Evidence against the Significance of C–S Hyperconjugation in Determining the Conformation of Allyl Methyl Sulphide†

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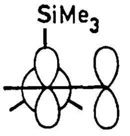
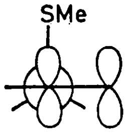
Summary Photoelectron spectroscopy indicates that C–S hyperconjugation with π ethylene systems (σ–π mixing) plays no special rôle, in contrast to C–Si hyperconjugation.

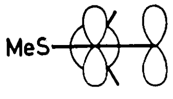
Recently[1] we demonstrated the use of photoelectron (PE) spectroscopy in studying molecular conformational problems. We unambiguously showed that allyltrimethylsilane (**1**) exists in conformation (I) with the C–Si bond parallel to the π lobes of the ethylene system, and that the HOMO energy of (**1**) indicates a strong hyperconjugative interaction between the C–Si bond[2] and the ethylene π system. We report here results on allyl methyl sulphide (**3**) which show that, contrary to the silicon case, C–S hyperconjugation plays no similar part in this molecule.



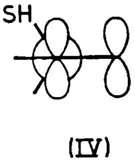
(I)



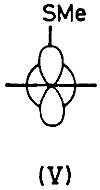
(II)



(III)



(IV)



(V)

The Figure shows parts of the photoelectron spectra of dimethyl sulphide (**2**) and allyl methyl sulphide (**3**). The two bands (A) and (B) on the low-energy side (ionization energy scale) in the spectrum of (**2**) are assigned to ionization of the two sulphur lone-pair MOs: (A) to the n_π MO (directed perpendicular to the CSC plane) and (B) to the n_σ MO (in the CSC plane).

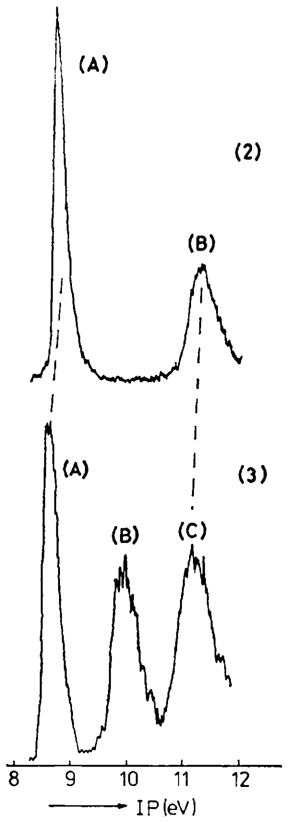


Figure. *Sections of photoelectron spectra of dimethyl sulphide* (**2**) *and allyl methyl sulphide* (**3**). *Measured vertical ionization potentials* (*in eV*); (**2**):[8] (A) 8·7, (B) 11·2$_5$; (**3**): (A) 8·6, (B) 9·9$_5$, (C) 11·1$_5$.

In the spectrum of allyl methyl sulphide (**3**) bands (A) and (C) appear at essentially the same positions as the uppermost bands in (**2**). As in both compounds the character of

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† For previous paper in series: 'Theory and Application of Photoelectron Spectroscopy,' see: A. Schweig, W. Schäfer, and K. Dimroth, *Angew, Chem.*, in the press.

the sulphur lone pairs is very similar we assign band (A) to the n_π MO and band (C) to the n_σ MO. Moreover, in (**3**) bands (A) and (C) are expected to remain in the same positions for both conformations (II) and (III).

The remaining band (B) at 9·95 eV must be assigned to an antibonding combination of the ethylene π MO and the neighbouring σ MOs.‡ The downward shift relative to the first band of ethylene (10·51 eV[3]) is a measure of the importance of σ–π mixing, which depends on the conformation of the molecule. In conformation (II), C–S hyperconjugation is possible, whereas in conformation (III) only C–H mixing is allowed. From the PE spectrum of propene[4] (first band at 9·9 eV) it is known that C–H mixing results in a downward shift of *ca.* 0·6 eV. CNDO/2[5] calculations, however, predict that (II) is 2·34 or 2·05 kcal/mol (*sp* and *spd* basis, respectively) more stable than (III). Moreover, previous investigations on allyl sulphide[6] (**5**) and the β-mercaptoethyl radical[7] (**6**) indicate (IV) and (V) as most stable conformations.

Therefore we conclude that (**3**) probably exists in conformation (II) showing that C–S hyperconjugation is not more effective than C–H mixing.

This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

(*Received, 7th April* 1972; *Com.* 589.)

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‡ This MO corresponds to the HOMO in allyltrimethylsilane (**1**).

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