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PHOTOELECTRON SPECTRA OF PLANAR SULFUR HETEROCYCLES

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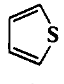
Abstract—The photoelectron spectra of benzo[b]thiophene (2), benzo[c]thiophene (3), thieno[3, 2-b]thiophene (4) and thieno[2, 3-b]thiophene (5) together with 2,1,3-benzothiadiazol (6) and benzofurazan (7) have been recorded and the first three bands have been assigned to π-orbitals on the basis of band shapes and semiempirical calculations. The good agreement obtained between measured and calculated ionization potentials suggests that sulfur 3d orbital participation must be very small.

In spite of the fact that thiophene and its derivatives are among the most thoroughly studied planar sulfur heterocyclic systems, there exists very little experimental evidence for the relative orbital energies of the π- and sulfur lone pair electrons relative to that of the π electrons. In a recent paper on the photoelectron spectrum (= PE spectrum) of thiophene (1), Derrick *et al.*,[1] have assigned the first three ionization bands (I_v = 8·9, 9·5 and 12·1 eV) to the π-orbitals $1a_2$, $3b_2$ and $2b_2$, respectively. (See also Ref 2). The fourth band (I_v = 12·7 eV) has been assigned to the orbital of the sulfur lone-pair of A_1 symmetry.

We report the PE spectra of the sulfur-containing derivatives benzo[b]thiophene (**2**), benzo[c]thiophene (**3**), thieno[2, 3-b]thiophene (**4**), thieno[3, 2-b]thiophene (**5**) and of the related compounds 2,1,3-benzothiadiazol (**6**) and benzofurazan (**7**), which were recorded in an attempt to provide further experimental evidence for the energy of the sulfur lone pair orbitals relative to that of π-orbitals.



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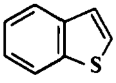

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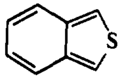

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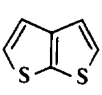

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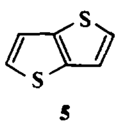

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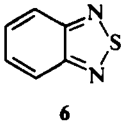

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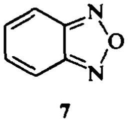

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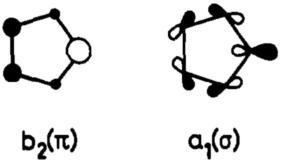
Such information is also of importance for the interpretation of the electronic spectra of such compounds.[3]

The PE spectra of **2–7** are shown in Figs 1 and 2. The ionization potentials (vertical) $I_{v,J}$ of the bands Ⓙ are given in Table 1 together with the proposed assignment.

All compounds were purified by sublimation before the spectra were taken. Benzo[c]thiophene (**3**) was prepared from 1,3-dihydrobenzo[c]thiophene-2-oxide according to Cava and Pollack.[4]

The spectra were recorded on a modified PS-15 photoelectron spectrometer of Perkin-Elmer Ltd., Beaconsfield, England (*cf* Turner[5]).

The lone-pair orbitals of a S atom taking part in a π-system (e.g. in **1**) hybridize, the p-type hybrid becoming part of the π-system (and donating two electrons to it) and the σ-type orbital mixing with other (semilocalized) orbitals of the same symmetry. This is shown qualitatively in (1). Consequently, it is to be expected that the π- and n-ionization bands in the PE spectra of **1** to **6** exhibit roughly the same characteristics as those of the PE spectra of azabenzenes and azanaphthalenes.[6] In the latter spectra the strongest component of the well-resolved vibrational fine-structure of the π-bands is usually the 0 ← 0 or 1 ← 0 transition, i.e. $I_{v,J} \approx I_{a,J}$ ($I_{a,J}$ = adiabatic ionization potential), whereas the n-bands are broad and poorly resolved, gaussian shaped peaks, i.e. $I_{a,J} < I_{v,J}$.



