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LOCALISED VS DELOCALISED MOLECULAR ORBITALS IN AROMATIC HYDROCARBONS

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Abstract—In many series of polycyclic aromatic hydrocarbons, e.g. the acenes, phenes, starphenes, pyrenes, perylenes and coronenes, the first two IP's follow simple rules and can be predicted with sufficient accuracy from the IP's of the basic chromophores. For example, the PE spectra of all angularly annellated anthracenes show a persistent ("autonomous") band at 7.4 eV; in the tetracenes such a band is found at 7.0 eV, in the pentacenes at 6.6 eV. The PE spectrum of hexaphene is essentially a superposition of the spectra of tetracene and anthracene, and the spectrum of heptaphene resembles that of tetracene, with all bands showing twice the normal integrated intensity. The bands in the spectra of the linearly annellated pyrenes can be classified into pyrene and acene-type bands of which only the latter respond to annellation ("moving" bands). Similar observations can be made in angularly annellated perylenes and the linearly annellated coronenes. Isotopic hydrocarbons, i.e. compounds with identical UV band positions, show surprising similarities in their PE spectra, despite the widely differing topologies. The origin of these regularities is discussed in terms of the sextet formalism and Hückel theory. Applications to structure elucidation are pointed out.

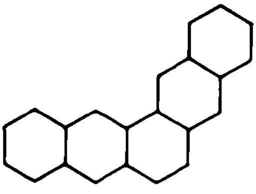
It is commonplace in inorganic chemistry to consider localised orbitals (e.g. lone-pairs, inner shells) within larger ones. It is therefore amazing that an analogous procedure has hardly been attempted in organic chemistry, perhaps because MO methods presume—symmetry permitting—complete electron delocalisation over the whole nuclear framework from the outset. However, one is forced by the large number of already existing PE spectra of aromatic hydrocarbons[1-12] to consider this view serious.

The anthracene series. In our paper on the PE and optical spectra of the acenes we stated and emphasised that there is a stationary PE band at 7.4 eV for all anthracenes, independent of the number of angular benzo rings, i.e. the number of aromatic sextets (Fig. 1). At first sight this appears surprising, given the huge difference in reactivity between anthracene 1 and tetrabenzanthracent 7, just to give the extreme cases. It is well known[13] that anthracene reacts with chromic acid or enters the diene reaction in the meso positions much more readily than tetrabenzanthracene. In between there is a gradual smooth decrease in reactivity,[14] despite the constant first IP. Obviously, one must give the excited state $\Delta p = IP_1 - E_p$ (E_p being the energy of the p-absorption band) a greater significance for chemical reactions.

In contrast to the constant first IP, the second IP is dependent on the number and, to a lesser degree, on the position of the angular benzo rings. Only in tetraphene 2 with one naphthalene complex comes IP_2 relatively close to IP_1 in naphthalene (8.15 eV). Obviously, there exists considerable interaction between the various naphthalene units (two in 3 to 5, three in 6, four in 7) so that IP_2 bears no simple relation to IP_1 of naphthalene.

The higher acenes. As was the case in the anthracene series, there is a persistent band, at 7.0 eV, in the PE spectra of tetracene **8** and its angular benzologues **9** to **13**. In the pentacene series **14** to **18**, this band is observed at 6.6 eV (Fig. 2). However, in contrast to the constant IP_1 within each series, the meso reactivity diminishes gradually on angular benzo annellation,[14] in accord with the sextet formalism.[13]

The phenes. Pentaphene **19** with two branches of the same length has two anthracene complexes which give rise to the two peaks at 7.27 and 7.39 eV; these figures compare well with the anthracene value at 7.41 eV. On passing to hexaphene **20**, the anthracene band remains at 7.39 eV whilst a tetracene band appears at 6.92 eV. In heptaphene **21** the peaks correlating with the two tetracene branches are both found at 6.89 eV. Naphthopentacene **22** comprises a pentacene and an anthracene



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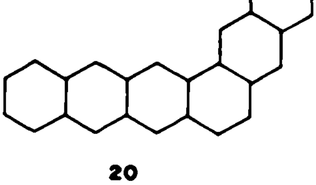

