Photoelectron Spectra of Iodobenzenes

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The photoelectron spectra of iodobenzene and 1,2-, 1,3-, and 1,4-di-iodobenzene have been recorded by using He^I excitation. The electronic structure of these compounds is discussed in terms of a simple model of interaction between known orbitals of the composite parts, *i.e.* the molecular orbitals of benzene and the $5p$ atomic orbitals of iodine, taking their energy and symmetry but no spin–orbit coupling into account. The assignment is simplified by the characteristic shapes of several systems, which holds especially for the lone-pair electrons on iodine. Orbital sequences are given down to ionisation energies of 17 eV. Assignments are supported by comparison with the photoelectron spectra of 1,2,3,4-tetrafluoro-5,6-di-iodo- and 1,2,4,5-tetrafluoro-3,6-di-iodo-benzene.

THE effect of substituents on the π-electron levels in substituted benzenes has been the subject of a number of investigations. Turner and his co-workers [1] have shown the effect of substituents lifting the degeneracy of the e_{1g} π-orbitals of benzene and discussed it in terms of π-electron perturbation by inductive and mesomeric effects. They also discussed in general terms the effect of multiple substitution (1,2-, 1,3-, 1,4-, and perfluoro-substitution) and the characteristics of systems associated with lone-pair electrons of substituents. Most of their conclusions are still valid. However, the progress in theoretical (computational) and instrumental methods (instruments with better resolution) made it of interest to study the substituted benzenes systematically in greater detail. Recently the effect of a substituent on the e_{1g} benzene orbitals was discussed theoretically by Marschner.[2] Inductive and mesomeric effects on the π-orbitals of fluoro-, chloro-, and bromo-benzenes were reported by Streets and Ceasar.[3]

We are interested in the dependence of interactions among lone-pair electrons on their positional relationship, and have therefore investigated the photoelectron (p.e.) spectra of the three isomeric di-iodobenzenes, which have not been reported hitherto.

EXPERIMENTAL

The p.e. spectra were recorded with a Vacuum Generators UV-G3 instrument.[4] The energy scale was controlled and calibrated by admitting a mixture of argon and xenon to

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[1] A. D. Baker, D. P. May, and D. W. Turner, *J. Chem. Soc.* (*B*), 1968, 22.

[2] F. Marschner, *Tetrahedron*, 1975, **31**, 2303.

[3] D. G. Streets and G. P. Ceasar, *Mol. Phys.*, 1973 **26**, 1037.

[4] L. Klasinc, B. Kovač, and B. Ruščić, *Kem. Ind.* (*Zagreb*), 1974, **23**, 569.

the sample. A temperature of 80 °C in the sample inlet produced satisfactory spectra under mild thermal conditions. The iodobenzenes and the two perfluoro-compounds are of commercial origin (Eastman Kodak and Bristol Organic Ltd., respectively) and were purified by recrystallization or distillation under vacuum.

RESULTS AND DISCUSSION

The p.e. spectrum of iodobenzene is given in Figure 1. The vertical ionisation energies are listed at the tops of the systems, and the adiabatic ionisation energies on the corresponding places at the bottom (±0.05 eV). They are in agreement (within ±0.1 eV) with the hitherto published first four values.[1,2,5] Under higher resolution the first three systems show vibrational structure (Figure 2). In the ground state of the molecular ion two vibrations of wavenumber 280 and 1 000 $\mathrm{cm^{-1}}$ are active. These are probably a low-wavenumber substituent-sensitive vibration and a ring vibration, respectively. The second system shows only weakly one vibration of 960 $\mathrm{cm^{-1}}$ which is probably also a ring motion. The third system has an unusual shape. There are two intense bands separated by 870 $\mathrm{cm^{-1}}$, yet the third member of the progression is observed only as a very weak shoulder near 10.0 eV. The abrupt drop in intensity from the second band to the shoulder is difficult to explain. It might be due to an unfavourable Franck-Condon factor coupled with broadening by predissociation. The bond most likely to break in iodobenzene is the C–I bond, and the active vibration (870 $\mathrm{cm^{-1}}$) leading to predissociation would then probably be ν_7, which involves a large amount of C–I stretching and has a wavenumber of 999 $\mathrm{cm^{-1}}$ in the molecular ground state.[6] Marschner [2] attributed the two maxima to spin–orbit split levels of the in-plane $5p_y$ electrons on the iodine atom, which is impossible.

