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ASYMMETRIC ANNELLATION EFFECTS—IV*

DIBENZACENES

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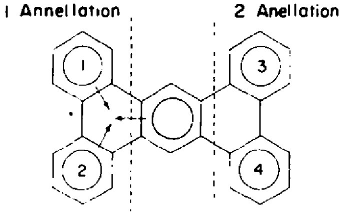
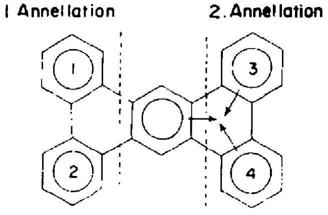
Abstract—The asymmetric annellation effects and the shift difference rule are explained on the basis of the two schemes A and B. The asymmetry of the annellation effects in passing from acenes to 1:2-benz-, and 1:2,3:4-dibenzacenes support the scheme B involving the view that the transition of a cyclic conjugated polyene into a benzenoid ring produces a violet spectral shift. Another set of asymmetric annellations is found in the heteronuclear dibenzacenes. This series can be started from ethylene. The merits of a symplified valence bond theory are considered for the interpretation of asymmetric annellation effects. The assumption of two transferable electrons capable of migrating through the rings of an acene leads to two π-electron levels for benzene with 4 π-electrons in two mobile double bonds in the lower level and 2 π-electrons moving freely about the ring and not belonging to any double bond.

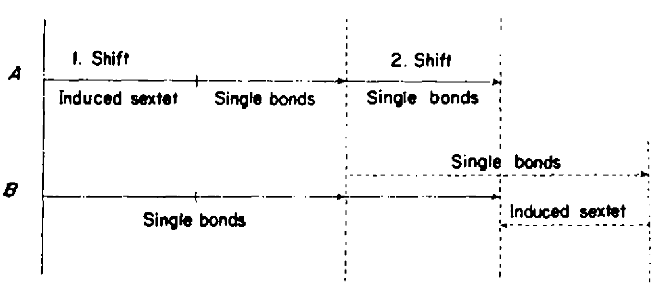
Asymmetric annellation effects are produced by two formally symmetrical substitutions of the benzene rings (1,2,3,4) to an acene system. These effects are observed as two very different red shifts of the β-bands. The nature of this electronic asymmetry becomes obvious if the second shift is subtracted from the first shift. This results in the extension of the initial acene system to the next higher acene, i.e. from benzene to naphthalene, from naphthalene to anthracene, from anthracene to tetracene and from tetracene to the pentacene system etc.[1]



Scheme A



Scheme B



There are two interpretations of this empirical rule possible. The first interpretation (A) was given recently and keeps in line with conventional ideas about

