

PHOTOELECTRON SPECTRA OF ACENES. ELECTRONIC STRUCTURE AND SUBSTITUENT EFFECTS

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Abstract - The valence-electronic structure of the first three members of the acene series, benzene, naphthalene and anthracene, seems to be confirmed now by their photoelectron (PE) spectra. This especially holds for the π -ionizations which, according to their specific behaviour, can be assigned to different ionization modes. The vibrational fine structure of the observed systems is discussed. The effects of a series of substituents on the electronic structure of the parent molecules were traced in their PE spectra and intercompared. The results for methyl, chloro, methoxy and cyano substitution are described in detail. The effect is most pronounced for the two lowest energy π -ionizations (i.e. HOMO and SHOMO in the Koopmans' picture) and can be described by the shift of the mean energy ("center of gravity") of HOMO and SHOMO, and the additional splitting compared to the unsubstituted molecule. Both parameters show good linear dependence for the three series of compounds, thus allowing to formulate general substituent parameters. A linear dependence of the lowest ionization energy with Hammett constants is found to exist as well.

INTRODUCTION

Acenes are a series of molecules whose properties often can be described as a monotonic function of the number of benzene rings, e.g. the similarities in position and intensity of bands in electronic spectra (1,2), first ionization energy (3), electron affinity (4-7), as well as reduction and oxidation potentials (8-10). It is known that these properties depend mainly on the characteristics of the outer, occupied and unoccupied, molecular orbitals, rather than on the total electronic configuration. Ionization energies of the valence electrons measured by molecular photoelectron (PE) spectroscopy provides, within the limitations of Koopmans' theorem, a valuable method for the determination of energies of the outer occupied molecular orbitals. In combination with quantum chemical calculations other characteristics as symmetry, space distribution and "origin" are obtained, all of them yielding a picture which is usually described as the electronic structure of a molecule. In this study the electronic structures of a number of monosubstituted benzenes, naphthalenes and meso-substituted anthracenes are compared with that of the non-substituted parent molecules in order to determine common effects of substituents which would enable to predict these effects in a quantitative way. Such an approach has been used several times as yet, but these studies have concerned mainly the effect of substituents on one of the molecules mentioned above. Pioneer work in the comparison of these effects can be found in the approach of Heilbronner (11) who indicated the parallelism of substituent effects on certain energy levels of benzene, naphthalene and anthracene. However, it is important to notice that until recently even the location of all π -ionizations in the PE spectra of naphthalene and anthracene was based mainly on considerably diverging calculations and thus was rather uncertain. Now consistent experimental evidence exists for the assignment of π -ionizations which certainly is necessary to rely on such correlations and makes the intended comparison more than worthwhile.

EXPERIMENTAL

Compounds: All compounds were of high purity, redistilled or recrystallized before use and checked by mass spectrometry. The 9-I- and 9-CF₃-anthracene were synthesized by Dr. M. Mintas.

PE spectra: All spectra were recorded on a Vacuum Generators UV-G3 spectrometer (12) using HeI (FWHM of ~ 35 meV and ~ 15 meV for fine structure determinations) and HeII (FWHM of ~ 50 meV) excitation. The inlet system was heated if necessary and the spectra calibrated by addition of argon and xenon to the sample gas flow.

Calculations: Standard PPP calculations of the π -electron levels were performed for most of the compounds. The correlation with assigned lower π -ionizations up to 15 eV is reasonably good.

RESULTS AND DISCUSSION

ELECTRONIC STRUCTURE OF THE PARENT MOLECULES: BENZENE, NAPHTHALENE AND ANTHRACENE

For the first three members of the acene series, benzene, naphthalene and anthracene, the valence electronic structure can now be considered as well established; different techniques of obtaining their PE spectra were of great help in the assignment. Thus, a comparison of HeI and HeII spectra (fig. 1) shows that cross sections of π -ionizations are relatively enhanced under HeII radiation (13,14). On the other hand, in the perfluorinated derivatives π -ionizations change their energy much less than σ -ionizations which are shifted to higher energy by 2-3 eV (15).