(1)

The shapes of the first three bands in the PE spectra of **1–5** are similar, the 0 ← 0 vibrational component being the most intense one of the progression, i.e. $I_{a,J} \approx I_{v,J}$. This suggests that the first three bands correspond to an ionization from a π-orbital. To check this, we have correlated the

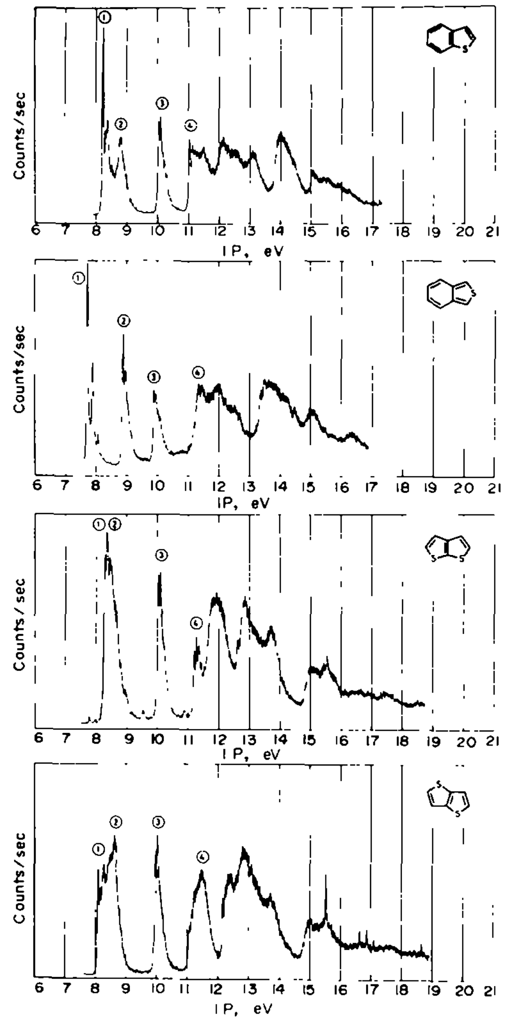


Fig 1. PE spectra of benzo[b]thiophene (**2**), benzo[c]thiophene (**3**), thieno[2,3-b]thiophene (**4**), thieno[3,2-b]thiophene (**5**) obtained using He 584-Å radiation.

first three measured ionization potentials of **1-5** with orbital energies obtained from an Extended Hückel (EH) calculation (Fig 4) and a PPP calculation (Fig 3), assuming Koopmans' theorem to hold.

The parameters for C, O, N and H in the EH calculations are those reported in the literature.[8] For the sulfur orbitals we have used the Slater exponents given by Clementi and Raimondi.[9] The valence state ionization potentials of these orbitals were assumed to be $H_{ll}(3s) = -20{\cdot}0$ eV and $H_{ll}(3p) = -13{\cdot}3$ eV. The parameters used in the PPP calculations for **1-5** are: $\beta_{C-C} = -2{\cdot}318$ eV, $\beta_{C-S} = -1{\cdot}62$ eV, $I_S = -20{\cdot}42$ eV, $I_C = -11{\cdot}42$ eV and $\gamma_{CC} = \gamma_{SS} = 10{\cdot}84$ eV. The two-centre integrals have been calculated according to the Mataga-Nishimoto formula.[10] All these parameters differ only marginally from those used by Zahradnik *et*

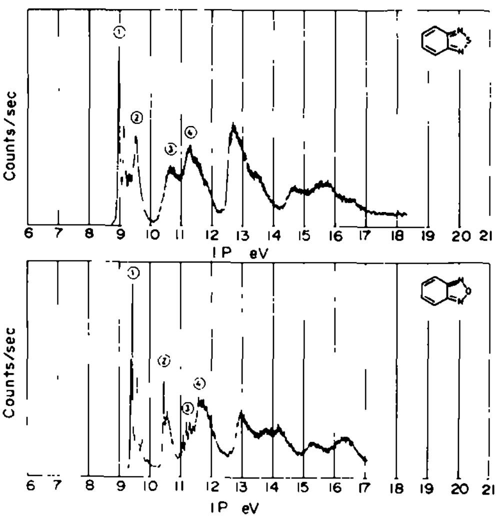
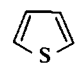
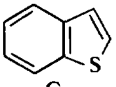
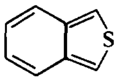
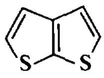
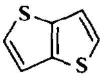
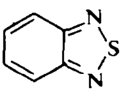
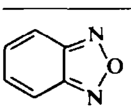


Fig 2. PE spectra of 2,1,3-benzothiadiazol (**6**) and benzofurazan (**7**).

