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ELECTRONIC STRUCTURE OF SULPHUR COMPOUNDS—VII[a]

PHOTOELECTRON SPECTRA OF THIOCARBONYL HETEROCYCLES

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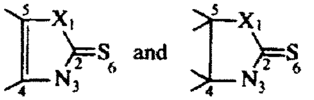
Abstract—The photoelectron spectra of α-substituted thiocarbonyl heterocycles have been analysed. By observing the effects of methyl substitution on the spectra, it was possible to assign the first five bands. These assignments were confirmed by semi-empirical calculations (CNDO/S).

INTRODUCTION

In a general study of the relationship between the reactivity of the thiocarbonyl group and its electronic structure,[1] we examined the photoelectron spectra of compounds of the type in order to



evaluate the n and π ionisation potentials of this group.

The examination of the spectra of molecules substituted in different positions has permitted a non-ambiguous interpretation. Furthermore since a theoretical study of the electronic spectra of some compounds has already been undertaken,[2] we have compared our experimental results with this data, using Koopmans' approximation.[3]

It was known that this approximation, which does not take account of correlation effects and ignores any electronic rearrangement, underestimates the values of the ionisation potentials. Nevertheless, for all the compounds studied, we found that the calculated order of the molecular orbitals is in agreement with that deduced by experimental analysis. This comparison has allowed us to correlate accurately the changes in localisation of the different molecular orbitals with the environment of the thiocarbonyl group.

Experimental and theoretical conditions

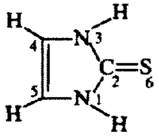
The spectra were recorded on a Perkin-Elmer P.S. 18 spectrophotometer using the $P_{1/2}$ and $P_{3/2}$ doublets of argon and xenon as references. A helium I lamp was used as the source of ionising radiation (wave length: 584 Å, that is, an energy of 21·21 eV). The ionisation potentials were determined to ±0·03 eV.

The theoretical study was carried out using the CNDO/S method extended to the d orbitals and with the parameterisation previously proposed by two of us.[4] The geometrical structures of the molecules used were deduced from X-ray structure determinations (see appendix). For all the structure calculations we only considered non-substituted molecules.

The preparations of the compounds studied have been previously given.[1]

Imidazoline-2-thione

The experimental values of the ionisation potentials of mono- and di-N-methyl substituted imidazoline-2-thione are given in Table I. The theoretical values were calculated for the non-substituted molecule.



The spectrum of N-methylimidazoline-2-thione (Fig 1) gives five distinct bands in the region 7-13 eV. The NN′-dimethyl derivative shows a displacement of all these bands to lower energies, the fourth

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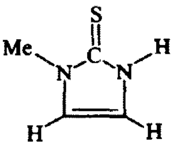
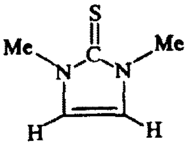
[a] Part VI—C. Guimon, D. Gonbeau, G. Pfister-Guillouzo, L. Asbrink and J. Sandstrom, *J. Electron Spectroscopy* 0000 (1974).

Table I. Experimental and theoretical ionisation potentials of imidazoline-2-thiones

		Non-substituted molecule		
Experimental values (eV)		Theoretical values (eV)	Contribution from the A.O. (%)	Nature of the M.O.
7·41 (700 cm^{-1})	7.27 (700 cm^{-1})	9.23	$S_6 = 72$; $N = 8$; $C_{4,5} = 4$	π
7·90 (1200 cm^{-1})	7·78 (1200 cm^{-1})	9·37	$S_6 = 98$; $N = 1$	n
10·09	9·87	12	$S_6 = 12$; $N = 4$; $C_{4,5} = 31$	π
10·68	10.30	13·48	$N = 46$; $C_{4,5} = 4$	π
12·4	12·23	13·82	$S_6 = 57$; $C_2 = 27$; $N = 4$	σ

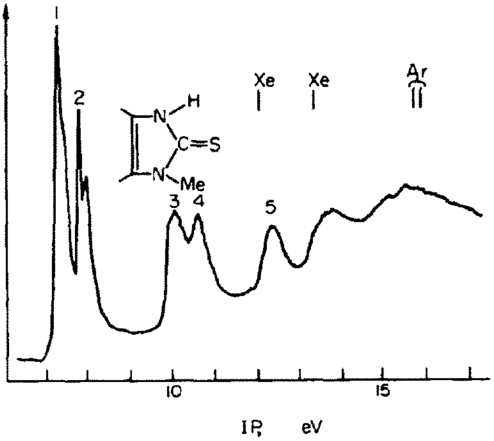


Fig 1.

band being the most senstive to the substitution at nitrogen.

