Photoelectron (He I) Spectra of Aromatic Thiocarbonyls and Corresponding S-Oxides

Fernando Bernardi *, Francesco Paolo Colonna **, Giuseppe Distefano **, Gaetano Maccagnani * and Giuseppe Spunta **

Z Naturforsch **33a**, 468–471 (1978); received December 1977

The low ionization energy regions of the photoelectron (He I) spectra of several p-p′-substituted thiobenzophenones $(X\text{-}C_6H_4)_2CS$ and of the corresponding S-oxides (sulphines) $(X\text{-}C_6H_4)_2CSO$ (where X=H, OCH_3, CH_3, I, Br, Cl and NO_2) have been assigned on the basis of perturbational molecular orbital theory arguments coupled with CNDO/2 computations and substituent effects.

For the thioketones, the ordering of the outermost MO's results to be n(S), π_7, π_6, π_5/π_4, π_3, n(S) being the HOMO; while for the sulphines the two outermost MO's have π character and correspond to π_7 and π_6 in the thioketones

In the light of the above results the different behaviour toward oxidation of these two classes of compounds can be rationalized.

Sulphines have already been the object of various investigations in this Laboratory. Previously studies have dealt mainly with stereochemistry [1], reduction and oxidation reactions of thiobenzophenones and sulphines [2], cycloaddition reactions [3] involving this pair of substrates, and theoretical investigations [4] on the geometry and charge distribution on H_2CS and H_2CSO.

In order to obtain further information on the electronic distribution of such compounds we have also carried out an UV photoelectron spectroscopy (UPS) study of some p-p′-thiobenzophenones $(X-C_6H_4)_2CS$ and of the corresponding sulphines $(X-C_6H_4)_2CSO$, with X=H, OCH_3, CH_3, I, Br, Cl and NO_2. Such information could, in fact, be quite useful for a better understanding of their chemical properties.

Experimental

The spectra were obtained with a Perkin Elmer PS 18 photoelectron spectrometer. Given that the substrates dealt with in this paper are rather complex molecules yielding complicated PE-spectra with several overlapping bands (see Figs.), the I.E. values are considered to have an uncertainty of the order of 0.1 eV except where they relate to well-resolved bands, in wich case the estimated error is ± 0.05 eV.

* Istituto di Chimica Organica dell' Universita, Viale Risorgimento 4 — Bologna — Italy.

** Laboratorio dei composti del carbonio contenenti eteroatomi e loro applicazioni del C.N.R. — Via Tolara di Sotto, 89 — Ozzano Emilia (Bologna) — Italy.

The compounds were obtained according to known procedures [5].

Results and Discussion

The IE values lower than about 11.5 eV of the p-p′-thiobenzophenones and of the corresponding sulphines investigated here are listed in Tables 1 and 2 and the low IE region of the photoelectron spectra are shown in Figs. 1 and 2 respectively.

The values quoted in the Tables refer to the maxima of the various bands which are assumed to correspond to the vertical IE values.

In the case of thiobenzophenone the assignment has been based on a qualitative Perturbational Molecular Orbital (PMO) analysis with the interacting fragments taken to be the two benzene rings and the C=S group. An estimate of the IE values of the π MOs of the two benzene rings in a similar situation can be taken from the spectrum of diphenylmethane [6] which shows a peak at 9.12 eV and two shoulders at 8.67 and 9.3 eV. The maximum has been assigned to ionization from the antisymmetric [7] π ring orbitals and the shoulders to the in phase and out-of-phase combinations of the symmetric π orbitals. The IE values of the relevant MOs of the C=S fragment can be taken from the spectrum of thioformaldehyde [8] where it has been found that the first two IE values at 9.33 and 11.90 eV correspond to the sulphur lone pair and the bonding π MO of the thiocarbonyl group respectively. The inductive effect of the phenyl groups certainly will lower both these values as has been observed in many thione derivatives [8, 9] where, in several cases, the HOMO (highest occupied mol-

Table 1. Ionization energy values with assignments for p-p′-substituted thiobenzophenones (eV).

X	n(S)	π_7	π_6	π_5/π_4	π_3	Halogen lone pair	K (l mol^{-1} s^{-1})[a]
OCH_3	7,61	$8,2_5$	$8,2_5$	$9,2_5$	9,8		
CH_3	7,80	$8,5_0$	$8,8_5$	$9,2_5$	$10,2_5$		66,0
H	8,0	8,77	9,4[b]	$9,2_1$	$10,6_2$		29,3
I	8,20	8,9	8,9	9,6 (sh)		$9,8_6$	
Br	8,21	$8,8_5$	9,08	9,7	$10,3_7$	$10,7_6$	
Cl	8,22	8,90	9,18	$9,7_5$	$10,6_1$	$11,4_2$	10,9
NO_2[c]	8,85	9,8					1,39

[a] Rate constant for the oxidation of thioketones to sulphines with perbenzoic acid, From Ref. [2].
[b] Despite the fact that the band corresponding to π_6 has a higher IE values than that denoted π_5/π_4, this nomenclature is used here because in all the other derivatives the corresponding MO is the second highest π MO.
[c] The NO_2 derivatives decompose in the target chamber to give mainly p-p′-dinitrobenzophenone (identified by comparison with the spectrum of a pure sample), The decomposition of sulphine is nearly complete, while the thioketone decomposes only in part, so that it has been possible to determine for the latter the IE values of the first two bands which appear at IE values lower than those of the decomposition product.

