Photoelectron Spectroscopy of Heterocycles. Indene Analogs

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The He(I) photoelectron (PE) spectra of indene, indole, benzofuran, benzothiophene, 1-, 2-, 3-, 4- and 6-methylindole and 4,5,6,7-tetrafluoroindole were measured and analysed. A close correlation between the π-ionisation energies of these compounds and the eigenvalues of the corresponding HMO-orbitals is found. A qualitative scheme for the assignment of the π-electron ionisations by orbital interaction of the constituents of the indene analogs i. e. of styrene and the p-orbital of the corresponding heteroatom, indicates that the energy levels in all the compounds investigated can be described by the same type of interaction and yields a value for the inductive effect of the hetero group ($-CH_3$ and $>CH_2$: 0.3 eV, $>NH$: 0.4, $>S$: 0.1, $>O$: negligible).

Introduction

The PE spectra of compounds with we call indene analogs, i. e. compounds which can be though as being obtained from indene by substituting its CH_2-group by a hetero group, have first been measured by Eland et al. [1,2], Johnstone et al. [3] and Heilbronner et alii [4]. We came to these compounds by our interest in the PE spectra of biologically active molecules [5]. Since in previous papers no complete assignment even of π-ionisations was given and our results from the direct use of some semiempirical methods (PPP, CNDO/2, MINDO/2) were rather confusing [5], we compared the PE spectra of the whole series and used a simpler theoretical approach, the HMO method with orbital interaction. The effect of methyl substitution and especially the "perfluoro effect" together with high resolution measurements yielded additional information on bonding properties and electron distribution of these molecules.

Experimental

The following compounds were investigated: indene, indole, benzofuran, benzothiophene, 1-methylindole, 2-methylindole, 3-methylindole, 4-methylindole, 6-methylindole and 4,5,6,7-tetrafluoroindole. Their PE spectra were recorded on a Vacuum Generators UV-G3 instrument [6] with He(I) excitation either at room or elevated temperature (indene,

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2-methylindole and 3-methylindole 50 °C; tetrafluoroindole 70 °C; indole and 4-methylindole 80 °C; 6-methylindole 200 °C) in the inlet system. Low resolution (30 — 50 meV) for the complete spectra, and high resolution (~ 15 meV) and expanded scale for individual systems was used. The energy scale of the spectra was calibrated by simultanious addition of small amounts of argon, xenon and nitrogen to the samples. All investigated compounds were of high purity, redistilled or recrystalised before use.

Results and Discussion

The full He(I) PE spectra of the investigated indene analogs are shown in Figures 1 — 4. The vertical ionisation energies, defined at the highest peak in a system, are listed above, and the adiabatic ionisation energies at the corresponding place below the spectrum (in eV ± 0.015 eV). Uncertain values are given in brackets. For diffuse, overlapping and unassigned systems the values are not given.
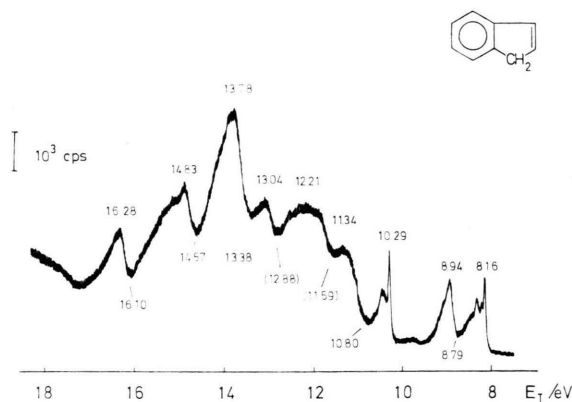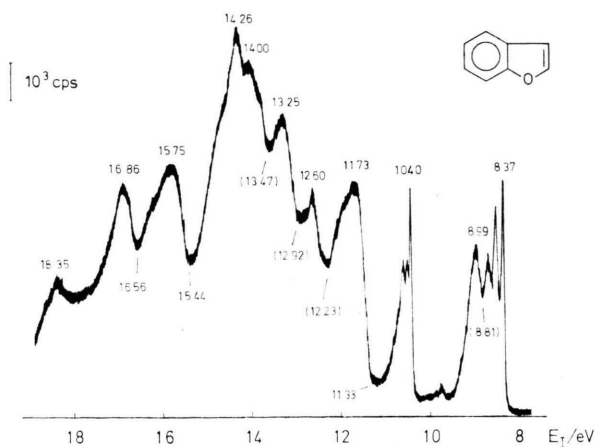

Fig. 1. He(I) PE spectrum of indene.

