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PHOTOELECTRON SPECTRA OF SUBSTITUTED DIALKYLPHENYLTHIOBORANES

F. BERNARDI

Istituto di Chimica Organica dell'Università, Viale Risorgimento, 4 Bologna (Italy)

R. DANIELI, G. DISTEFANO

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

A. MODELLI

Istituto Chimico "G. Ciamician", Via Selmi 2, Bologna (Italy)

and A. RICCI

Istituto di Chimica dell'Università, Via G. Capponi 9, Firenze (Italy)

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Summary

The photoelectron He(I) spectra of some thioboranes $\text{XC}_6\text{H}_4\text{SB}(\text{n-C}_3\text{H}_7)_2$ ($\text{X} = p\text{-Cl, } m\text{-Cl, } p\text{-Br, H, } p\text{-CH}_3, m\text{-CH}_3 \text{ and } p\text{-OCH}_3$) have been recorded and assigned respective to those of related simple molecules and by a perturbational molecular orbital analysis and CNDO/2 calculations on the simpler thioborane $\text{C}_6\text{H}_5\text{SBH}_2$. The interaction between the phenyl ring and the SBR_2 group is briefly discussed.

Introduction

Ultraviolet photoelectron spectroscopy (UPS) has been widely employed to investigate the electronic structure of boron derivatives in which boron forms a partial double bond with neighbouring atoms containing one or two lone pairs. In particular halo-, oxy- and amino-boranes have been extensively studied [1–4] *, while thioboranes have received much less attention [5,6]. Since we are interested in the properties of sulphur-containing substituents, we have investigated by means of UPS a series of thioboranes $\text{XC}_6\text{H}_4\text{SB}(\text{n-C}_3\text{H}_7)_2$ (X

* Most of the recent literature is cited by Berger et al. [1].

TABLE I
ANALYTICAL DATA AND PHYSICAL PROPERTIES OF $\text{XC}_6\text{H}_4\text{SBR}_2$

X	B.p. (°C/mmHg) ^a	Yield (%)	Found (calcd.) (%)		
			C	H	S
<i>p</i> -OCH ₃	175/25	62	65.7 (66.1)	9.12 (8.96)	13.8 (13.6)
<i>p</i> -CH ₃	162/25	56	70.4 (70.9)	9.37 (9.61)	14.8 (14.6)
<i>m</i> -CH ₃	158/25	70	70.6 (70.9)	9.44 (9.61)	14.3 (14.6)
H ^b	125/12				
<i>p</i> -Cl	90/0.1	53	60.2 (59.9)	7.46 (7.54)	13.6 (13.3)
<i>p</i> -Br	165/3.0	45	51.0 (50.6)	6.28 (6.36)	11.6 (11.2)
<i>m</i> -Cl	85/0.1	60	60.1 (59.9)	7.59 (7.54)	13.5 (13.3)

^a Uncorrected. ^b See ref. 7.

= *p*-Cl, *m*-Cl, *p*-Br, H, *p*-CH₃, *m*-CH₃ and *p*-OCH₃). Our attention was mainly focussed upon the electronic and steric interactions between the phenyl ring and the SBR₂ group, in a comparative analysis of the properties of this substituent with those of the better known SCH₃ and SH.

Experimental

The spectra were obtained with a Perkin-Elmer photoelectron spectrometer PS 18, and were calibrated against Xe and Ar lines. The accuracy of the ionization energy (*IE*) values is estimated to be ±0.05 eV.

Phenylthioboranes were made by Mikhailov's procedure [7], involving reaction of tri-*n*-propylborane with the suitable thiols. All the compounds were freshly distilled before use.

Physical constants and analytical data are listed in Table 1.

Results and discussion

The *IE* values below about 11 eV of the thioboranes are shown in Fig. 1, together with the assignments and variations for the different X substituents. The *IE* values quoted here refer to the centre of the various bands and are assumed to correspond to the vertical *IE* values. The corresponding regions of the photoelectron spectra are shown in Fig. 2. The assignments of the first few bands as shown in Fig. 1, are based on a perturbational molecular orbital (PMO) analysis [8] which focusses upon the interactions occurring between the XC₆H₄ and SBR₂ fragments. However, the extent of such interactions and the type of group orbitals involved in the interactions depend upon the conformation of the molecule. On the other hand, the equilibrium conformation of such molecules is unknown. In order to obtain information on this point we have carried out CNDO/2 computations, with and without the inclusion of sulphur 3*d* orbitals,