The first band at 7·41 eV possesses a slight vibrational structure (700 cm^{-1}). Thus it corresponds unambiguously to the ionisation of a π-electron localised on the extracyclic S atom (calc: 72%).

The second band at 7·90 eV shows a much larger vibrational splitting (1200 cm^{-1}) and so can only be the result of the ionisation of a non-bonding S electron. Its calculated localisation is particularly high (98%). For these two bands, as indicated in Fig 8, these vibrational spacings are easily identified being unaccompanied by other modes of vibration.

These two peaks are shifted by about 0·15 eV when the hydrogen on nitrogen is replaced by a Me group. This destabilisation is related to the hyperconjugative effect of the Me group and also to the steric effect.

The third (10·09 eV) and fourth (10·68 eV) bands are, upon substitution, displaced to 9·87 eV and 10·30 eV, that is, by 0·22 eV and 0·38 eV respectively. In accordance with the theoretical data, these bands can be attributed in the following manner:

Third band: ionisation of an electron from a molecular orbital localised on the carbon-carbon double bond (62%).

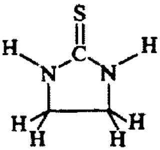
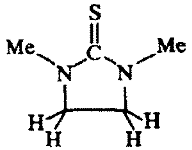
Fourth band: ionisation of an electron from an anti-symmetric molecular orbital localised on the two N atoms (92%).

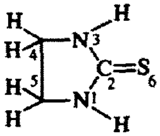
The fifth band (12·4 eV) corresponds to the ionisation of an electron from the σ-molecular orbital localised on the C═S bond (84%).

Imidazolidine-2-Thione

As in the case of imidazoline-2-thione, we compared the spectra of imidazolidine-2-thione and NN′-dimethylimadazolidine-2-thione. The experimental and theoretical values of the ionisation potentials are given in Table II.

Table II. Experimental and theoretical ionisation potentials of imidazolidine-2-thiones

		Non-substitued molecule		
Experimental values (eV)		Theoretical values (eV)	Contribution from the A.O. (%)	Nature of the M.O.
8·15	7·95	9·14	$S_6 = 97$	n
8·15	7·99 (650 cm^{-1})	9·25	$S_6 = 84$; $C_2 = 4$; $N = 6$	π
9·46	8·62	11·98	$N = 44$; $C_{4,5} = 3$	π
12·6	11·77	13·37	$S_6 = 53$; $C_2 = 27$; $N = 4$	σ



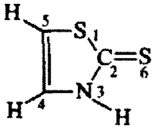
It can be seen that the behaviour of these compounds is similar to that of the previous one. The first two bands which are in practice superimposed, are displaced, upon substitution by about 0·2 eV while the third is displaced by 0·84 eV. This latter can only correspond to the molecular orbital localised on the N atoms (Fig 2).

The order n, π was proposed from the theoretical data and by analogy with the attribution proposed by two of us[5] for thiourea (a) and tetramethylthiourea (d) (see Table III).

The comparison of the spectra of the thioureas (a, b, d) with those of the variously substituted imidazolidine-2-thiones (c,e) (Table III) confirms our interpretation, once we have taken account of substituent and cyclisation effects.

