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CORRELATIONS BETWEEN PHOTOELECTRON AND ULTRAVIOLET ABSORPTION SPECTRA OF POLYCYCLIC HYDROCARBONS AND THE NUMBER OF AROMATIC SEXTETS

E. CLAR*
Department of Chemistry, University of Glasgow, Glasgow W.2, Scotland

and

W. SCHMIDT
Institut für Organische Chemie der Universität, Karlstr.23, D-8 München-2, Germany

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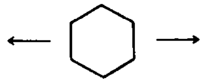
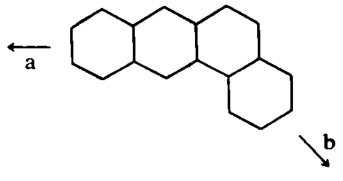
Abstract—Comparison of the β- and p-bands in the visible and UV absorption spectra with the first IP's obtained from the photoelectron spectra shows that only the p-bands are related to the latter. This allows the determination of the upper level of the p-bands which are near to $R/4 = 3{\cdot}4$ eV, where R is the IP of the H atom. Deviations from this value can be related to the number of aromatic sextets in polycyclic systems; these are also important for the ground states. The α- and β-bands are related to photoelectron bands with higher IP's which have no clear vibrational structure. The upper level of the α- and β-bands is very near to 4·9 eV which is the vertical IP of graphite. The asymmetric annellation effects reported in earlier work and observed when diphenyl or styrene complexes are fused to an acene, beginning with benzene, are confirmed independently. In the series acene, 1:2-benzacene and 1:2, 3:4-dibenzacene, the annellation effects are asymmetric for the β-bands but symmetric for the p-bands and the first IP's.

In order to begin with a correlation of visible and UV absorption bands it is necessary to base it on a reliable classification scheme. The first classification of bands in different series of polycyclic hydrocarbons was based on the annellation effect, i.e. the shift of the bands observed when benzene rings are fused together in different directions.[1-5]

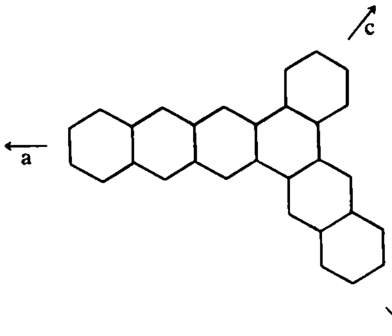
1. *The acene series.* There the annellation effect is very pronounced for the p-bands but smaller for the α- and β-bands. With an increasing number of rings strong shifts towards the red are observed for the p-bands, the shifts being constant in $\sqrt{\text{Å}}$. The shifts of the α- and β-bands are also constant but smaller which causes the less intense α-bands to become hidden behind the more intense p-bands in anthracene and tetracene.



2. *The phene series.* There are similar strong shifts towards the red of the α- and β-bands for each additional ring in this series as in the acenes. They are of the same magnitude for both annellation directions a and b. However, the red shift of the p-bands depends entirely on the number of benzene rings in the longest branch a of a phene, whilst annellation to the shorter branch b produces small violet shifts. As far as the p-bands are concerned, aromatic conjugation appears to be limited to the longest branch a, whilst there is participation of both branches a and b in conjugation for the α- and β-bands.



3. *The starphene series.* Here, as in the phene series, the two longest branches a and b are in aromatic conjugation and determine the position of the α- and β-bands. However, the third branch c is ineffective in that respect and produces mostly very small violet shifts. As in the phene series only the longest branch a counts for the position of the p-bands, the branches b and c causing very small shifts towards the violet. Neither for the p-bands nor for the α- and β-bands the third branch c appears to be in aromatic conjugation with the other branches a and b.



Keeping these simple rules in mind one can compare the visible and UV spectra with the photoelectron spectra and establish their relation. Mistakes as with the use of the molecular axes and the polarization direction for the interpretation of the bands cannot occur.[6-9]

The lowest ionization potentials (IP's) of a number of kata-annellated hydrocarbons, as obtained from the first band of their photoelectron spectra,[10] are presented in

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*Address correspondence to this author at: Punta Chullera Km 144, Estepona, Prov. Malaga, Spain.

Fig. 1 and Table 1. These range between 9·24 eV for benzene to 6·44 eV for hexacene. There are a number of simple rules to be derived from the comparison.

In the series of the simple benzene derivatives the IP's decrease from benzene (9·24 eV) to diphenyl (8·31 eV) and fluorene (8·15 eV). In the series of the hydrocarbons with not more than two linearly annellated rings the IP's depend on the number of aromatic sextets which can be written into systems with the same number of rings. This results in the sequence: naphthalene (1 sextet, 8·15 eV), phenanthrene (2 sextets, 7·86 eV), triphenylene (3 sextets, 7·89 eV). According to the above annellation rule No. 3, the latter has three branches one of which must be ineffective, so that triphenylene has practically the same IP as phenanthrene. Chrysene and 3:4-benzophenanthrene have both two sextets in four rings. Their IP's, 7·60 and 7·60 eV, are therefore approximately equal. A remarkable low IP is reached with dibenzochrysene (7·26 eV) in which four sextets are in six rings, whilst in the isomeric hexacene one sextet is shared between six rings. This causes the IP to fall to 6·44 eV.