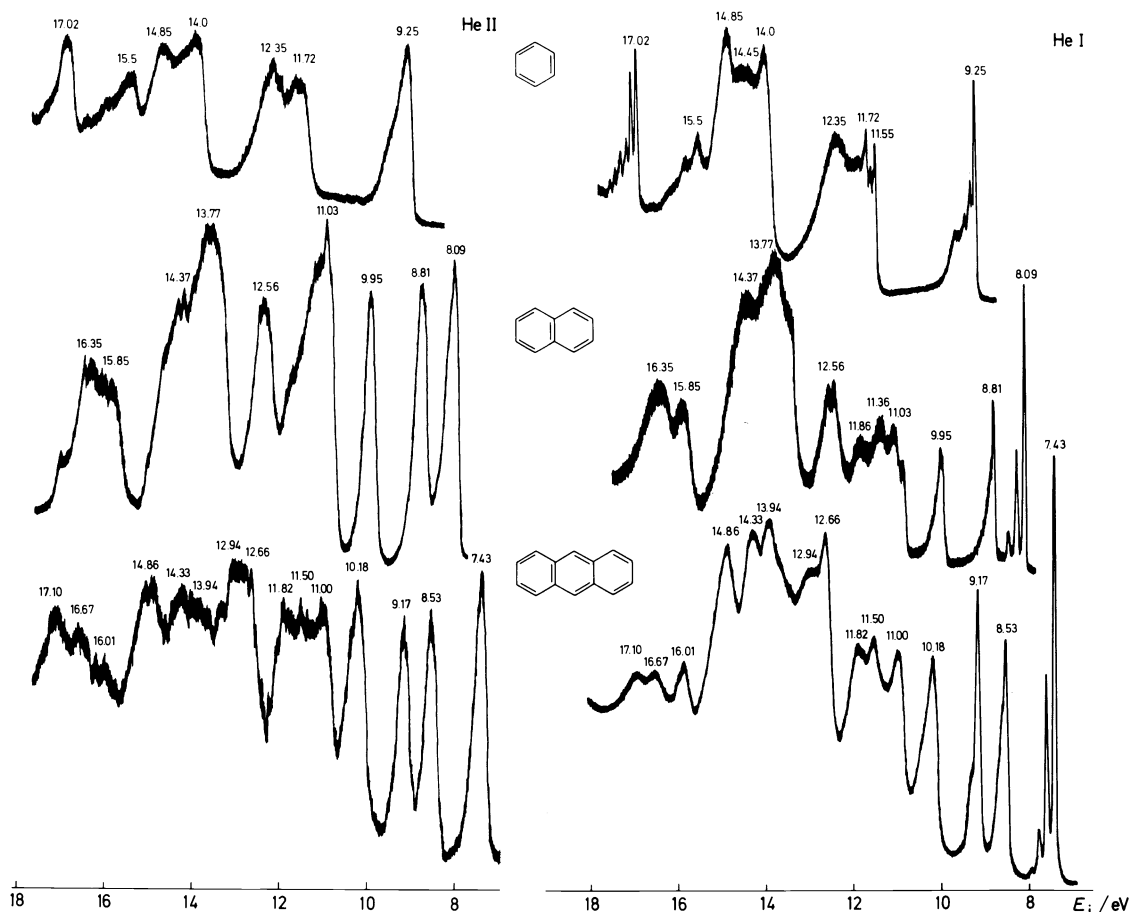
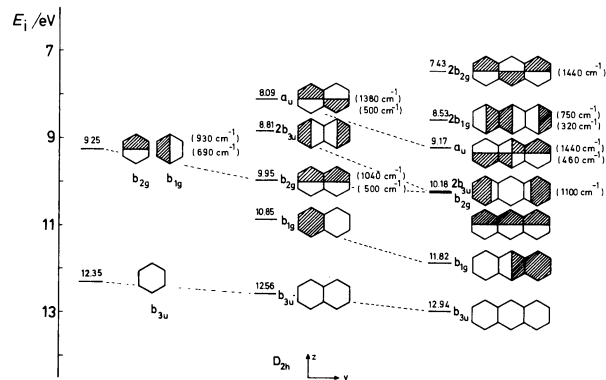


Fig. 1. HeI and HeII photoelectron spectra of benzene, naphthalene and anthracene

Especially under Penning ionization the π -ionizations observed are pronounced (16). All this in combination with quantum chemical calculations yielded the following π -electronic structures (fig. 2); the listed energies correspond to vertical ionizations and the wave numbers to observed vibrational modes.

Fig. 2. Correlation of π -systems of benzene, naphthalene and anthracene



The vibrations can be classified into four groups (17): (i) Kekulé type CC-stretchings of about 1400 cm^{-1} , (ii) in phase ring breathing ($700\text{--}750\text{ cm}^{-1}$) with CC bonds along the short axis of the molecule shortening at the same time, (iii) out of phase ring breathing (1000 cm^{-1}) where this shortening shortening alternately and (iv) vibrations which include CCC-bending and CC-stretching along the long axis and are therefore strongly dependent on the number of rings (500 cm^{-1} in naphthalene, 390 cm^{-1} in anthracene). It would follow that Kekulé type vibrations are excited only in the highest MO's with nodal plane along the short and long axes, that breathing is found in systems where the corresponding MO has no nodal plane parallel to the short axis and that bending with stretching is excited when the electron comes from an orbital with a smaller number of nodal planes parallel to the short axis. Thus, in the X systems of naphthalene and anthracene, very intensive 0-0 transitions of Kekulé type vibrations are observed. The vibration of the molecules along the longer axes with wave numbers of 500 cm^{-1} in naphthalene and 480 cm^{-1} in anthracene are seen only as asymmetry of the Franck-Condon (FC) envelopes. The same two vibrations are found in the system of anthracene, but here bending with stretching is more pronounced and FC envelopes of 0-0 and 1-0 transitions become diffuse since the 1-0 transition nearly coincides with the 0-0 transitions. Such an explanation is in agreement with that given by Ohno (17). However, the present description of the vibrational structure of the B system of naphthalene and A system of anthracene differs from that of Ohno which on the basis of calculated FC factors were attributed to long axis bending and ring breathing, respectively. Our high resolution spectra indicate in the A system of anthracene