Indeed, passing from (a) to (b), that is, the substitution of the hydrogen on each N atom by a Me group, lowers all the ionisation potentials, particularly the third which corresponds to the loss of a π-electron localised on the N atoms. Cyclisation, that is, passing from (b) to (c) has very little effect on the first two potentials but raises the next two. This change, due to the restriction brought about by cyclisation had already been observed in passing from methyl trithiocarbonate to ethylene trithiocarbonate,[5] and also, to a greater extent, in passing from tetramethylthiourea (α) to NN'-dimethylimidazolidine-2-thione (e) where the non-planarity of tetramethythiourea involves a weaker conjugation.

Thiazoline-2-Thione



The spectrum of thiazoline-2-thione (Fig. 3) closely resembles that of imidazoline-2-thione. As expected, given the electronegativities and mesomeric properties of sulphur as compared with nitrogen, the values of the vertical potentials are displaced to higher energies.

Taking account of the effects of N-substitution

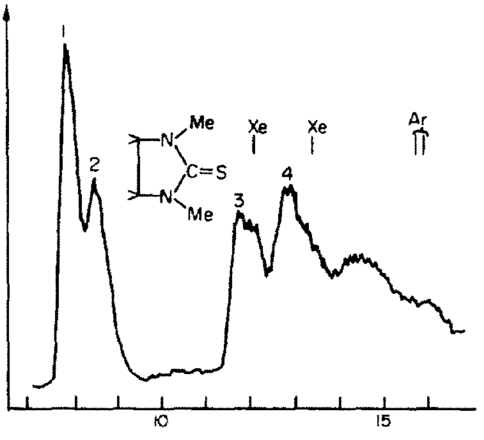


Fig 2.

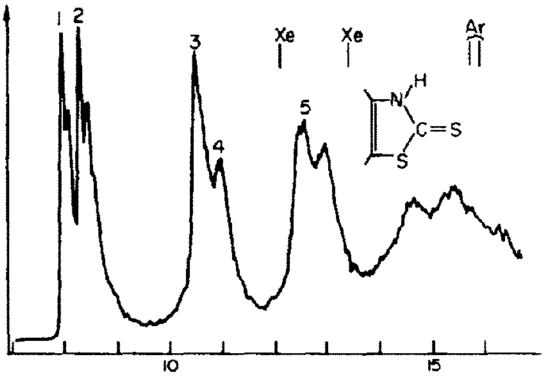
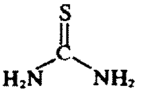
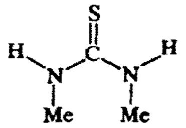
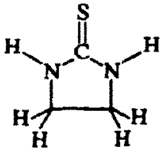
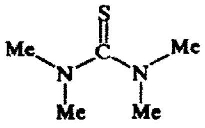
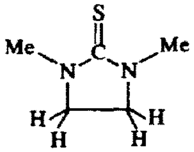


Fig 3.

Table III. Experimental ionisation potentials of thioureas derivatives (eV unit)

 (a)	 (b)	 (c)	 (d)	 (e)	Nature of the M.O.
8·41	8·08	8·15	7·82	7·95	n
8·41	8·08	8·15	8·09	7·99	π
10·50	9·18	9·46	8·58	8·62	π
12·82	12·1	12·60	11·28	11·77	σ

and in agreement with the theoretically calculated order, we were able to propose the following attributions (Table IV):

First band at 7·74 eV: ionisation of a π-electron from the thiocarbonyl group (calculated: 60%);

Second band at 8·12 eV: ionisation of a non-bonding electron from the extracyclic sulphur (calculated: 94%);

Third band at 10·32 eV: ionisation of a π-electron delocalised over the S=C—S—C=C segment;

Fourth band at 10·82 eV: ionisation of a π-electron localised on the intracyclic sulphur (63%) and nitrogen (28%);

Fifth band at 12·48 eV: ionisation of a σ bonding electron localised on the S=C—S segment of the molecule.

As in the case of the previous compounds, we were interested in following the evolution of the spectrum of thiazoline-2-thione with different substituents, on the one hand at nitrogen (Table IV) and on the other hand at carbons 4 and 5 (Table V).