In the series with not more than three linearly annellated rings (anthracene type) the lowest IP's are practically the same from anthracene to tetrabenzanthracene, namely about 7·4–7·5 eV. This is an amazing result if the very different reactivities of these hydrocarbons are considered.

The same observation can be made in the tetracene series. The six benzologues up to tetrabenzotetracene have IP's which are all near 7·0 eV. In the pentacene series the benzologues up to tetrabenzopentacene have all IP's close to 6·7 eV. As far as the hexacene series is concerned, only the parent hydrocarbon (IP 6·44 eV) and 1:2-benzohexacene have been synthesized. The latter decomposed too quickly in the gas phase so that its PE spectrum could not be measured.

By extrapolation one would expect the first heptacene band to come at about 6·2 eV. We had hoped to generate heptacene directly in the ionization chamber of the spectrometer, using suitable precursors such as 5,18-dihydroheptacene, 6,17-dihydroheptacene 6,17,8,15-tetrahydroheptacene and 5,18,7,16,9,14-hexahydroheptacene. All these compounds vaporized smoothly in the temperature range 290–360° and gave well resolved spectra, but there was no evidence for bands due to heptacene in the 6–6·7 eV region. On scanning the low-energy region at higher sensitivity, only the Heβ satellites of the first bands of the starting materials could be detected. Thus, it appears that the equilibrium between the hydroheptacenes and heptacene itself is strongly on the side of the former, or that the high temperatures required to vaporize the precursors seriously damage if not completely destroy any higher acene. It is clear that the possible identification of heptacene in the dehydrogenation products requires a flow system which we hope to build in the near future.

The relation of the lowest IP's with the visible and UV data is also shown in Fig. 1 and Table 1. The upper series of points is obtained by subtracting the energy of the p-bands, E_p, from the first IP's. The E_p values were mostly taken from the absorption spectra in solution which were corrected for the gaseous state as follows: solution in ethanol, methanol, hexane, cyclohexane plus 900 cm^{-1}, solution in benzene plus 1200 cm^{-1}, solution in methylnaphthalene plus 1500 cm^{-1}, solution in trichlorobenzene plus 1400 cm^{-1}. The points of the upper series at $\Delta p = IP - E_p$ are all located in the neighbourhood of $R/4 = 3{\cdot}4$ eV, which is the level of the first excited state of the hydrogen atom. In this context it must be remembered that this upper level for the p-bands has already been considered before for different reasons.[5]

Figure 1 makes it immediately clear that only the p-bands can be related to the first IP's. However, there are some highly significant deviations from the line at $R/4 = 3{\cdot}4$ eV. The upper level of the simple hydrocarbons benzene, diphenyl and fluorene, which contain benzene rings that are not in aromatic conjugation, are all slightly above this line. The other hydrocarbons beginning with naphthalene have upper levels which are below this line. Their levels approach this line gradually with annellation and with an increasing number of aromatic sextets (these are marked with cycles). Thus triphenylene, which is a fully benzenoid hydrocarbon having no π electrons or double bonds outside the sextets, has an upper level which is exactly at 3·4 eV. Other hydrocarbons with two sextets like phenanthrene, chrysene or 3:4-benzophenanthrene have upper levels only very little below the line whilst dibenzochrysene with four sextets comes very close to it.

As mentioned above, the first IP's of anthracene and its benzologues are very close together, namely at 7·5 eV. However, the upper levels, Δp, show bigger deviations from the line at 3·4 eV depending on the number of sextets. Thus, the upper level of the anthracenes approaches gradually the line at 3·4 eV, as shown by the following data: anthracene 4·05 eV, 1:2-benzanthracene 3·87 eV, 1:2,3:4-dibenzanthracene 3·78 eV, 1:2,5:6-dibenzanthracene 3·73 eV, 1:2,7:8-dibenzanthracene 3·75 eV, 1:2,3:4,5:6-tribenzanthracene 3·66 eV, and tetrabenzanthracene 3·58 eV.

This rule holds also in the tetracene series. Here again the number of sextets determines the extent to which the upper levels deviate from the line at 3·4 eV. These deviations are bigger than in the anthracene series because these hydrocarbons are less benzenoid, i.e. they have more π electrons which do not simultaneously belong to a sextet. However, the gradation of the Δp values is the same as in the anthracene series: tetracene 4·30 eV, 1:2-benzotetracene 4·11 eV, 1:2,3:4-dibenzotetracene 4·02 eV, 1:2,7:8-dibenzotetracene 4·04 eV, 1:2,3:4,7:8-tribenzotetracene 3·96 eV, and tetrabenzotetracene 3·95 eV. The latter, not being a fully benzenoid hydrocarbon, has a Δp value considerably below the line.

This trend is even more pronounced in the pentacene series: pentacene 4·44 eV, 1:2-benzopentacene 4·32 eV, 1:2,3:4-dibenzopentacene 4·22 eV, 1:2,8:9-dibenzopentacene 4·24 eV and tetrabenzopentacene 4·13 eV.