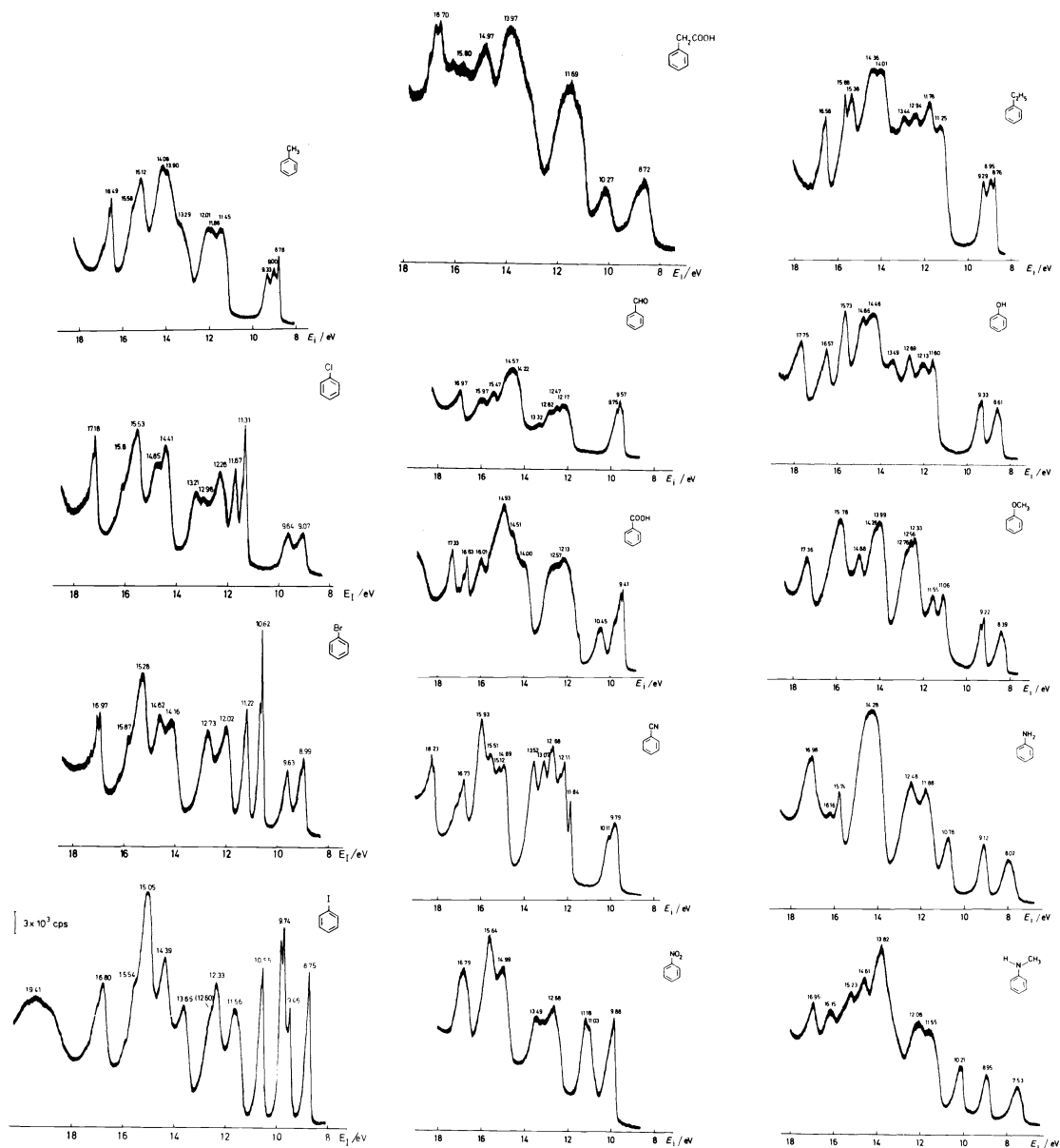


Fig. 3. HeI photoelectron spectra of monosubstituted benzenes

progressions of 750 cm^{-1} (Fig. 2) and, unexpectedly with the assumed character of the corresponding orbital, also progressions of 320 cm^{-1} . Similarly, in the B system of naphthalene, besides the expected bending along the y -axis, also ring breathing is observed which for reasons of orbital symmetry, is conform with ionizations from $2b_{3u}$ and b_{1g} orbitals rather than from the b_{2g} orbital corresponding in the B system. This "incompleteness" of the molecular orbital description is presumably also the reason why no fine structure is observed in the A system of naphthalene. This system is very diffuse and progressions are undiscernible which indicates possible mixing with σ -systems and excitation of a greater number of vibrational modes.

ELECTRONIC STRUCTURE OF SUBSTITUTED MOLECULES

In this study PE spectra of fourteen monosubstituted benzenes, twelve 1-substituted naphthalenes, ten 2-substituted naphthalenes and ten 9-substituted anthracenes with Me, Et, *t*-Bu, F, Cl, Br, I, OH, OMe, NH_2 , HNMe, NMe₂, CHO, COMe, COOH, CH_2OH , CF_3 , CN and NO_2 as substituents were recorded and investigated. Most of the low resolution HeI PE spectra are reproduced in Figs. 3-6. The number on the top of the observed systems correspond to vertical ionization energies, E_i , expressed in eV. The number of compounds is so great that it is impossible to discuss all of them in detail, but this will be done with some representative substituents such as methyl, chloro, methoxy and cyano groups for which also all four compounds were investigated. The other substituents will be used to find out whether some general rules can describe their effects on the electronic structures of the parent compound.