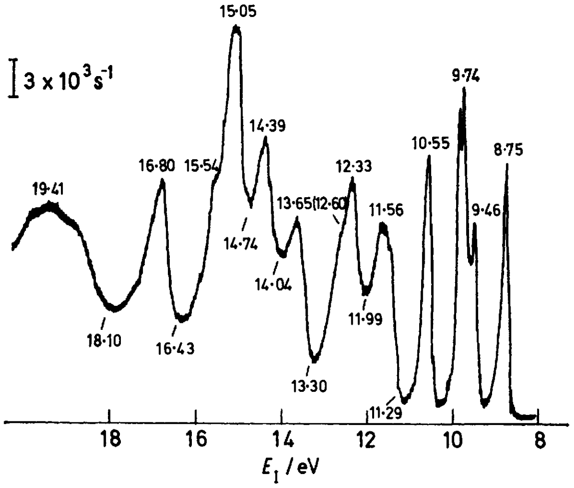

FIGURE 1 The He$^{\mathrm{I}}$ photoelectron spectrum of iodobenzene

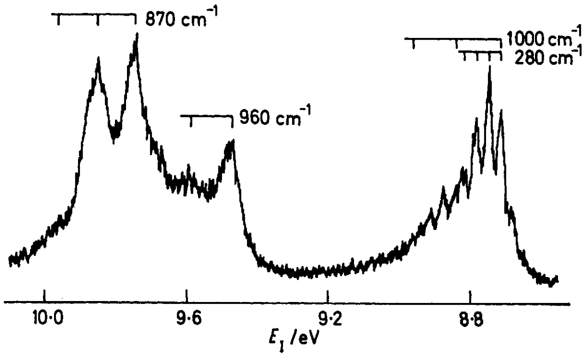

FIGURE 2 High resolution p.e. spectrum of the first three systems of iodobenzene

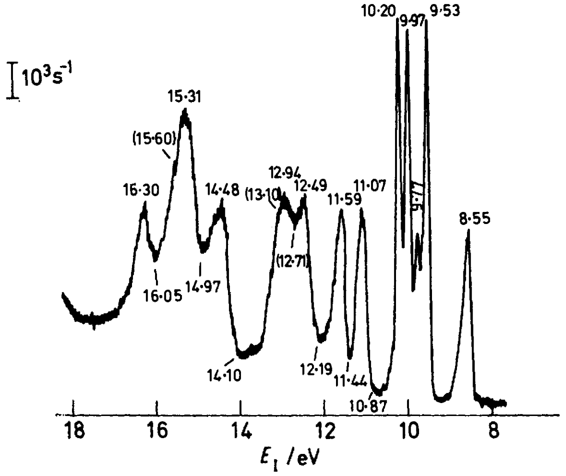

FIGURE 3 The p.e. spectrum of 1,4-di-iodobenzene

The p.e. spectra of the three di-iodobenzenes (Figures 3—5) show no fine structure, but some systems have a characteristic shape which can be followed through all the spectra, thus providing a major guide for the present assignment. The systems arising by ionisation from the top two π-orbitals, corresponding to the benzene e_{1g} orbitals, can thus be distinguished clearly from the significantly narrower systems caused by ionisation of the iodine lone-pair electrons. The splitting is increased