Table 1. Ionization potentials of **1-7**. All values in eV. Values in brackets refer to shoulders

Compound	Band J	Orbital	$I_{v,J}$
 C_{2v} **1**	①	$a_2(\pi)$	8·90
	②	$b_2(\pi)$	9·50
	③	$b_2(\pi)$	12·10
	④	$a_1(n)$	12·70
 C_s **2**	①	$a''(\pi)$	8·20
	②	$a''(\pi)$	8·76
	③	$a''(\pi)$	10·08
	④	$a'(\sigma)$?	11·03
 C_{2v} **3**	①	$a_2(\pi)$	7·75
	②	$b_2(\pi)$	8·90
	③	$a_2(\pi)$	9·90
	④	$a_1(\sigma)$?	11·33
 C_{2v} **4**	①	$b_2(\pi)$	8·32
	②	$a_2(\pi)$	8·41
	③	$b_2(\pi)$	10·08
	④	$a_1(\sigma)$?	11·27
 C_{2h} **5**	①	$a_u(\pi)$	8·10
	②	$a_u(\pi)$	8·61
	③	$b_g(\pi)$	10·04
	④	$a_g(\sigma)$?	11·50
 C_{2v} **6**	①	$a_2(\pi)$	8·98
	②	$b_2(\pi)$	9·52
	③	$a_1(n_-)$	10·64
	④	$a_2(\pi)$	11·31
	⑤	$b_1(n\ )$	(11·6)
 C_{2v} **7**	①	$a_2(\pi)$	9·37
	②	$b_2(\pi)$	10·44
	③	$a_1(n_-)$	11·18
	④	$a_2(\pi)$	11·58
	⑤	$b_1(n_-)$	(12·0)

al.[3,11] In the case of **6** and **7** the additional parameters $\beta_{N-C} = -2{\cdot}318$ eV, $\beta_{N-S} = -1{\cdot}6$ eV, $\beta_{N-O} = -2{\cdot}318$ eV, $I_N = -14{\cdot}12$ eV, $I_O = -21{\cdot}08$ eV, $\gamma_{NN} = 12{\cdot}30$ eV, $\gamma_{OO} = 22{\cdot}50$ eV were used. The two-centre integrals were calculated according to Ref. 12. Sulfur 3d-orbitals have not been included in the basis set for either of the methods. The following bond distances and angles have been assumed throughout: C—C = 1·4 Å, C—S = 1·7 Å, ∡ CCC = 120°.

The calculated orbital energies ϵ_J^{PPP} and ϵ_J^{EH} are given in Table 2. As can be seen, both methods yield the same order for the three highest occupied π-orbitals of each compound and the same differences between the orbital energies. The PPP results are of interest in that the use of the same set of parameters for both the ground and the excited states, with the inclusion of configuration interaction for the latter, satisfactorily reproduce the position of the first bands in the electronic spectra of the compounds **1** to **5**. As our results are practically the same as those of Fabian, Mehlhorn and Zahradnik,[3] we shall not give them explicitly.

A linear regression analysis based on the observed (ϵ_J) and calculated (ϵ_J^{calc}) π-orbital energies of the compounds **1** to **5**, i.e.

$$\epsilon_J = A + B\epsilon_J^{calc} \tag{2}$$

yields the following results (degree of freedom for

Table 2. Comparison between the π-ionization potentials of 1–7 with EHT and PPP calculations. All values in eV.

Compound	Orbital	$I_{v,J}$	$\Delta I_{v,J}$	$-\epsilon_J^{PPP}$	$\Delta\epsilon_J^{PPP}$	$-\epsilon_J^{EH}$	$\Delta\epsilon_J^{EH}$
1	a_2	8·90		9·51[a]		12·51	
			0·60		0·76		0·29
	b_2	9·50		10·27[a]		12·80	
			2·60		2·81		2·06
	a_2	12·10		13·08[a]		14·86	
2	a″	8·20		9·24[a]		11·97	
			0·56		0·66		0·42
	a″	8·76		9·90[a]		12·39	
			1·32		1·22		0·82
	a″	10·08		11·12[a]		13·21	
3	a_2	7·75		8·50[a]		11·50	
			1·15		1·72		1·17
	b_2	8·90		10·22[a]		12·67	
			1·00		0·71		0·45
	a_2	9·90		10·93[a]		13·12	
4	b_2	8·32		9·00[a]		11·79	
			0·09		0·05		0·21
	a_2	8·41		9·05[a]		12·00	
			1·67		0·68		1·21
	b_2	10·08		10·73[a]		13·21	
5	a_u	8·10		8·74[a]		11·65	
			0·51		0·66		0·52
	a_u	8·61		9·40[a]		12·17	
			1·43		1·25		0·90
	b_g	10·04		10·65[a]		13·07	
6	a_2	8·98		9·85[b]		12·43	
			0·54		0·62		0·21
	b_2	9·52		10·47[b]		12·64	
			1·79		1·69		1·31
	a_2	11·31		12·16[b]		13·95	
7	a_2	9·37		10·10[b]		12·43	
			1·07		1·25		0·77
	b_2	10·44		11·35[b]		13·20	
			1·14		1·10		0·73
	a_2	11·58		12·45[b]		13·93	