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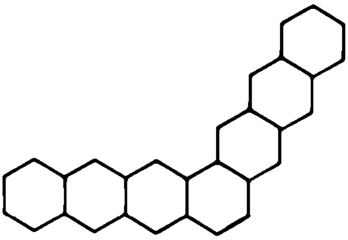

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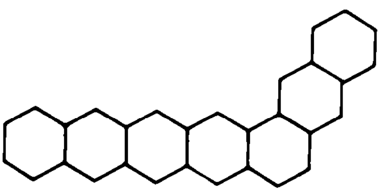


22

complex; the first two IP's, 6.59 and 7.33 eV, approach closely to the pentacene and anthracene values at 6.61 and 7.41 eV, respectively.

The analogy between the IP's of the phenes and those of the acene fragments extends in part to the higher PE bands. For example, the 8.25 and 8.53 eV peaks in the hexaphene spectrum can be classified as higher tetracene and anthracene bands whose IP's in the parent hydrocarbons are 8.41 and 8.54 eV, respectively. Similar assignments can be advanced for the higher bands of 19, 21 and 22. However, the numerical agreement becomes progressively worse for the higher PE bands.

The higher starphenes. The first three hydrocarbons in Fig. 3 show clear and simple first PE bands which can only be related to the two tetracene branches; this agrees with the fact that the integrated area of these bands assumes twice the normal value. On the other hand, anthracenoheptaphene 26 with three tetracene branches has an amazingly complex first band accommodating

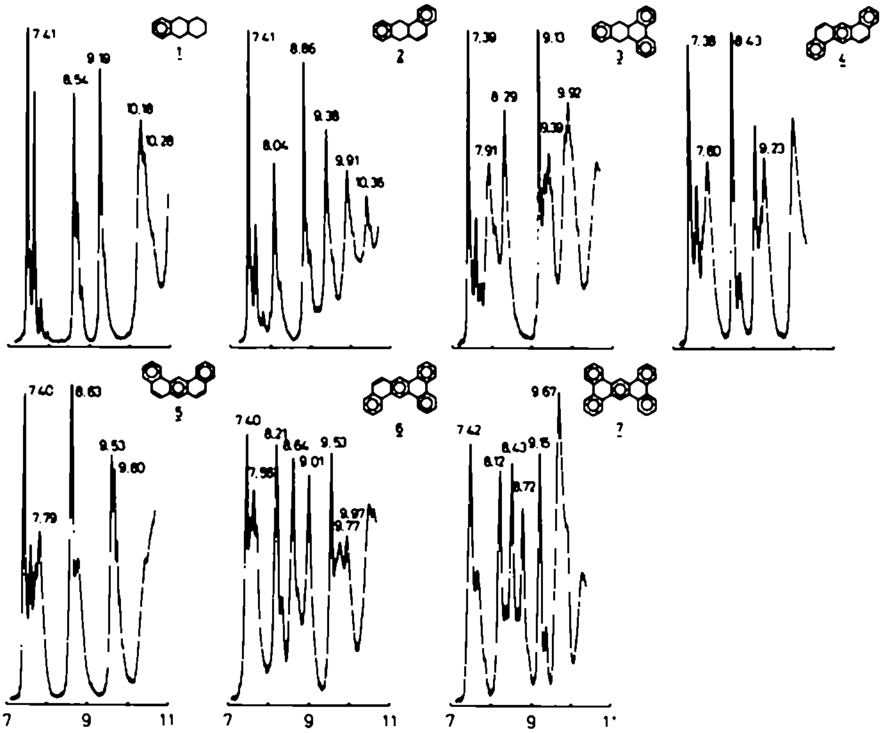


Fig. 1. PE spectra of the anthracene series. Here and in the following figures all hexagons symbolize aromatic rings; only localized double bonds of the phenanthrene type are marked.