If the experimental values are compared, it can be seen that the substitution at nitrogen of a Me group (Tables IV and V) has a similar effect on both the first (π) and second (n) bands, which indicates that there is an interaction, as important as the hyperconjugative effect, at a distance between these groups and the extracyclic sulphur. Finally the fourth band, resulting from the ionisation of a π-electron partially localised on the nitrogen undergoes a more marked shift to lower energies than the third hand, particularly in the case of 4,5-dimethyl compound.

Conversely, the presence of Me groups on the C=C bond (Table V) has a larger effect on the first band (π) than on the second (n). This seems logical since a Me group in this position interacts mainly by its hyperconjugative effect. This hypothesis was confirmed by the theoretical results since the π-molecular orbital corresponding to the first ionisation potential is delocalised by 14% on the intracyclic sulphur and with weighting of 7% and 4% on the C atoms C_4 and C_5. This agreement between the theoretical calculation and the experimental spectrum is confirmed in the case of methylation of C_5, which affects the fourth band more than the third (Table V).

Finally, it can be seen from Table IV and V that N-methylation causes a larger shift in the fifth band than does methylation on the C=C band. This band, as previously mentioned, results from the ionisation of an electron from a σ-type bonding molecular orbital localised on the S=C—S segment and so must be sensitive to steric type interactions introduced by N-methylation.

Table IV. Experimental and theoretical ionisation potentials of thiazoline-2-thiones

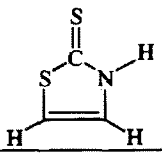
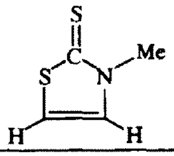
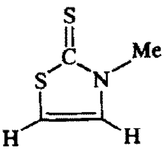
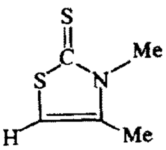
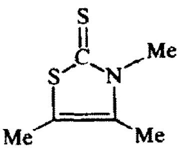
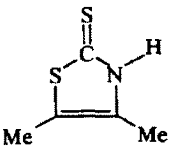
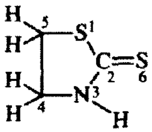
		Non-substitued molecule		
		Theoretical values (eV)	Contribution from the A.O. (%)	Nature of the M.O.
Experimental values (eV)				
7·74 (800 cm^{-1})	7·68 (800 cm^{-1})	9·45	$S_6 = 60$; $S_1 = 14$; $N = 12$; $C_4 = 4$; $C_5 = 7$	π
8·12 (1000 cm^{-1})	8·02 (1150 cm^{-1})	9·64	$S_6 = 94$	n
10·32	10·12	11·98	$S_6 = 18$; $C_2 = 18$; $S_1 = 21$; $C_5 = 18$; $C_4 = 25$	π
10·82	10·53	12·70	$S_1 = 63$; $N = 28$; $C_5 = 19$	π
12·48	12·18	13·61	$S_6 = 35$; $C_2 = 26$; $S_1 = 24$	σ

Table V. Experimental ionisation potentials of thiazoline-2-thiones (eV unit)

				Nature of the M.O.
7·68 (800 cm^{-1})	7·55 (800 cm^{-1})	7·45 (800 cm^{-1})	7·56 (800 cm^{-1})	π
8·02 (1150 cm^{-1})	7·98 (1200 cm^{-1})	7·94 (1100 cm^{-1})	8·04 (1050 cm^{-1})	n
10·12	9·90	9·76	9·91	π
10·53	10·28	10·00	10·44	π
12·18	12·00	11·94	12·16	σ

Thiazolidine-2-Thione



As well as thiazolidine-2-thione (Fig 4) we have analysed the spectra of the N-methyl- and 4,4-dimethyl derivatives. The experimental values of the ionisation potentials are given in Table VI. In agreement with what we have previously observed, N-methylation produces a larger shift in the first two vertical ionisation potentials. In contrast with imidazolidine-2-thione, the first two peaks are separated and they display a vibrational spacing of $800\ cm^{-1}$ on the higher energy side, which serves to confirm the theoretically forecast order n, π.