The biggest deviation is reached with hexacene where Δp is 4·46 eV. With a high degree of annellation and only one sextet in their system the Δp values of the polyacenes appear to approach the lower line at 4·9 eV which is the IP of graphite.[11]

The relation between the higher IP's and the α- and β-bands is represented in Fig. 2. It becomes immediately clear that the upper level for these bands must be 4·9 eV, the vertical IP of graphite. The upper levels are obtained from the differences $IP_\alpha - E_\alpha$ and $IP_\beta - E_\beta$, respectively. As could be expected, there are deviations, particularly for benzene. Its photoelectron spectrum shows no band which could be related to any α-band. This is also the case in the photoelectron spectrum of coronene.[12] Therefore the absence of these bands must be related to the symmetry of benzene and coronene. However there are

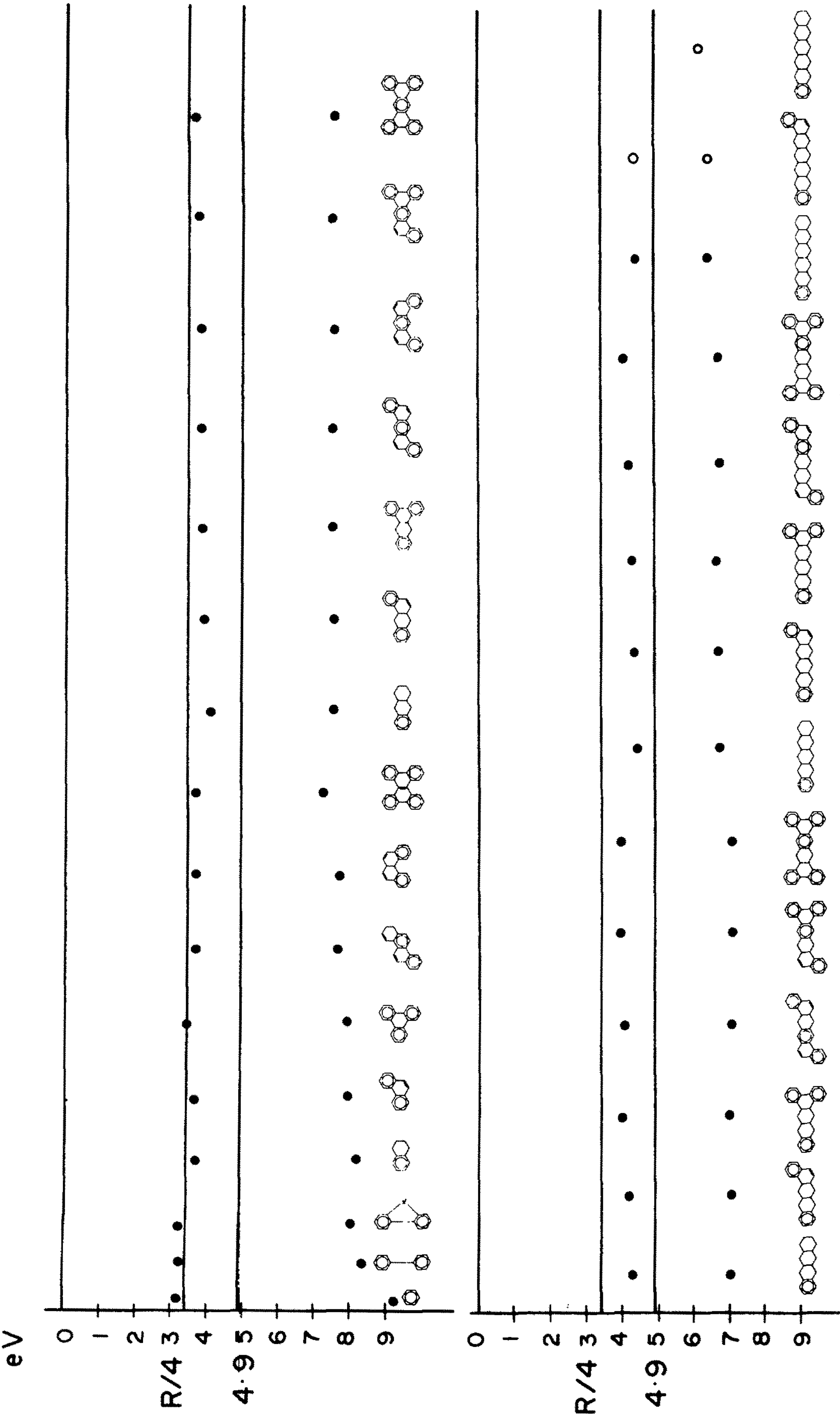


Fig. 1. Relation between the first IP's (lower series of points), the Δp values (upper series of points), and the number of linearly annellated rings in kata-condensed hydrocarbons.