Fig. 2. He (I) PE spectrum of benzofuran.
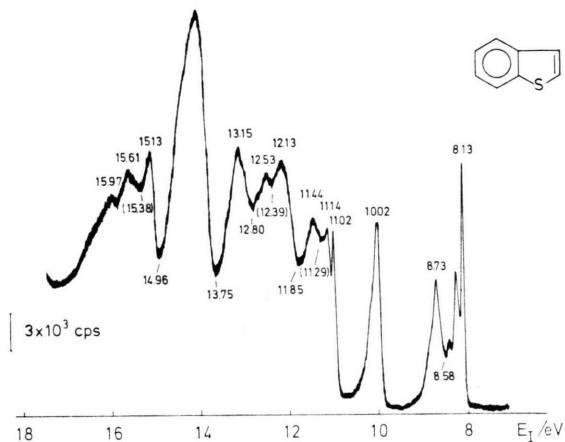
Fig. 3. He (I) PE spectrum of benzothiophene.

Fig. 4. He (I) PE spectrum of indole and 4,5,6,7-tetra-fluoroindole.

For all indene analogs a HMO calculation was performed. The following heteroatom parameters [7] have been applied (X, h_X and k_{CX} are given): NH, 1.0, 0.9; O, 2.0, 0.9; S, 1.0, 0.5; F, 2.5, 0.5; CH_3 and CH_2, $h_{a-C} = -0.5$ (inductive). The assignment of the π-ionisations was tried on the basis of the following simple qualitative reasoning. Suppose we know the energies and the symmetry properties of the molecular orbitals in two compounds (e. g. benzene and ethylene) which are the constituent parts of a new compound (e. g. styrene) whose π-ionisations we wish to estimate. The resulting energies will be a function of the energies of the constituent parts and of the (unknown) interaction parameters and will be, in a good approximation, given as eigenvalues of an interaction matrix. Symmetry arguments can be of great help to neglect cer-
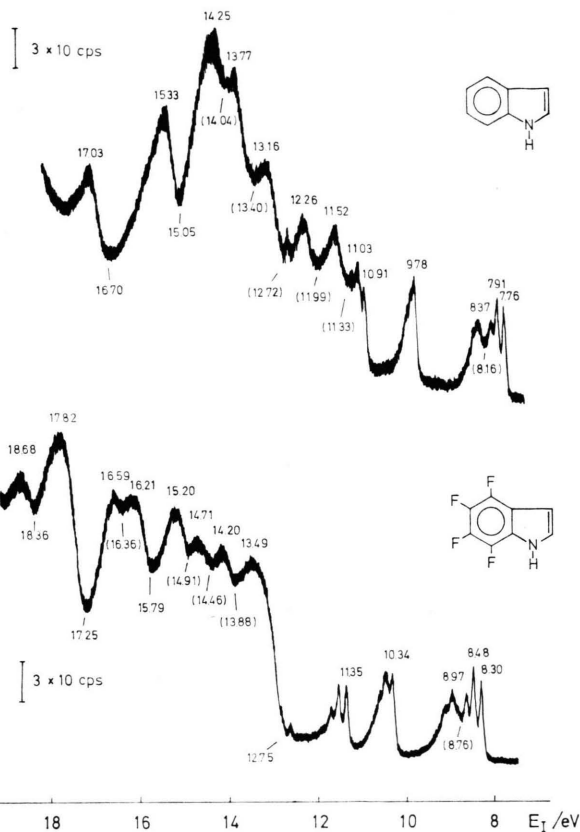
tain interactions. This is well demonstrated in the case of benzene and ethylene yielding styrene (Figure 5). In benzene (D_{6h}) there are three occupied π-orbitals $\pi_1(a_{2u})$ and the doubly degenerate $\pi_{2,3}(e_{1g})$ corresponding to PE vertical ionisation energies of 12.35 and 9.23 eV, respectively [8]. Ethylene (D_{2h}) has one filled $\pi(b_{3u})$ orbital (10.51 eV) [9]. The PE-spectrum of styrene [10] (in a first approximation C_{2v} symmetry) shows that ionisation from its $\pi_3(1a_2)$ orbital (9.30 eV) corresponds nearly to the same energy as from π_3 in benzene. This orbital, because of its symmetry, cannot have π-interaction with ethylene, and the unchanged energy value indicates that the inductive effect is also negligible. The energy values of the other orbitals are changed by interaction with the ethylene orbitals. Setting the interaction matrix elements equal to one and the ionisation energies of the interacting orbitals at the diagonal, we obtain a symmetric interaction matrix