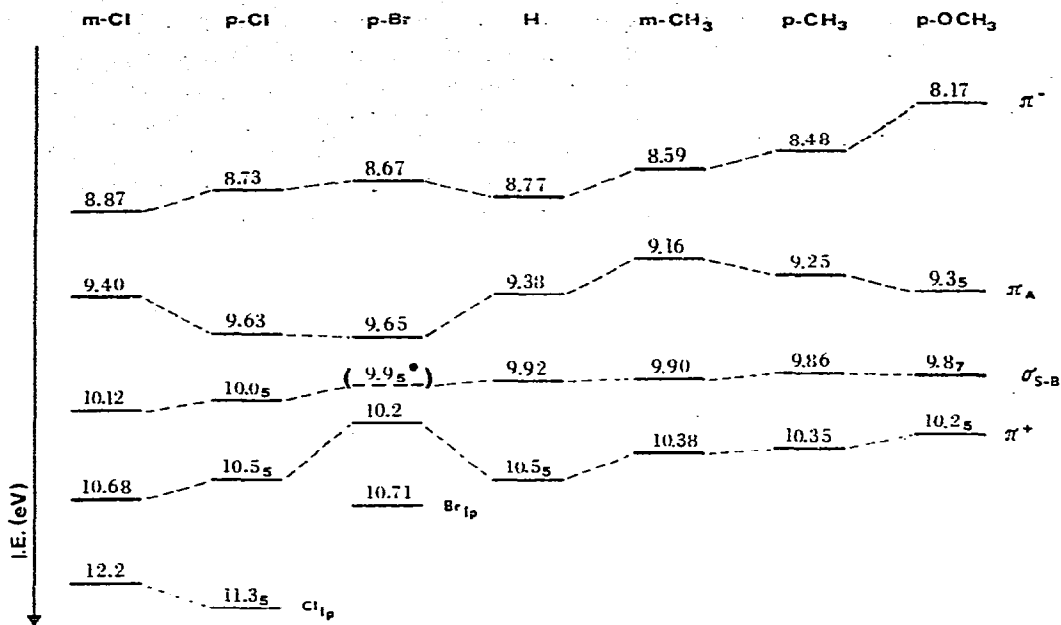
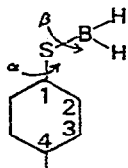


Fig. 1. Partial energy level diagrams, with assignments, of thioboranes $XC_6H_4SB(n-C_3H_7)_2$. * Estimated value.

on the simplest thioborane of this type, i.e.:

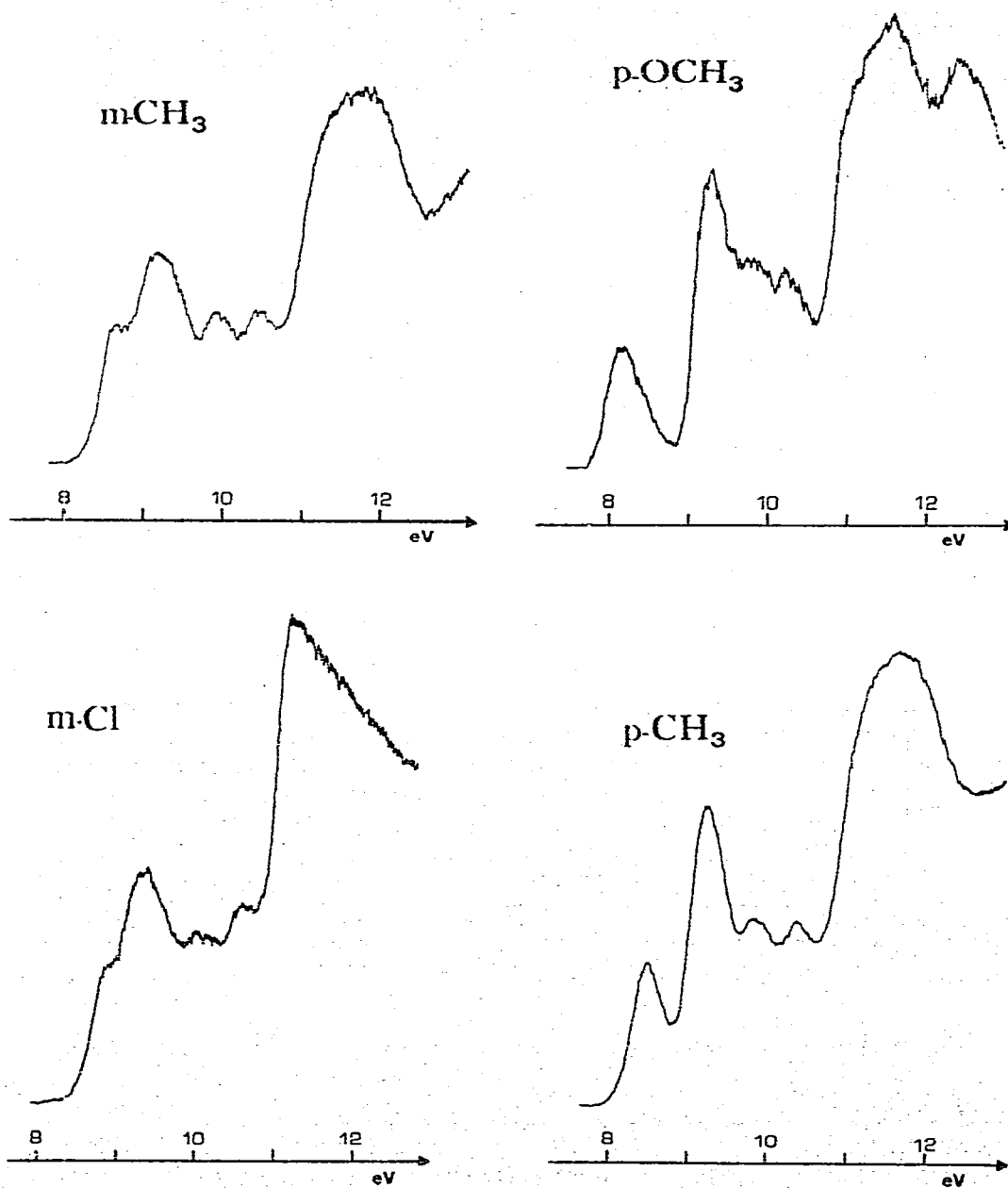


In order to study the conformational properties of this molecule, two rotational motions must be investigated, viz. rotation about the $C(1)-S$ bond (described here in terms of the torsional angle α) and rotation around the $S-B$ bond (described here in terms of the torsional angle β). However, recent ab initio calculations indicate that the barrier to rotation around the $S-B$ bond in $HSBH_2$ is ca. 20 kcal/mol [9], while that around the $C(1)-S$ bond in $p-FC_6H_4SCH_3$ must be negligible [10]. Therefore we have limited our conformational study to that of rotation about the $C(1)-S$ bond. The CNDO/2 results show that the optimum conformation of species 1 occurs for α values of 45° and 40° , respectively, for computations with and without sulphur $3d$ orbitals. Therefore the phenyl ring

is not coplanar with the plane defined by $C(1)-S-B$. Furthermore, even

though the π orbitals of the phenyl ring can mix not only with the π orbitals but also with the σ orbitals of the SBH_2 fragment (and vice versa), the CNDO/2 calculations show that such $\pi-\sigma$ mixing is almost negligible at the computed

equilibrium α values. Although the situation in the simple thioborane I is slightly different from those in the species experimentally investigated, nevertheless the experimental results (as shown below) can be interpreted on the basis of α values and π - σ mixing in agreement with those found for I. We can now discuss the assignment of the first few bands of the unsubstituted compound ($X = H$). The highest occupied MO's of the two interacting fragments are shown in Fig. 3. The ordering of the highest occupied benzene MO's is well known,



