

## C - S HYPERCONJUGATION <sup>1</sup>

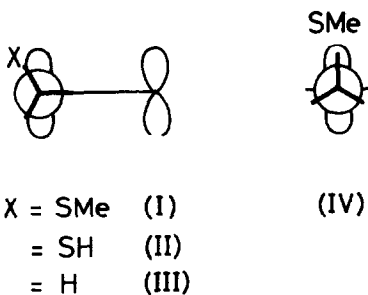
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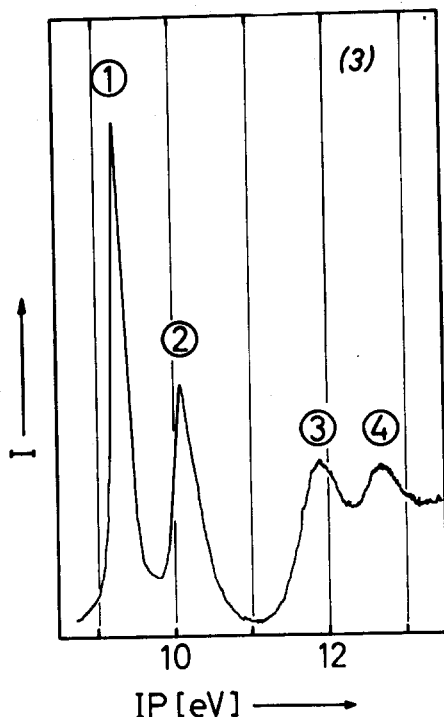
Assuming <sup>2</sup> allyl methyl sulphide,  $\text{CH}_2=\text{CH}-\text{CH}_2-\text{SMe}$  (1) to be in the gauche form (I) we previously <sup>3</sup> concluded that C-S hyperconjugation ( $\sigma/\pi$  mixing between the C-S bonding MO and the vinyl  $\pi$  MO) is not more effective than C-H hyperconjugation ( $\sigma/\pi$  mixing between a C-H bonding MO of the  $\text{CH}_3$  group and the vinyl  $\pi$  MO of propene,  $\text{CH}_2=\text{CH}-\text{CH}_3$  (2)). The conclusion suffers from two drawbacks. First, the conformation of (1) is not known experimentally <sup>2</sup>. Second, a possible inductive effect of the SMe group has not been considered. In this communication we remedy the two defects and thereby confirm our conclusion rigorously.



Contrary to (1), allyl sulphide,  $\text{CH}_2=\text{CH}-\text{CH}_2\text{SH}$  (3) is known experimentally to exist only in the gauche form (II) <sup>4</sup>. Likewise, (2) appears only in form (III) <sup>5</sup>. Therefore a direct comparison between (2) and (3) is valid.

The Figure shows the photoelectron (PE) spectrum of (3) <sup>6</sup>. Band (1) must be assigned to the sulphur lone pair which in methyl sulphide is observed at 9.42 <sup>7</sup>

(9.44) eV<sup>8</sup>. Band (2) results from ionization of the highest occupied  $\pi$  MO. This MO represents an antibonding combination of the vinyl  $\pi$  MO and the neighboring  $\sigma$  MOs of the CH<sub>2</sub>SH substituent.



**Figure** Section of photoelectron spectrum of allyl sulphide (3). Measured vertical ionization potentials (in eV): (1) 9.25, (2) 10.05, (3) 11.90, (4) 12.75

It is interesting to note that the  $\pi$  band which appeared in (1) at 9.95 eV<sup>3</sup> is found for (3) at 10.05 eV and thus again has just about the same value as the  $\pi$  MO in (2)<sup>9</sup>. Neglecting a possible inductive effect of the SMe and SH groups in both sulphur compounds this result confirms directly our previous conclusion<sup>3</sup>.

Besides the destabilizing hyperconjugative effect exerted on the vinyl system by the neighboring  $\sigma$  bonds, a stabilizing inductive effect due to the SMe and SH groups could also be involved. We now show that this effect is small.

Not being able to separate the two effects in the allyl sulphides themselves we try to estimate the inductive effects from the  $\pi(a_2)$  MO<sup>10,11</sup> of the corresponding phenyl sulphides (PhSMe = - 0.04 eV<sup>12</sup> and PhSH = - 0.14 eV<sup>7</sup>). Subtracting these inductive effects from the total (hyperconjugative and inductive) measured shifts (as compared to the 10.51 eV<sup>13</sup> of the  $\pi$  MO in ethylene), (1) = 0.56 eV<sup>3</sup>, (3) = 0.46 eV, we finally obtain for the bare hyperconjugative effects the following values: (1) = 0.60 eV, (3) = 0.60 eV. These values are

comparable to the hyperconjugative effect of the C-H bonding MOs in (2) which is 0.63 eV<sup>9,14</sup>.

These results rigorously demonstrate that the hyperconjugative ability of C-S and C-H bonds are nearly equal.

### References and Notes

- \* Address correspondence to this author.
1. Part 21 of Theory and Application of Photoelectron Spectroscopy. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. - Part 20: W.Schäfer, A.Schweig, G.Märkl, H. Hauptmann, and F.Mathey, submitted for publication.
  2. The assumption was based on the following arguments. First, allyl sulphide (3) exists only in the gauche form<sup>4</sup>. Second, the  $\beta$ -mercaptoethyl radical appears in the eclipsed conformation (IV)<sup>15</sup>.
  3. W.Schäfer and A.Schweig, Chem.Comm., 1972, 824.
  4. K.V.L.N.Sastry, S.C.Dass, W.V.F.Brooks, and A.Bhaumik, J.Mol.Spectroscopy, 31, 54 (1969).
  5. D.R.Lide and D.Christensen, J.Chem.Phys. 35, 1374 (1961); D.R.Lide and D.E.Mann, J.Chem.Phys. 27, 868 (1957).
  6. The He-I (584 Å) photoelectron spectra were measured on a PS-16 photoelectron spectrometer from Perkin-Elmer, Beaconsfield, England.
  7. D.C.Frost, F.G.Herring, A.Katrib, C.A.McDowell, and R.A.N.McLean, J. Phys.Chem., 76, 1030 (1972).
  8. H.Bock and G.Wagner, Angew.Chem., 84, 119 (1972).
  9. U.Weidner and A.Schweig, J.Organometal.Chem., 39, 261 (1972).
  10. B.Narayan and J.N.Murell, Mol.Phys., 19, 169 (1970).

11. H.Schmidt and A.Schweig, submitted for publication.
12. H.Bock, G.Wagner, and J.Kroner, *Tetrahedron Lett.*, 1971, 3713.
13. D.W.Turner, C.Baker, A.D.Baker, and C.R.Brundie: *Molecular Photoelectron Spectroscopy*, Wiley-Interscience, London 1970.
14. The ( $a_2$ ) band being observed in toluene at 9.28 eV the inductive effect of the  $CH_3$  group is negligible.
15. P.J.Krusic and J.K.Kochi, *J.Amer.Chem.Soc.*, 93, 846 (1971).