As with the fourth band of thiazoline-2-thione, the sensitivity of the third band (9·47 eV) to N-methylation (shifted by 0·45 eV) can only be interpreted as the ionisation of an electron from the π molecular orbital localised mainly on the intracyclic sulphur and, with a weighting of 21% on the nitrogen. Finally, the steric perturbations caused by Me disubstitution at C_4 manifest themselves by a change in ionisation potential of the molecular orbital delocalised over the whole σ system.

As previously, we have examined the influence of cyclisation on the photoelectron spectrum of S-methyl-N-methyl dithiocarbonate (Table VII, Fig 5). The results are identical; cyclisation has very little effect on the first three molecular levels (thiocarbonyl n and π, and π of the single-bonded

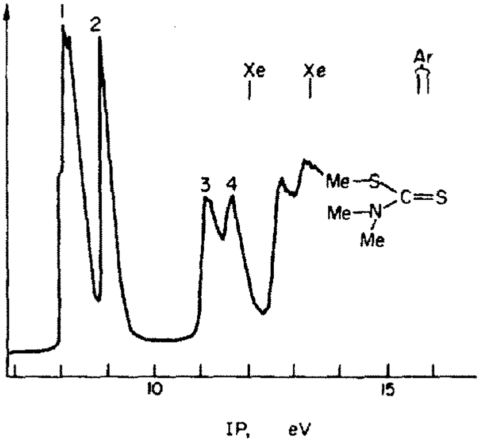


Fig 5.

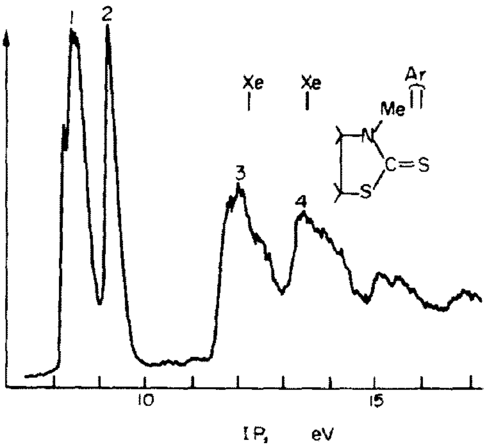


Fig 4.

Table VII

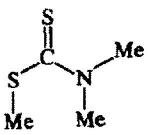
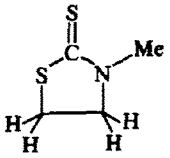
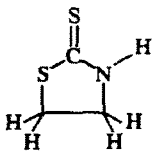
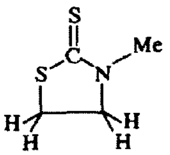
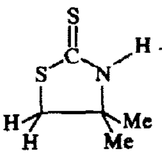
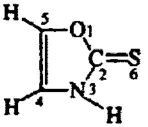
Experimental values (eV)		
		Nature of the M.O.
8·01	8·04	n
8·23	8·23	π
8·97	9·02	π
11·13	11·71	σ

Table VI. Experimental and theoretical ionisation potentials of thiazolidine-2-thiones

			Non-substitued molecule		
Experimental values (eV)			Theoretical values (eV)	Contribution from the A.O. (%)	Nature of the M.O.
8·25	8·04	8·18	9·42	$S_6 = 94$	n
8·48 ($800\ cm^{-1}$)	8·23 ($700\ cm^{-1}$)	8·36 ($800\ cm^{-1}$)	9·56	$S_6 = 74$; $C_2 = 5$; $N = 11$	π
9·47	9·02	9·18	11·52	$S_1 = 69$; $N = 21$	π
11·97	11·71	11·47	13·26	$S_6 = 36$; $S_1 = 18$; $C_2 = 27$; $C_5 = 7$	σ

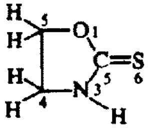
sulphur and nitrogen) and a much larger effect on the σ level, as a result of the changes introduced by the geometric strain of the ring.

Oxazoline-2-Thione



In this series we have examined only the N-methyl- and 4,5-dimethyloxazoline-2-thiones (Fig 6). For these two compounds the attribution of the bands corresponds to the order: $\pi_{C=S}$, n_S, $\pi_{C=C}$, $\pi_{N,O}$, σ_{C-S} (Table VIII).

