PHOTOELECTRON SPECTRA OF CONJUGATED MOLECULES

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Abstract - The various approaches to the assignment of
molecular ultraviolet photoelectron spectra are described. An
interpretation of π-electron structure of selected classes of
cyclic, heterocyclic and substituted conjugated molecules is
given in terms of common constituent parts. The results are
supported by molecular orbital calculations, photoelctron
spectra of fluorinated compounds and comparison of spectra
recorded under HeI and HeII excitation, as well as by symmetry
considerations.

Molecular ultraviolet photoelectron (PE) spectroscopy (Ref. 1,2) measures
ionization energies of valence electrons of free molecules. Interaction of
radiation of sufficient energy and a free molecule in the gas phase releases
electrons from the latter and produces positive ions in various electronic
states. The process can be described by

$$M(^1\Psi_0) + h\nu \rightarrow M^+(^2\Psi_k) + e^-(T_k)$$
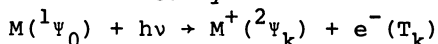
where $M(^1\Psi_0)$ stands for a neutral molecule in its singlet ground state
described by the electronic wave function $^1\Psi_0$, $h\nu$ the incident photon,
$M^+(^2\Psi_k)$ the ion in the k-th doublet state described by $^2\Psi_k$ and $e^-(T_k)$ the
released photoelectron with a kinetic energy T_k. Since $m_M >> m_e$, the energy
difference

$$h\nu - T_k = \varepsilon(^2\Psi_k) - \varepsilon(^1\Psi_0) \equiv E_{i,k}$$

is an important experimental quantity of a molecule and is called the k-th
ionization energy. The ionization energy can be determined by employing
constant (monochromatic) radiation and by analysing and counting the
electrons of given kinetic energy. A plot of thus counted electrons vs. their
energy (or the difference $h\nu-T_k$) is called a PE spectrum. The quantity $E_{i,k}$
depends on both - the ground and the ionic state. The energy of the ground
state $e(^1\Psi_0)$ is relatively easy to determine e.g. describing the wave
function $^1\Psi_0$ of the 2N electrons in a single determinantal form

$$^1\Psi_0 = ||\Psi_1\bar{\Psi}_1 \cdots \Psi_k\bar{\Psi}_k \cdots \Psi_N\bar{\Psi}_N||$$

and minimizing the energy by a Hartree-Fock procedure yielding

$$F\Psi_0 = \varepsilon_i\Psi_i$$

where ε_i are the orbital energies of the canonical orbitals Ψ_i.

The same set of canonical orbitals Ψ_i is usually used as an approximation for
the spacial part of $^2\Psi_k$ as

$$^2\Psi_k\alpha = ||\Psi_1\bar{\Psi}_1\ldots\Psi_k\ldots\Psi_N\bar{\Psi}_N||$$

$$^2\Psi_k\beta = ||\Psi_1\bar{\Psi}_1\ldots\bar{\Psi}_k\ldots\Psi_N\bar{\Psi}_N||$$

within a so-called restricted Hartree-Fock calculation. Such calculation by handling separately electrons with α and β spins takes into account the effect of electron correlation.

Koopmans (Ref. 3) has shown that the description of (2N-1) spin orbitals of $^2\Psi$ of M^+ in terms of 2N spin orbitals of $^1\Psi_0$ of M may yield an optimum description of M^+. In other words ionization energies correspond to negative orbital energies

$$E_{i,k} = -\epsilon_k$$

what is known as Koopmans´ theorem. However, it is valid only under the assumption that orbitals of M^+ are the same as orbitals of M despite that one electron has been removed from them. Two effects speak against this assumption: the electron correlation, and reorganization which can accompany the ionization process. Electron correlation and reorganization are usually counteracting effects and under a further assumption that they cancel each other Koopmans´ theorem is applicable again. The result of such a situation is that in describing the phenomenon of photoionization we have two kinds of visualization which yield two different approaches in the assignment and interpretation of the information contained in a PE spectrum.
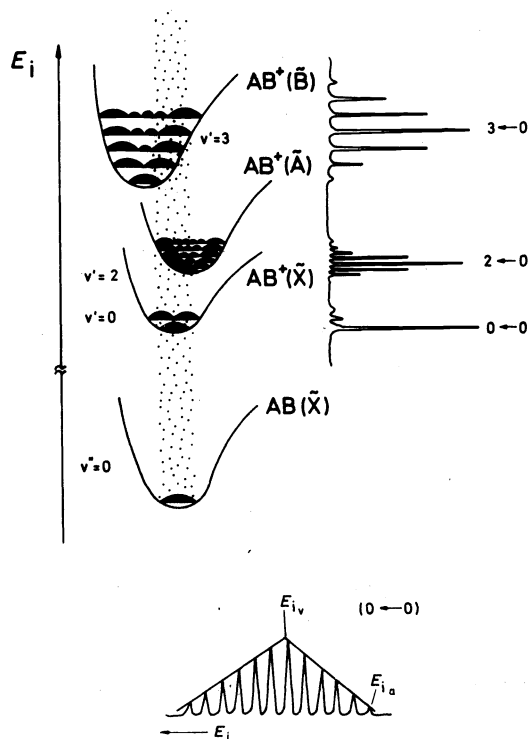

Fig. 1. Photoelctron spectrum of a diatomic molecule AB visualized as a result of Franck-Condon transitions to states of AB^+.