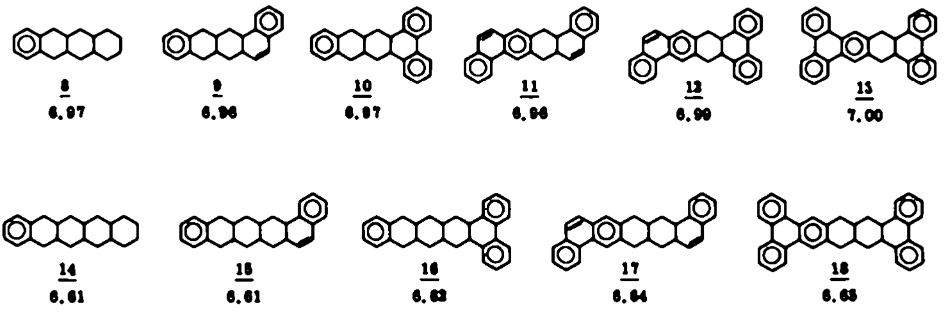


Fig. 2. IP$_1$ values in eV of the tetracene (above) and pentacene series (below).

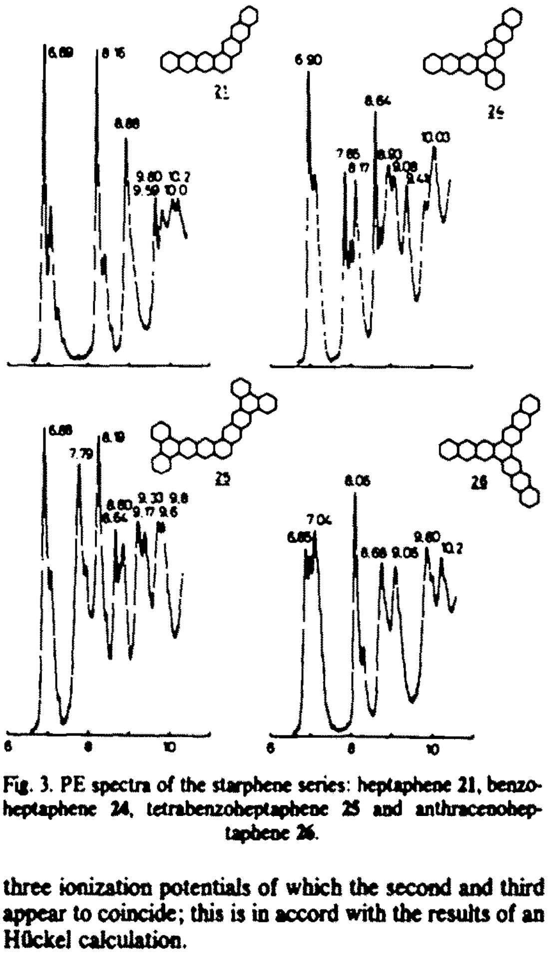
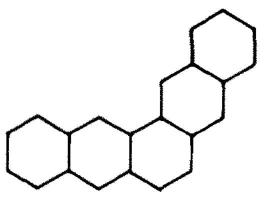
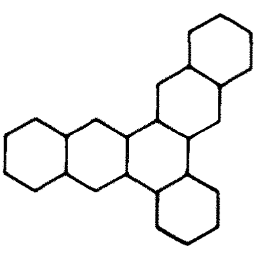


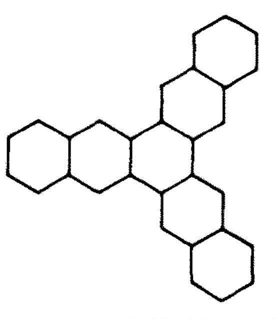
Fig. 3. PE spectra of the starphene series: heptaphene 21, benzoheptaphene 24, tetrabenzoheptaphene 25 and anthracenoheptaphene 26.

three ionization potentials of which the second and third appear to coincide; this is in accord with the results of an Hückel calculation.

Analogous observations are made in the following annellation series:


7.27/7.39


7.36/~7.5


7.35/7.35/7.35

As the above figures show, pentaphene and benzopentaphene have two anthracene bands in the expected energy region whilst naphthopentaphene has three. In addition to the two anthracene bands, benzopentaphene shows a naphthalene band at 8.04 eV.