Table 2. Ionization energy values of p-p′-substituted diphenylsulphines (eV).

X	I_1	I_2	I_3[a]	I_4	I_5[b]	10^4 K_2 (l mol^{-1} s^{-1})[c]
OCH_3	7,66	$8,4_5$	9,3			31,5
CH_3	7,94	9,0 (sh)	9,3	$9,7_5$ (sh)		5,32
H	8,25		$9,4_5$	10,2		1,28
Br	8,33	9,15	9,8		10,83	
Cl	8,35	9,3	$9,8_5$		11,50	1,20

[a] Broad intense band. [b] Halogen lone pair.
[c] Rate constants for the oxidation of sulphines to ketones with perbenzoic acid. From Ref. [2].

ecular orbital) has been assigned [9] to a π-MO mainly localized on the sulphur atom.

In addition we have also carried out CNDO/2 computations on thioformaldehyde and on thiobenzophenone. Thioformaldehyde has been taken at the experimentally found geometry, while thiobenzophenone (whose geometry has not been determined experimentally) has been investigated in a non planar geometry with a dihedral angle between the two phenyl rings of $\sim 56°$ (the latter is the value of the dihedral angle experimentally found [10] in benzophenone), a C—S bond length at the same value as in thioformaldehyde and the remaining geometrical parameters at standard values. The relevant computational results are listed in Table 3.

The CNDO/2 computations have been used mainly to assess the nature of the first band. The computational results suggest that the first band should be assigned to ionization from the sulphur lone pair (denoted here by n(S)). The remaining bands have been assigned mainly on the basis of PMO arguments.

Table 3. Computed and experimental ionization energies of the first two bands of thioformaldehyde (A) and thiobenzophenone (B) (eV).

	A		B	
	Comp.	Exp.	Comp.	Exp.
n(S)	11.96	9.23	10.69	8.00
π(C—S)	13.69	11.90	10.99	8.77
Δ	1.73	2.67	0.30	0.77

Consequently the bands peaking at 8.77, 9.4 and 10.62 eV are assigned to the three combinations (out-of-phase, non-bonding and in-phase) of the π-MO of the C=S fragment with the two combinations of the symmetric π ring orbitals, denoted here by π_7, π_6 and π_3. The band at 9.2_1 eV is assigned to ionization from the degenerate antisymmetric π-MO's of the phenyl groups because of its intensity and by analogy with 1-1-diphenylmethane and will be denoted by π_5/π_4.

Comparison between computed and experimental ionization energies for thioformaldehyde shows that at the CNDO/2 level the ionization energy of the π(C—S)MO is overestimated compared with that

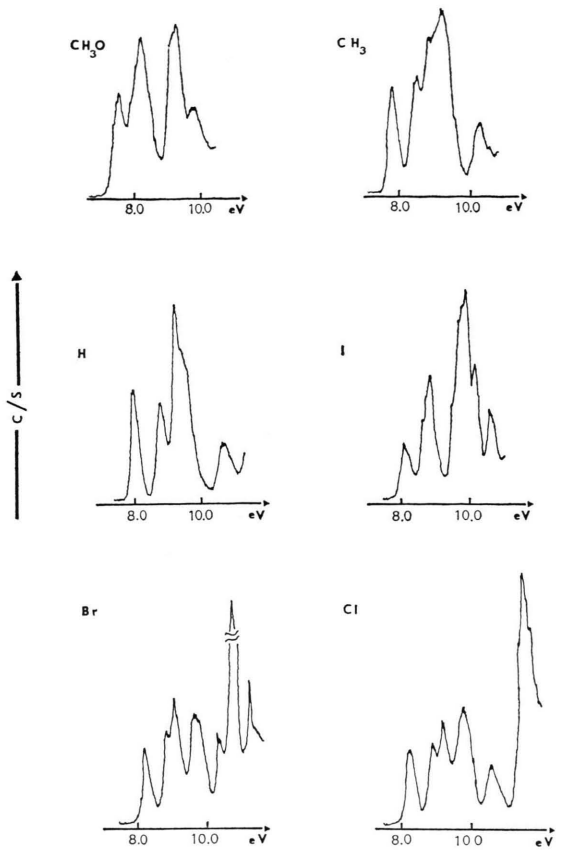

Fig. 1. Low ionization energy region of the photoelectron (He I) spectra of p-p′-substituted thiobenzophenones.