In the first as shown in Fig. 1 taking a diatomic molecule AB as an example, by the action of light, states $\tilde{X}$, $\tilde{A}$, $\tilde{B}$ etc. of AB^+ are populated in a vertical manner according to the Franck-Condon principle. The intensity of individual bands corresponds to the population of respective vibrational states within an electronic state and is determined by the overlap of vibrational wave functions in the ground and final state (Franck-Condon factors). All bands which belong to an electronic state in the spectrum are called electronic band system (or system). The band of lowest energy usually corresponds to the zero point vibration of the corresponding ion and is called the adiabatic ionization energy $E_{i,a}$ whereas the band of highest intensity (or better said the center of gravity of the system) is called the vertical ionization energy $E_{i,v}$. In a polyatomic molecule with 3N-6 vibrational modes vibrational structure is rarely observed although generally only the totally symmetric modes are being excited in PE spectroscopy. Here $E_{i,a}$ is taken at the onset and $E_{i,v}$ at the center of gravity of the system. Knowing the vibrational frequencies of the neutral molecule one can from the observed frequencies in M^+ say if the loss of electron has changed the interatomic distances in the ion or not.

The other picture, as indicated in Fig. 2, based on the validity of Koopmans' theorem assigns to each system in the spectrum a flux of electrons which up

$$hv = E_i + E_k$$

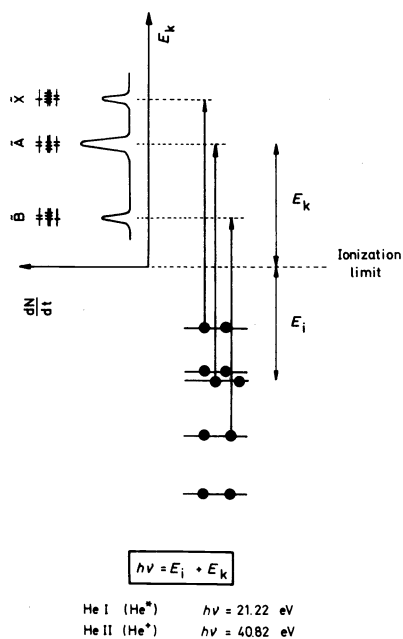He I (He*) hv = 21.22 eV
He II (He*) hv = 40.82 eV

Fig. 2. Photoelectron spectrum of a molecule visualized according to Koopmas' theorem.

to an ionization limit depending on the energy of radiation can be ejected from their doubly occupied orbitals in the molecules.

As a consequence in the interpretation of PE spectra different assignments can occur which do not necessarily exclude or disprove each other.

Namely, a true assignment in terms of energy of states would need the knowledge of equilibrium geometries, potential hypersurfaces, normal vibrational modes of radical ions in the gas phase and transition probabilities and is practically impossible.

However, an assignment is possible on the basis of correlation between calculated states for M^+ and characteristics of PE spectra. This assignment is usually given in terms of ionization energies, ordering of states, changes in geometry on photoionization including determination of Franck-Condon factors, cross-sections etc.

Another assignment is based on the molecular orbital model and using experimental and theoretical results for the molecular ground state, as well as study of related compounds. This assignment in terms of orbital energies and electronic structure (π-, σ-, lone pair-, antibonding, bonding, nonbonding etc.) and using symmetry considerations yields a wide range of information going from ground state conformation, heteroatom and substituent effects to structure-activity relationships. Within this assignment, if any, the definition of aromaticity in PE spectroscopy can be tried. Therefore, a closer examination of the features of PE spectra of cyclic planar conjugated molecules within this assignment will be of interest. A lot of work has been done on these compounds, especially on polycyclic hydrocarbons.

In these molecules a separation of π- and σ-ionizations can be taken for granted. However, systems corresponding to low σ-ionizations appear in the spectrum before the higher π-ionizations.