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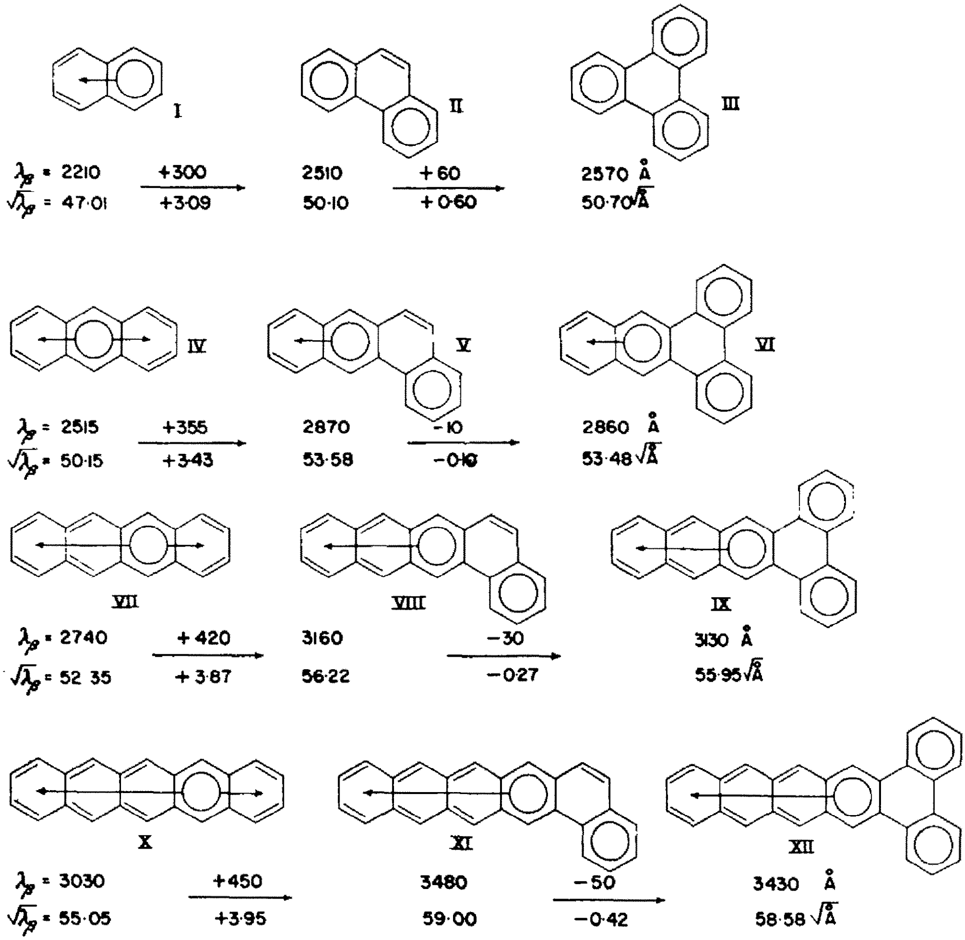
* Part III: *Tetrahedron* **6**, 358 (1959).

[1] E. Clar, *Tetrahedron* **6**, 355 (1959).

spectral conjugation and spectral shifts. Here the first shift consists of the sum of the shifts due to two single bonds, providing conjugation of the aliphatic type and to the shift resulting from the formation of an induced aromatic sextet, as indicated by the arrows. The deduction of the second shift gives the pure aromatic shift which thus must be towards the red.



In the second interpretation (B) the first shift is attributed to the single bonds alone, whilst the second one is considered to be the difference of the same shift *minus* the aromatic shift which must then be towards the short wave end of the spectrum. This means that a benzene molecule represented by one fixed Kekulé structure should absorb light at a longer wavelength than benzene with 6 mobile π-electrons, in an aromatic sextet.* The rule that the difference between the two shifts gives an increase amounting to one aromatic ring is valid in both interpretations (A and B).

A decision in favour of the scheme (B) can be reached if the annellation series I-XII is considered. The shifts are recorded in Å and $\sqrt{\text{Å}}$, the latter being a scale for the reciprocal nuclear charges. The first shifts (300, 355, 420 and 450) in these

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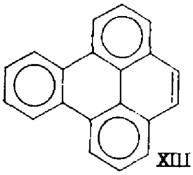
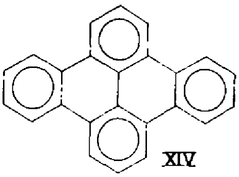
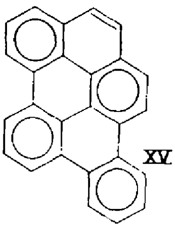
* The aromatic sextet was first introduced by T. W. Armit and R. Robinson, *J. Chem. Soc.* 1604 (1925). In this paper its use is directly derived from it not involving the latter subdivision given to it.

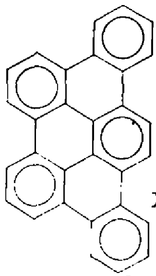
four asymmetric annellation series are much bigger than the second ones (+60, −10, −30 and −50). If the principle of the maximum number of aromatic sextets is applied, then the acenes (I, IV, VII, X) can have only one benzenoid ring. The two transferable electrons can move through the system as indicated by the arrows. The fusion of the angular ring in (II, V, VII and XI) restricts this movement to one ring less, and this is the ring at the angle in which a double bond becomes fixed. This ring must therefore lose its acene character and thus produce a red shift. The fusion of the new ring with the third sextet has apparently very little influence, since the connection of the butadiene system in this ring brings about the same amount of red-shift just as the formation of the third sextet causes a violet-shift.