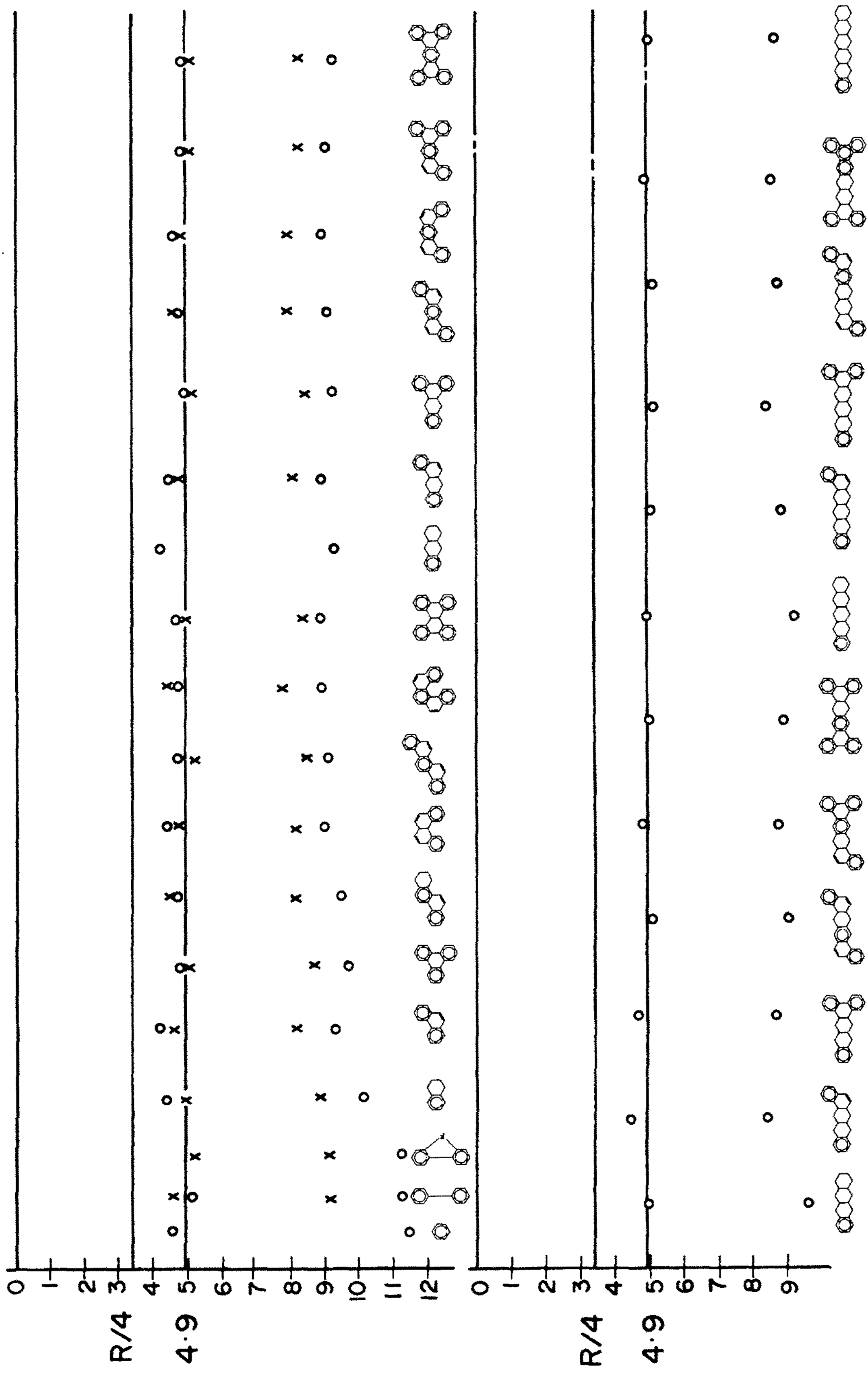
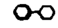
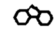
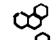
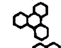
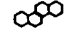
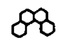
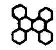
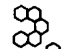
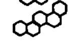
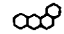
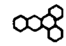
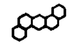
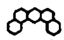
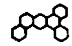
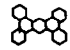
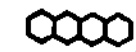
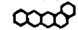
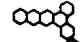
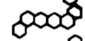
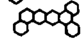
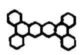
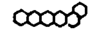
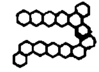
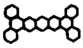
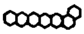


Fig. 2. Relation between the α-photoelectron and α-ultraviolet bands (marked with crosses), and between the β-photoelectron and β-ultraviolet bands (marked with circles). The upper level is 4·9 eV, the IP of graphite.

Table 1. Singlet energies from the visible and UV spectra and vertical IP's (eV).

	p	IP_p	IP_p-E_p	α	IP_α	IP_α-E_α	β	IP_β	IP_β-E
	6.08	9.24	3.16	4.80			6.93	11.49	4.56
	5.07	8.31	3.24		9.11		6.16	11.26	5.10
	4.86	8.15	3.29	4.16	9.03	4.87	5.96	11.22	5.26
	4.46	8.15	3.69	4.08	8.87	4.79	5.72	10.08	4.36
	4.35	7.86	3.51	3.63	8.15	4.52	5.05	9.28	4.23
	4.48	7.89	3.41	3.67	8.66	4.99	4.93	9.68	4.75
	4.00	7.60	3.60	3.47	8.10	4.63	4.75	9.46	4.71
	4.05	7.60	3.55	3.36	8.00	4.64	4.52	8.95	4.43
	3.64	7.26	3.62	3.27	8.23	4.96	4.23	8.84	4.61
	3.87	7.47	3.60	3.16	7.70	4.54	4.12	8.81	4.79
	3.92	7.54	3.62	3.42	7.70	4.28	4.46	9.05	4.59
	3.42	7.47	4.05				5.04	9.23	4.19
	3.60	7.47	3.87	3.26	8.05	4.79	4.43	8.86	4.43
	3.66	7.44	3.78	3.35	8.30	4.95	4.45	9.16	4.71
	3.68	7.41	3.73	3.17	7.84	4.67	4.26	9.04	4.78
	3.68	7.43	3.75	3.17	7.83	4.66	4.23	8.84	4.61
	3.74	7.40	3.66	3.24	8.17	4.93	4.23	8.99	4.76
	3.87	7.45	3.58	3.28	8.14	4.86	4.34	8.14	4.94
	2.74	7.04	4.30				4.64	9.60	4.96
	2.89	7.00	4.11				4.03	8.44	4.41
	2.96	6.98	4.02				4.05	8.68	4.63
	2.98	7.02	4.04				3.96	8.98	5.02
	3.08	7.04	3.96				3.93	8.64	4.71
	3.13	7.08	3.95				3.88	8.79	4.91
	2.30	6.74	4.44				4.24	9.09	4.85
	2.40	6.72	4.32				3.71	8.74	5.03
	2.45	6.67	4.22				3.76	8.31	4.55
	2.53	6.77	4.24				3.69	8.64	4.95
	2.64	6.77	4.13				3.66	8.48	4.82
	1.98	6.44	4.46				3.66	8.56	4.90
	2.08								