Experimentally the shape of the particular systems especially under conditions of different excitation energy and the effect of substituents are of great help in their distinction. This is shown in Fig. 3 on the example of naphthalene. In comparison with the HeI spectrum, the HeII spectrum of naphthalene exhibits enhanced intensities of systems at 8.09, 8.81, 9.95, 10.85 and 12.5 eV. The first three are undoubtedly π-ionizations, the last two being potential candidates. In comparison the PE spectrum of octafluoro naphthalene, in which according to the "perfluoro-effect" (Ref. 4) the π-ionizations are uncovered by the stronger shift of σ-ionizations to higher energies the same candidates are found. This coincidence strongly indicates their assignment to π-ionizations, which is also supported by molecular orbital calculations. As shown in Fig. 4 the low energy π-ionizations in acenes can be nicely correlated and discussed in symmetry terms (Ref. 5). Different levels of semiempirical calculations (HMO, PPP, EHT, MINDO/2) as reported by Eland at al (Ref. 6), Schmidt at al (Ref. 7) and Heilbronner at al (Refs. 2,5) give excellent correlations between experimental and calculated ionization energies. For this reason nowadays mostly simple HMO
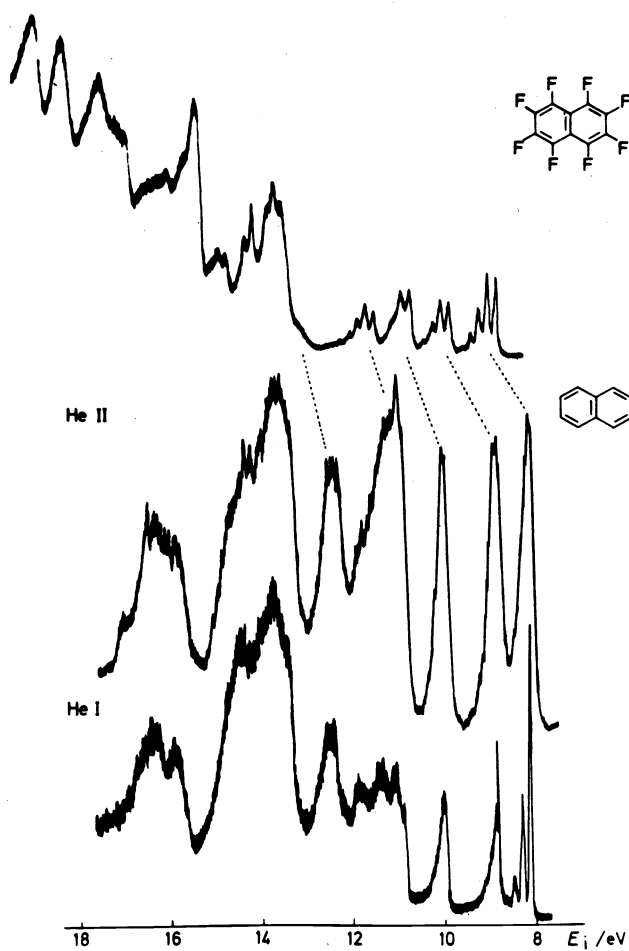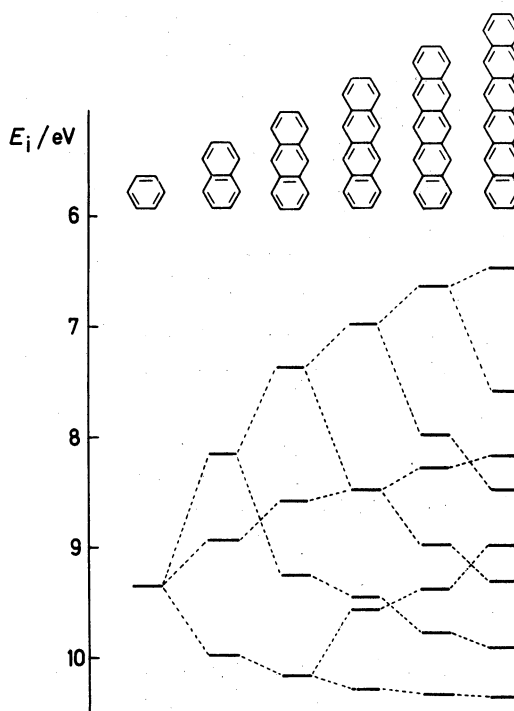
Fig. 3. Photoelectron spectra
of octafluoro naphthalene (top)
and naphthalene under HeI and
HeII excitation.

He II

He I

18   16   14   12   10   8 E_i /eV

Fig. 4. Correlation between low energy
ionizations in acenes (Ref. 5).

E_i /eV

calculations are used to draw orbital correlations from PE spectra. In the last years we tried such studies using the model of constituent parts to build more and more complicated molecules. The PE spectra of these molecules were interpreted starting from the known electronic structure of constituent parts and taking into account their interaction. The main constituent parts as shown in Table 1 are ethylene and benzene, and the model also employs

CONSTITUENT PARTS FOR CONJUGATED MOLECULES
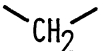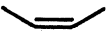
ETHYLENE	BENZENE
-X-	-R
—	-ME
H H	-F
CH₂	-CL
NH	-BR
O	-I
S	-VINYL
═	-PHENYL
LINK	SUBSTITUENT

Table 1

links and substituents which additionally help the assignment. Six classes of such compounds are indicated by following formulae. Thus, the first
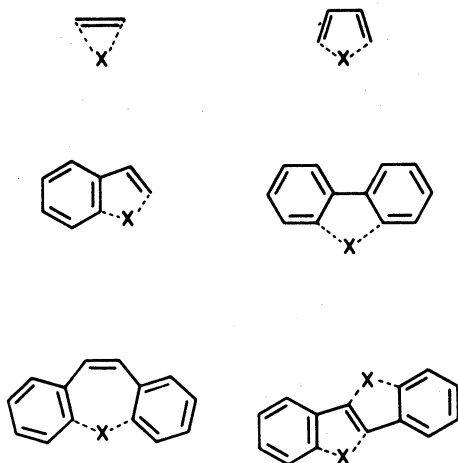
starts with acetylene and ends with cyclobutadiene, the second goes from cyclobutadiene to benzene (cyclohexatriene) etc. Here results will be presented on the three classes of compounds which according to the names of their CH$_2$-linked representatives were called indene (Ref. 8), fluorene(Ref.9) and 5H-dibenzo(a,d)cycloheptene analogues (Ref. 10).