[a] $\gamma_{\mu\nu}$ calculated according to [10].
[b] $\gamma_{\mu\nu}$ calculated according to [12].

the standard errors SE, $\phi = 13$; r = correlation coefficient):

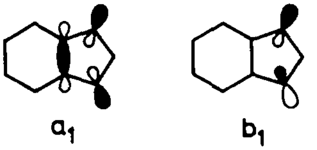
$\epsilon_J^{\text{calc.}}$	A eV	SE(A) eV	B	SE(B)	r	
ϵ_J^{EH}	7·269	0·662	1·306	0·053	0·9897	(3)
ϵ_J^{PPP}	0·168	0·501	0·932	0·050	0·9820.	

The quality of both regressions is the same (*cf* r-values). However, the PPP-regression does not miss the origin $\epsilon_J = \epsilon_J^{\text{PPP}} = 0$ by a significant amount. Also, the 90% confidence limits for B^{PPP} are 0·844 and 1·020, which include $B^{\text{PPP}} = 1{\cdot}000$, so that the PPP-calculations can be said to reproduce the "observed" Koopmans π-orbital energies faithfully within the 90-percent confidence limits. In the range of interest these limits span an interval of approximately 1 eV. On the basis of (2) and (3) and the calculated values ϵ_J^{EH} and ϵ_J^{PPP} (Table 2) for **6** and **7** the following 90% lower and upper confidence limits $\epsilon_{J,l}$, $\epsilon_{J,u}$ have been determined (all values in eV)

		$-\epsilon_{1,l}$	$-\epsilon_{1,u}$	$-\epsilon_{2,l}$	$-\epsilon_{2,u}$	$-\epsilon_{3,l}$	$-\epsilon_{3,u}$	
6	EH	8·66	9·27	8·93	9·54	10·62	11·28	
	PPP	8·61	9·41	9·19	10·00	10·73	11·61	
								(4)
7	EH	8·66	9·27	9·66	10·28	10·59	11·25	
	PPP	8·85	9·65	10·00	10·83	10·98	11·90.	

The resulting assignment of π-bands in the PE spectra of **6** and **7** is shown in Table 2.

For the three highest occupied π-levels of **6**, both methods predict that the first two lie close together, with an orbital energy difference of 0·21 eV (EH), 0·62 eV (PPP). The separation of the third π-level from the second one is calculated to be 1·3 eV (EH), 2·7 eV (PPP). These results suggest that the PE bands at 8·98, 9·52 and 11·31 eV correspond to ionization from a π-orbital. This assignment leaves the bands at 10·64 and the shoulder at 11·6 eV in the PE spectrum of **6**, as corresponding to the two combinations a_1 and b_1 of the nitrogen lone pair orbitals. The measured energy separation of ~ 1 eV compares favorably with the 0·73 eV value obtained by the EH method. The calculations indicate that the a_1 orbital lies above b_1 because of the dominant through-bond coupling[13] between the lone-pair basis orbitals, which involves the central CC–σ–bond, as indicated in the diagrams (5):



(5)

The same procedure applied to the PE spectrum of **7** yields the result that the PE bands at 9·37 eV and 10·44 eV correspond to π-electron ionization. The third π-band is again part of the broad feature between 11 and 12·5 eV. According to (4) the prominent maximum at 11·58 eV is most likely the one belonging to the π-band, especially in view of the sharp onset at 10·5 eV. The EH procedure predicts the two nitrogen lone-pair combinations a_1 and b_1 to have an orbital energy separation of 0·60 eV, with a_1 lying again above b_1 because of