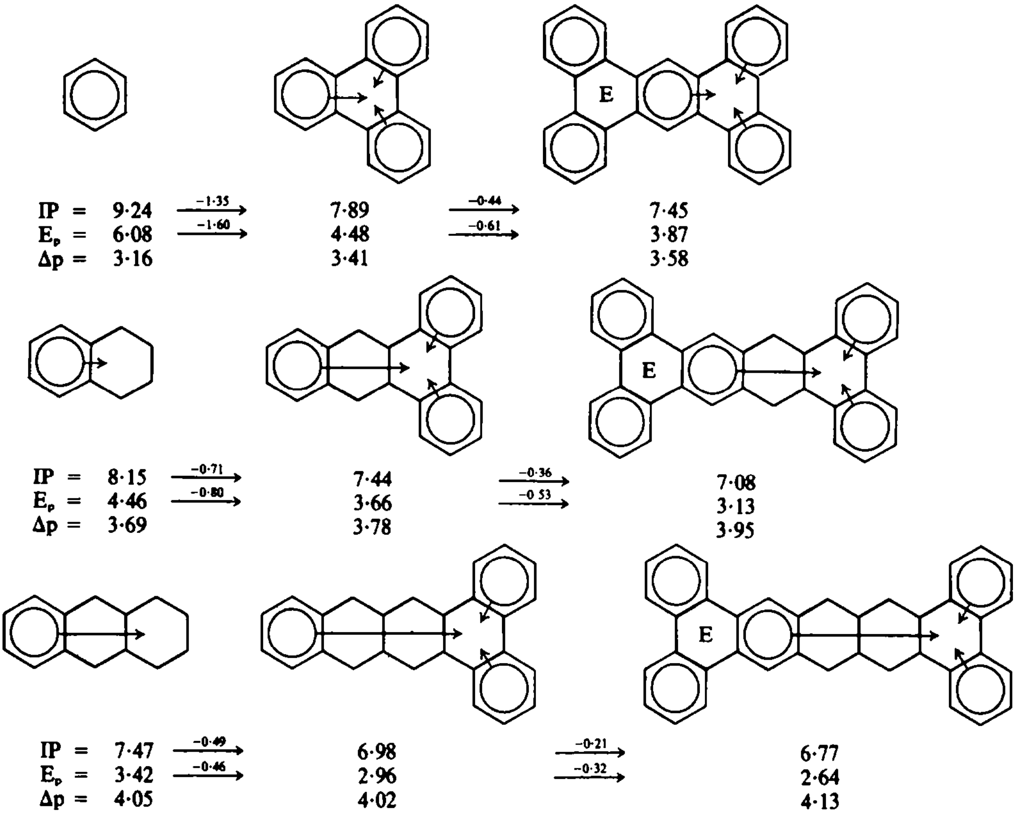
α- and β-bands in the photoelectron spectra of biphenyl and fluorene. (In order to correct the α-bands for the gaseous state from the solution, 250 cm^{-1} were added for alcohol, and 350 cm^{-1} for benzene solution).

As in the series of the p-bands there is a tendency for hydrocarbons with a bigger number of sextets to converge closer to the theoretical upper level of 4·9 eV. This is most pronounced in the fully benzenoid hydrocarbons triphenylene and 1:2,7:8-dibenzochrysene. The lower levels are more dependent on the longest aromatic conjugation which results in a lower IP. However, this does exclude the third branch, as shown before, for example, in triphenylene and 1:2,7:8-dibenzochrysene. Anthracene has a high IP for the β-band and a low upper level. Like in the higher acenes tetracene, pentacene and hexacene, there is no band in the photoelectron spectrum which could be related to an α-band in the absorption spectrum. Under these circumstances any deformation of the minima following the p-bands in the absorption spectrum should be treated with caution before it is ascribed to a hidden α-band system.

However, distinct α-bands (marked with crosses) are found in the absorption and photoelectron spectra, and their relation is obvious from Fig. 2 and Table 1. As shown by the β-bands (marked with circles), the third branch has a negligable influence. Thus the values for tetrabenzanthracene are near to the ones for the dibenzanthracenes.