For indene and fluorene analogues a HMO calculations were performed using the following heteroatom parameters (Ref. 11) (x: h_X, and k_{CX}, respectively): O: 2.00, 0.09; NH: 1.00, 0.9; S: 1.00, 0.50; F: 2.5, 0.5; CH$_3$ and CH$_2$: h_C=-0.50 (inductive). The assignment of the π-ionizations was supported by a calculation involving diagonalization of the interaction matrices between the constituent parts of the molecule obtained using their experimental ionization energies. Briefly, the molecule investigated is divided into constituent parts (usually the parent molecule and the heteroatom). The π-ionization energies, or, with the validity of Koopmans' theorem, the π-orbital energies of both parts of the composite molecule constitute the diagonal elements of the matrix, while the off-diagonal elements are set to zero if the respective π-orbitals do not interact, or to 1 eV if they do. This value is approximately half the value of the Hückel resonance integral β. The method is rather insensitive to meaningful values of the non-zero off-diagonal elements of the matrix. The eigenvalues obtained from diagonalization of the matrix must be corrcted for an inductive effect which is a function of the difference between the ionization energies of the constituent parts (i.e., the sum of diagonal elements of the interaction matrix) and the experimental π-ionization energies of the composite molecule. The correction is applied with the same weight to every eigenvalue and has a characteristic value for every heteroatom. This value can be estimated as

$$I = (Tr - \sum_{i=1}^{n} E_i)/n$$

where Tr is the trace of the matrix, E_i are the experimental π-ionization

energies and n the number of π-orbitals. In practice only substantial
effects for the NH and CH_3 (or CH_2) groups of -0.4 eV and -0.3 eV
respectively, were found. For all the others the inductive effects amounted
0.1 eV and less being within the limits error.

The PE spectra of the indene analogs i.e. indene, indole, benzofuran,
benzotiophene are reproduced in Fig. 5.   The π-electron structure of indene
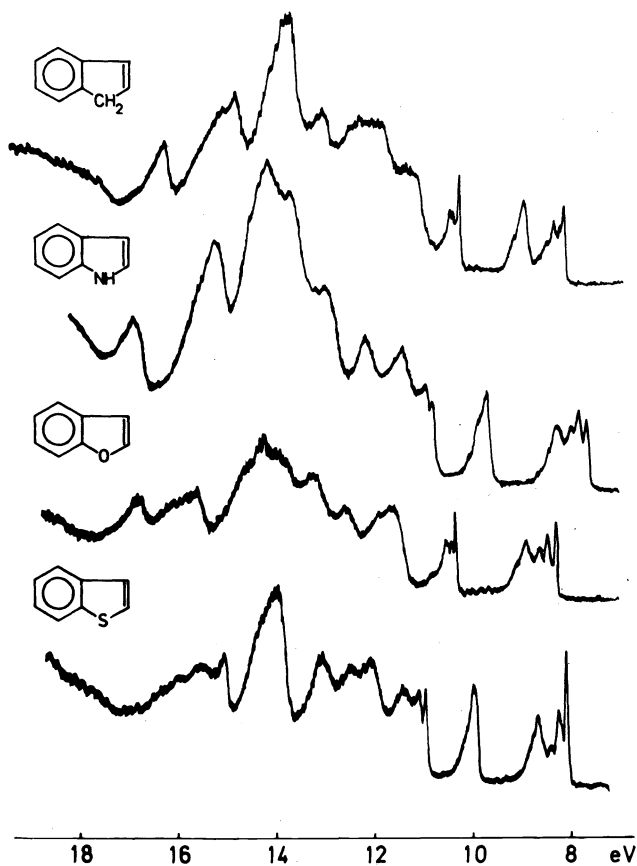

Fig. 5. HeI photoelectron spectra of indene, indole,
benzofuran and benzothiophene.

appears as an inductively destabilized structure of styrene which as shown
in Fig. 6 can be rationalized by interaction of its constituent parts
benzene and ethylene. In this interaction one of the benzene e_{1g} orbitals
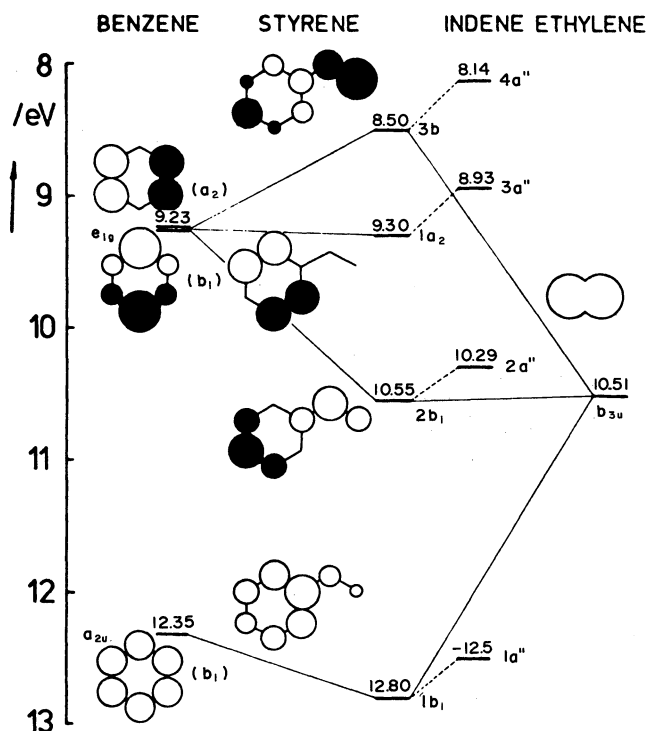does not take part because of symmetry reasons.