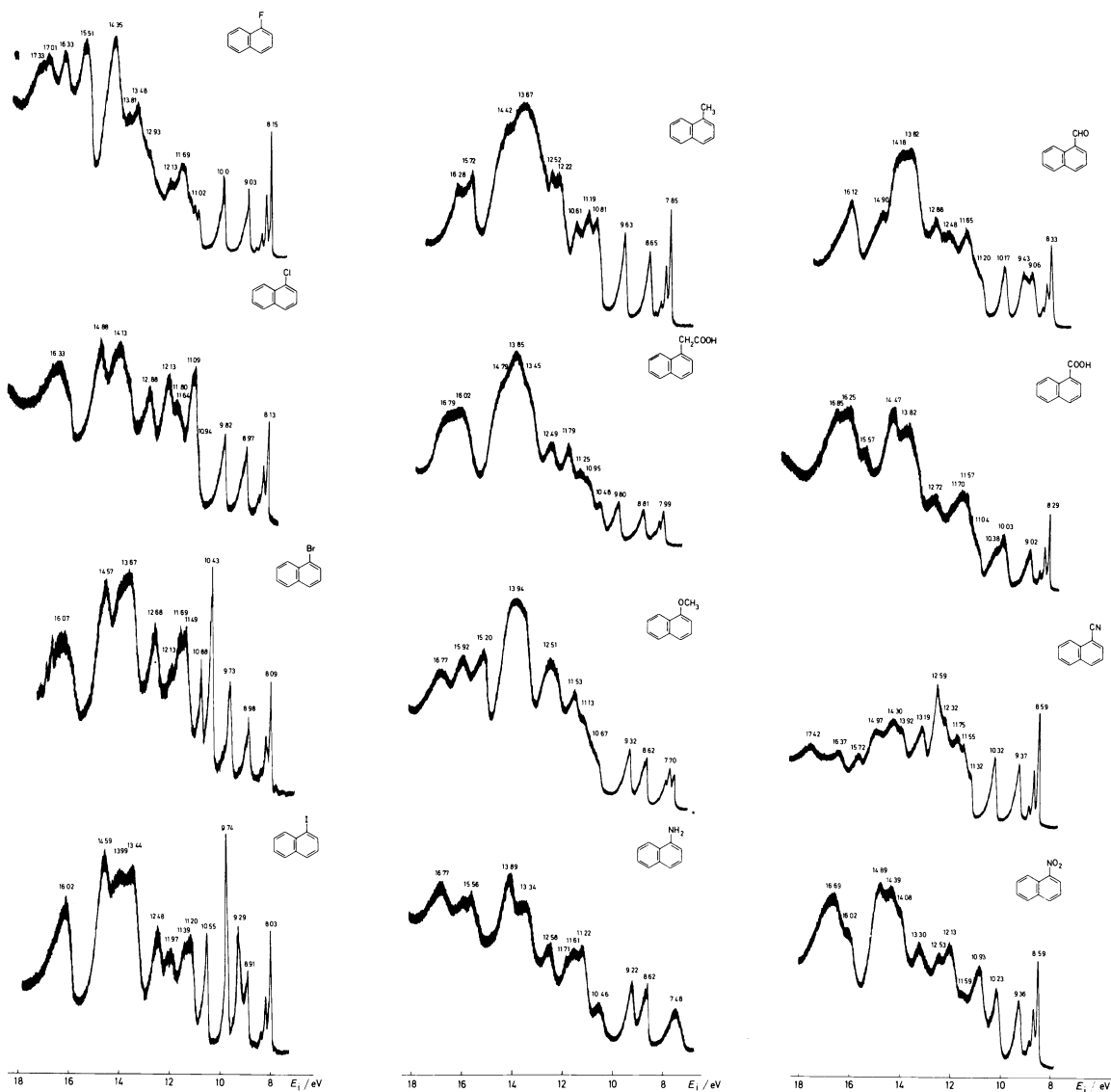


Fig. 4. HeI photoelectron spectra of 1-substituted naphthalenes

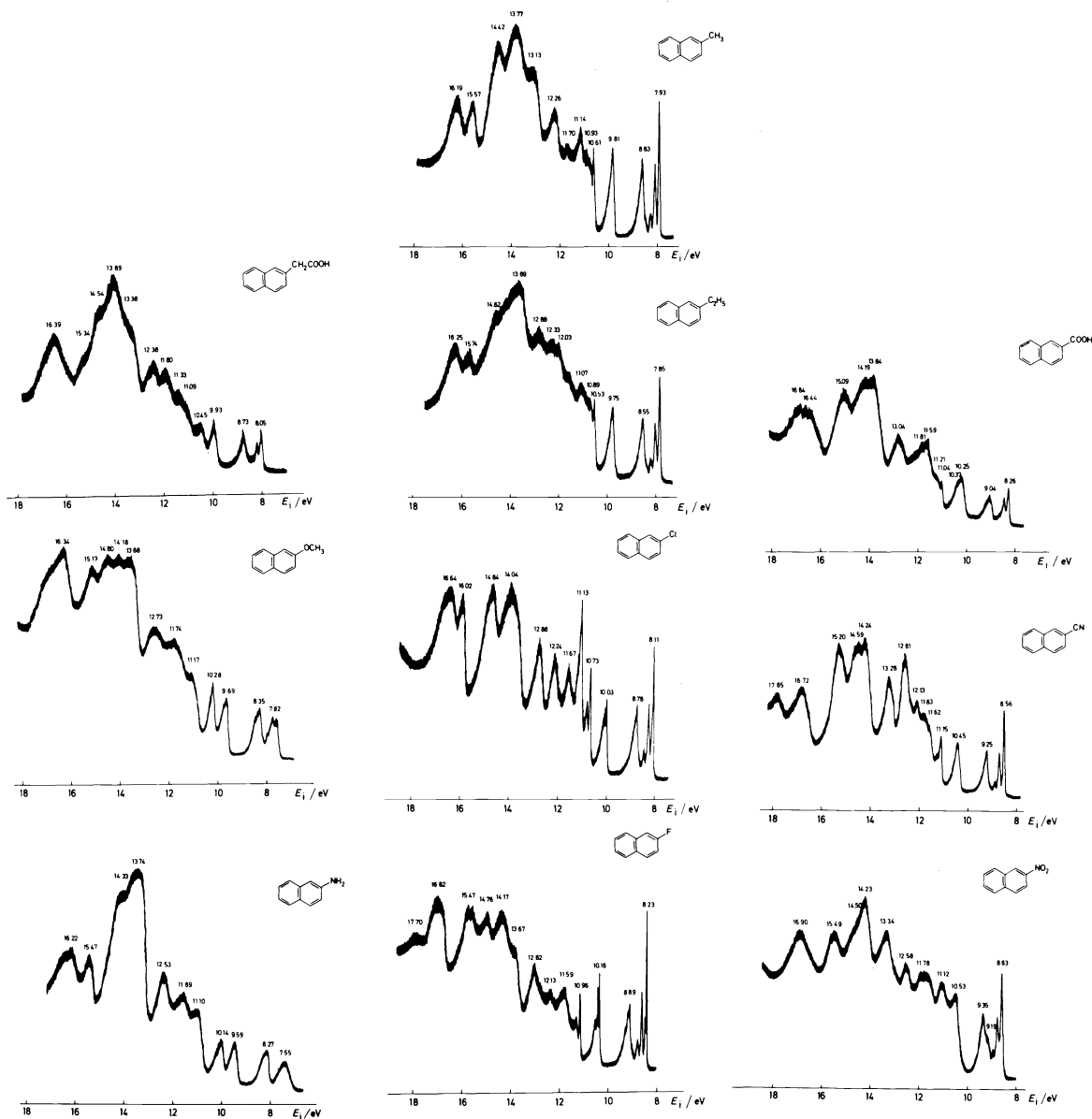


Fig. 5. Photoelectron spectra of 2-substituted naphthalenes

Methyl- and chloro-substitution

Both, methyl and chloro substitution can be considered as a weak interaction with the π -electron levels of the parent compounds, although for different reasons. In the case of methyl (fig. 7) which, as is well known, destabilizes π -ionizations, this is caused by the much higher energy of the interacting methyl orbital, whereas in chloro substitution (fig. 8) the $3p$ electron pairs of the chloro atom have too low an electron density in the space important for the interaction. Chlorobenzene is a nice example for the description of the interaction of the electrons, especially those of in-plane and out-of-plane lone pair orbitals, of the substituent with the electronic structure of the parent molecule. The assignment is presented in a diagram (fig. 8) correlating the experimental ionization energies of chlorobenzene, chlorine and benzene and showing the approximate shape of the corresponding orbitals as obtained from the MO coefficients (18, 19). Systems X and A correspond to ionizations from π -orbitals obtained by lifting the degeneracy of the e_{1g} benzene orbital. The splitting in chlorobenzene (0.57 eV) compares with the related values for fluorobenzene (0.44 eV), and bromobenzene (0.64 eV) and iodobenzene (0.71 eV) and can be qualitatively explained by the energy difference of the interacting orbitals, i.e. benzene e_{1g} and halogen p orbital. Systems B and C correspond to ionization from the in-plane ($9b_2$) and out-of-plane ($3b_1$) lone pairs of chlorine which are split by 0.36 eV as a result of different interactions with benzene orbitals. The out-of-plane lone pair is destabilized by antibonding interaction with the $1a_{2u}$ benzene orbital, although this is an additional, but weaker bonding interaction with the b_1 component of the $1e_{1g}$ benzene orbital. The in-plane is destabilized by a series of antibonding interactions with benzene σ -orbitals, whereby the strongest being with the b_2 component of $3e_{2g}$, a somewhat weaker interaction with the b_2 of $3e_{1u}$ and the weakest with $1b_{2u}$.

