Inner Ionization Potentials of Aromatic Compounds

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Photoelectron spectra of indene, naphthalene, azulene, biphenyl, quinoline and isoquinoline are reported, and some inner ionization potentials of naphthalene, azulene, biphenyl and biphenylene measured by an electron impact method are also given. A close correlation is found between the inner ionization potentials of the hydrocarbons and π-electron orbital energies given by the zero-overlap Hückel approximation.

A controversy has recently arisen over the assignment of the inner ionization potentials of benzene found by photoelectron spectroscopy[1]. The differences between the first two ionization potentials of benzene[1] and diacetylene[2] are in agreement with the predictions of simple Hückel molecular orbital theory for π-electron ionization using a value of 2.2 eV for the parameter β. More elaborate calculations[3] on the other hand, suggest that some σ-electron orbitals should have lower ionization potentials than the second π-electron orbitals.

Experimental

Energy spectra of electrons produced in photoionization by 584 Å radiation from a helium lamp have been measured using a photoelectron spectrometer with a parallel plate electrostatic analyser to be described in detail elsewhere. Because of the rather low volatility of the compounds studied the highest resolution was not sought, wide slits being used to obtain high sensitivity. Resolution in the spectra presented is about 100 mV at the highest energies. Introduction of the aromatic compounds caused considerable (0.5 volt) contact potential changes in the apparatus. To establish correct energy scales a mixture of argon, krypton and xenon was admitted with each compound and the least squares regression of apparent electron energy on the ionization potential was calculated for the six sharp peaks produced by the rare gases. The experimental method used in the electron impact studies has already been described[4]. The compounds were commercially available samples and were used without further purification.

Results

The photoelectron spectra of indene, naphthalene, azulene, quinoline, isoquinoline and biphenyl are shown in Figs. 1 to 3 and the first four ionization potentials of each compound are given in Table 1. Where there is resolved vibrational structure the position of the first peak is given; the other tabulated values are the positions of onsets of bands. The electron impact results given in Table 1 refer to the centres of steps which were found in first derivative ionization efficiency curves sharpened by a modifi-

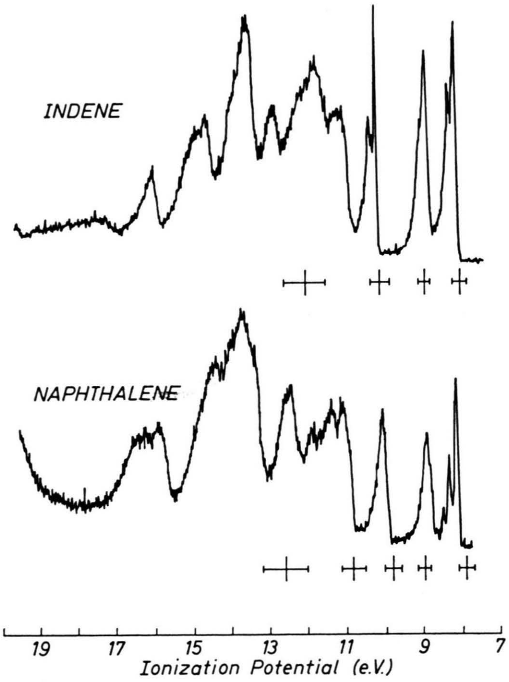

Fig. 1. Photoelectron spectra of indene and naphthalene. The vertical lines under each spectrum show the ionization potentials calculated from Eq. (1) with indications of the standard deviations of each point.

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[1] M. J. Al Joboury and D. W. Turner, J. Chem. Soc. **1964**, 4434.

[2] C. Baker and D. W. Turner, Chem. Comm. **1967**, 797.

[3] M. J. S. Dewar and J. Kelemen, Tetrahedron Letters **1967**, 2341.

[4] J. H. D. Eland, P. J. Shepherd, and C. J. Danby, Z. Naturforschg. **21 a**, 1580 [1966].