Fig. 6. Orbital correlation diagram for benzene, styrene,
indene and ethylene. The listed values are experimental
vertical ionization energies.

In Fig. 7 it is shown how in terms of interaction between styrene and
the nitrogen lone pair (10.85 eV in ammonia), and taking the -0.4 eV
inductive shift into account, the π-ionizations of indole can be described.
Their assignment is supported by inductive shift of about 0.3 eV on
methylation as shown in Fig. 8 by comparison of PE spectra of indole and
three methyl indoles and the "perfluoro-effect" in the PE spectrum of
4,5,6,7-tetrafluoroindole reproduced in Fig. 9. Finally, the nice
correlation between thus assigned π-ionizations vs. the m_k coefficients
from the HMO calculations defining the energy ε_k of the molecular orbital
by

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

and resonance integrals

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

$$\beta_C = (2.73 \pm 0.08) \text{ eV}$$
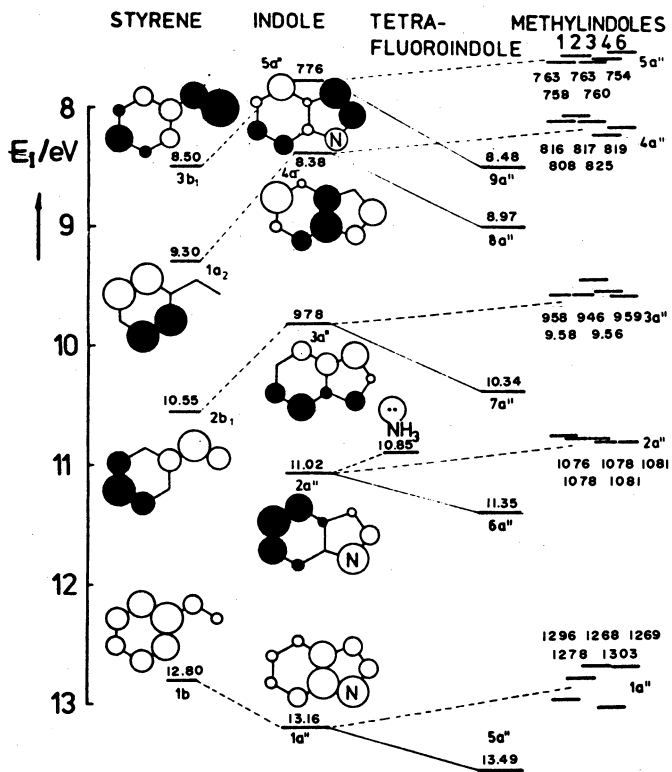
and is shown in Fig.10.

Fig. 7. Orbital correlation diagram for styrene, indole, 4,5,6,7-tetrafluoroindole and the 1-, 2-, 3-, 4- and 6-methylindoles. The listed values are experimental vertical ionization energies.
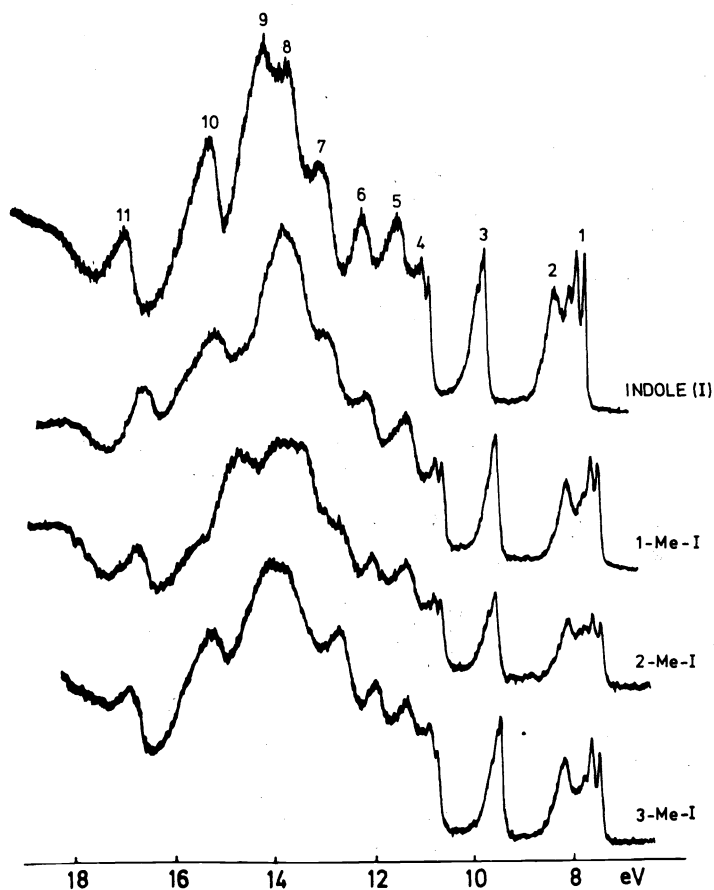
Fig. 8.   HeI photoelectron spectra of indole, 1-methylindole,
2-methylindole and 3-methylindole.

Similarly as in the case of indene the π-electron structure of fluorene
as shown in Fig. 11   results from inductive destabilization of biphenyl
whose electronic structure is rationalized through interaction of two
benzenes (Ref. 12). The PE spectra of some fluorene analogues: fluorene,
carbazole, dibenzofuran, and dibenzothiophene and the correlation of their
π-ionizations with results of HMO calculations are shown in Fig. 12
and 13 respectively.

