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APPLICATION OF PHOTOELECTRON SPECTROSCOPY TO CONFORMATIONAL ANALYSIS OF 1,2,4-TRITHIOLANES (1)

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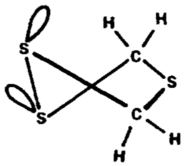
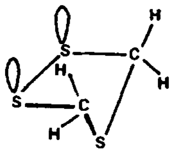
In a recent study of 3,5-dialkyl 1,2,4-trithiolanes by P.M.R. spectroscopy S.B.TJAN and al (2) put forward for these compounds the existence of two configurational isomers showing pseudorotation whose barrier was estimated to be smaller than 6 kcal/mole. Later, after an investigation by vibrational spectroscopy (3), we were able to specify that the pseudorotation could only imply an envelope (C_S) of half-chair (C_2) form.



Half-chair form (C_2)



Envelope form (C_S)

We show, in this study how the use of P.E.S. can remove the indetermination about the nature of the equilibrium conformation of 1,2,4-trithiolane.

We actually know that, when two neighbouring heteroatoms are in interaction, the observed splitting of the first PE band is in a clear dependence on the dihedral angle θ of the heteroatom electron pairs (4 - 10).

In the case of the S-S bond, H. BOCK and G. WAGNER (5, 9) have studied this splitting for different values of θ. However the authors have only examinated a variation of that angle between 60° and 110°. We have investigated again some disulfides adding lipoïc acid (Fig.1a) which shows a θ angle about 30° (11) ; so that we could extend the range of the values of the dihedral angles. These results are reported in Table I.

If, in vapour phase, the trithiolane showed a pseudorotation between an envelope $\theta = 0°$ and an half-chair form $0 < \theta < 60°$ (taking into account the angle observed in 1,2-dithiane) we could expect the presence of two doublets in the PE spectra with a different separation (15). Particularly for the envelope form, this separation should be greater than the observed value for lipoïc acid (1.80 e.V.).

It seems that the spectra observed for 1,2,4-trithiolane and its 3,3,5,5-tetramethyl derivative (Fig.1b) can only be explained by the existence of one single conformation.

When we pass from 1,2,4-trithiolane to its tetramethyl derivative, we can observe a displacement of the whole spectra towards the low energies.

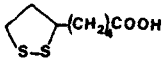
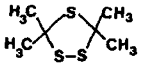
COMPOUNDS		IE_{n^-}	IE_{n^+}	ΔIE	θ	$IE_{\sigma S-S}$
RSSR	R					
	H	10.10	10.28	0.27 (a)	90.4° (12)	12.6 (a)
	CH_3	8.97	9.21	0.24 (a)	84.7° (13)	
		9	9.25	0.25 (b)		11.27 (b)
	C_2H_5	8.70	8.92	0.22 (a)		
		8.77	9	0¿23 (b)		10.96 (b)
	C_3H_7	8.62	8.87	0.25 (a)		
	$CH(CH_3)_2$	8.54	8.76	0.22 (a)		
		8.51	8.74	0.23 (b)		10.70 (b)
	C_4H_9	8.51	8.72	0.21 (b)		10.76 (b)
	$C(CH_3)_3$	8.17	8.82	0.65 (a)	∿ 110°	
		8.15	8.75	0.60 (b)		10.50 (b)
		8.36	9.31	0.95 (a)	60° (14)	10.9 (a)
		8.02	9.82	1.80 (b)	∿ 30° (11)	
		8.72	10.19	1.47 (b))		11.06 (b)
		8.12	9/78	1.66 (b)		10.36 (b)

TABLE I – Vertical ionization potentials (IE), n^-/n^+ splitting (ΔIE) and dihedral angles (θ) of disulfides derivatives.

(a) : reference (8) ; (b) : this work

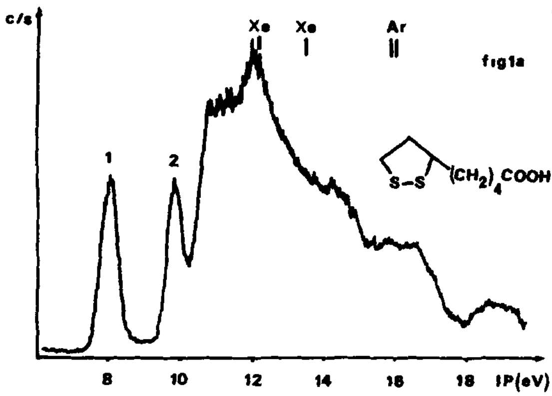


Fig. 1a – PE spectrum of lipoïc acid.

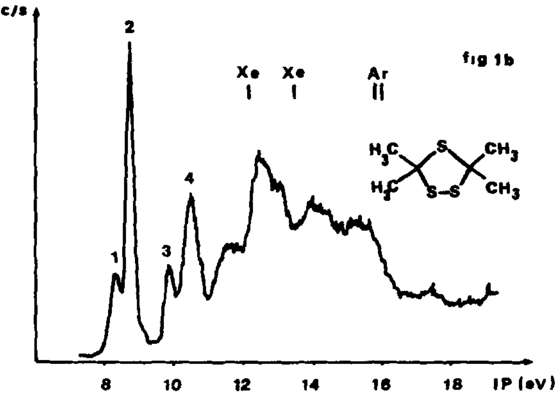


Fig. 1b – PE spectrum of 3,3,5,5-tetramethyl 1,2,4-trithiolane.

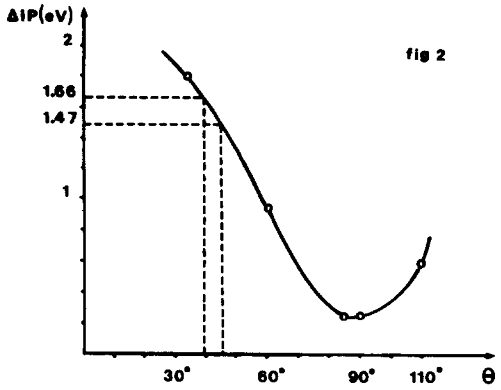


Fig.2 : n^-/n^+ splitting correlation diagram as a function of θ

For these two compounds, the bands of strong intensities (respectively at 9.10 eV and 8.58 eV) can be assigned to the ionization of one electron of the lone pair of the S_4 sulfur. These two values are to be compared to the one observed for dimethyl sulfide at 8.67 eV (8).

The first and third bands correspond to the antisymetric and symetric combination of the sulfur atoms of the disulfur bond.

The fourth band, sensitive to the substitution by methyl groups results from the ionization of an electron of a σ molecular orbital delocalised on the sulfur atoms and the C-S bonds.

Thus, we can notice a splitting of 1.47 eV (1,2,4-trithiolane) and 1.66 eV (3,3,5,5-tetramethyl 1,2,4-trithiolane) between the lone pairs of the sulfur atoms of the disulfide bond. From these data, we can conclude for 1,2,4-trithiolane to the existence, in vapour phase, of the half-chair form only. Considering the profile of the curve ΔIP = f(θ) (Fig.2) we can approximately estimate the dihedral angle formed by (CS_2S_2) and (S_1S_2C) plans at about 40°.

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