That this is the case is shown by the second annellation stage leading to (III, VI, IX and XII). Since the double bonds in the positions 3 and 4 are already fixed by the first annellation, the new rings fused to these positions must produce about the same amounts of red and violet shifts, thus resulting in a very small overall shift in comparison with the shift caused by the first annellation. Very small positive or negative annellation effects therefore are an indication of fixed double bonds at the position where a new ring has been fused. This can also be shown in the pyrene and perylene systems XIII and XV, where the application of the maximum number of benzenoid rings (marked with circles) enforces the fixation of double bonds. The annellation effects in passing to XIV and XVI are small violet-shifts (−30 and −55 Å respectively).


XIII


XIV


XV

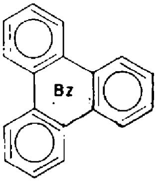

XVI

$$\begin{array}{lcl} \lambda_\beta = 2890 & \xrightarrow{-30} & 2860 \\ \sqrt{\lambda_\beta} = 53{\cdot}76 & -0{\cdot}28 & 53{\cdot}48 \end{array} \qquad \begin{array}{lcll} 3095 & \xrightarrow{-55} & 3040 & \text{Å} \\ 55{\cdot}64 & -0{\cdot}50 & 55{\cdot}14 & \sqrt{\text{Å}} \end{array}$$

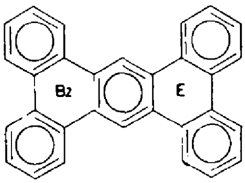
If the asymmetric annellation scheme (B) is accepted it is still not clear why an induced benzenoid ring is not formed in the first stage of the annellation leading to triphenylene III. An explanation might be given using a simplified version of the valence bond theory with a drastic reduction of the multitude of Kekulé structures to manageable proportions.

If the chemical inertness and high stability of benzene is secured by only two Kekulé structures there is no reason why there should be more Kekulé structures per benzenoid ring in fully benzenoid hydrocarbons of equal stability. There is also no reason why the double bonds in the benzenoid rings should exchange their places independently from one another, thus giving rise to a large number of structures which are not needed to explain the stability.

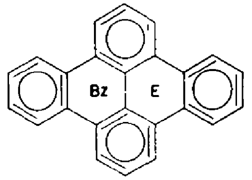
However if the movement of double bonds is synchronized in such a way that the maximum number of induced benzenoid rings (marked Bz) and a minimum number of empty rings (E) are formed, an interpretation of scheme (B) can be given. Thus triphenylene has only two Kekulé structures XVIIa and XVIIb. Only in



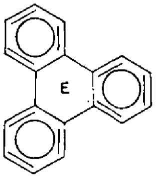
XVIIa



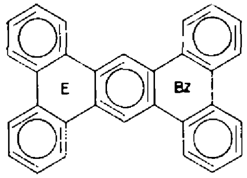
XVIIIa



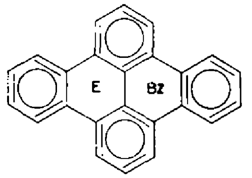
XIXa



XVIIb

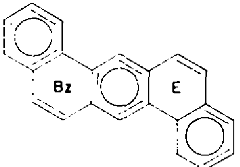


XVIIIb

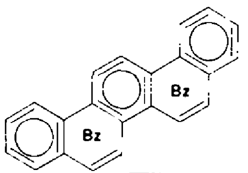


XIXb

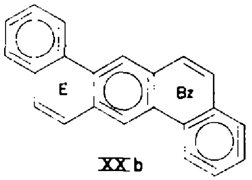
structure XVIIa are there three double bonds in the central ring which could thus have aromatic character. This is apparently not enough. In tetrabenzanthracene both structures XVIIIa and XVIIIb each have one induced benzenoid ring (Bz) and an empty ring (E). The overall benzenoidity is thus increased from 5 inherent benzenoid rings to 6. This accounts well for the fact that, according to scheme (B) a second annellation of a diphenyl system to benzene is required to produce the induced sextet. In dibenzopyrene the two Kekulé structures XIXa and XIXb have the same effect as the annellation of two *o*-phenylene systems to diphenyl.