The CH_2-linked representatives of the next clases 5H-dibenzo(a,d)cyclo-
heptene and diindene with their PE spectra reproduced on the botton of
Fig. 14 are very interesting as examples for fixed conformations of
cis-stilbene and trans-stilbene (Ref. 13) whose PE spectra are given in
the middle of Fig. 14. The behaviour of the five top π-orbitals on
rotating the phenyl rings is nicely reproduced by PPP calculations thus
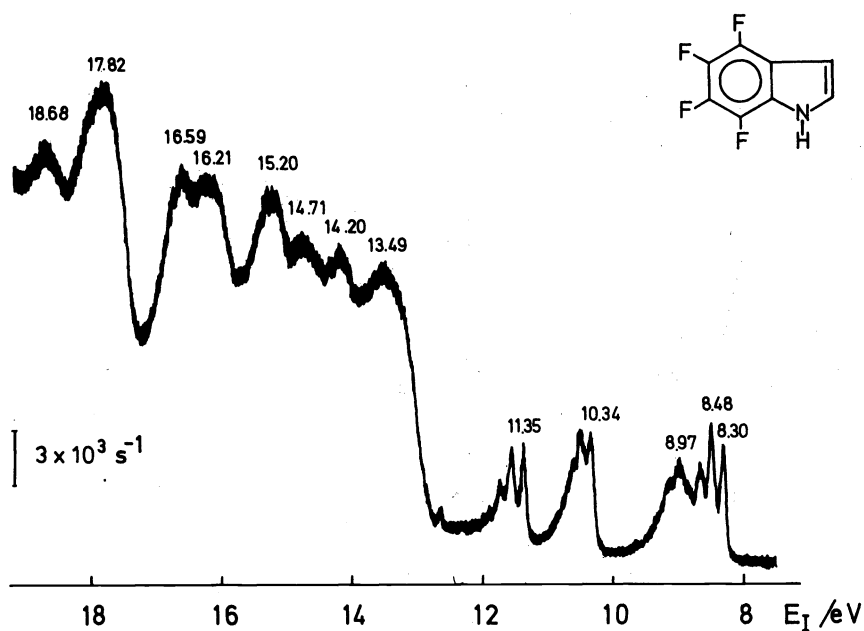allowing the predict ion conformation by comparison of PE spectra with

Fig. 9. HeI photoelectron spectrum of 4,5,6,7-tetrafluorindole.

calculation results. This was done in the case of nonplanar 5H-dibenzo-
(a,d)cycloheptene analogues (Ref. 10) whose PE spectra are shown in Fig. 15.
However, such an approach can not be generally applied since π-electron
structure often ends to be rather insensitive on conformation.

In conclusion a few words on the topic of our Symposium - aromaticity.
We have seen that conjugative interaction between orbitals of constituent
parts forming a π-system can readily be observed if interpreting a PE
spectrum within the molecular orbital concept. However, frankly speaking
I am convinced that aromaticity is not observable in PE spectroscopy. But
neither is it a molecular orbital a concept of enormous importance in
chemistry and PE spectroscopy. Thus the concept of aromaticity which
certainly has a long tradition and as we have seen broad use in classifying
certain properties of compounds need not be banned. I think that one
must only be aware of possible dangers when providing this concept with
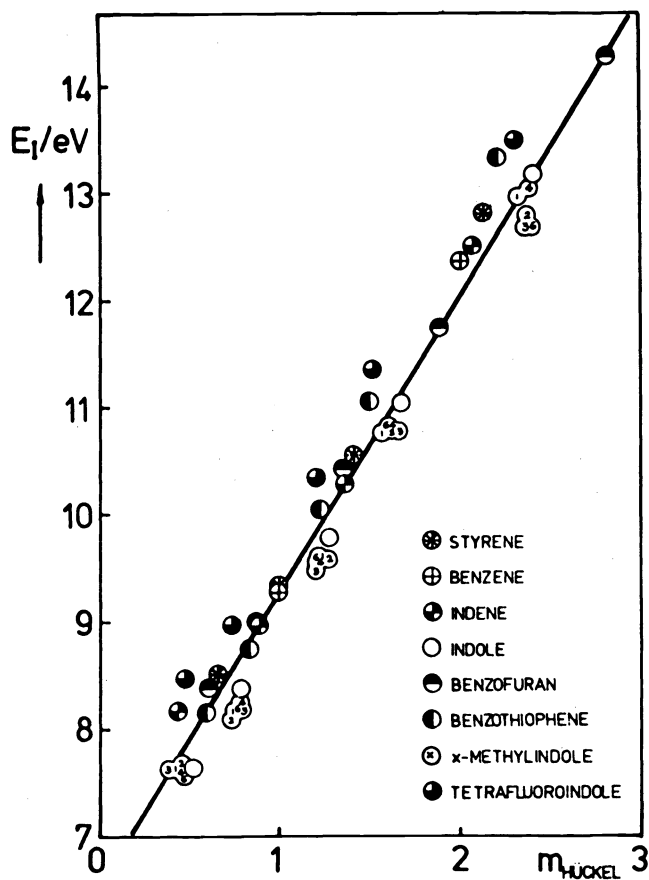numbers trying to make it quantitative.

Fig. 10. Least-square regression of the observed π-ionization energies vs. HMO calculation results for indene analogs.