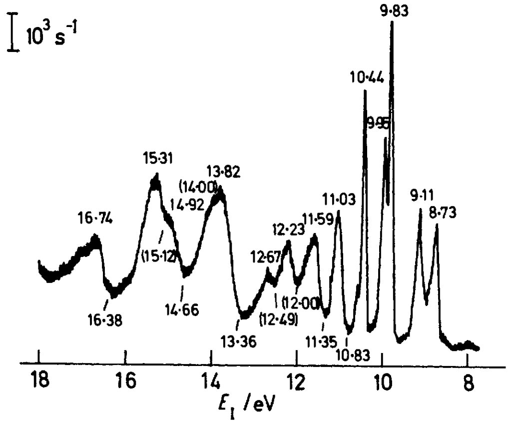

FIGURE 4 The p.e. spectrum of 1,3-di-iodobenzene

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[5] D. W. Turner, C. Baker, A. D. Baker, and C. R. Brundle, 'Molecular Photoelectron Spectroscopy,' Wiley–Interscience, London, 1970.

[6] D. H. Whiffen, *J. Chem. Soc.*, 1956, 1350.

on going from iodobenzene to 1,4-di-iodobenzene from 0.71 to 0.98 eV, with the b_1 orbital having the higher energy. In 1,3-di-iodobenzene the order is reversed and the b_1 orbital with the nodal plane through the bonds is below the a_2 orbital. In 1,2-di-iodobenzene the orbital with the nodal plane across the bonds is again of highest energy but of a_2 symmetry since the axis of symmetry passes also through the bonds. This is in agreement with observations on other substituted benzenes.[3,7] The correlation of ionisation energies of di-iodobenzenes with those of iodobenzene, benzene, and iodine is given in Figure 6. The assignment for benzene is taken from ref. 8; for iodine the first ionisation energy of the atom was taken.

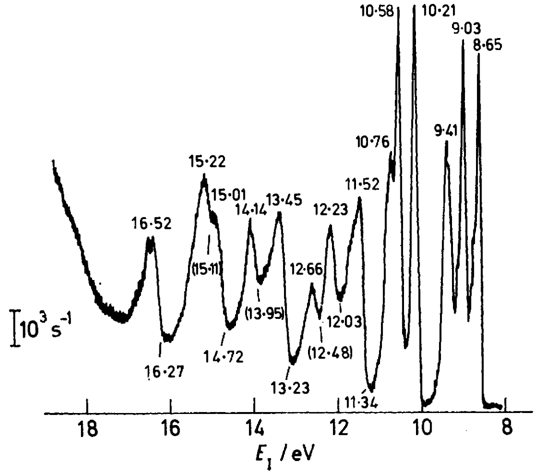

FIGURE 5 The p.e. spectrum of 1,2-di-iodobenzene

In iodobenzene the two lone-pair orbitals on iodine, one of b_2 (in-plane) and one of b_1 (perpendicular to the molecular plane) symmetry, have different interactions with the benzene ring. Since the interaction with the higher lying π-orbitals is stronger than with the low lying σ-orbitals the b_1 orbital will be shifted below the b_2 orbital. The stronger bonding character of the b_1 orbital is observed as a broader system in the p.e. spectrum. In the disubstituted compounds there are two pairs of lone-pair orbitals. Under higher resolution the sharper systems corresponding to the in-plane orbitals can be clearly distinguished from the broader systems corresponding to the out-of-plane orbitals. The in-plane orbitals are split by 0.67 eV in 1,4-di-iodobenzene indicating a relatively strong through-bond interaction as in *p*-benzoquinone.[9] In 1,3-di-iodobenzene this splitting is approximately the same (0.61 eV) whereas in 1,2-di-iodobenzene it is increased to 1.55 eV owing to strong through-space interaction. The out-of-plane lone-pair orbitals are split by 1.1 eV in 1,4-di-iodobenzene, indicating a stronger interaction with the π-orbitals in the benzene ring.

The negative combination of $5p_x$ orbitals has a bonding interaction with the higher lying π-orbital and will be thus lower in energy than the b_{2u} orbital which can interact only with the low lying π_1-orbital. This separation again remains almost the same (1.08 eV) in 1,3-di-iodobenzene and is changed drastically when the iodine atoms are on adjacent carbon atoms. Here the positive combination of $5p_x$ orbitals will have a lower energy owing to both stronger bonding interaction with the π-orbitals and the stabilizing through-space interaction (Figure 6).