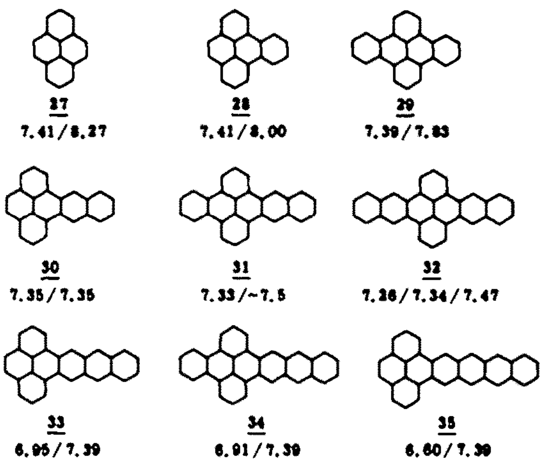


Fig. 4. IP_1 and IP_2 values in eV of the pyrene series.

The pyrene series. There is a persistent band at 7.4 eV in the spectra of pyrene 27, benzopyrene 28 and dibenzopyrene 29 which can only originate from the pyrene unit with first IP of 7.41 ev (Fig. 4). In naphthopyrene 30, benzonaphthopyrene 31 and dinaphthopyrene 32 there appears, in addition to the pyrene band, an autonomous band corresponding to the anthracene complex(es). Since pyrene and anthracene have the same first IP (7.41 eV), the first band in the spectra of 30 and 31 shows twice the normal integrated intensity whereas 32 exhibits three maxima with trice the normal intensity. Thus, the comparison of naphtho- and dinaphthopyrene gives the seemingly paradox result that the hydrocarbon of lower symmetry has a clearer and simpler first PE band; the same observation was made above in the case of heptaphene 21 and anthracenoheptaphene 26.

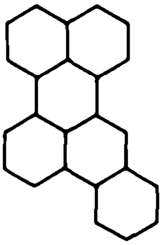
The participation of an anthracene complex is impossible in anthracenopyrene 33 and benzoanthracenopyrene 34 so that the first PE bands, at 6.95 and 6.91 eV, resp., can only originate from the tetracene chromophore with first IP of 6.97 eV. The second PE bands which are found at 7.39 eV in both hydrocarbons appear at practically the same position as the first band in pyrene.

In the last hydrocarbon given in Fig. 4, tetracenopyrene 35, the analogy to the pentacene and pyrene IP_1 values is almost perfect.

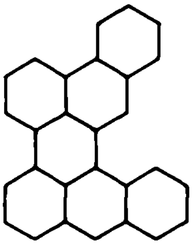
Benzonaphthopyrene 31 and benzoanthracenopyrene 34 show bands at 7.96 and 7.87 eV, resp., which can be interpreted as naphthalene bands. However, as mentioned above, assignments for the higher PE bands should be taken with caution, pending a more thorough theoretical analysis of the "fragment" method which we hope to present in the near future.

The perylene series. As discussed in Ref. 10, the first IP in the benzologues and naphthologues of perylene is strongly influenced by the number of aromatic sextets.

The angular benzologues 37 and 38 show a well-pronounced band at 7.9 eV which can only originate from the naphthalene complex as no such band is found in perylene 36 itself. In the hydrocarbons 39 and 40 with two angular benzo rings this band is increased in in-



37
7.86



38
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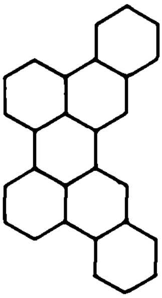
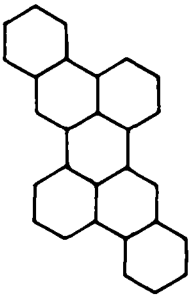


39
7.84/8.07



40
7.81/8.08

tensity and marginally split into subbands whose IP's fit very well the naphthalene range.

Naphthoperylene **41** with an anthracene complex shows an autonomous band at 7.47 eV. On passing to dinaphthoperylene **42** this band is split in separate bands at 7.24 and 7.57 eV whose mean value (7.41 eV) complies with IP_1 in anthracene. Precisely the same observations are made with the two isomeric benzonaphthoperylenes **43** and **44** and with benzodinaphthoperylene **45** (Fig. 5).

Thus, the sextet formulation accounts very well not only for the lowering of IP_1 of perylene due to benzo and naphtho annellation, but also for the appearance of autonomous bands originating from the individual naphthalene and anthracene complexes.