Legend:
⊛ STYRENE
⊕ BENZENE
◐ INDENE
○ INDOLE
⊖ BENZOFURAN
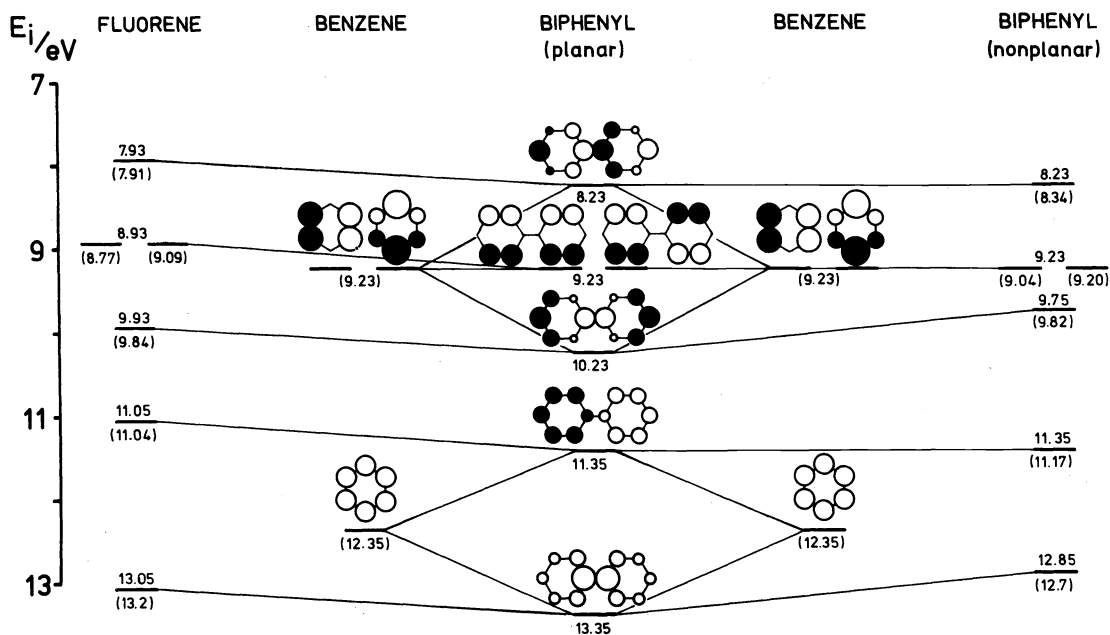◑ BENZOTHIOPHENE
⊗ x-METHYLINDOLE
◕ TETRAFLUOROINDOLE

Fig. 11. Schematic representation of the π-ionization energies in eV calculated by the matrix method for biphenyl and fluorene. Experimental data are indicated in parentheses.
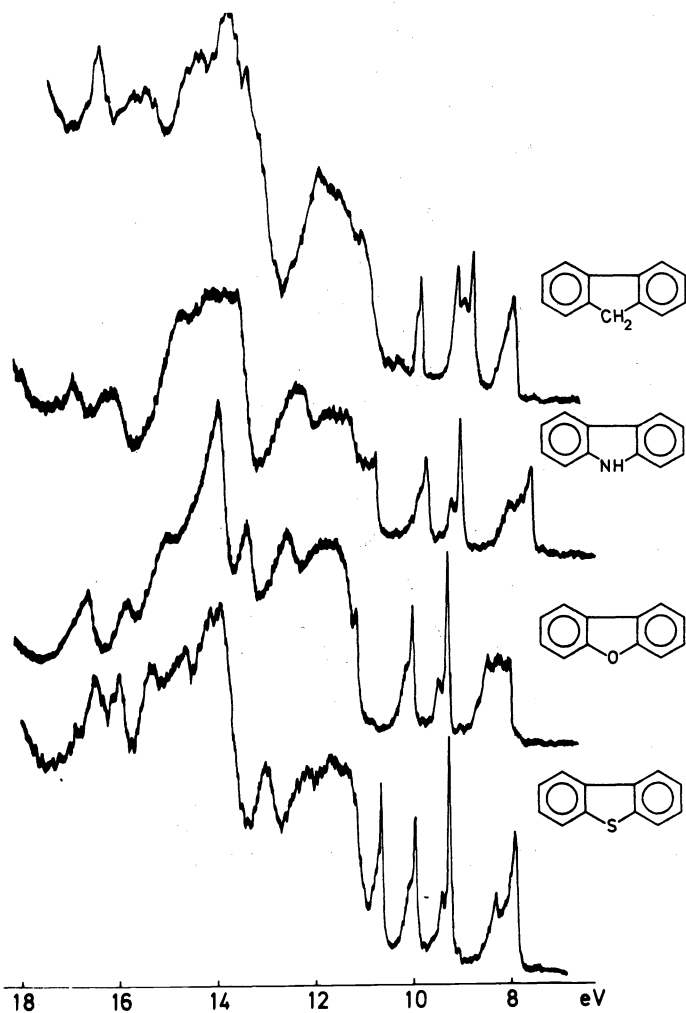
Fig. 12. HeI photoelectron spectra of
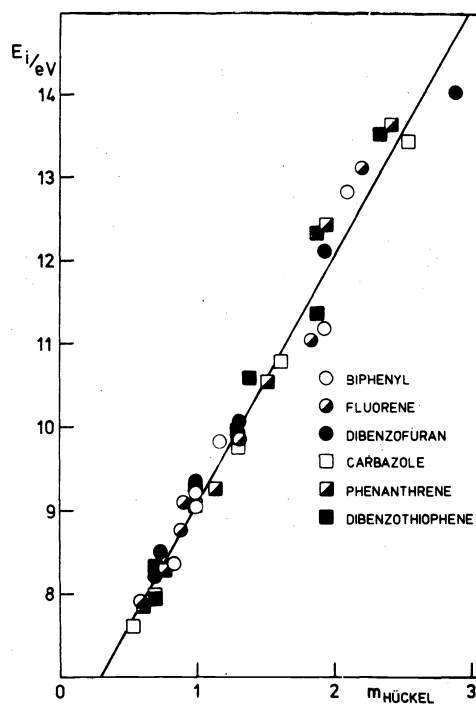fluorene, carbazole, dibenzofuran and
dibenzothiophene.