The higher acenes beginning with tetracene show no α-bands in the photoelectron spectrum. The upper levels of the β-bands are all very close to 4·9 eV, i.e. the hydrocarbons are becoming more graphite-like. The number of sextets shifts the lower levels of the β-bands towards lower IP's. The β-band of hexacene was obtained from the spectrum of crystalline hexacene.[13]

Although there are no photoelectron bands following the β-band in the higher acenes which could be classified as α-bands, there are other bands which show the characteristic vibrational structure of p-photoelectron

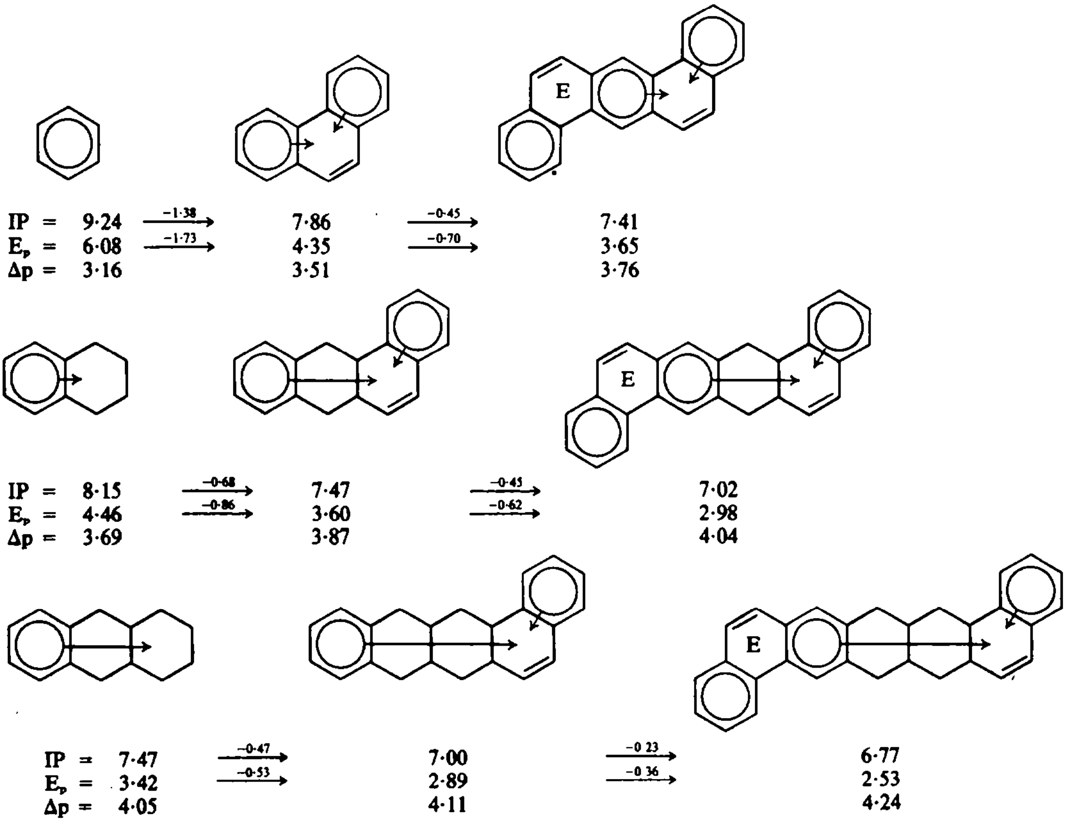


IP = 9·24 $\xrightarrow{-1\cdot35}$ 7·89 $\xrightarrow{-0\cdot44}$ 7·45
E_p = 6·08 $\xrightarrow{-1\cdot60}$ 4·48 $\xrightarrow{-0\cdot61}$ 3·87
Δp = 3·16 3·41 3·58

IP = 8·15 $\xrightarrow{-0\cdot71}$ 7·44 $\xrightarrow{-0\cdot36}$ 7·08
E_p = 4·46 $\xrightarrow{-0\cdot80}$ 3·66 $\xrightarrow{-0\cdot53}$ 3·13
Δp = 3·69 3·78 3·95

IP = 7·47 $\xrightarrow{-0\cdot49}$ 6·98 $\xrightarrow{-0\cdot21}$ 6·77
E_p = 3·42 $\xrightarrow{-0\cdot46}$ 2·96 $\xrightarrow{-0\cdot32}$ 2·64
Δp = 4·05 4·02 4·13

Fig. 3. Asymmetric annellation effects of the p- and β-bands in the series acene, 1:2,3:4-dibenzacene and tetrabenzacene.



IP = 9·24 $\xrightarrow{-1\cdot38}$ 7·86 $\xrightarrow{-0\cdot45}$ 7·41
E_p = 6·08 $\xrightarrow{-1\cdot73}$ 4·35 $\xrightarrow{-0\cdot70}$ 3·65
Δp = 3·16 3·51 3·76

IP = 8·15 $\xrightarrow{-0\cdot68}$ 7·47 $\xrightarrow{-0\cdot45}$ 7·02
E_p = 4·46 $\xrightarrow{-0\cdot86}$ 3·60 $\xrightarrow{-0\cdot62}$ 2·98
Δp = 3·69 3·87 4·04

IP = 7·47 $\xrightarrow{-0\cdot47}$ 7·00 $\xrightarrow{-0\cdot23}$ 6·77
E_p = 3·42 $\xrightarrow{-0\cdot53}$ 2·89 $\xrightarrow{-0\cdot36}$ 2·53
Δp = 4·05 4·11 4·24

Fig. 4. Asymmetric annellation effects of the p- and β-bands in the series acene, 1:2-benzacene and dibenzacene. All hexagons symbolize aromatic rings. Only localized double bonds of the phenanthrene type are marked.

bands. It is striking that the number of these bands corresponds to the number of different p-positions which have H-atoms. There is just one p-position of this kind in naphthalene from which the p-band at 8·15 eV originates. Anthracene has two different p-positions causing the bands at 7·47 and 8·57 eV. Tetracene has also two such p-positions, with the corresponding bands at 7·04 and 8·44 eV. Pentacene has three p-positions and p-bands at 6·74, 8·03 and 8·40 eV. Hexacene has also three at 6·44, 7·53 and 8·13 eV. With this new classification a complete correlation of the lower IP's with the structural formula appears possible.