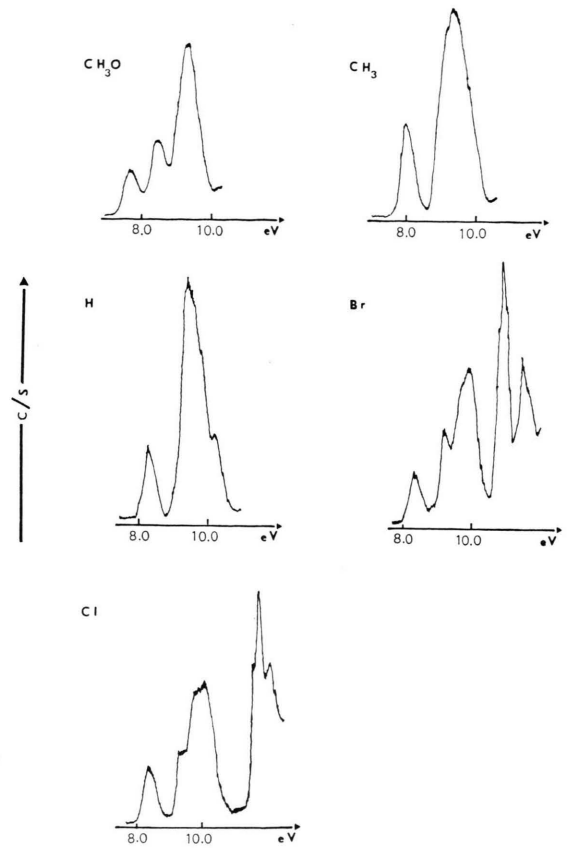

Fig. 2. Low ionization energy region of the photoelectron (He I) spectra of p-p′-substituted diphenylsulphines.

of the n(S)MO. This feature of the CNDO/2 calculations provides indirect evidence for the proposed assignment of the first two bands. We should expect this ionization energy in fact to be overestimated also in thiobenzophenone. However, despite this fact, the HOMO is found to be n(S).

To obtain further support for the assignment, various p-p′-disubstituted thiobenzophenones have been investigated. It has been found that the first two I.E. values change in a parallel way with the substituents (see Table 1): their separation being 0.7 ± 0.1 eV in all cases. The constancy of this separation gives no information on the nature of the corresponding MO's. On the other hand, the behaviour of π_6 as a function of the substituent is much more pronounced than that of the first two bands. It can be observed that the introduction of two p-I or p-OCH_3 groups, which have π orbitals (9.46 [11] and 10.25 [12] eV respectively) of energy intermediate between those of π_6 and π_3 in thiobenzophenone, causes such a large destabilization of π_6 that the corresponding band overlaps the second one. This effect indicates that the latter band corresponds to an MO that experiences a much smaller substituent effect with respect to π_6. The CNDO/2 results provide an explanation of the more pronounced substituent effect on π_6. The latter MO corresponds to the out-of-phase combination of the two symmetric MO's of the phenyl rings. By symmetry this MO does not mix with the π(C—S) MO and consequently the values of the coefficients in the para positions of the two phenyl rings are larger than in the π_7MO, and therefore also its sensitivity to the substituent effect will be larger.

The general trends of π_7, π_6, π_5, π_4 and n(S), as a function of substituents, are those expected from the known properties of the substituent groups [11, 13, 14] confirming the assignment proposed.

In the case of the related diaryl sulphines, a complete assignment of the low IE region of the spectra

is hampered by extensive overlap of bands (see Fig. 2) and only two bands (one for the H and p-CH_3 derivatives) are resolved below about 9.3 eV.

On going from H_2CS to H_2CSO, n(S) is greatly stabilized (n(S) is at 9.3 eV in H_2CS [8] while the corresponding n(S, O) in H_2CSO is at 10.7 eV [15]) and in H_2CSO the HOMO (at ca. 10.35 eV [15]) has π character. It follows that ionization from the n(S, O)MO of diarylsulphines will occur at an energy not lower than ca. 9.5 eV and that the first band in the spectrum of the unsubstituted sulphine is to be ascribed to ionization from a π MO, while in the substituted sulphines both the first two bands (I_1 and I_2) are to be assigned to ionization from π MOs. This assignment is supported by the following considerations.

i) The trends, of I_1 and I_2 as a function of substituents, closely parallel those of π_7 and π_6 respectively of the corresponding thioketones (in fact good linear relationships exist between π_7 and I_1 and between π_6 and I_2, the slope being in both cases close to 1).

ii) In the sulphines, the outermost π MO is destabilized (by ca. 0.5_5 eV) with respect to π_7 in thioketones in agreement with the destabilization of the first π MO on going from H_2CS to H_2CSO [8, 15].

