Photoelectron Spectra of Bromo- and Iodo-thiophens

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The photoelectron spectra of bromo- and iodo-thiophens with the halogen(s) in the 2-, 3-, 2,5-, 3,4-, 2,3,5-, and 2,3,4,5-positions, have been recorded with He^{I} radiation, and the ionisation energies have been assigned down to 13 eV. The spectra were analysed on the basis of qualitative molecular orbital description, by mutual comparison and comparison with the spectra of bromo- and iodo-benzenes. Interactions between halogen lone-pair electrons are discussed.

A SIMPLE approach based on symmetry arguments for interactions between molecular orbitals of the basic molecular frame and those of the substituents has proved to be successful in the analysis of the photoelectron (p.e.) spectra of iodobenzenes;[1] we wished to apply the same procedure to substituted thiophens. Thiophen appears especially suitable for such a study since the three lowest ionisation energy band systems in its p.e. spectrum are assigned to π-ionisations.[2,3] However, recent calculations[4] indicate that the correct orbital ordering in thiophen is π_3, π_2, σ, π_1. In any case, the additional systems in halogenothiophens coming from ionisations of the halogen lone-pair electrons are of lower energy than any σ-ionisation of thiophen.

The p.e. spectrum of the parent compound has been analysed previously,[2,3,5,6] and Rabalais *et al.*[7] have analysed the p.e. spectra of 2- and 3-bromothiophen extensively. The p.e. spectra of some other substituted thiophens have also been reported[8] from the point of view of their analytical application.

EXPERIMENTAL

2-Bromo-, 3-bromo-, 2,5-dibromo-, tetrabromo-, and tetraiodo-thiophen were of commercial origin (EGA Chemie); 2-iodo- and 2,5-di-iodo-thiophen,[9] 3-iodo- and 2,3,5-tri-iodo-thiophen,[10] 3,4-di-iodothiophen,[11] 3,4-dibromothiophen,[12] and 2,3,5-tribromothiophen[13] were synthesized by reported methods. All compounds were recrystallised or redistilled under vacuum before use. The spectra were recorded with a Vacuum Generators UV G3 photoelectron spectrometer[14] under low (*ca.* 35 meV) and high resolution (<15 meV measured relative to argon) using He^{I} excitation. In some cases heating of the inlet system was required to obtain sufficiently high vapour pressures (3-iodo- and 3,4-di-iodo-thiophen 30 °C, 2,5-di-iodothiophen 70 °C, 2,3,5-tri-iodothiophen 110 °C, tetrabromothiophen 130 °C, and tetraiodothiophen 200 °C). Only in the case of tetraiodothiophen was some decomposition observed. The p.e. spectra were calibrated by admission of small quantities of rare gases (Ar, Xe) during the measurement.

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RESULTS

The correlation between energy levels corresponding to the π and lone-pair electron vertical ionisations in the p.e. spectra of mono-, di-, and tetra-substituted thiophens is given in Figures 1 and 2 for bromo- and iodo-substitution, respectively. The p.e. spectra with the indicated vertical ionisation energies of the investigated compounds (excluding 2- and 3-bromothiophen, reported in ref. 6) are given in Figures 3—7, available with Figure 8 as Supplementary Publication No. SUP 22064 (8 pp).*

Vibrational structure can be observed in many band systems and the obtained vibrational wavenumbers in the ionic states of mono- and di-substituted thiophens are summarised in the Table.

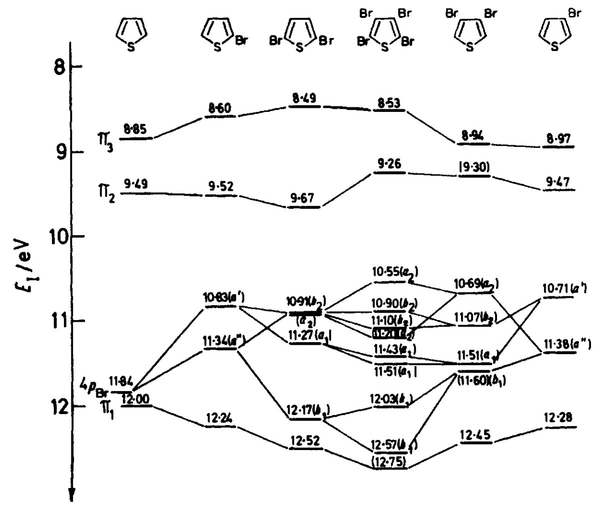

FIGURE 1 Correlation of vertical ionisation energies for π and n orbitals of five bromothiophens

Wavenumbers (ν/cm^{-1}) of active vibrations in the p.e. spectra of substituted thiophens (uncertain values are in parentheses)

X	Position of substitution	Electronic system of the ion				
		X̃	Ã	B̃	C̃	Others
Br	2	1 300, 350	1 080	600, 280	900, 600	H̃ 890
	3	1 200	1 120	520	560	D̃ 220
	2, 5	1 280, 240	1 040			
	3, 4	1 360, 280				
I	2	1 290, 320	1 000, 640	(480)	640, 240	
	3	1 250, 860, 260	1 210	(740)	760, 230	D̃ 720 (Ẽ 640)
	2, 5	1 200				
	3, 4	1 200				

The first band systems in the p.e. spectra of substituted thiophens resemble closely the first system of thiophen. Two vibrations can in most cases be identified: one of 1 100—1 300 cm^{-1} and one of low wavenumber (240—350 cm^{-1}).