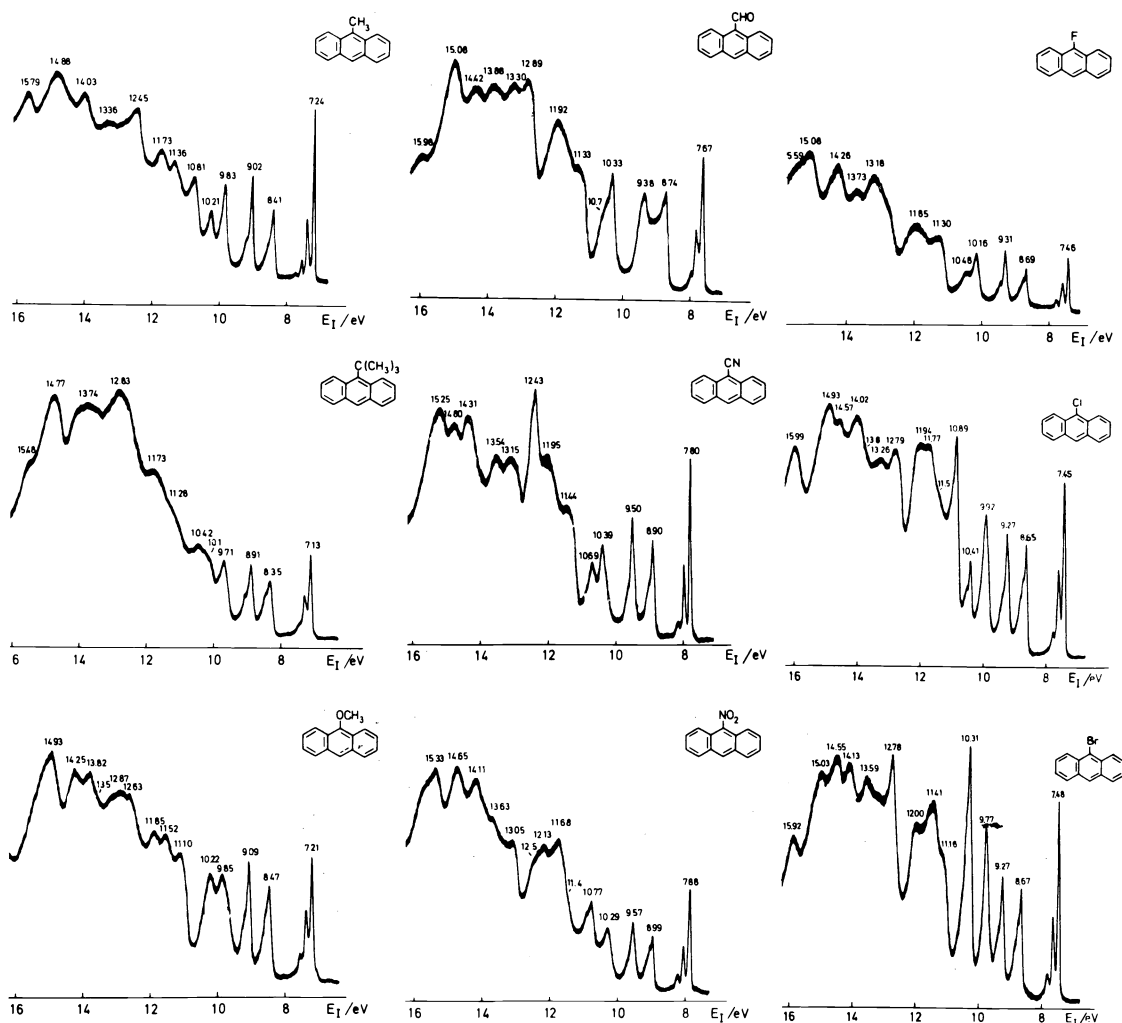
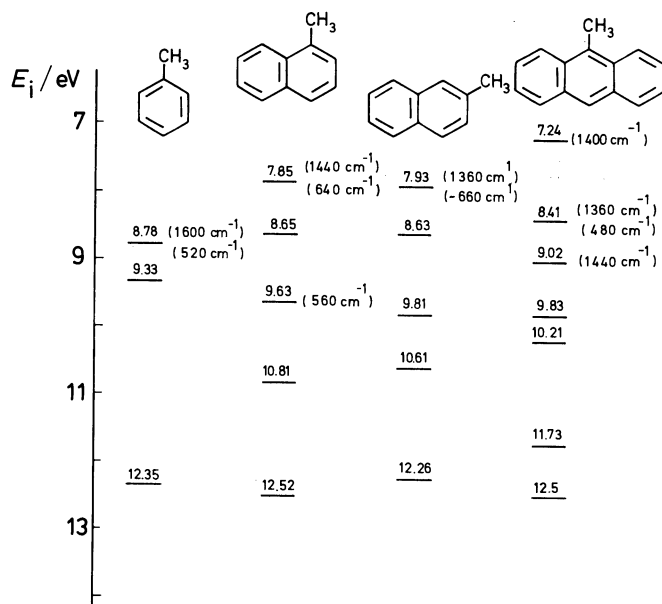
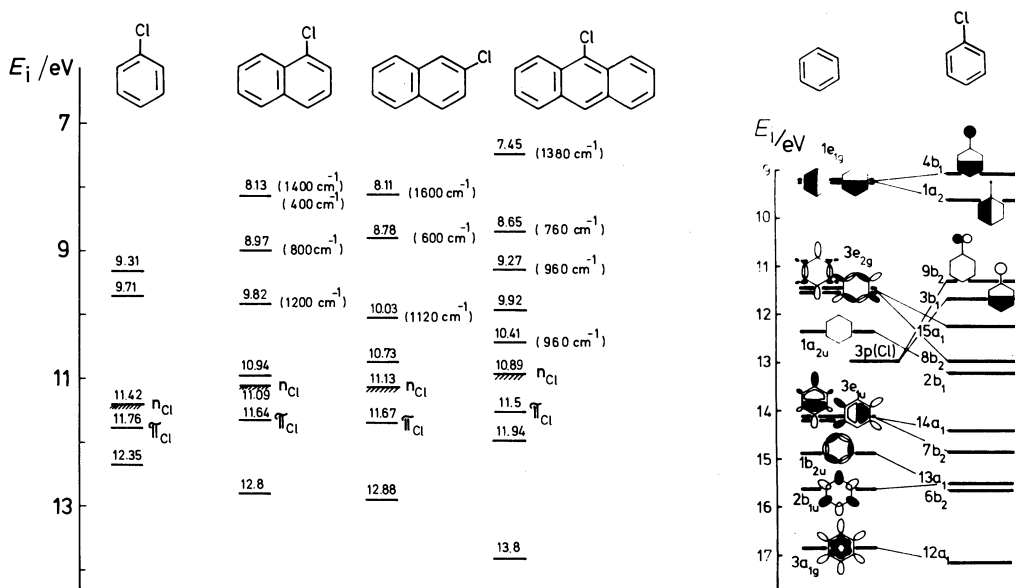


Fig. 6. HeI photoelectron spectra of 9-substituted anthracenes

This explains why the in-plane chlorine lone pair is more destabilized than the out-of-plane one. Such an assignment of B and C systems also suggested by *ab initio* results (19), is supported by the emission spectra of chlorobenzene radical cation (20) where no B-X transition is observed.