$$\begin{pmatrix} 9.23 & 0 & 1 \\ 0 & 12.35 & 1 \\ 1 & 1 & 10.51 \end{pmatrix}$$
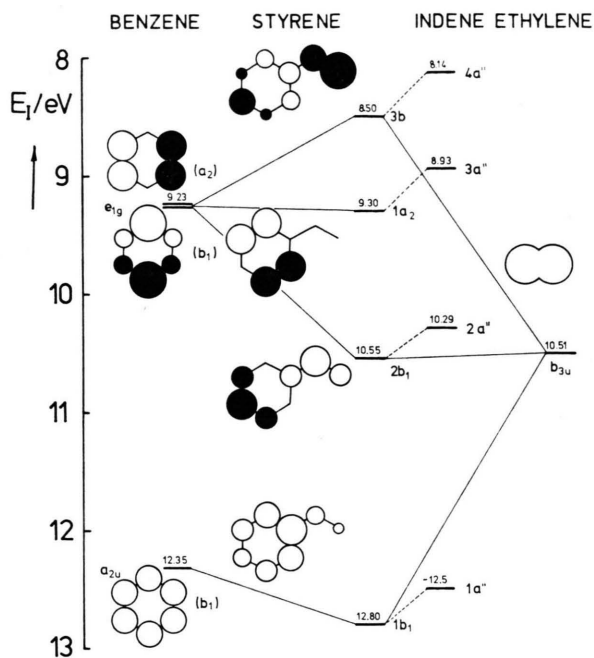
Fig. 5. Orbital correlation diagram for benzene, styrene, indene and ethylene. The listed values are experimental vertical ionisation energies.

whose eigenvalues ε: 8.62, 10.64 and 12.84 eV are in good agreement (within 1%) with the observed ionisation energies of styrene. (The π_3 orbital of benzene was not taken into account, since its interaction matrix element with all orbitals is zero.) This allows to assign the $\tilde{X}$, $\tilde{A}$, $\tilde{B}$ and $\tilde{F}$ systems of styrene at 8.50, 9.30, 10.55 and 12.80 eV as π-ionisations, and at the same time to calibrate the HMO eigenvalues assuming that linear correlation exists. The σ-ionisations corresponding to overlapping systems $\tilde{C}$ and $\tilde{D}$ and the system $\tilde{E}$ appear as peaks at 11.50 and 12.25 eV, respectively. The assignment is supported by the PE spectrum of 2,3,4,5,6-pentafluorostyrene. The top three vertical ionisation energies in this compound at 9.33, 9.67 and 11.13 eV can be correlated with ionisations from shifted π_4, π_3 and π_2 orbitals of styrene, the double peak at about 12.80 eV to overlapping σ- (mainly σ_{CH} of the ethylene part) and π_1-orbitals whereas the other two σ-orbitals are strongly shifted to higher ionisation energies (> 14 eV).

The application of this simple method of π-orbitals assignment is demonstrated with the PE spectra of the indene analogs.