Oxazolidine-2-Thione



The interpretation of the spectrum of oxazolidine-2-thione corresponds to those proposed for the other saturated compounds, that is: n_S, $\tau_{C=S}$, $\pi_{N,O}$, σ_{C-S} (Table IX, Fig 7).

ANALYSIS OF RESULTS

In the case of the 4,5-saturated heterocycle, the occupied molecular orbital of highest energy is non-bonding, the next lowest being a π orbital. While the spacing of the first two peaks in imidazolidine-2-thione is practically zero, in the case of thiazolidine-2-thione it is 0·23 eV and for oxazolidine-2-thione 0·33 eV.

In addition, if we compare the values of the first two ionisation potentials of these three molecules, we can see that the stabilisation produced by N, S and O in the position α the thiocarbonyl group increases in the order N;S;O.

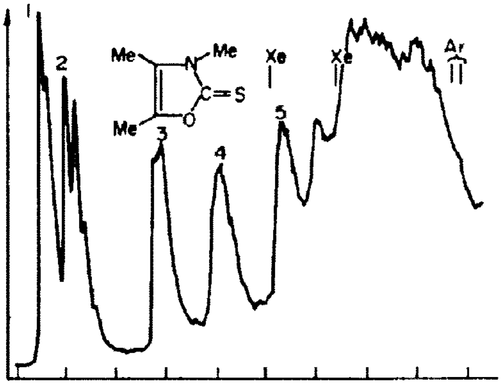


Fig 6.

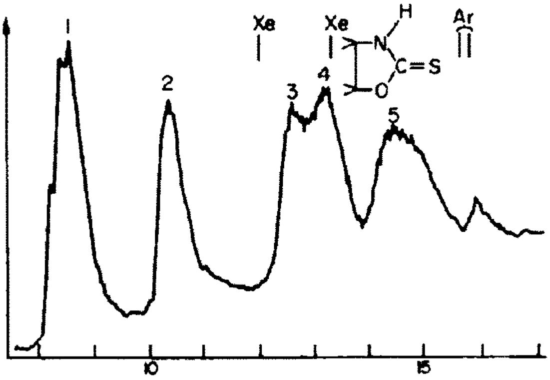


Fig 7.

Thus the mesomeric effect of the heteroatom α to the thiocarbonyl group seems to have more influence on the π level than does the electronegativity on the n level.

The third band (π) associated with these two heteroatoms is particularly sensitive to their mesomeric ability.

Table VIII. Experimental and theoretical ionisation potentials of oxazoline-2-thiones

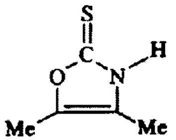
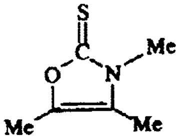
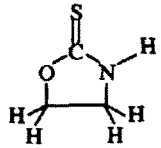
		Non-substitued molecule		
		Theoretical values (eV)	Contribution from the A.O. (%)	Nature of the M.O.
Experimental values (eV)				
7·74 (1150 cm^{-1})	7·54 (900 cm^{-1})	9·58	S = 66; O = 7; N = 13; $C_5 = 7$; $C_4 = 5$	π
8·22 (1250 cm^{-1})	8·03 (1200 cm^{-1})	9·74	S = 97	n
10·11	9·90	12·20	S = 15; $C_2 = 18$; O = 2; N = 4; $C_5 = 31$; $C_4 = 30$	π
11·71	11·15	14·55	O = 38; N = 52; $C_4 = 8$	π
12·58	12·33	14·43 –	S = 63; $C_2 = 25$; O = 2; N = 2	σ

Table IX. Experimental and theoretical ionisation potentials of the oxazolidine-2-thione

	Non-substitued molecule		
Experimental values (eV)	Theoretical values (eV)	Contribution from the A.O. (%)	Nature of the M.O.
8·37	9·55	$S = 98$	n
8·70 (800 cm^{-1})	9·71	$S = 77$; $C_2 = 6$; $O = 4$; $N = 11$	π
10·48	12·67	$O = 30$; $N = 43$	π
12·81	13·76	$S = 54$; $C_2 = 26$; $N = 5$	σ
13·28	15·34	$N = 38$; $C_2 = 23$; $C_4 = 23$	σ

In comparison with the above saturated compounds, examination of the spectra of the 4,5-unsaturated heterocycles shows an inversion in the order of the first two ionisation potentials, associated with molecular orbitals of the type n and π.