A measurement of system areas in HeI and HeII spectra of chlorobenzenes provides additional evidence for this assignment since the relative intensity of the B system in going from HeI to HeII excitation is reduced to less than a half, while the C system retains about the same relative intensity. The F system at 13.21 eV corresponds to the ionization of the lowest π -orbital ($2b_1$) in agreement with the PE spectra of higher substituted chlorobenzenes (19), earlier investigations (21,22) and *ab initio* results (19). Its stabilization by 0.86 eV as compared to the parent benzene $1a_{2u}$ orbital is due to bonding interaction with the energetically near chlorine $3p$ orbital. The $3e_{2g}$ and $3e_{1u}$ benzene orbitals yield in chlorobenzene two pairs of orbitals, $15a_1$ and $8b_2$, and $14a_1$ and $7b_2$, respectively. The stabilization of a_1 can be explained by the fact that the $3p$ chlorine orbital taking the role of the $1s$ hydrogen orbital increasing the overlap with the carbon $2p$ orbital. This type of interaction is not very strong and rapidly decreases with the energy difference between the interacting orbitals, as can be seen for the $12a_1$ orbital, which has nearly the same energy as the parent $3a_1$ orbital of benzene. Where symmetry allows it, ring σ -orbitals enter into a much stronger interaction with in-plane chlorine lone pair and this interaction accounts for the strong stabilization of $8b_2$ and destabilization of $9b_2$. The same holds for $7b_2$ and $6b_2$ orbitals, although their stabilization is weaker because of the greater energy difference between chlorine $3p$ and parent benzene orbitals.

Fig. 7. Correlation diagram of π -systems in methyl substituted acenesFig. 8. Correlation diagram of π -systems and chlorine lone pair ionizations in chloro substituted acenes (left) and of benzene and chlorobenzene (right)

Methoxy substitution

The methoxy group here constitutes an example of an electron donating substituent. The influence of a methoxy group on benzene π -ionizations was explained already by Maier and Turner (23). As indicated in the correlation diagram on fig. 9 starting from phenol, its PE spectrum is, as expected, destabilized by the methyl group, i.e., going to anisole. In the naphthalene derivatives, in agreement with Bock et al. (24), again the greater splitting of lowest energy ionizations in the 1-compound and the greater stabilization of the next ionization in the 2-compound is observed. The system corresponding mainly to the oxygen lone pair ionization is steadily destabilized towards anthracene in this series. In accordance with its electron donating properties the overall effect of the substituent is to destabilize the low energy systems in the substituted molecules. The lowering of the first E_i , the broadening of this system in the spectra and its vibrational structure with pronounced 1-0 transition

indicate, in agreement with Bock *et al.* (24), substantial mixing with the oxygen lone pair electrons.

Cyano substitution

The effect of the cyano group, known as a strong electron withdrawing substituent stabilizing the π -levels of the parent molecule, has been already studied for cyanobenzene (25), 1- and 2-cyanonaphthalenes (26) and 9-cyanoanthracene (27), as well. The correlation of observed ionizations in terms of electronic structure of these compounds is shown in fig. 9. The stabilizing effect is well pronounced. As in previous cases, the splitting of the lowest energy levels in 2-cyanonaphthalene is smaller than in 1-cyanonaphthalene, whereas the next system is more stabilized in the former. The inversion of the two π -systems while going from cyanobenzene over 1-cyanonaphthalene towards 2-cyanonaphthalene is indicated by calculations.

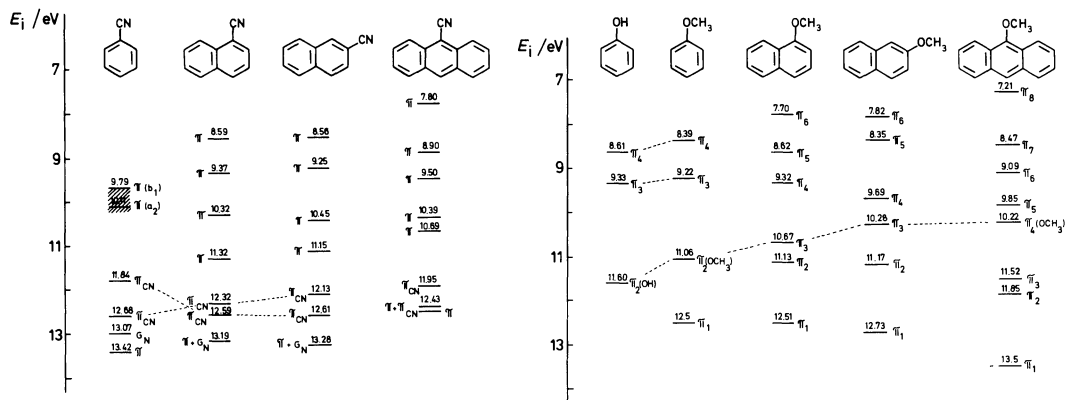


Fig. 9. Correlation diagram of π -systems in phenol and substituted methoxy acenes (right) as well as in cyano substituted acenes (left)