If the above correlation between p-bands and the first IP's is correct then it should also apply to the unusual asymmetric annellation effects which have been reported before.[14] These effects have been measured by the shifts of the β-bands, and were explained by an asymmetric conjugation of the rings, caused by the mobility of only one pair of π electrons capable of moving in a straight direction through linearly fused rings (see Fig. 3). Thus, an induced sextet can be formed by three pairs of π electrons, as indicated by arrows in triphenylene. This cannot be repeated a second time in tetrabenzanthracene because the middle ring has only one pair of π electrons with interring mobility. The result must be an empty ring marked "E". The scheme represented in Fig. 3 shows that this is also true for the p-bands and the first IP's.

In passing from benzene to triphenylene and tetrabenzanthracene, the first IP's decrease by 1·35 and 0·44 eV, respectively. The corresponding decrease in the energy of the p-bands, E_p, is 1·60 and 0·61 eV. In going from naphthalene to 1:2,3:4-dibenzanthracene and tetrabenzotetracene, these differences are for the first IP's 0·71 and 0·36 eV, and for the p-bands 0·80 and 0·53 eV, respectively. In the series anthracene, 1:2,3:4-dibenzotetracene and tetrabenzopentacene, the differences for the first IP's are 0·49 and 0·21 eV, and for the p-bands 0·46 and 0·32 eV, respectively. Thus, in all cases the asymmetries reported earlier[14] for the absorption bands are independently confirmed by different methods. The possible objection that a comparison of absorption bands involves a ground and an excited state and therefore introduced an element of uncertainty is not valid anymore.[15]

According to the third annellation rule mentioned above the third branch in a hydrocarbon of the triphenylene type