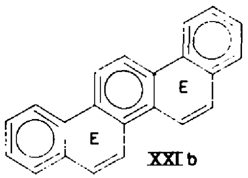
XXa



XXIa

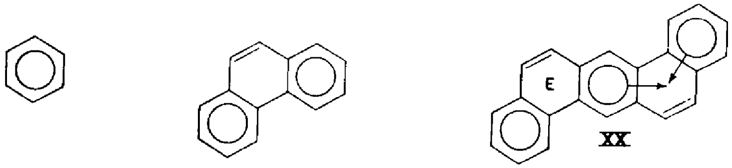


XXb



XXIb

If this interpretation is correct then it should apply also in systems where two benzenoid rings are replaced by two fixed double bonds, as in XXa and XXb. Building up 1:2,5:6-dibenzanthracene XX from benzene by successive annellation of two styrene complexes results in an asymmetric annellation effect. The shift-difference rule again shows that benzene has been extended to a naphthalene system. However the agreement is not so good as that obtained on building up picene XXI in an analogous way from benzene. The difference between these two examples can only be explained by a change in the fine structure of the central ring in dibenzanthracene XX. The dibenzotetracenes XXII and XXIII and dibenzopentacenes XXIV can be obtained



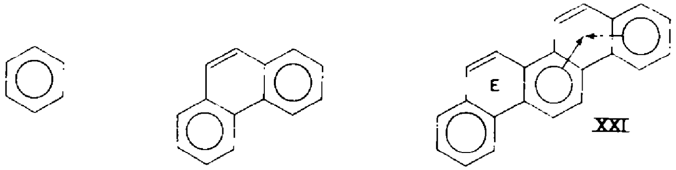
XX

$$\lambda_\beta = 1790 \xrightarrow{+720} 2510 \xrightarrow{+460} 2970\ \text{Å}$$

$$\sqrt{\lambda_\beta} = 42{\cdot}31 \xrightarrow{+7{\cdot}79} 50{\cdot}10 \xrightarrow{+4{\cdot}40} 54{\cdot}50\ \sqrt{\text{Å}}$$

$$50{\cdot}10 - 4{\cdot}40 = 45{\cdot}70 \quad \triangleq \quad 2089\ \text{Å}$$

β-Band of Naphthalene, found 2210 Å



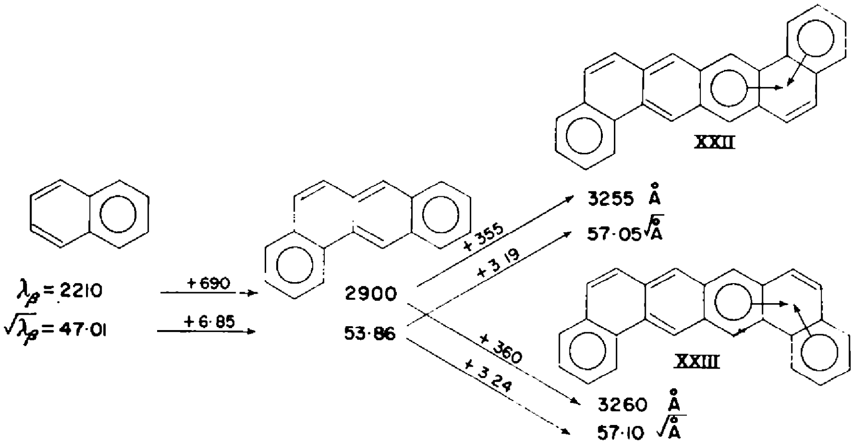
XXI

$$\lambda_\beta = 1790 \xrightarrow{+720} 2510 \xrightarrow{+335} 2845\ \text{Å}$$

$$\sqrt{\lambda_\beta} = 42{\cdot}31 \xrightarrow{+7{\cdot}79} 50{\cdot}10 \xrightarrow{+3{\cdot}25} 53{\cdot}35\ \sqrt{\text{Å}}$$

$$50{\cdot}10 - 3{\cdot}25 = 46{\cdot}85\ \sqrt{\text{Å}} \quad \triangleq \quad 2195\ \text{Å}$$