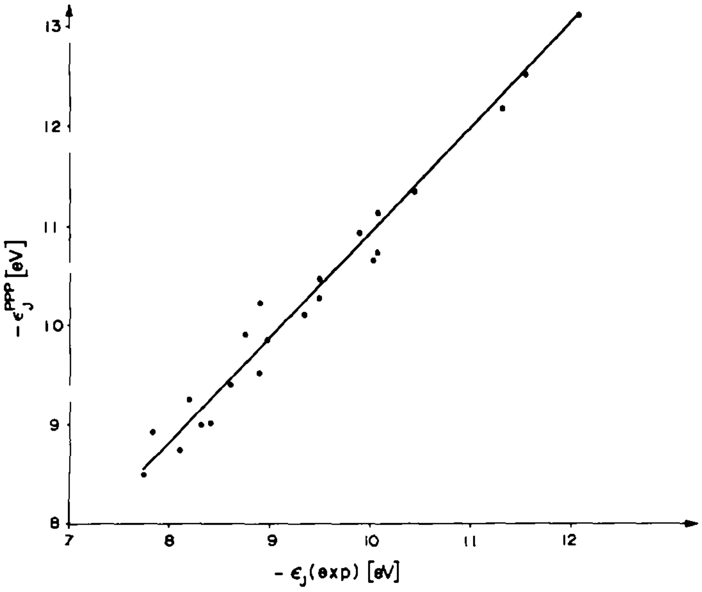


Fig 3. Regression $\epsilon_J^{\text{PPP}} = -0{\cdot}603 + 1{\cdot}026\,\epsilon_J$ (r = 0·9879) based on the calculated (PPP) and observed orbital energies of Table 2.

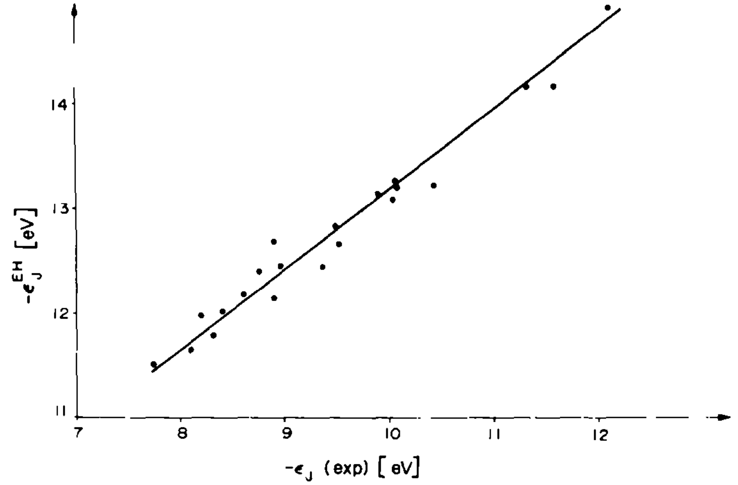


Fig 4. Regression $\epsilon_J^{EH} = -6{\cdot}138 + 0{\cdot}695\ \epsilon_J$ ($r = 0{\cdot}9813$) based on the calculated (EH) and observed orbital energies of Table 2.

through-bond interaction. We assign tentatively the band at 11·18 eV and the shoulder at 12·0 eV to ionization from these orbitals.

Our assignment of the π-bands is based on a consideration of band shapes and on semiempirical calculations, in which we have neglected sulfur 3d orbital participation. That 3d participation must indeed be quite small is indicated by the rather good agreement obtained between measured and calculated ionization potentials, as shown in Figs 3 and 4. This conclusion supports recent *ab initio* calculations on thiophene,[13] in which the addition of sulfur 3d functions has been shown to have only a minor effect on the π-orbital energies. The same conclusion had been reached previously by Di Lomardo and Zauli[14] (see also Ref. 15).

Unfortunately this analysis does not provide an answer to the question of which orbital energy should be assigned to the sulfur lone-pair basis orbital. In view of the complexity of the spectra of 2 to 5 in the region above 11 eV, it is not possible to locate those bands which correspond to the ejection of an electron from a lone-pair orbital. The only conclusion that can be drawn with some confidence is that the energy of the sulfur lone-pair basis orbitals must be lower than −11 eV.

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