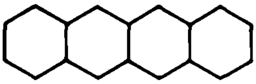
Other series. The first IP in the angularly annellated pyrenes approaches gradually to that of the acene of the same length:

Thus, the pyrenes become more and more acene-like; this is in accord with the sextet formulation as well as their chemical behaviour (rates of maleic anhydride addition[14]). On the basis of the above comparison, it is feasible to predict the first IP of the elusive hydrocarbon heptacene. However, the second PE band in the above pyrene series cannot be associated with the pyrene or acene fragments.

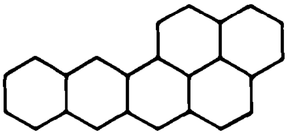
In the coronene series, the first IP appears to converge to that of the acene containing one benzene ring less:

Thus, naphthocoronene approaches to tetracene, anthracenocoronene to pentracene. The second IP is related to the coronene complex as it remains almost constant at 7.3 eV across the series (IP_1 of coronene 7.29 eV).

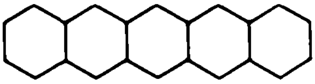
There are insufficient data to check whether similar regularities hold in the following series:



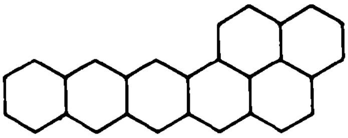
6.97



6.82



6.61



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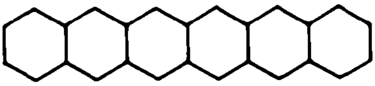

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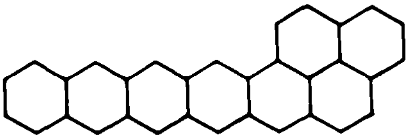

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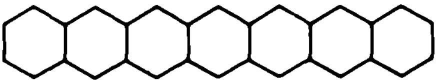

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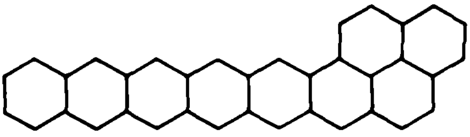

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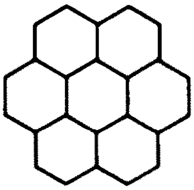
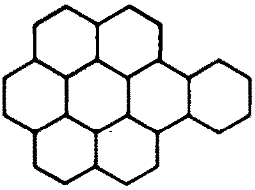
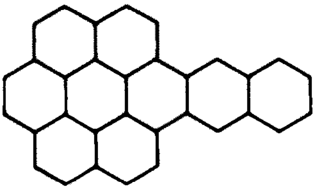