The non-bonding electrons give rise to sharp band systems which can be identified easily. In the mono-substituted molecules there are always two such systems present, one at lower energy which is extremely narrow and the other showing pronounced vibrational structure. Such an example is shown in Figure 8 (Supplementary Publication). When the substituent is in position 3 the difference is even greater, and the broader system has a maximum intensity in the vibronic 1–0 band.

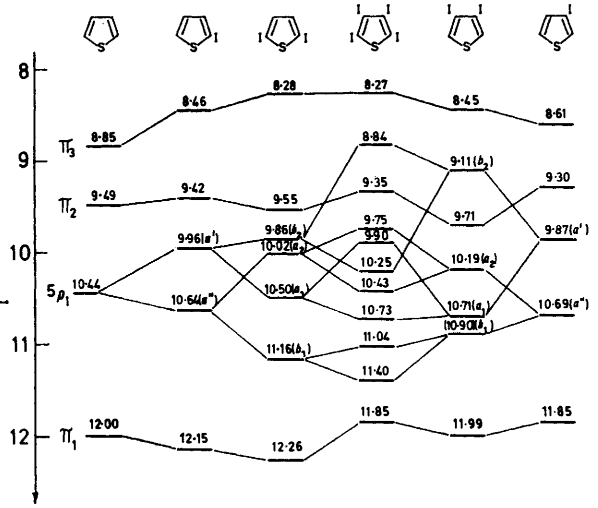

FIGURE 2 Correlation of vertical ionisation energies for π and n orbitals of five iodothiophens

DISCUSSION

The spectra of monosubstituted bromo- and iodo-thiophens are very similar at first sight. In the case of polysubstituted compounds this similarity is not so obvious and we were interested in finding out whether a close relationship still existed.

The electrons of halogeno-substituted thiophens can be divided into three groups: σ, π, and lone pair (n) electrons. The corresponding band systems in the p.e. spectra can be easily identified on the basis of their energy, shape, and fine structure. The σ electrons have significantly greater ionisation energies than the π or n electrons, which makes the analysis easier.

The thiophen π orbitals can be thought of as being derived from the orbitals of benzene by replacing two CH groups by a sulphur atom. The highest occupied orbitals π_2 and π_3 thus correlate with the e_{1g} orbitals of benzene. The π_3 orbital has a nodal plane passing through the S atom (a_2 symmetry), whereas in the π_2 orbital the nodal plane crosses the two C–S bonds (b_1 symmetry).[2,3,5,6] The corresponding band systems in the p.e. spectra of thiophen are found at ionisation energies of 8.25 and 9.49 eV for π_3 and π_2 orbitals,

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* For details of Supplementary Publications see Notice to Authors No. 7, *J.C.S. Perkin II*, 1976, Index issue.

respectively, and they show characteristic vibrational structure. The analogous systems in the spectra of substituted thiophens are also easy to identify by the energy and almost identical vibrational structure. The system which we assign to the ionisation from the lowest π orbital, π_1, with no nodal plane perpendicular to the ring, is also not difficult to identify. In some cases a long progression in the ring breathing vibration indicates a strong ring-bonding character which can be attributed to this orbital. It is also easily recognized by its characteristic shape and area. In all compounds investigated it is the first peak after the lone-pair electron ionisations.

There is some doubt only in the case of tetraiodothiophen, where the system assigned to π_1 could possibly be that at 12.65 instead of that at 11.85 eV. However, this is not thought to be so for two reasons: (i) because of the characteristic shape of the peak at 11.85 eV, which is smaller and broader than the next highest system corresponding to an a'' lone pair orbital, and (ii) because this would represent the only case in which one of the σ ionisations appeared at lower energy than that of π_1. On the other hand if one looks for the centre of gravity of the π_1, π_2, and π_3 systems (*i.e.* their mean E_{I} value) then, for comparison with thiophen for which this centre is at 10.11 eV, in all bromothiophens it appears at 10.18 ± 0.06 eV and in iodothiophens at 10.00 ± 0.05 eV, with the exception of tetraiodothiophen, where with the 11.85 or 12.65 eV system assigned as π_1 it amounts to 9.71 or 10.09 eV, respectively. The constancy of the centre of gravity indicates a negligible inductive effect of the halogens on the π orbitals of the thiophen ring, but of a different sign for bromo- than for iodo-substitution. However, in view of the controversy concerning the ordering of orbitals in thiophen [2-4] the assignment of π_1 must be considered as tentative.