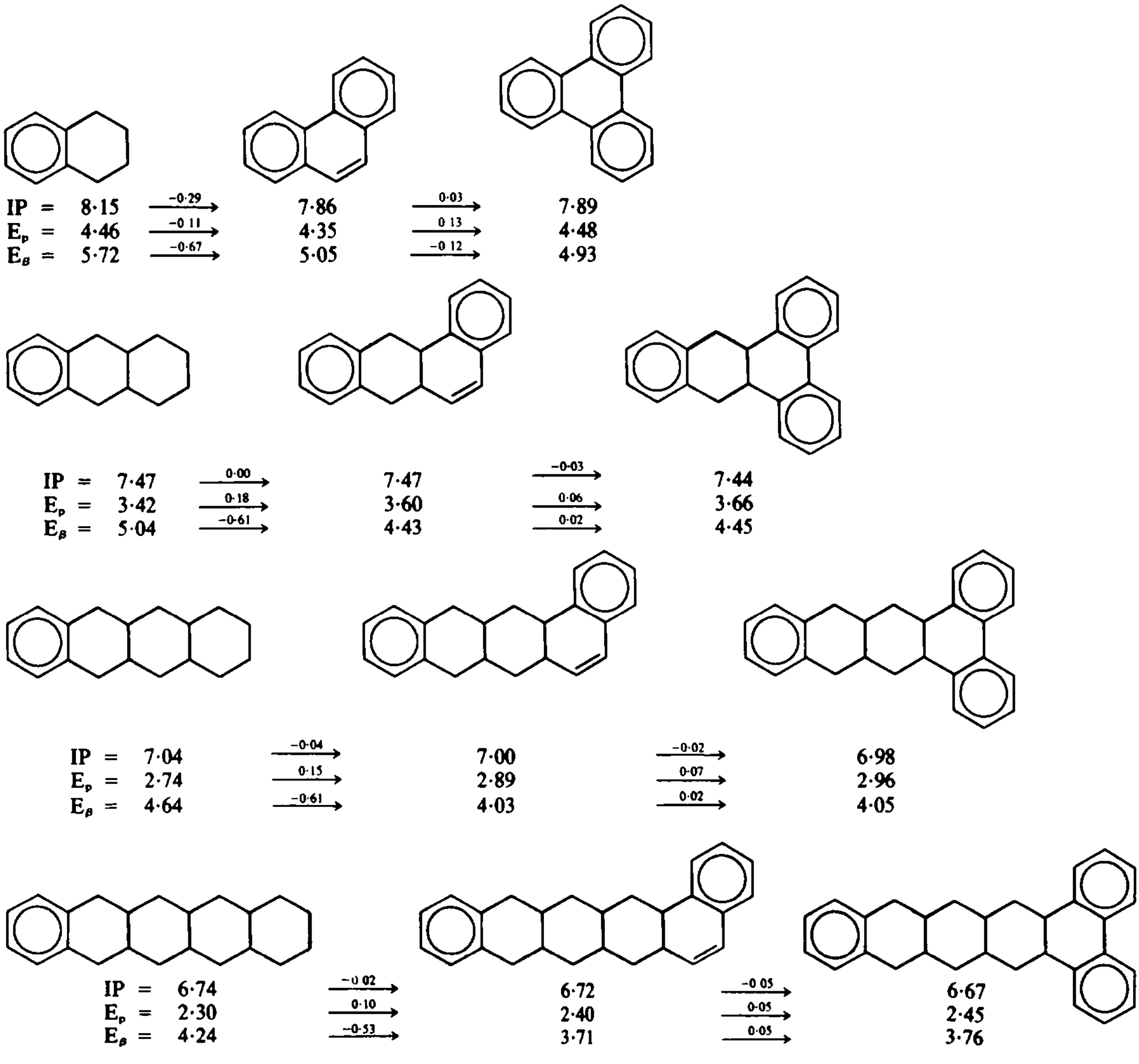


Fig. 5. Asymmetric annellation effects of the p- and β-bands in the series acene, 1:2-benzacene and 1:2,3:4-dibenzacene. All hexagons symbolize aromatic rings. Only localized double bonds of the phenanthrene type are marked. The possible, different aromatic conjugations are here not indicated by arrows.

is not in aromatic conjugation with the other two branches. It has been demonstrated earlier for the β-bands[16,17] that in all systems comprising the triphenylene nucleus (see Fig. 3), the third ring can be removed with no effect on the asymmetric annellation. In order to rule out any doubt as to the validity of this kind of comparison, we are reporting in Fig. 4 the IP's and E_p values for the acenes, 1:2-benzacenes and dibenzacenes. In passing from benzene to phenanthrene and 1:2,5:6-dibenzanthracene, the differences of the IP's are 1·38 and 0·45 eV, respectively, and for the p-bands 1·73 and 0·70 eV, respectively.

For the series naphthalene, 1:2-benzanthracene and 1:2,7:8-dibenzotetracene, the corresponding differences of the IP's are 0·68 and 0·45 eV, and for the p-bands 0·86 and 0·62 eV, respectively. For the series anthracene, 1:2-benzotetracene and 1:2,8:9-dibenzopentacene, the recorded differences for the IP's are 0·47 and 0·23 eV, and for the p-bands 0·53 and 0·36 eV, respectively. This is in complete agreement with earlier comparison of the β-bands,[16,17] the asymmetries being confirmed in all cases.

There are very strong asymmetric annellation effects in the series of the acenes, 1:2-benzacenes and 1:2,3:4-dibenzacenes, if measured with the β-bands (see Fig. 5). This is reasonable because according to the second and third annellation rules only two branches of a polycyclic system can be in aromatic conjugation simultaneously, the third being ineffective.[14] As a result of this there can be no doubt that the polarization of the β-bands is along the long axis of the molecule.

This is not so with the p-bands. The changes in this series are small and almost symmetric for the two angular benzo rings (see Fig. 5). The same observation can be made with the first IP's. This shows clearly that only the p-bands can be related to the first IP's, and that the transition moment of the p-bands must be along the short axis of the molecules.

That this is so for the first IP's is also demonstrated by the series phenanthrene, triphenylene, 1:2,3:4-dibenzanthracene, 1:2,3:4-dibenzotetracene and 1:2,3:4-dibenzopentacene (Fig. 6). As in the other series, the p-bands shift parallel with the IP's to lower energies. It is obvious that this behaviour is connected with the long axes of the molecules. However, the next band in the photoelectron spectra is almost stationary at about 7·9 eV through the whole series. In that case it would be logically correct to correlate this transition to the phenanthrene complex, formed by the angular benzo rings which remain unchanged in this series and should not be simultaneously in aromatic conjugation with the third, longer branch.

A more detailed analysis, based on MO calculations and including a wider range of hydrocarbons, will be published in due course.

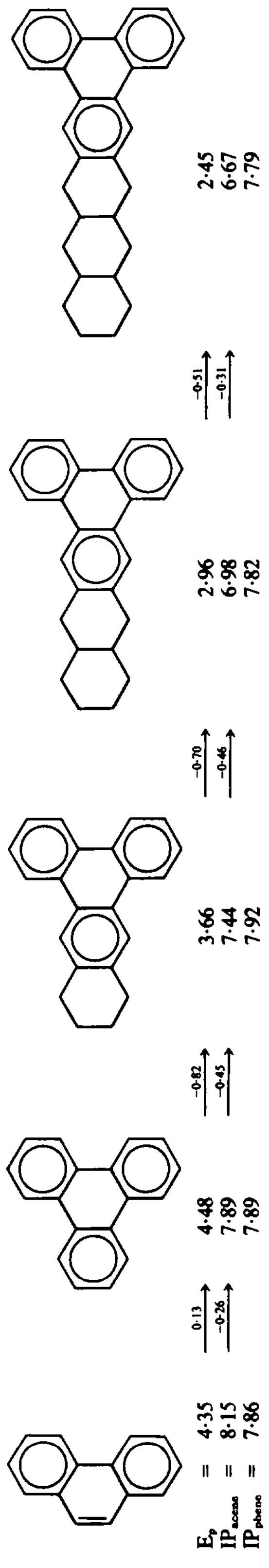


Fig. 6. Symmetric annellation effects of the p-bands in the 1:2,3:4-dibenzacenes. All hexagons symbolize aromatic rings. Only localized double bonds of the phenanthrene type are marked. The possible aromatic conjugations are here not indicated by arrows.

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