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APPLICATION OF PHOTOELECTRON SPECTROSCOPY TO CONFORMATIONAL ANALYSIS OF TWO 1,3-DITHIA COMPOUNDS (1)

Claude GUIMON, Marie-Françoise GUIMON and Geneviève PFISTER-GUILLOUZO
Laboratoire de Chimie Organique Physique, I.U.R.S., 64016 PAU - (FRANCE).

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One of the numerous interests of photoelectron spectrometry is the quantitative estimation of orbital interactions existing in molecules. In particular the interaction between atomic orbitals associated with the identical lone pairs of heteroatoms is observed as a splitting of the bands associated with these orbitals (2-5). As the splitting is proportional to the spatial interaction of orbitals its analysis has provided solutions to several conformational problems (6-9).

Our aim in this work has been to examine what information could be obtained by this method concerning the preferential conformations of 2,4-dithiapentane and dimercapto ethane in the vapour phase.

For 1,3-dithia compounds with a planar molecular structure, a "through bond" interaction between two π lone pairs is observed. The result is that the symmetric combination interacting with methylene group is energetically less stable than the antisymmetric combination (10) With non-planar structure, there is "through space" interaction causing a smaller splitting with $IP(n^-) < IP(n^+)$.

The 2,4-dithiapentane spectrum (fig.1) shows, in the region of low IPs, two peaks partially overlapping each other (8.67 and 8.92 eV).

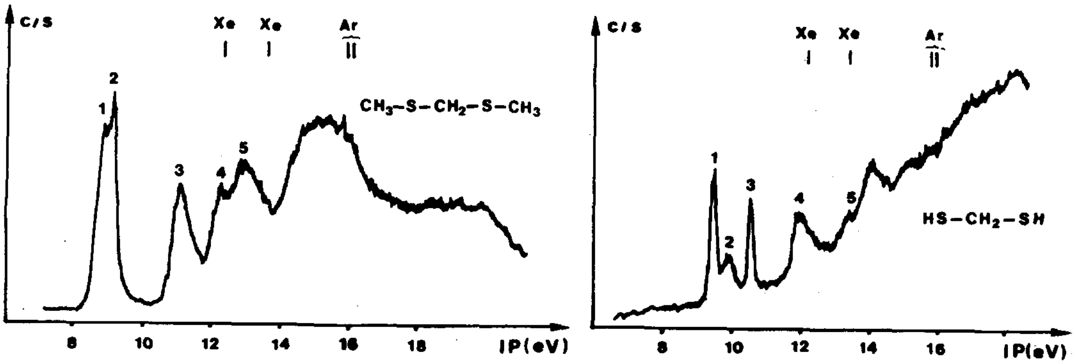


Figure 1 - P.E. spectra of 2,4-dithiapentane and dimercapto ethane.

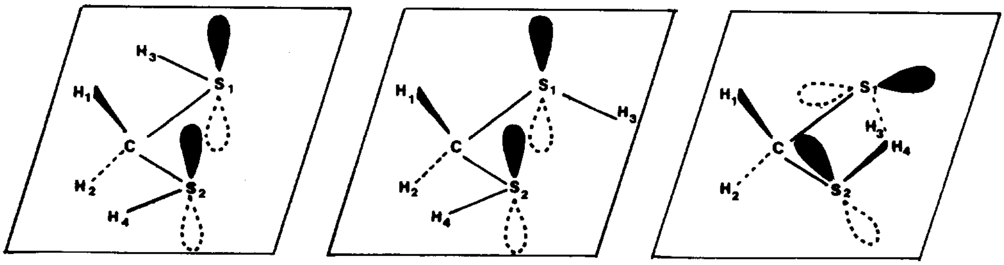
In agreement with BOCK and WAGNER (10), we associate with these two peaks the molecular orbitals arising from π symmetric and antisymmetric combinations of lone pairs respectively. The slight difference between the two values, corresponds to a "through bond" mechanism. This molecule therefore has a planar conformation showing a C_{2v} or C_s symmetry. A non-planar conformation would increase the splitting. These conclusions are corroborated by a C.N.D.O./S calculation* (11) (Table I).

IP_{exp}		IP_{calc}	
		Planar form	Non-planar form
S_π	8.67	10.63	10.94
A_π	8.92	10.80	10.18
A_σ	10.95	13.04	12.74
S_σ	12.14	13.36	14.16

TABLE I - Vertical experimental and C.N.D.O./S calculated ionisation potentials of 2,4-dithiapentane. Potentials (S_π) and (A_π) respectively correspond to π symmetric and antisymmetric combinations of the lone pairs of the sulfurs. Potentials (A_σ) and (S_σ) are associated with antisymmetric and symmetric combinations of σ lone pairs and $_{C-S}$ bonds. The same notation is used in table II.