β-Band of Naphthalene, found 2210 Å



XXII

XXIII

$$\lambda_\beta = 2210 \xrightarrow{+690} 2900 \xrightarrow{+355} 3255\ \text{Å}$$

$$\sqrt{\lambda_\beta} = 47{\cdot}01 \xrightarrow{+6{\cdot}85} 53{\cdot}86 \xrightarrow{+3{\cdot}19} 57{\cdot}05\ \sqrt{\text{Å}}$$

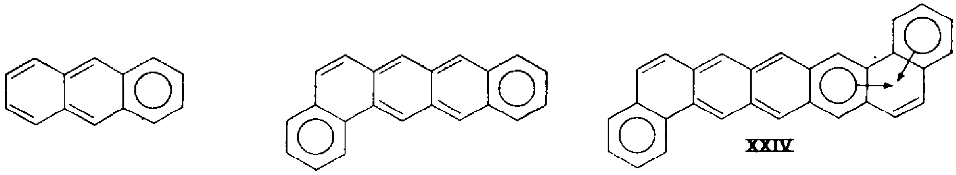
$$2900 \xrightarrow{+360} 3260\ \text{Å}$$

$$53{\cdot}86 \xrightarrow{+3{\cdot}24} 57{\cdot}10\ \sqrt{\text{Å}}$$

$$53{\cdot}86 - 3{\cdot}19 = 50{\cdot}67\ \sqrt{\text{Å}} \quad \triangleq \quad 2567\ \text{Å}$$

$$53{\cdot}86 - 3{\cdot}24 = 50{\cdot}62\ \sqrt{\text{Å}} \quad \triangleq \quad 2562\ \text{Å}$$

β-Band of Anthracene, found 2534 Å (corrected for Benzene soln.)



XXIV

$$\lambda_\beta = 2515 \xrightarrow{+675} 3190 \xrightarrow{+315} 3505\ \text{Å}$$

$$\sqrt{\lambda_\beta} = 50{\cdot}10 \xrightarrow{+6{\cdot}34} 56{\cdot}49 \xrightarrow{+2{\cdot}71} 59{\cdot}20\ \sqrt{\text{Å}}$$

$$56{\cdot}49 - 2{\cdot}71 = 53{\cdot}78\ \sqrt{\text{Å}} \quad \triangleq \quad 2892\ \text{Å}$$

β - Band of Tetracene, found $\left\{\begin{matrix}2930\\2740\end{matrix}\right\} \triangleq$ 2865 Å (corrected for Benzene soln.)

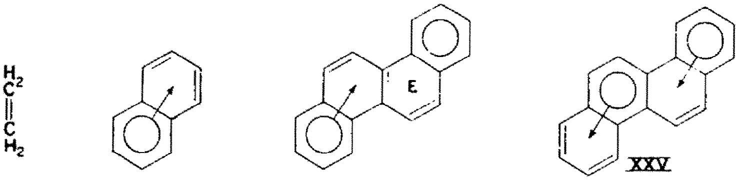
Alc soln.

by asymmetric annellation from naphthalene and anthracene respectively. The shift-difference rule gives the correct answer in all three cases.