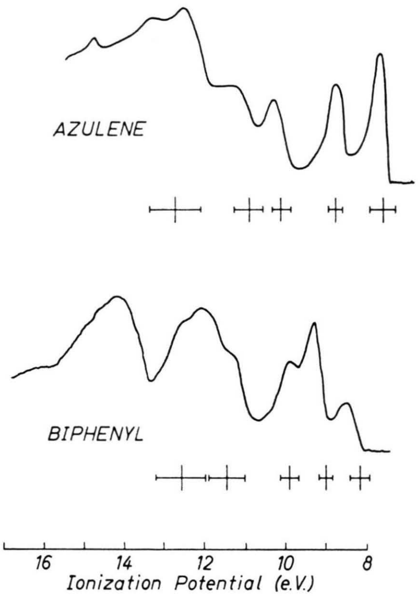

Fig. 2. Photoelectron spectra of azulene and biphenyl.

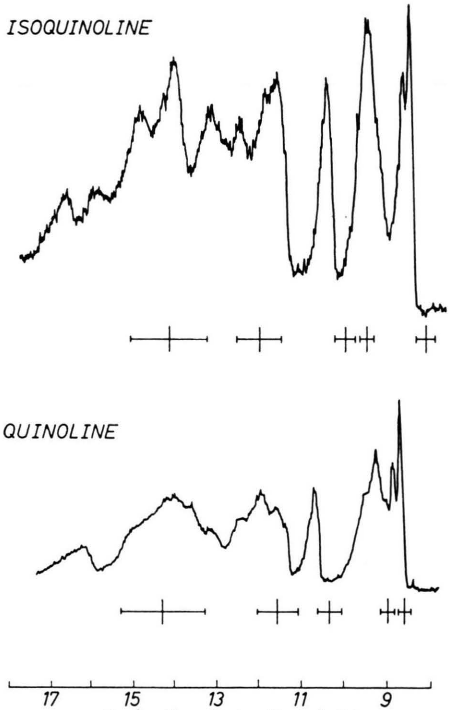

Fig. 3. Photoelectron spectra of quinoline and isoquinoline.

Compound	Method	Ionization Potentials			
Indene	p.e.s.	8.13	8.95	10.29	11.58
Naphthalene	p.e.s.	8.12	8.90	10.00	10.85
	e.i.	8.24	8.70	9.75	
Azulene	p.e.s.	7.42	8.49	9.91	10.81
	e.i.	7.76	8.75	9.55	
Biphenyl	p.e.s.	8.20	9.08	9.70	11.02
	e.i.	8.22	8.85	9.70	10.82
Quinoline	p.e.s.	8.67	(9.00)	10.63	11.37
Isoquinoline	p.e.s.	8.53	9.16	10.32	11.43
Biphenylene	e.i.	7.95	9.20	10.10	(10.80)

Table 1. p.e.s. = photoelectron spectrum. e.i. = electron impact. The estimated precision is ±0.05 eV for p.e.s. results not in parenthesis, and ±0.30 eV for the e.i. values.

cation of the Fourier transform technique described by MORRISON[5]. The resolution of the unfolded curves was about 0.40 volts. The agreement between these electron impact results and the photoelectron spectra in the cases of naphthalene and biphenyl suggests that autoionization processes cannot be very important for these compounds. Biphenylene was too involatile for its photoelectron spectrum to be measured with our apparatus in its present form, so only electron impact results are available. Comparison with the other compounds suggests that confidence limits of about ±0.3 volt should be used.

Discussion

A striking feature of the photoelectron spectra is the similarity between those of indene, naphthalene, quinoline and isoquinoline. In each case there are three sharp peaks at low ionization potential, the first showing vibrational structure, followed by the onset of overlapping and broader bands at an ionization potential of about 11 volts. The resolved vibrational spacings are all about 180 mV. In view of the sharpness of the first two ionization levels of benzene and diacetylene it is tempting to consider sharpness to be indicative of π-electron ionizations. In azulene the first two bands are fairly sharp, but no vibrational structure has been resolved, while in biphenyl all the bands are broad. This may be due to strong vibrational excitation of the interannular bond on ionization.