The PE spectrum of indene (Fig. 1) is very similar to that of styrene. Its $\tilde{X}$, $\tilde{A}$ and $\tilde{B}$ systems (at 8.14, 8.93 and 10.29 eV) have already been assigned to photoionisations from $\pi_4(4a'')$, $\pi_3(3a'')$ and $\pi_2(2a'')$ orbitals [5]. The broadness of the peak at 12.21 eV in the indene PE spectrum indicates that it contains at least two unresolved systems ($\tilde{D}$ and $\tilde{E}$). The correlation with HMO calculation using the established calibration would place the $\pi_1(1a'')$ of indene at about 12.5 eV, which is very likely true. A comparison with styrene shows that all the π-levels of indene are shifted by practically the same amount (~ 0.3 eV) to lower ionisation energies, a fact which we ascribe to the inductive effect of the CH$_2$-group. The described HMO procedure is visualised in Figure 5.

Thus, within the model of the interaction matrix the effect of the CH$_2$-group on the π-levels is described as addition of a constant value (-0.30 eV) to all diagonal elements. By assuming that the inductive effects of other groups will also be constant for all π-energy levels, one can define the inductive effect of a group as the difference between the sum of the assigned π-energies of a molecule and the corresponding sum for the orbitals of constituent parts, divided by the number of considered levels.

In the PE spectrum of indole (C$_s$-symmetry, five occupied π-orbitals) the top four systems at 7.76, 8.38, 9.78 and 11.02 eV (Fig. 4) are assigned to π-ionisations. On the basis of the "calibrated" HMO-calculations the $\tilde{F}$ system at 13.16 eV can be assigned as the $\pi_1(1a'')$ ionisation. This assignment is strongly supported by the PE spectrum of tetrafluoroindole (Figure 4). Although only four of the seven hydrogen atoms of the indole molecule are substituted by fluorine they exhibit a remarkable "perfluoro effect" shifting all the σ-ionisations below the π-ionisations. The top four systems in the PE spectrum of tetrafluoroindole at 8.48, 8.97, 10.34 and 11.35 eV are easily assigned by comparison with the spectrum of indole, as well as the π_1 at 13.49, which only collapses with some σ-ionisation. Employing the above described interaction matrix procedure and using the styrene energy levels and the nitrogen lone-pair energy in ammonia of 10.85 eV [9], i. e. diagonalising the matrix

$$\begin{pmatrix} 8.50 & 0 & 0 & 0 & 1 \\ 0 & 9.30 & 0 & 0 & 1 \\ 0 & 0 & 10.55 & 0 & 1 \\ 0 & 0 & 0 & 12.80 & 1 \\ 1 & 1 & 1 & 1 & 10.85 \end{pmatrix}$$

the eigenvalues ε: 7.90, 8.98, 10.10, 11.64 and 13.38 eV are obtained.

From the sum of the above assigned energy levels of indole their sum differs by -1.90 eV, and if this energy is randomly distributed over the resulting orbitals then a value of $(-1.90/5) = -0.38$ eV corresponds to the inductive effect of the NH-group. Adding this amount to the calculated eigenvalues, the values 7.52, 8.50, 9.72, 11.26 and 13.00 eV are obtained, in very good agreement with the experimental ionisation energies. The correlation of the experimental π-ionisation energies of styrene, indole, ammonia, tetrafluoroindole and methylindoles is shown in Figure 6. Clearly, the assumption of the

Fig. 6. Orbital correlation diagram for styrene, indole, 4,5,6,7-tetrafluoroindole and the 1-, 2-, 3-, 4- and 6-methyl-indoles. The listed values are experimental vertical ionisation energies.

random distribution holds only to the first approximation. This is indicated by the real inductive effect of the methyl group on the π-energies of the methylindoles here studied. The experimental ionisation energies are spread within about 0.1 eV, but the correlation is still good enough to assign a value