COMMON SUBSTITUENT EFFECTS

The few examples presented above indicate that there are effects on the electronic structure of the parent acene molecule which could serve to formulate the influence of the substituent more generally. Most of the electronic systems in the spectra of substituted molecules can easily be recognized to correspond either to ionizations from perturbed orbitals of the parent molecules or to the new ones from electron pair(s) of the substituent. There are only a few cases of systems, occurring in the region where the interacting orbitals are very close in energy ($E_i > 10$ eV), for which above qualitative assignment is impossible, due to substantial mixing of these two "types" of ionizations (28). Therefore, low energy ionizations ($E_i < 10$ eV) seem to be best suited for tracing of substituent effects. Besides for monosubstituted benzenes, 1-substituted naphthalenes and 9-substituted anthracenes, the two lowest energy ionizations corresponding in the Koopmans' picture to removal of electrons from the highest occupied and the second highest occupied molecular orbitals (HOMO and SHOMO), are especially interesting. Their nodal properties are such (fig. 2) that one of them has a maximum of electron density at the position of substitution, whereas the other has a node there, and, consequently, should be insensitive to the substituent. However, the PE spectra show that electron donating substituents destabilize and electron withdrawing substituents stabilize both of these orbitals. This finding reflects the already discussed observation of types of vibration in the corresponding electron systems. Let such a pair of orbitals be discussed as an entity. Thus, for the unsubstituted molecules two parameters can be defined: their mean energy ("Center of gravity") and their splitting. The corresponding values are 9.25, 8.45 and 7.98 eV for the mean energy, and zero, 0.72 and 1.10 eV for the splitting in benzene, naphthalene, and anthracene, respectively. On substitution, the center of gravity can be shifted to lower or higher values, whereas all the splittings become greater. These mean energies for substituted benzenes are linearly correlated with those of 1-naphthalenes ($r^2 = 0.95$) and 9-anthracenes ($r^2 = 0.92$). The same holds for the splittings. Moreover, the different slopes for the energy shifts (1 : 0.66 : 0.49) are inversely proportional to the number of carbon atoms in the parent molecule, whereas the slopes of the splittings (1 : 0.4 : 0.2) are proportional to the inverse square. On the other hand, as also found earlier (29-31), a surprisingly good correlation of the lowest ionization energies of the investigated compounds exists with Hammett σ_p values, or in the case of 2-naphthalenes with $(\sigma_m + \sigma_p)$ values (fig. 10). The observed slopes for these correlations, in agreement with the second order perturbation theory, are roughly proportional to the square of the HOMO coefficient of the parent acene at the position of substitution. Above results suggest that the effect of substituents is transferable within the acene series.

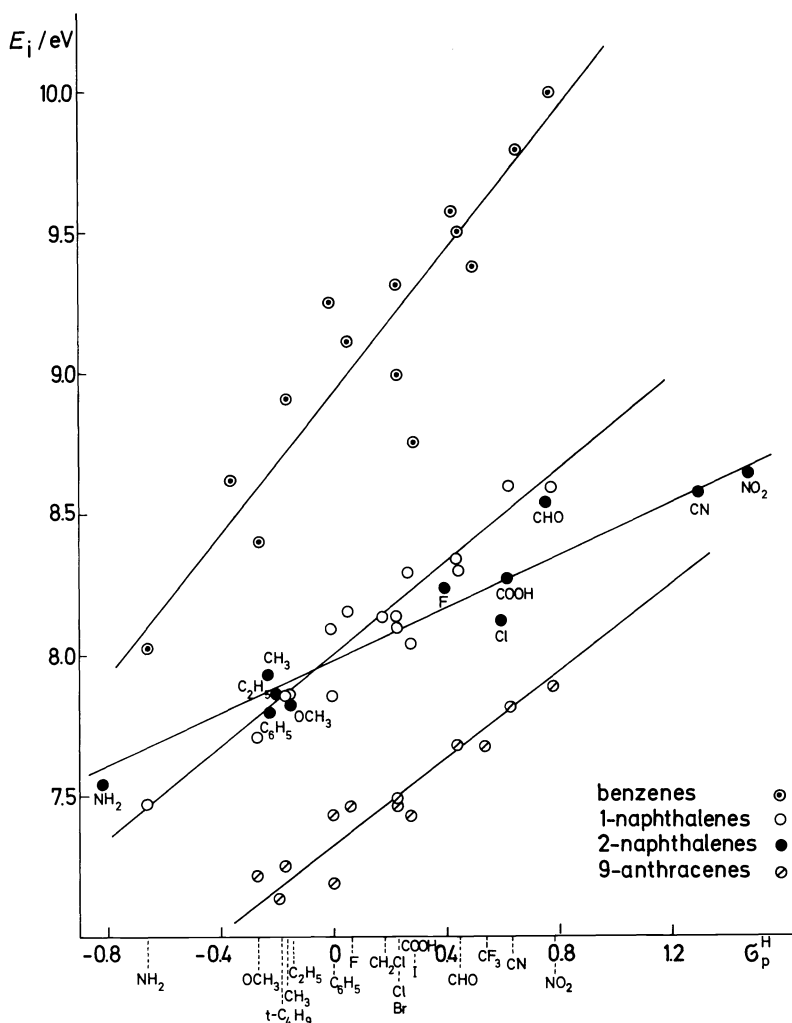


Fig. 10. Correlations of lowest ionization energies with Hammett's σ_{p^-} and $(\sigma_p + \sigma_m)$ -values (●) for substituted acenes.

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