To relate the observed photoelectron spectra to H.M.O. theory we have plotted the first three ionization potentials of indene, naphthalene, azulene and biphenyl against the H.M.O. coefficients (m) of β[6] (Fig. 4). The points lie close to a straight

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[5] J. D. MORRISON, J. Chem. Phys. **39**, 200 [1963].

[6] C. A. COULSON and J. I. STREITWIESER, JR., A Dictionary of π-Electron Calculations, Pergamon Press, London 1965.

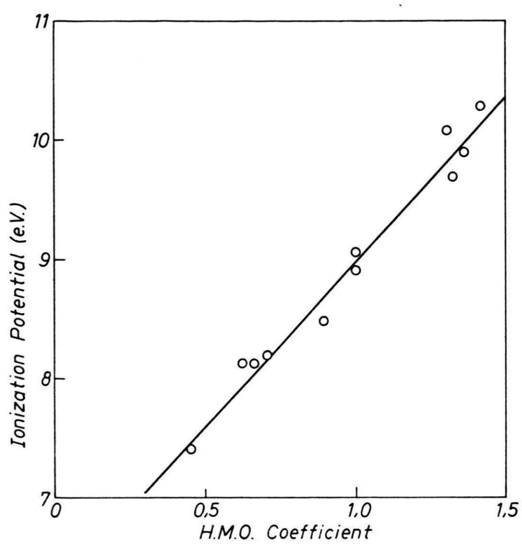

Fig 4.

line for which least squares analysis gives:

$$I.P. = 6.22 + (2.77 \pm 0.15)\, m\,. \qquad (1)$$

This value of (2.77 ± 0.15) eV for β is in agreement with other estimates made from properties related to ionization potentials [7, 8].

We have used Eq. (1) to estimate all the π-electron ionization potentials of the compounds studied: the calculated values are shown as arrows below the curves in Figs. 1 to 6 with bars giving the standard deviations of the predictions. For benzene Eq. (1) gives (8.99 ± 0.15) eV and (11.76 ± 0.45) eV in fair agreement with experiment and for biphenylene the calculated values are (7.43 ± 0.3), (8.65 ± 0.15), (9.68 ± 0.20), (10.04 ± 0.23) and (11.21 ± 0.4) eV. The electron impact results for biphenylene given in Table 1 seem to be displaced +0.5 volt from the predicted positions, but have the same spacing. This may be due to an unsuspected experimental effect. It is interesting to observe that the second ionization peak of biphenyl is about twice as intense as the first, in accordance with the double degeneracy of the second π-orbital in H.M.O. theory.

In order to calculate orbital energies for quinoline and isoquinoline in the Wheland approximation it is necessary to choose h and k parameters for nitrogen. A moderately good fit is obtained with $h = 1$, $k = 1$ in the case of quinoline, but not with isoquinoline, all of whose observed ionization potentials fall outside the standard deviations of the predicted values. It appears that a more sophisticated theoretical treatment may be desirable for hetero-molecules; this is currently being investigated.

Conclusions

Zero overlap Hückel molecular orbital theory with an appropriate choice of parameters provides good predictions for the first and inner π-electron ionization potentials of aromatic hydrocarbons. The quantitative correlation between ionization potentials and orbital energies in the Wheland approximation for quinoline and isoquinoline is not so close but their general pattern is well predicted by the simple theory.

The correlation found is close and the identification of the first inner ionization potentials of the substances studied with π-electron loss seems inescapable.

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[7] E. S. Pysh and N. C. Yang, J. Am. Chem. Soc. **85,** 2124 [1963].

[8] A. R. Lepley, J. Am. Chem. Soc. **84,** 3577 [1962].