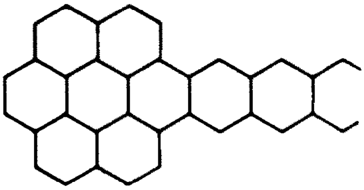
7.29/7.29



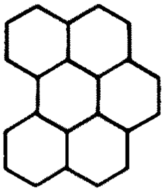
7.08/7.35



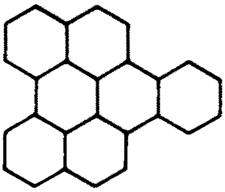
6.88/7.36



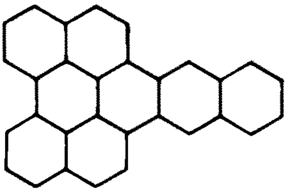
6.64/7.33



7.15/7.81



6.96/7.80



6.77/7.71

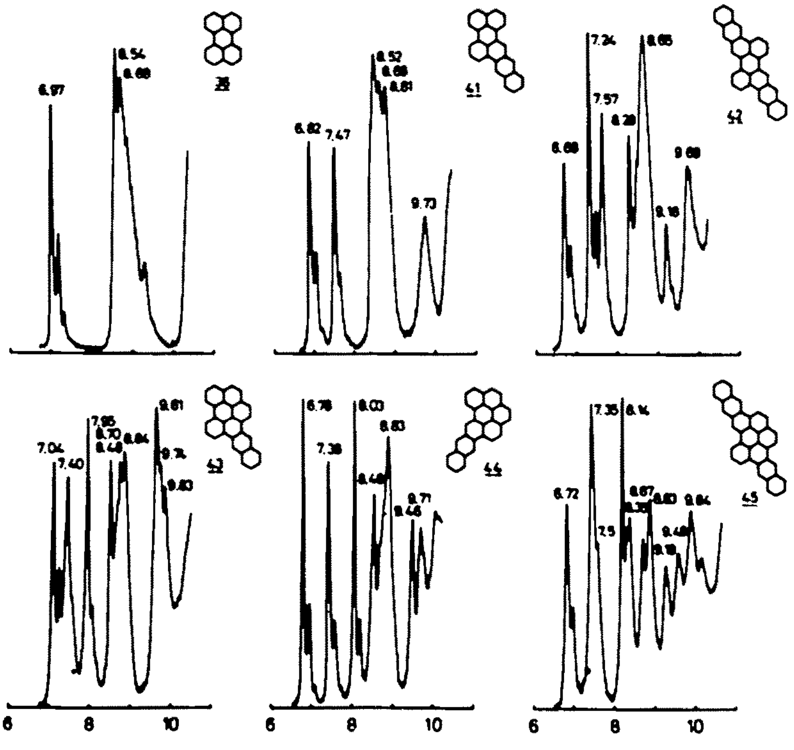


Fig. 5. PE spectra of perylene 36 and the naphthologues of perylene and benzoperylene.

Again, there is a "moving" band associated with the acene chromophore, and a stationary band related to the benzoperylene fragment.

Applications to structure elucidation. The appearence, in the PE spectra, of autonomous and moving bands (the latter responding to annellation) provides a most useful means for checking whether the assumed structure is consistent with the observed PE spectrum. This is an important consideration in aromatic hydrocarbon chemistry as many synthetically useful procedures, e.g. the Friedel–Crafts reaction, the Elbs reaction and $AlCl_3$ catalyzed cyclodehydrogenations,[13] are occasionally accompanied by skeletal rearrangements. Due to poor solubility and the difficulty in obtaining single crystals, the NMR and X-ray diffraction methods are of limited value for aromatic hydrocarbons so that structural proof rests largely on the UV spectra for which powerful rules have been developped ("annellation principle"[13,15]). However, application of these rules is often hampered by the diffuseness of the UV spectra and the appearance of additional bands which do not fit in the α-, p-, β- and β'-scheme.

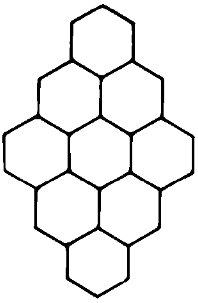
The PE spectra, on the other hand, are clear and simple, even in the case of structurally non-rigid, overcrowded hydrocarbons; all π bands show sharp 0-0 transitions and have the same integrated intensity so that overlapping bands are readily recognized. Sample purity is easily checked by monitoring the spectrum at different temperatures, thus allowing complex reaction mixtures to be analyzed. The peak positions can be successfully correlated with eigenvalues calculated by simple one-electron procedures, e.g. the Hückel scheme. Isotopic hydrocarbons[12] (i.e. compounds with the same α-, p-, β- and β'-band energies) such as dibenzoperopyrene and isoviolanthrene or anthanthrene and dibenzopyrene can be distinguished as they differ in the third and higher IP's.

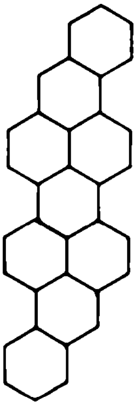
Two simple examples may illustrate how the regularities reported in this paper can be used to choose between structural alternatives.

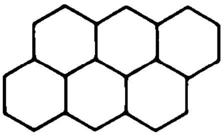
In the synthesis[16] of naphthopentacene **22**, rearrangement to the isomer **23** could have occurred. Both isomers comprise a pentacene chromophore so that the IP_1 values and therefore the p-band energies would be practically identical. However, IP_2 is governed by the second branch which is of the anthracene type in **22** and of the phenanthrene type in **23**. Since the IP_1 values of anthracene and phenanthrene differ considerably (see structural forumlas above), a clear-cut answer is possible. The experimental findings ($IP_1 = 6.59$ eV, $IP_2 = 7.33$ eV) show beyond reasonable doubt that structure **22**, deduced in Ref. 16 on other grounds, is the correct one.