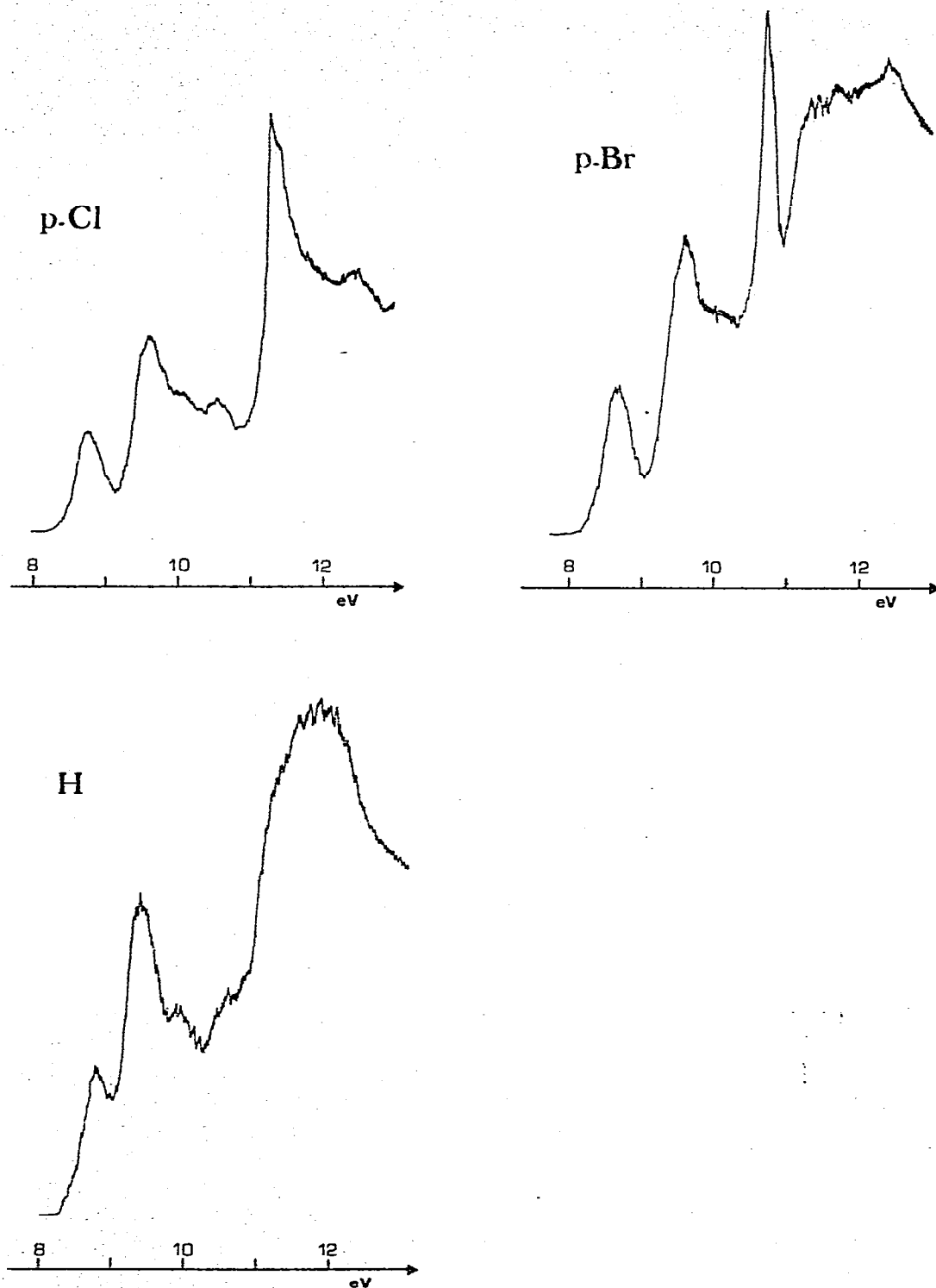


Fig. 2. Low ionization energy region of the photoelectron He(I) spectra of thiorboranes $\text{XC}_6\text{H}_4\text{SB}(\text{n-C}_3\text{H}_7)_2$ ($\text{X} = \text{p-Cl}, \text{m-Cl}, \text{p-Br}, \text{H}, \text{p-CH}_3, \text{m-CH}_3$ and p-OCH_3).

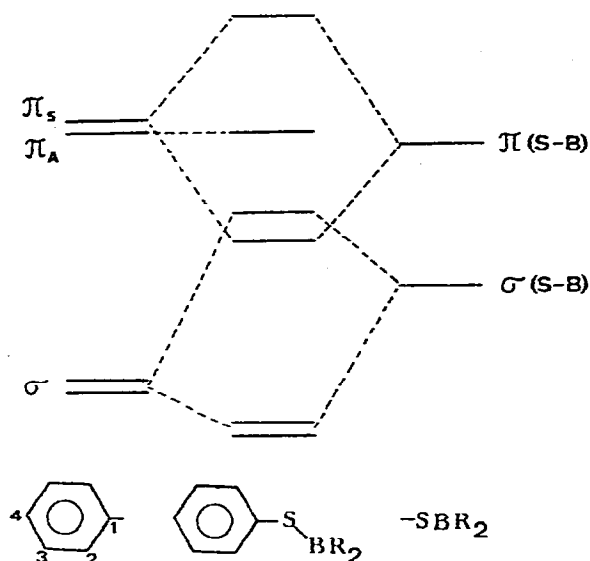


Fig. 3. Interaction diagram of the highest occupied orbitals of the phenyl and SBR₂ fragments. The symmetry properties of the benzene π-orbitals are defined with respect to a plane passing through C(1) and C(4).