The a_{2u} π_1-orbital of benzene corresponds to an ionisation energy of 12.35 eV (ref. 8) and if we assume that it has only very weak interaction with the $5p_x$ orbitals of iodine, the ionisation energies will remain approximately constant in all the compounds investigated.

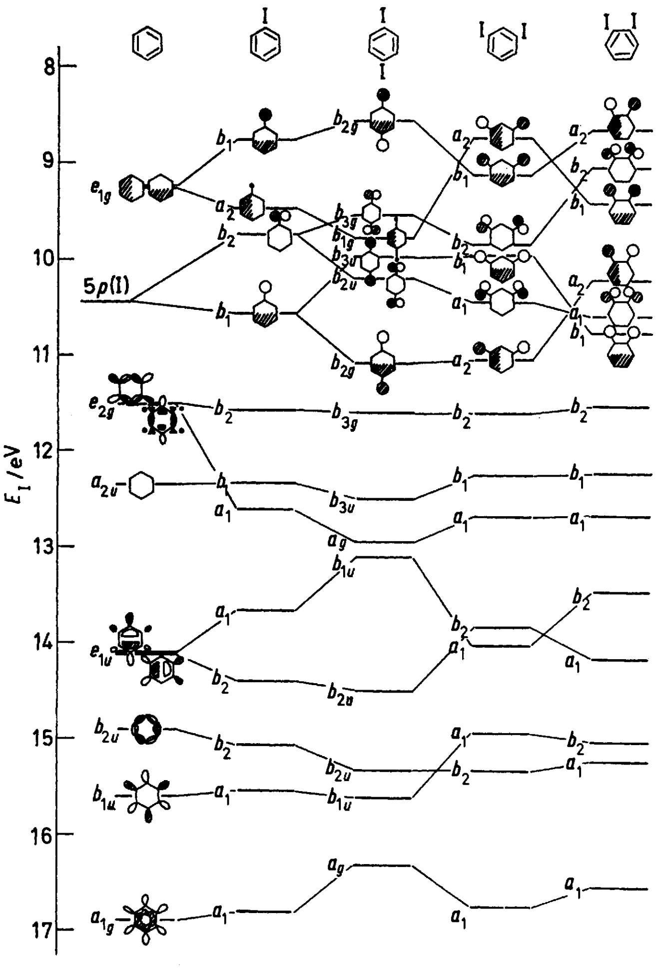

FIGURE 6 Correlation diagram for iodo- and di-iodo-benzenes with benzene and iodine

The assignment of the σ-levels given in Figure 6 is less definite. It is mainly based on the recent assignment for benzene.[8] In benzene the e_{2g} orbitals at 11.5 eV are above the lowest π-level (a_{2u}). On substitution this degeneracy is lifted. In iodobenzene and 1,4-di-iodo-

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[7] (*a*) D. G. Streets, W. E. Hall, and G. P. Ceasar, *Chem. Phys. Letters*, 1972, **17**, 90; (*b*) T. Kobayashi and S. Nagakura, *Bull. Chem. Soc. Japan*, 1974, **47**, 2563.

[8] J. Almlöf, B. Roos, U. Wahlgren, and H. Johansen, *J. Electron Spectroscopy Related Phenomena*, 1973, **2**, 51.

[9] T. Kobayashi, *J. Electron Spectroscopy Related Phenomena*, 1975, **7**, 349.

benzene there is also a system at *ca.* 11.5 eV which must be a σ-level and can be attributed to one component of the benzene e_{2g} level with the nodal plane across C-1 and C-4, thus having no interaction along the C–I bonds. The second component is then near the π_1-level. We assume that the same order is retained in 1,3- and 1,2-di-iodobenzene. The shapes of these systems in the p.e. spectra of the latter two compounds are almost identical (*cf.* Figures 4 and 5). The splitting pattern corresponding to the e_{1u} level resembles that of the e_{1g} π-level since the symmetry of the interacting orbitals is the same except with respect to the plane of the molecule. The b_{2u} level is shifted only by an inductive effect, slightly more in the disubstituted molecules than in the monosubstituted compound. The a_{1g} level is associated with a system of characteristic shape which can be seen in all the spectra. The correlation with the remaining b_{1u} orbital of benzene then follows automatically.