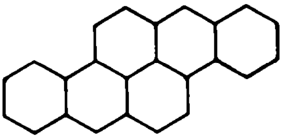
The second example concerns 1:2, 3:4-dibenzopyrene **47**, a hydrocarbon important for experimental cancer research. Three independent syntheses[13] have been worked out and numerous derivatives prepared along these lines. Later studies[17] showed, however, that the assumed structure is incorrect and that the hydrocarbon obtained in the above syntheses is in fact dibenzofluoranthene **49**. The true 1:2, 3:4-dibenzopyrene has meanwhile been synthesized by two independent routes;[18] the 1:2, 4:5 isomer **48** is also known.[13]

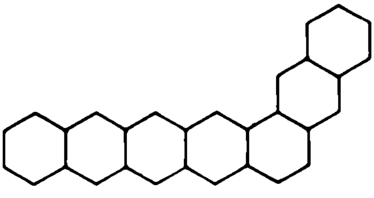
It would have been a trivial task to settle the above controversy if the PE spectra were available at that time. As has been shown with numerous examples[7,11] (see also Figs 1 and 2), benzo annellation at fixed double bonds has little or no effect on IP_1 whilst IP_2 is lowered. Thus, on passing from 3.4-benzopyrene **46** to **47** and **48**, the first PE band should remain stationary whereas the second one should move to lower energies. Except for a slight lowering of all IP's in **47** due to overcrowding, this is the case indeed. Dibenzofluoranthene, on the other hand, has a significantly higher first IP which does not fit in the 3.4-benzopyrene range.





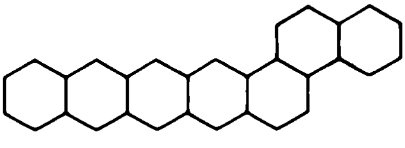






22

6.61/7.41



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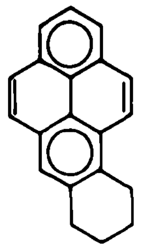
6.61/7.86



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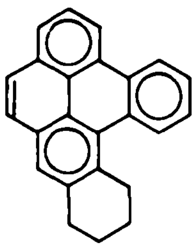
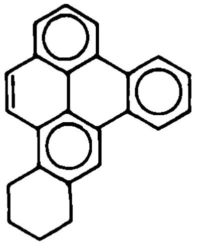
7.10/8.01



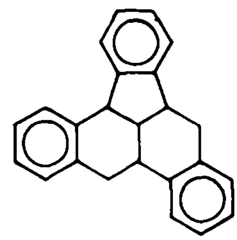
47

7.07/7.72



48

7.11/7.87



49

7.24/7.79

In the course of our studies, several other hydrocarbons have been found whose structure has to be revised. This will form the subject of a future paper.

Comparison with Hückel theory. It seemed of interest to check whether the spectral regularities and resemblances reported here, in particular the existence of autonomous and moving bands, shows also up in Hückel theory.

As discussed above, the IP_1 values of the angularly annellated anthracenes cluster at 7.4 eV, those of the tetracenes at 7.0 eV, and those of the pentacenes at 6.6 eV. On the other hand, the Hückel eigenvalue coefficients of the highest occupied orbitals of the anthracenes range from 0.414 (anthracene) to 0.577 (tetrabenzanthracene) and overlap with those of the tetracenes which range from 0.295 to 0.425; these in turn overlap with those of the pentacenes which range from 0.220 to 0.313. Thus, the appearance of autonomous anthracene, tetracene and pentacene bands is not reproduced by the eigenvalue coefficients, at least not in Koopmans' approximation. This failure of Hückel theory is not removed if double bond fixation[3,4] is taken into account. It appears that the size of the molecules plays an important role, i.e. large hydrocarbons have generally lower IP's than small ones, even if the eigenvalue coefficients are equal.

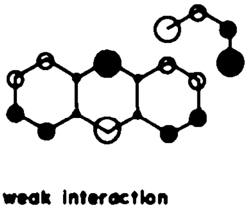
The observation that starphenes with three branches of the same length show first PE bands with trice the normal intensity, is in keeping with the eigenvalue coefficients. Hückel theory also correctly predicts that all π orbitals of heptaphene **21** appear in near-degenerate pairs whereas they are well separated and non-degenerate in hexaphene **20** or naphthopentacene **22**. The numerical trends are only poorly reproduced by Hückel theory, however. For example, whereas the first IP decreases slightly in the series tetracene, heptaphene **21** and anthracenoheptaphene **26** (6.97, 6.89 and 6.85 eV), the eigenvalue coefficients of the highest occupied orbital (0.295, 0.326 and 0.340) would predict the opposite.