Therefore, from a chemical point of view, the most interesting result is that the HOMO in the thiobenzophenones is mainly sulphur lone pair while in the corresponding sulphines is a MO of π symmetry. The outer MO's are of basic importance in determining the reactivity of the molecules for it is usually the most loosely bound electrons which partake readily in chemical reactions [16]. The assignment proposed for the present molecules is in agreement with the major features of the chemical reactivity of substrates containing the CS and CSO groups. In particular the different behaviour of thioketones and sulphines in the oxidation reaction with perbenzoic acid might be rationalized in terms of the different nature of the HOMO in the two cases. In fact if has been suggested [2] that the oxidation reactions of thiocarbonyls leads to sulphines involving the sulphur lone pair, in agreement with the HOMO beings mainly sulphur lone pair, while the oxidation reaction of sulphines leads to ketones and sulphur monoxide, *via* a cyclic sulphinic ester, in agreement with a HOMO of π symmetry delocalized on the CSO group. Furthermore the reactivity orders, as a function of substituent [2], in the oxidation reactions of thiobenzophenones to sulphines and of sulphines to ketones parallel the trends shown by the HOMO's i.e. they increase with the tendency of the substrate to donate its electrons as measured by the IE values (see Tables 1 and 2).

[1] S. Ghersetti, L. Lunazzi, G. Maccagnani, and A. Mangini, Chem. Comm. 834 (1969); B. F. Bonini, L. Lunazzi, G. Maccagnani, and G. Mazzanti, J.C.S. Perkin I, **1973**, 2314

[2] L. Lunazzi, G. Maccagnani, G. Mazzanti, and G. Placucci, J Chem. Soc B, 162 (1971); A. Battaglia, A. Dondoni, P. Giorgianni, G. Maccagnani, and G. Mazzanti, J. Chem. Soc. B, **1971**, 1547; A. Battaglia, A. Dondoni, G. Maccagnani, and G. Mazzanti, J.C.S. Perkin II, **1974**, 609.

[3] A. Battaglia, A. Dondoni, G. Maccagnani, and G. Mazzanti, J. Chem. Soc. B, **1971**, 2096; B. F. Bonini, G. Maccagnani, A Wagenaar, L. Thijs, and B. Zwanenburg, J.C.S. Perkin I, **1972**, 2490; B. F. Bonini, G. Maccagnani, L. Thijs, and B. Zwanenburg, Tetrahedron Letters **1973**, 3569.

[4] F. Bernardi, G. Maccagnani, and A. Mangini, An. Quim. **70**, 1199 (1974).

[5] B. F. Bonini, S. Ghersetti, G. Maccagnani, and G. Mazzanti, Boll. Sci. Fac. Chim. Ind. Bologna **27**, 401 (1969).

[6] G. Distefano, S. Pignataro, L. Szepes, and J. Borossay, J. Organomet. Chem. **104**, 173 (1976).

[7] Antisymmetric (or symmetric) with respect to a plane perpendicular to the ring plane and passing through the substituted carbon atom and that in the para position.

[8] C. Guimon, D. Gonbeau, G. Pfister-Guillouzo, L. Åsbrink, and J. Sandström, J. Electron Spectr. **4**, 49 (1974).

[9] C. Guimon, G. Pfister-Guillouzo, M. Arbelot, and M. Chanon, Tetrahedron **30**, 3831 (1974).

[10] E. B. Fleischer, N. Sung, and S. Hawkinson, J. Phys. Chem. **72**, 4311 (1968).

[11] A. D. Baker, D. P. May, and D. W. Turner, J. Chem. Soc. B **1968**, 22; J. P. Maier and D. W. Turner, J. Chem. Soc. Faraday II **1973**, 521.

[12] F. Bernardi, G. Distefano, A. Mangini, S. Pignataro, and G. Spunta, J. Electron Spectr. **7**, 457 (1975).

[13] G. Lawer, W. Schäfer, and A. Schweig, Chem. Phys. Letters **33**, 312 (1975); W. Schäfer, A. Schweig, G. Maier, and T. Sayrac, J. Amer. Chem. Soc. **96**, 279 (1974).

[14] F. Bernardi, F. P. Colonna, G. Distefano, L. Forlani, and P. E. Todesco, J. Electron Spectr. **9**, 217 (1976) and references cited therein.

[15] E. Block, H. Bock, S. Mohamand, P. Rosmus, and B. Solowki, Angew. Chem. Int. Ed. Engl. **15**, 383 (1976).

[16] K. Fukui, Modern Quantum Chemistry, Part. I, O. Sinanogh, Ed., Academic Press, New York 1965.