while that of the two highest occupied MO's of the SBR₂ fragment has been taken from the values obtained [5] for CH₃SB(CH₃)₂, i.e. 9.40 eV for π(S-B) and 10.39 eV for σ(S-B). According to the interaction diagram, the first band is assigned to the out of phase combination of the benzene symmetric highest occupied MO (HOMO) π_s with the occupied π-MO of the SBR₂ fragment (π(S-B)). The second band is assigned to the benzene antisymmetric HOMO π_{as} (according to the CNDO/2 calculations π_{as} interacts negligibly with the other MO's) and the third band to the out of phase combination of σ(S-B), i.e. the σ bond of the SBR₂ fragment mainly localized in the S-B region, with the highest occupied σ MO's of benzene. Support for this assignment is given by: (i), the *IE* value of π_{as} must be expected to be close to that of the corresponding MO in benzene (9.25 eV); (ii) the value of the σ(S-B) MO is expected to be smaller than that found for CH₃SB(CH₃)₂, because of the larger σ interaction in the present case.

The fourth band is then assigned to the in phase combination of π_s with π(S-B). Therefore these *IE* values can be denoted as: *I*₁(π⁻), *I*₂(π_{as}), *I*₃(σ(S-B)) and *I*₄(π⁺). This assignment is confirmed by the substituent effect on the various bands. In particular the trends shown by *I*₁(π⁻) and *I*₂(π_{as}) are similar to those observed [11] for *I*₁ and *I*₂ in *para*-substituted anisoles and thioanisoles, confirming the π character of these MO's.

It has already been pointed out that the first band of anisole shows a sensitivity to substituent effect greater than that shown by the first band of thioanisole. This different sensitivity has been described to a large (anisole) or small (thioanisole) ring character of the respective HOMO. Since the *IE* of the unperturbed π(S-B) MO is intermediate between those of the HOMO's of the SCH₃ and OCH₃ fragments (8.80 and 10.24 eV respectively [11]), we would expect the

ring character of the HOMO of the unsubstituted thioborane to be intermediate between those of thioanisole and anisole, and consequently that the magnitude of the substituent effect would also be intermediate. However, the substituent effect observed in the present thioborane is slightly larger than even that for anisole, indicating a ring character in the HOMO of the unsubstituted thioborane ($X = H$) even larger than that in anisole. A plausible explanation could be formulated in terms of a reduced overlap between the two interacting orbitals, i.e. π_s and $\pi(S-B)$, of the two interacting fragments, i.e. the phenyl ring and SBR_2 , in agreement with the results of the CNDO/2 calculations. Also the stabilization of I_1 and I_4 and the destabilization of I_2 in going from the *para* to *meta* CH_3 and Cl derivatives further confirm the proposed assignment. On the other hand, I_3 shows only a very small sensitivity to substituent effects ($\Delta I_3 = 0.2$ eV) in agreement again with expectations based on the assignment proposed.

The results allow us to obtain some information about the interaction with aromatic rings of the $SB(n-C_3H_7)_2$ substituent compared with those of better known sulphur containing substituents such as SCH_3 or SH . It has been suggested [12,13] that the IE values related to π_{as} in monosubstituted benzenes can provide a measure of the inductive effect of the substituents. The comparison of the IE values relating to π_{as} in $C_6H_5SB(C_3H_7)_2$ (9.38 eV), in thioanisole (9.28 eV) [14] and thiophenol (9.38 eV) [15] indicates that the $SB(n-C_3H_7)_2$ group has an electron-withdrawing inductive effect slightly larger than that of the SCH_3 group and of the same order of magnitude as that of the SH group. However, this result does not imply that the charge transfer in the SBR_2 fragment is of the same type and order of magnitude as that in SCH_3 or SH . In fact, the comparison of the HOMO IE values for CH_3SCH_3 and $CH_3SB(CH_3)_2$ (8.70 [14,16] and 9.40 [5] eV respectively) suggests that in $CH_3SB(CH_3)_2$ there is a large interaction between the sulphur lone pair and the boron vacant p orbital and consequently a large π -charge transfer from sulphur to boron, which should produce a large positive charge on sulphur. Since the inductive withdrawal by the SBR_2 group is only slightly larger than that by SCH_3 there must be an associated σ -charge transfer from the BR_2 group towards the sulphur atom, which reduces the charge on sulphur. This conclusion is in agreement with the results of various theoretical investigations on several classes of boranes [4,9,17-19].

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