of ~ 0.25 to the inductive effect (Figure 7). The adiabatic (A) and vertical (V) ionisation energies of methylindoles are given in Table I. One must not forget that we also have attributed the same value (1.0) to all the non-zero interaction off-diagonal
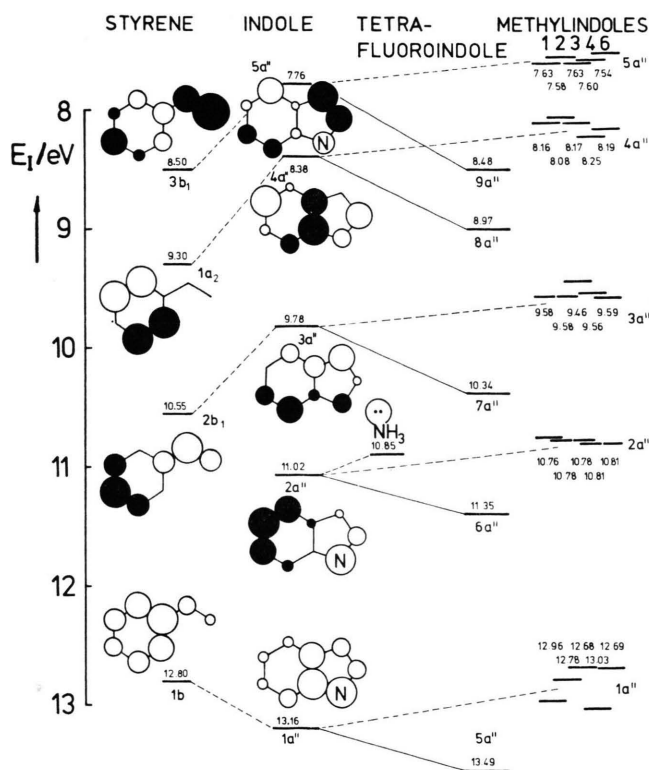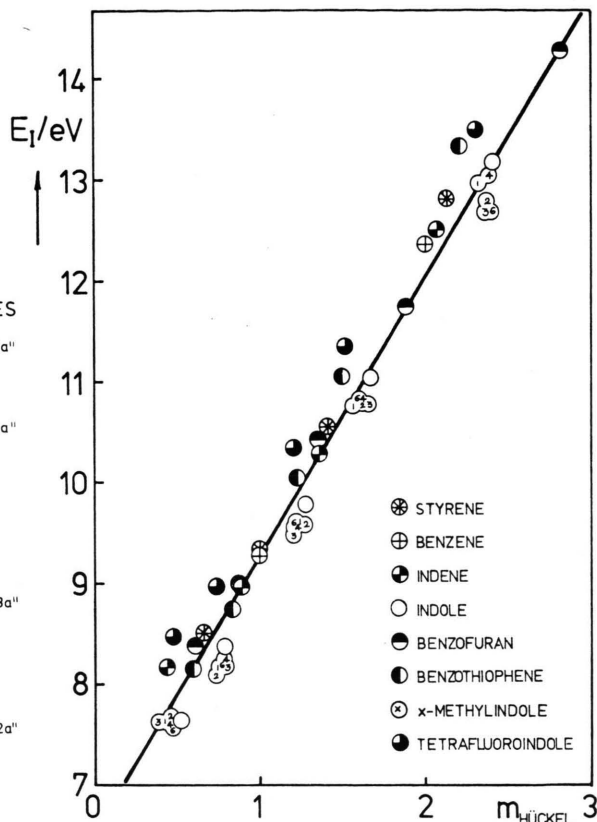

Fig. 7. Least-squares regression of the observed π-ionisation energies vs. HMO calculation results for indene analogs.

elements. Some change in the off-diagonal elements could certainly improve the correlation, but setting the interaction parameter just one if interaction exists and zero if there is none is quite a good assumption. It is also good enough to assign the energy levels of the other molecules of the studied series e.g. benzofuran and benzothiophene from styrene and H_2O [$E_I(O_{2p})$: 12.61 eV] and H_2S [$E_I(S_{3p})$: 10.48 eV], respectively [9]. Hereby, the inductive effect of the O-group appeared to be practically zero, and those of the S-group less than 0.1 eV. Besides the four top systems which in both compounds arise from π-ionisation, the π_1 levels are assigned at 14.26 eV (benzofuran) and 13.15 eV (benzothiophene) (Figs. 2 and 3).

Table I. Adiabatic (A) and vertical (V) ionisation energies of methylindoles in eV.