Dimercapto ethane shows a totally different photoelectron spectrum (fig.1). Two relatively sharp and intense peaks (9.42 and 10.49 eV) are observed, on either side of a rather broad band of lower intensity (9.9 eV). Thus it seems that, in contrast to the previous compounds, there are two stable conformers of dimercapto ethane in vapour phase. The most stable form must correspond to the two intense peaks.

As the important splitting (1.07 eV) results from a particularly high "through space" interaction, the preferential conformer corresponds to non-planar form. The first peak, slightly greater in intensity than the second, is then associated with the antisymmetric combination of lone pairs. The 9.9 eV band most certainly corresponds to planar conformer of molecule (C_{2v} or C_s). The two symmetric and antisymmetric components are then energetically very close (less than 0.2 eV) since the corresponding peaks almost totally overlap each other.



C_{2v} Planar forms C_s Non planar form

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* The C.N.D.O./S parameterisation initially proposed for electronic spectra, allows a good evaluation of the ionisation potentials (12-14).

The theoretical results (table II) are in excellent agreement with these conclusions since the difference between the first two ionisation potentials is equal to 1.02 eV (1.07 eV experimentally) in the case of non-planar form, and 0.27 eV for the planar form. The correlation between experimental and calculated values turns out to be very good for the first four IPs of non-planar form, since a regression analysis gives a variance of only 0.005 with the relation (eV) :

$$IP_{exp} = 0.853\ IP_{calc.} + 0.536$$

Planar form				Non-planar form		
IP_{exp}	IP_{calc}			IP_{exp}	IP_{calc}	
	C_{2v}		C_s			
9.9	11.01	S_π	11.04	9.42	10.50	A_π
	11.28	A_π	11.31	10.49	11.52	S_π
	13.47	A_σ	13.32	11.90	13.37	A_σ
	14.36	S_σ	13.87	13.40	15.07	S_σ

TABLE II - Vertical, experimental and calculated ionisation potentials of dimercapto ethane. For planar forms, we have taken two examples : one showing C_{2v} symmetry, the other showing C_s symmetry. As for 2,4-dithiapentane the non-planar form of dimercapto ethane shows S_1H_3 and S_2H_4 bonds respectively in the bisecting planes of angles (S_2CH_2) and (S_1CH_1), with the two planes forming an angle of 120°.

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REFERENCES

(1) Part XIV of "Electronic structure of sulfur compounds"
Part XIII : "Orbital interactions in amino ketones and thioketones".
J. Chem. Soc. (Farad. II) - submitted for publication.

(2) D.A. SWEIGART and D.W. TURNER - J. Amer. Chem. Soc., 94, 5599, (1971)

(3) S.F. NELSEN and J.M. BUSCHEK - Ibid, 96, 2392, (1974)

(4) G. WAGNER and H. BOCK - Chem. Ber., 197, 68, (1974)

(5) C. BATICH and W. ADAM - Tetrahedron Letters, 16, 1470, (1974)

(6) P. RADEMACHER - Angew. Chem. Int. Ed., 12, 408, (1973)

(7) A.D. BAKER, M. BRISH and M. GELLENDER - J. Elect. Spect., 3, 227, (1974)

(8) A.H. COWLEY, M.J.S. DEWAR, D.W. GOODMAN and M.S. PADOLINA -
J. Amer. Chem. Soc., 96, 2648, (1974)

(9) M.F. GUIMON, C. GUIMON and G. PFISTER-GUILLOUZO - Tetrahedron Letters, 7, 441, (1975)

(10) H. BOCK and G. WAGNER - Angew. Chem. Int. Ed., 11, 150, (1972)

(11) C. GUIMON, D. GONBEAU and G. PFISTER-GUILLOUZO - Tetrahedron, 29, 3399, (1973)

(12) C. GUIMON, D. GONBEAU, G. PFISTER-GUILLOUZO, L. ASBRINK and J. SANDSTROM -
J. Elect. Spect., 4, 49, (1974)

(13) C. GUIMON, M. ARBELOT, M. CHANON and G. PFISTER-GUILLOUZO -
Tetrahedron, 30, 3831, (1974)

(14) D. GONBEAU, C. GUIMON, J. DESCHAMPS and G. PFISTER-GUILLOUZO -
J. Elect. Spect., 6, 99, (1975)

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