) 2264.
9 B. Gimarc, *J. Amer. Chem. Soc.*, 93 (1971) 593.
10 J. Pople and D. Beveridge, *Approximate Molecular Orbital Theory*, McGraw Hill, New York, 1970.