Chrysene XXV can be derived in an analogous way from ethylene. It is remarkable that the first shift (234 Å) is a small one because the newly formed ring in naphthalene has induced benzenoid character. The magnitude of the second shift is influenced by the transformation of the structure XXVa to XXVb. The latter contains a diphenyl system whose transfer to the two adjoining rings produces two fused naphthalene systems and no empty ring. The shift-difference rule gives correct figures for the α- and β-bands of benzene even in this extreme case.

$$\lambda_\alpha = 3110 \xrightarrow{+490} 3600 \ \text{Å}$$

$$\sqrt{\lambda_\alpha} = 55{\cdot}78 \xrightarrow{+4{\cdot}22} 60{\cdot}00 \ \sqrt{\text{Å}}$$



XXV

$$\lambda_\beta = 1976 \xrightarrow{+234} 2210 \xrightarrow{+460} 2670 \ \text{Å}$$

$$\sqrt{\lambda_\beta} = 44{\cdot}45 \xrightarrow{+2{\cdot}56} 47{\cdot}01 \xrightarrow{+4{\cdot}67} 51{\cdot}68 \ \sqrt{\text{Å}}$$

$$55{\cdot}78 - 4{\cdot}22 = 51{\cdot}56 \ \sqrt{\text{Å}} \ \hat{=} \ 2658 \ \text{Å}$$

α-Bond of Benzene, found 2604 Å

$$47{\cdot}01 - 4{\cdot}67 = 42{\cdot}34 \ \sqrt{\text{Å}} \ \hat{=} \ 1792 \ \text{Å}$$

β-Bond of Benzene, found 1790 Å

Building up tetrabenzonaphthalene XXVI in an analogous way follows a different course. The first annellation produces a big shift and an empty middle ring in phenanthrene. The second shift is much smaller. To measure it correctly the β-band of tetrabenzonaphthalene must be corrected in order to account for the over-lapping H atoms (marked by x) which shifts the β-band to the red.[2] The comparison of the β-band of chrysene with the β-band of the isomeric 3:4-benzophenanthrene which has two overlapping H atoms shows a red-shift of 140 Å. This is the minimum correction which has to be applied. Using this corrected β-band, the deduction rule gives a β-band at 2173 Å, which is very near to the β-band of naphthalene (at 2210 Å in alcohol). A bigger correction for over-lapping would give an even closer agreement. It is thus obvious that in the second annellation two induced benzenoid rings (Bz) have been formed in the centre. The central double bond must therefore participate in both central sextets.

It is already somewhat difficult to explain the asymmetric annellation effect leading to picene on the basis of the two structures XXIa and XXIb, one with two induced sextets and the other with none. But it can be claimed that on average there is only one induced sextet. However, this explanation fails in the case of tetra-benzonaphthalene. Neither with the structure XXVIa and XXVIb nor in any other pair of structures can two induced sextets on the average be obtained. It is obvious that the limit of application of the simplified valence bond scheme is reached.

The role of the double bond between two rings must be more closely defined.

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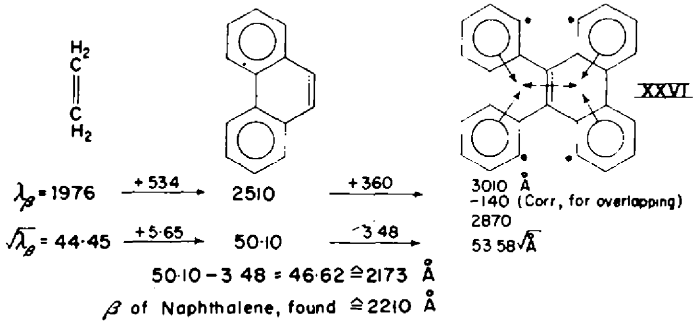
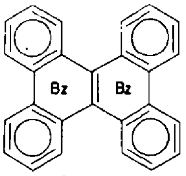
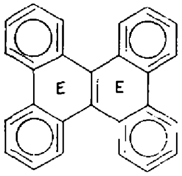
[2] E. Clar and D. G. Stewart, *J. Amer. Chem. Soc.* 74, 6235 (1952).



XXVI



XXVI a



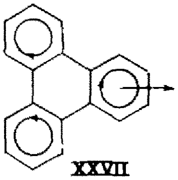
XXVI b

This can be done by identifying it with the transferable pair of electrons which can migrate through an acene and participation of which in the formation of an induced sextet is essential.[1] Since there is only one mobile pair of these electrons available in one inherent benzenoid ring, the central ring in picene XXI can only produce one induced sextet in one of the adjoining rings. In tetrabenzonaphthalene XXVIa the four inherent benzenoid rings and the central double bond provide five pairs of electrons symbolized by the five double bonds between the rings which form a system of five fused naphthalene complexes.