The assigned orbital sequence in 1,2- and 1,4-di-iodobenzene is supported by the p.e. spectra of the corresponding perfluoro-compounds. In agreement with the known perfluoro-effect the spectra show an increase in ionisation energies of *ca.* 0.5 eV for π- and non-bonding electrons on iodine and about four times as large for the σ-electrons.

In 1,2,4,5-tetrafluoro-3,6-di-iodobenzene the iodine lone-pair orbitals correspond to the following ionisation energies: 10.08 (b_{3g}), 10.37 (b_{1g}), 10.72 (b_{3u}), and 11.63 (b_{2g}) eV; thus there is an almost constant shift of 0.5 eV with respect to 1,4-di-iodobenzene. The same shift is observed for the lowest π-orbital (b_{3u}) which is found at 12.87 eV. The separation between the top two π-orbitals (b_{2g} and b_{1g}) is reduced by fluoro-substitution, the corresponding ionisation energies being 9.05 and 9.58 eV, respectively. This might have been expected, since in 1,2,4,5-tetrafluorobenzene the orbital sequence is reversed.[3]

In 1,2,3,4-tetrafluoro-5,6-di-iodobenzene the π-electron ionisation energies are 9.46 (a_2), 9.83 (b_1), and 12.63 (b_1) eV; thus there are increases of 0.8 eV for the top level and 0.4 eV for the other two relative to those in 1,2-di-iodobenzene. A similar shift is observed for the iodine lone-pair electrons, the corresponding E_{I} values being 9.08 (b_2), 10.58 (a_2), 11.01 (a_1), and 11.20 (b_1) eV. The top level is here hardly shifted because of the counteracting repulsion of the fluorine and iodine lone-pair electrons.

The strongest shifts on perfluoro-substitution are observed in σ-levels, leading to the disappearance of the σ-level near 11.5 eV in the tetrafluoro-compounds. Thus, the two levels corresponding to the e_{2g} level of benzene are at 13.9 and 14.73 eV in 1,2,4,5-tetrafluoro-3,6-di-iodobenzene and at 12.92 and 14.06 eV in 1,2,3,4-tetrafluoro-5,6-di-iodobenzene.

In conclusion, the described treatment can easily be extended to bromo- or chloro-substituents and to conjugated molecules other than benzene. The major guidelines to be used in the analysis are the shapes and intensities of the photoelectron band systems and the relative energies of the interacting orbitals. Simple interaction schemes within the symmetry rules lead to an assignment which necessarily relies on the assignment for the molecular frame, which is in our case benzene.[8] In the present discussion spin–orbit interaction has not been taken into account since there is no place for it in such a simple scheme. It is believed, however, on the basis of the similarity of the spectra of bromo- and iodo-compounds that the main ring–substituent interaction is conjugative and that inclusion of spin–orbit interaction will not change the assignment. The same conclusion was reached in the study of p.e. spectra of bromo- and iodo-thiophens.[10] Through-space interaction of the lone-pair orbitals is important only when the iodine atoms are on adjacent carbon atoms; then, however, it becomes a dominant effect.

This work has been performed on the basis of a German–Yugoslav scientific co-operation programme. Financial support by Internationales Büro, Kernforschungsanlage Jülich, and the Republic Fund for Scientific Work of Croatia is gratefully acknowledged.

[6/1331 *Received, 8th July,* 1976]

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[10] J. Božić, T. Cvitaš, K. Humski, and L. Klasinc, in preparation; reported in part at the International Congress on Heterocyclic Chemistry, Ljubljana, July 1975.