Conversely, the order of stabilisation introduced by the heteroatoms α to the thiocarbonyl group remains the same as that observed for the saturated compounds (i.e., N; S; O).

The vibrational structures of the first two bands (π and n) associated with the thiocarbonyl group correspond respectively to the frequencies:

700 cm^{-1} and 1200 cm^{-1} for imidazoline-2-thione (Table I)

800 cm^{-1} and 1000 cm^{-1} for thiazoline-2-thione (Table IV)

1150 cm^{-1} and 1250 cm^{-1} for oxazoline-2-thione (Table VIII)

These vibrational spacings are easily identified on Figs 8, 9 and 10.

The frequencies associated with the n band approach that of a pure C=S double bond as we pass from thiazoline-2-thione to imidazoline-2-thione and to oxazoline-2-thione. Ignoring differences in coupling between these three molecules, this difference between thiazoline-2-thione and the other two compounds corresponds in the theoretical results to a certain degree of delocalisation of the molecular orbital associated with this band.

In the case of oxazoline-2-thione, the fourth band, corresponding to the ionisation of an electron from a molecular orbital possessing π symmetry and localised on the O (38%) and N (52%) atoms, is, upon N-methylation, displaced by a larger extent

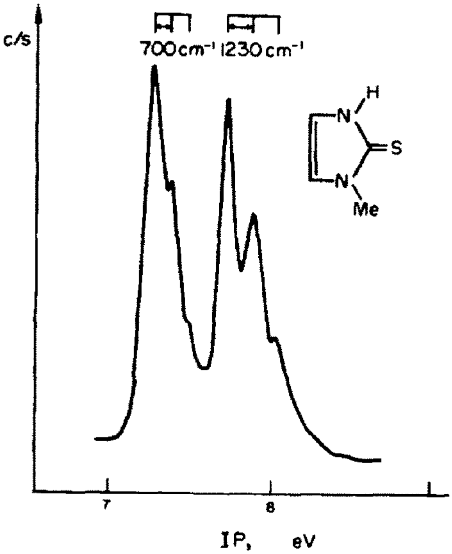


Fig 8.

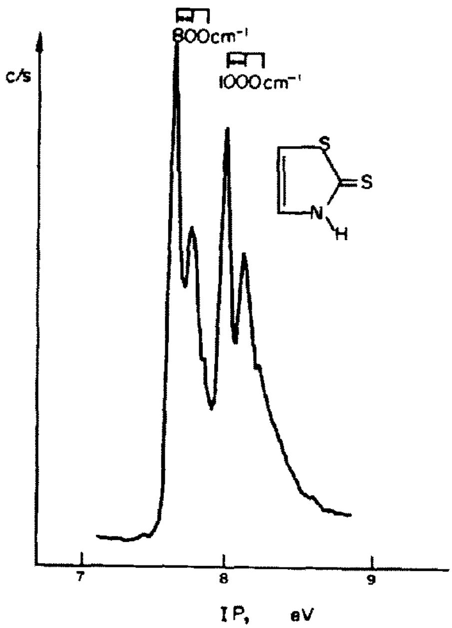


Fig 9.