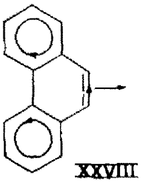
The assumption of a transferable pair of electrons symbolized by arrows becomes a necessity because the aromatic sextets alone do not indicate the asymmetry of the annellation and cannot predict in which of the two stages the formation of the first induced sextet takes place. The Kekulé structures alone can do this, but do not show the asymmetry of the annellation because both methods can give only the answer which is inherent in the choice of the symbols.

In order to understand why no induced aromatic sextet is formed in triphenylene it is necessary to define where the two transferable electrons, which have a greater mobility than the other π-electrons, are located in a benzenoid ring. If one electron rotates around the whole ring above the molecular plane the other electron must rotate in the opposite sense, below the plane. Although the momenta are compensated within the ring, there are two different ways to combine them with another electron pair of this kind in another ring. The interchange between these two pairs can be bonding or antibonding. In the ground state they will be bonding in diphenyl but it is not possible to add a third ring with a bonding pair of these electrons as in triphenylene. The situation can be best illustrated by marking the momenta of the electrons only on one side of the molecule (XXVII) because on the other side the momenta are exactly opposite. A coupling between the three pairs of electrons is just as impossible as the coupling of the rotation of three wheels touching each other. The result is that the third ring tends to be repelled by the other two, as indicated by the straight arrow in XXVII. This causes a big red-shift with no reduction produced by an aromatization of the central ring. The bond distance between the three rings should be intermediate between a single bond in diphenyl and two single bonds of the paraffinic type.

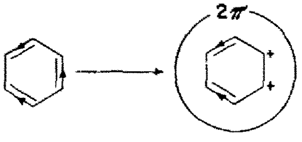
This repulsion of the third ring is counteracted by the additional rings in tetrabenzanthracene XVIII and dibenzopyrene XIX and the formation of an induced sextet can take place.



XXVII



XXVIII



XXIX a XXIX b

The situation is quite similar in phenanthrene XXVIII except that one ring is replaced by one double bond. It had been shown at the beginning of this paper that a benzenoid ring can be replaced by a fixed double bond with little effect on the β-band and the asymmetric annellation. It must be concluded that a double bond can be substituted for a benzenoid ring in the interaction between benzenoid rings. This leads necessarily to the assumption that in a double bond one π-electron is above and the other below the molecular plane, both having opposed orbital momenta. This being the case the interaction of cyclic conjugated double bonds must be analogous to that between benzenoid rings.

In a Kekulé structure XXIXa there must be one double bond, antibonding relatively to the other two. Accordingly, Kekulé benzene, an alternant hydrocarbon in terms of marked carbon atoms, becomes a nonalternant hydrocarbon in terms of marked double bonds. Since the space in benzene is more limited than in triphenylene a relief of the strain is obtained by transferring two π-electrons out of one double bond to a higher level, where they belong to the ring as a whole and to no particular double bond. The remaining two double bonds can then move into any position which is the most favourable in a particular derivative. In XXIXb they receive more positive charge than in XXIXa which accounts for the extra aromatic energy in comparison with a single Kekulé structure.

There are also two electronic levels as in Hückel's term scheme,[3] the difference being that in the latter case the lowest level is occupied by two and the next higher by four π-electrons, whilst in XXIX the inverse distribution is applied, thus creating only two particularly mobile π-electrons which can migrate from one ring to another through the whole length of an acene. This gives mobility to the "background" double bonds within their rings and to the positive charges through the whole length of an ocene. It also accounts for the asymmetric annellation effect, because the pair of transferable electrons can be effective only on one side of an acene simultaneously.

[3] E. Hückel, *Grundzüge der Theorie der ungesättigten and aromatischen Verbindungen* p. 71. Verlag Chemie (1938).