Fig. 13. Least-square regression of the
π-ionization energies assigned vs.
results of HMO calculations for fluorene
analogues.

Fig. 14. HeI photoelectron
spectra of 5H-dibenzo(a,d)-
cycloheptene, <u>cis</u>-stilbene,
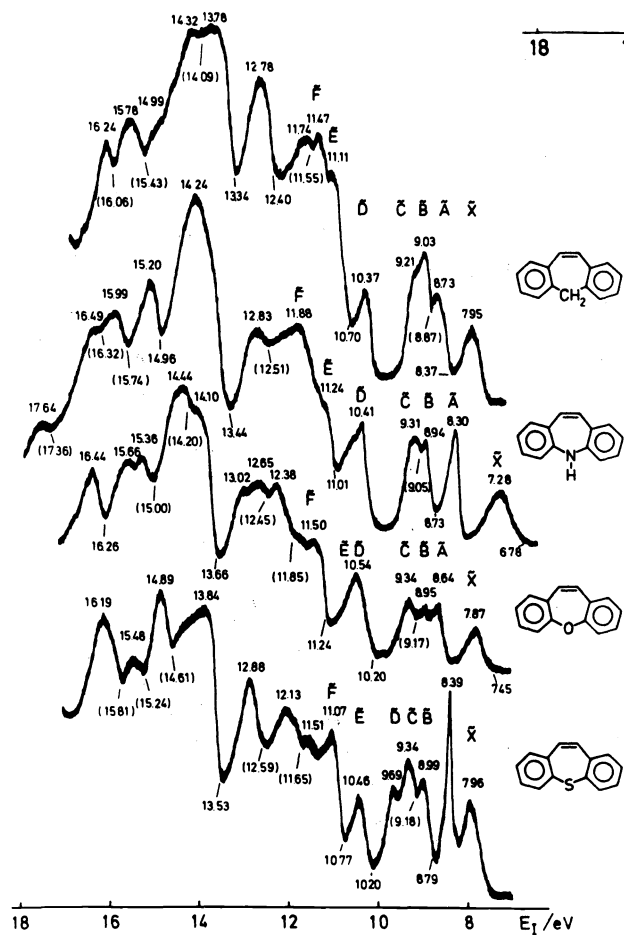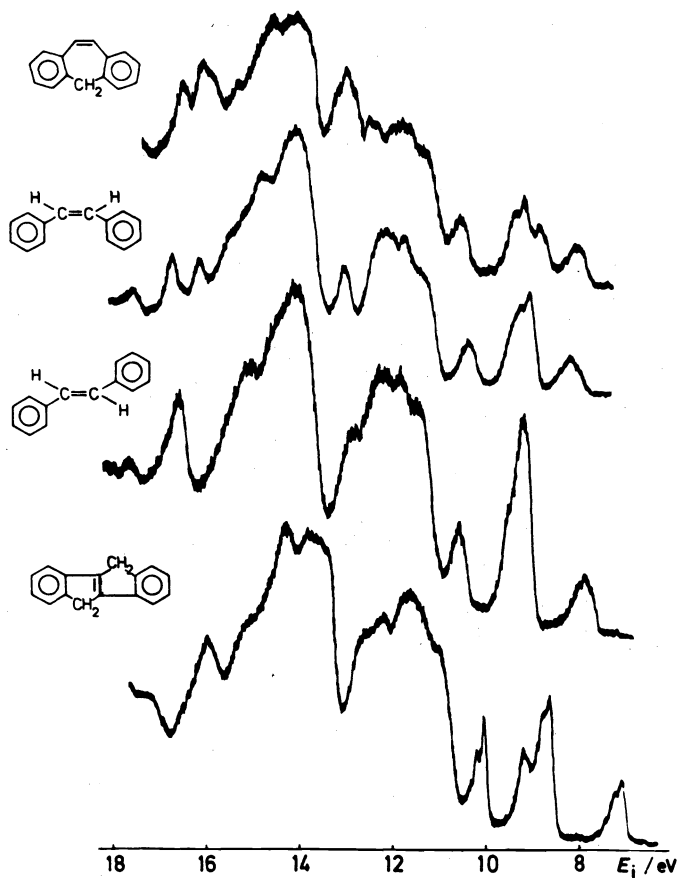<u>trans</u>-stilbene and diindene
(top to bottom).

Fig. 15. HeI photoelectron
spectra of 5H-dibenzo(a,d)-
cycloheptene analogues.

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