Similar comments apply to the linearly annellated pyrenes **27** to **35**. The autonomous pyrene band at 7.4 eV is associated with eigenvalue coefficients which vary as a result of the increasing molecular size from 0.445 in pyrene to 0.594 in dinaphthopyrene. Interestingly, the symmetry species of this orbital is always the same, namely b_1 in point group C_{2v} which is common to all pyrenes (molecules oriented in the y, z plane). The moving band(s) originating from the acene fragments correspond to eigenvalue coefficients which are roughly comparably (but generally higher, depending on molecular size) to those of the acene(s). These orbitals belong all to symmetry species a_2 as in the acenes. In accord with the observed high integrated intensity of the first band in dinaphthopyrene, Hückel theory yields two near-degenerate anthracene-type orbitals with coefficients 0.476 and 0.536, besides the pyrene-type orbital with coefficeint 0.594.

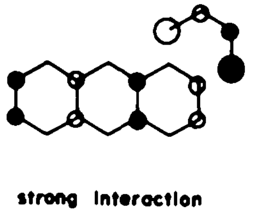
The spectral regularities observed in the remaining series are similarly masked by the above mentioned size effect on the Hückel eigenvalue coefficients. It is therefore not surprising that the existence of orbitals of constant energy in hydrocarbons as diverse as anthracene and tetrabenzanthracene or dibenzoperopyrene and isoviolanthrene (though implicit in the sextet formalism[13]) escaped the attention of earlier workers who used the MO method to calculate ionisation potentials and UV spectra.

We are thus lead to the conclusion that the delocalised picture implied by Hückel theory (if properly applied) and the localised view of the sextet formalism give identical results as far as the energy levels are concerned. How can this be understood? We think that both theories are equivalent and that it is simply a matter of convenience which picture is preferred.

The insensitivity to angular annellation of IP_1 in the acene series can be qualitatively understood on the basis of perturbation theory using Hückel orbitals.[9] Consider anthracene as an example. If a cis-butadiene fragment is added to give tetraphene, no first-order interaction between the highest occupied fragment orbitals is possible because their local symmetries do not match; second-order interaction of the highest occupied anthracene orbital with deeper or higher lying butadiene levels is insignificant due to the large energy gaps.



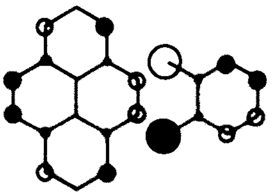
weak interaction



strong interaction

On the other hand, the second-highest anthracene orbital is able to interact with the highest occupied butadiene level and is consequently raised in energy, as is experimentally observed (see Fig. 1).

Similarly, the lack of conjugation in naphthopyrene **30** can be rationalised on the basis of the different symmetries of the highest occupied fragment orbitals, viz. pyrene (b_1 within C_{2v}) and *o*-xylylene (a_2):



no interaction

As these two examples show, annellation at bonds which have a high double-bond character in the sextet formulation,[13] produces at best small second-order effects in IP_1, whereas IP_2 is significantly lowered. Conversely, annellation at quasi-single bonds (2–3 bond in anthacene, 3–4 bond in pyrene) gives strong first-order effects for IP_1 whilst IP_2 is essentially unaffected. However, such perturbation arguments are difficult to extend to the deeper lying orbitals and would therefore not explain, for example, the similarity of the PE spectra of heptaphene and tetracene.

If the appearance of autonomous bands in the PE spectra of polycyclic hydrocarbons is a general phenomenon, a more general theory is clearly needed. We believe that a more promising approach would be to use an MIM ("molecules in molecules") procedure in which the orbitals of tetraphene are expressed as linear combinations of the orbitals of anthracene and naphthalene; naphthopyrene is similarly treated using the orbitals of pyrene and anthracene. Such a model would retain the conceptual simplicity of the sextet fromalism and perhaps reveal new, yet undiscovered regularities.

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