The lone-pair electrons on the halogen substituent are in p orbitals, one of which lies in the molecular plane (a' symmetry in the C_s point group) whereas the other is perpendicular to it (a''). For symmetry reasons only the a'' orbital can interact with the π electrons of the thiophen ring and this interaction is observed as a broadening of the corresponding electronic system in the p.e. spectrum. The a' orbital can interact only with the low lying σ orbitals and is therefore shifted to lower ionisation energy than the a'' orbital, which interacts with the higher lying π_2 and π_3 orbitals.

In molecules with more substituents there should be observed as many pairs of such electronic systems as there are halogen atoms. The spectra still have the same features that all systems arising from ionisations from a' orbitals have significantly narrower peaks than those from a'' orbitals and that in both sets of observed systems the width increases on going to higher ionisation energies. The few cases of overlapping can easily be resolved, *e.g.* the peak at 10.91 eV of 2,5-dibromothiophen, where the upper a' and a'' ionisations coincide in energy, but evidently yield a peak of double intensity. Some broadening of the lowest energy a' ionisation is observed in the case when it appears between the π_2 and π_3 ionisations (compounds with adjacent iodine substituents), which is explained by the strong antibonding interaction and out-of-plane position of such atoms. Even in such cases (3,4-di-iodo-, 2,3,5-tri-iodo-, and tetraiodo-thiophen) it is not difficult to distinguish these systems from the higher lying π_2 and lower lying π_3 ionisation in the low and especially in the high resolution p.e. spectra. Therefore the correlation of the π_2 and π_3 orbitals as shown in Figures 6 and 7 follows in a nearly straightforward manner.

The assignment of the electronic systems of 2,3,5-tribromo- and 2,3,5-tri-iodo-thiophen is not given in Figures 6 and 7 but is easily derived from the p.e. spectra and by comparison with the other compounds. In 2,3,5-tribromothiophen π_3 and π_2 appear at 8.55 and 9.47 eV, respectively; the systems at 10.91, 11.15, and 11.39 eV correspond to a' ionisations, and those at 10.77, 11.74, and 12.42 eV to a'' ionisations. The last peak at 12.42 eV also contains the π_1 system, as indicated by the doubled area. In 2,3,5-tri-iodothiophen π_3, π_2, and π_1 are at 8.27, 9.63, 12.03 eV, the a' ionisations at 9.07, 9.87, and 10.47 eV, and the a'' ionisations at 10.17, 10.77, and 11.32 eV. The correlation is easily seen with the corresponding 2-mono- and 3,4-di-substituted compounds, indicating that the (unrecorded) p.e. spectra of the 2,3-disubstituted thiophens might closely resemble those of the 3,4-disubstituted thiophens.

Only in 3,4-dibromothiophen are the π_3 and π_2 systems collapsed, which is easily seen by the doubled area of the first peak, but is not as easy to understand. In 3,4-di-iodothiophen the π_3 and π_2 levels are, as expected, diverging. The π_3 and π_2 orbitals in the other bromo- and iodo-thiophens as shown in Figures 6 and 7 show a roughly similar behaviour. Because of the considerably higher ionisation energy of the $4p$ orbital of bromine (11.48 eV) in comparison with the energy of the π_2 and π_3 orbitals of thiophen, in all bromo-compounds ionisations from the π_3 and π_2 orbitals are well separated from the n ionisations. This is not so in the iodothiophens, although, as already mentioned, with iodines in adjacent positions one of the a' ionisations appears between π_3 and π_2. However by following the above rules the assignment is easy in both series. If the halogens are not in adjacent positions the overall splitting of the n ionisations is of similar magnitude for bromo- and iodo-thiophens (0—0.2 eV greater for the iodo-compounds). In 3,4-di-iodo-, 2,3,5-tri-iodo-, and tetraiodo-thiophen the splitting of the iodine lone pairs is greater by 0.78, 0.59, and 0.54 eV, respectively. Through-space interaction (of the a' orbitals) is probably largely responsible for this difference. The through-bond interaction of the a' orbitals is most pronounced in the 2,5-derivatives as also found for the related 1,4-di-iodo- and dibromobenzene. However, through-space interaction with sulphur d orbitals could also play a part.

In general, the π interaction between the halogen lone-pair electrons is stronger in the bromothiophens, whereas the corresponding σ-interaction is greater in the iodothiophens. This can be recognised from the splittings between the highest and lowest a'-type and a''-type orbitals in the di-, tri-, and tetra-substituted compounds. As a result the lowest energy lone-pair ionisation in all iodothiophens is of a' type, but in bromothiophens with two or more bromine atoms it is of a'' symmetry.

In conclusion the present results, although derived without computation, indicate that the effects of bromo- and iodo-substitution in the p.e. spectra of aromatic molecules can easily be rationalised in terms of π interaction with the basic aromatic frame and of through-bond and through-space interaction of halogen p orbitals. The main differences in p.e. spectra arise from the large σ-through-space interaction of iodine p orbitals in adjacent positions, and the greater π interaction of bromine substituents. In the present discussion spin–orbit interaction has not been taken into account; however the similarity of the spectra of bromo- and iodo-thiophens as well as of other halogen-substituted compounds[15] makes us confident that its inclusion would not influence the assignment.

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