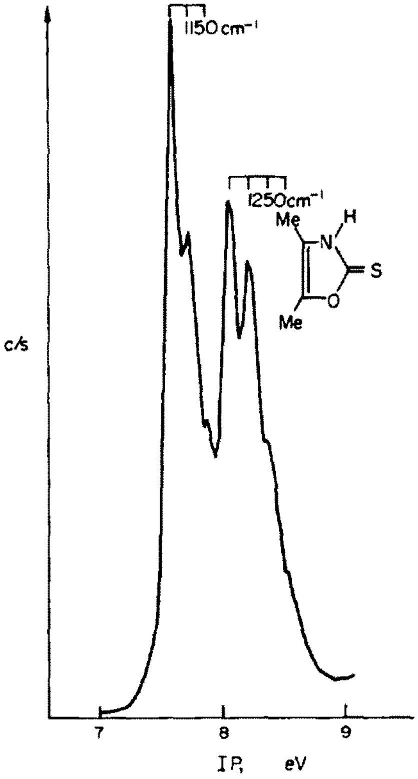


Fig 10.

(0·69 eV) than in the other two compounds (0·37 eV and 0·29 eV). This agrees perfectly with the calculations which give as weighting of the atomic orbital of nitrogen in the considered molecular orbital:

28% for thiazoline-2-thione (0·29 eV shift)
46% for imidazoline-2-thione (0·37 eV shift)
52% for oxazoline-2-thione (0·69 eV shift)

Finally it should be noted that in passing from the conjugated compound to the corresponding saturated compound has little effect on the ionisation potential of a σ-electron localised on the C—S bond. It is however lowered by the larger delocalisation of this orbital in the thiazoline- and thiazolidine-2-thiones.

CONCLUSION

The interpretation of the photoelectron spectra of thiocarbonyl heterocyclic compounds has allowed us to elaborate the electronic structure of the thiocarbonyl group.

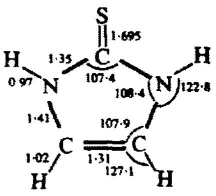
We propose to use these new data in the interpretation of the nucleophilic behaviour of this group.[10]

REFERENCES

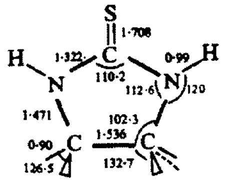
[1] M. Arbelot, R. Gallo, M. Chanon and J. Metzger, *Int. J. Sulfur Chem.* to be published (1974)
[2] M. Arbelot, C. Guimon, D. Gonbeau and G. Pfister-Guillouzo, *J. Mol. Struct.* **20**, 487 (1974)
[3] T. Koopmans, *Physica* **1**, 104 (1934)
[4] C. Guimon, D. Gonbeau and G. Pfister-Guillouzo, *Tetrahedron* **29**, 3399 (1973).
[5] C. Guimon, D. Gonbeau, G. Pfister-Guillouzo, L. Asbrink and J. Sandstrom, *J. Ed. Spect.* Part VI (1974) in press
[6] G. B. Ansell, D. M. Forkey and D. W. Moore, *Chem. Commun.* 56 (1970)
[7] P. J. Wheatley, *Acta Cryst.* **6**, 369 (1953)
[8] G. J. Kruger and G. Gafner, *Ibid.* **B.28**, 272 (1972)
[9] P. Groth, K. Davidkov and D. Simov, *Acta Chem. Scand.* **26**, 1931 (1972)
[10] M. Arbelot, M. Chanon, J. Metzger, C. Guimon and G. Pfister-Guillouzo, to be published

APPENDIX

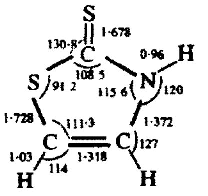
The geometric data used for all our calculations were determined by X-ray. For those molecules whose structure was not known, we evaluated a geometry consistent with that of compounds of know structure.



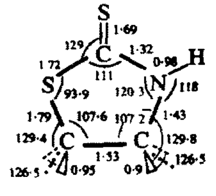
Imidazoline-2-thione[6]



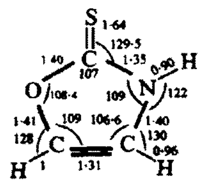
Imidazolidine-2-thione[7]



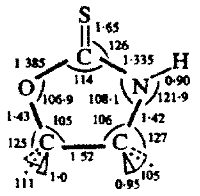
Thiazoline-2-thione[8]



Thiazolidine-2-thione



Oxazoline-2-thione[9]



Oxazolidine-2-thione