Indole		System									
		1	2	3	4	5	6	7	8	9	10
1-Methylindole	A	7.48	(7.97)	9.58	10.63	(11.08)	(11.92)	12.53		(14.84)	(16.43)
	V	7.63	8.16	9.58	10.76	11.36	12.17	12.96	13.82	15.20	16.62
2-Methylindole	A	7.44	(7.93)	9.58	10.64	(11.08)	(11.78)		(13.17)	(14.30)	(16.48)
	V	7.58	8.08	9.58	10.78	11.32	12.03	12.78 sh	13.66	14.64	16.73
3-Methylindole	A	7.54	(8.08)	9.46	10.74	(11.13)	(11.76)	(12.37)		(14.98)	(16.56)
	V	7.63	8.17	9.46	10.78	11.33	11.93	12.68	14.02	15.23	16.90
4-Methylindole	A	7.60	8.13	9.56	10.67	11.11	(11.72)	12.48	13.48	(14.75)	16.32
	V	7.60	8.25	9.56	10.81	11.31	11.98	13.03	13.69	15.24	16.60
6-Methylindole	A	7.54	(8.03)	9.59	10.63	(11.07)	(11.83)	12.38	(13.57)	(14.96)	16.62
	V	7.54	8.19	9.59	10.81	11.36	12.05	12.69	13.97	15.11	16.92
7-Methylindole	A	7.53	(8.01)	9.47	10.72	(11.09)	(11.79)	12.43	(13.44)	14.93	(16.45)
	V	7.53	8.16	9.47	10.84	11.37	12.01	12.87	14.08	15.10	16.85

A least square regression of the observed ionisation energies of the indene analogs assigned as π-ionisations vs. the m_k coefficients from the HMO calculations defining the energy E_k of the molecular orbital by

$$E_k = \alpha_C + m_k \beta_{CC}, \quad k = 1, 2, \ldots, n$$

gave the following values of the Coulomb and resonance integrals

$$\alpha_C = (6.54 \pm 0.12) \text{ eV},$$

$$\beta_{CC} = (2.73 \pm 0.08) \text{ eV}$$

and is shown in Figure 7.

The lowest ionisation energy systems ($\tilde{X}$ and $\tilde{A}$) of indene, benzofuran and benzothiophene show a characteristic fine structure under high resolution recording.

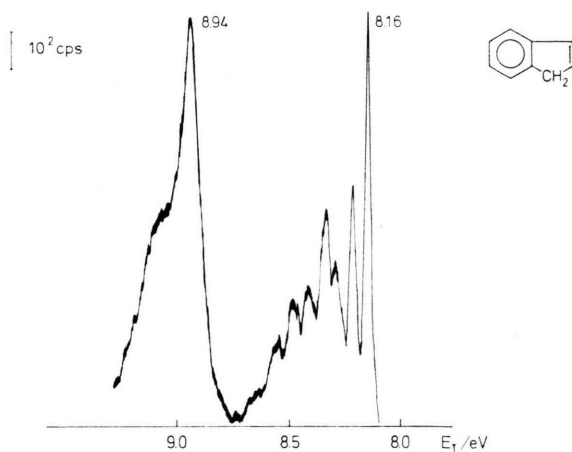The high resolution spectrum in the first two systems of indene is illustrated in Figure 8.

Fig. 8. High resolution PE spectrum of $\tilde{X}$ and $\tilde{A}$ system of indene.

While the $\tilde{A}$ system in all compounds is strongly bonding, the $\tilde{X}$ system is more of nonbonding character. The $0-0$ band of the $\tilde{X}$ system is by far the highest in indene, benzofuran and benzothiophene. Only in indole the $0-0$ and $0-1$ bands are of comparable intensity. In the $\tilde{X}$ systems there are three fundamental vibrations observable corresponding to the following wavenumbers, indene: 530, 1170 and 1500 cm^{-1}, benzofuran: 560, 1170 and 1550 cm^{-1} and benzothiophene: 500, 820 and 1350 cm^{-1} (all values with an uncertainty of ± 30 cm^{-1}). They correspond to three ring vibrations of which the first two can be attributed mainly to the five and six membered ring, respectively. These values for indene and benzofuran are different from those quoted previously[5] (540, 1370, 1530 and 400, 600, 1130, respectively) and are within the experimental error identical for both compounds. There is only a difference in the intensity distribution.

Simple HMO calculations in connection with the applied orbital interaction shows that the π-levels of the compounds investigated can be assigned with great confidence. We are currently using this procedure in the interpretation of the PE spectra of other classes of organic compounds[11].

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