Tetrahedron, 1961, Vol. 16, pp. 113 to 118. Pergamon Press Ltd. Printed in Northern Ireland

ASYMMETRIC ANNELLATIONS—V

PHENYLACENES

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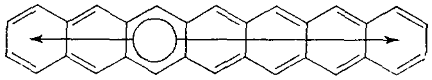
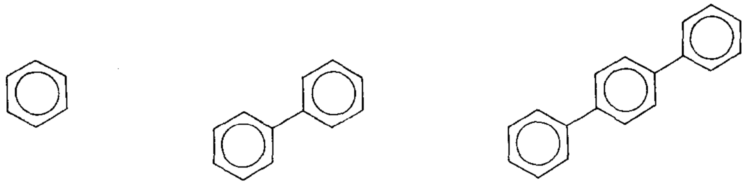
(*Received* 9 *May* 1961)

Abstract—An asymmetric annellation effect is recorded in passing from an acene to a phenylacene and then to a diphenylacene if the formation of an exocyclic electron quartet is possible. This is considered an important unit in a polycyclic system. The electronic structures are discussed involving a subdivision of the π-electrons into π_α and π_β electrons.

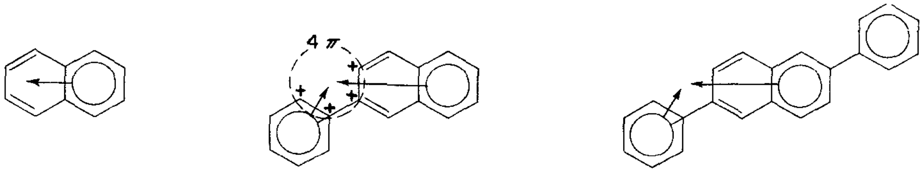
THE existence of aromatic sextets in an acene is only possible if two π_α-electrons of the sextet have a greater mobility than the other electrons located in the double bonds. Migrating through the acene as indicated by the arrows they can give each ring a sextet and a share of benzenoidity.[1]



If phenyl-complexes each having an aromatic sextet are condensed a small annellation effect is recorded. Passing from benzene to diphenyl and terphenyl the red shifts of the β-bands are small. Contrary to this a strong asymmetric annellation effect is observed in the series napthhalene, 2-phenylnaphthalene and 2,6-diphenylnaphthalene (Fig. 1):



$\lambda_\beta = 1835 \xrightarrow{145} 1980 \xrightarrow{85} 2065$ Å (in heptane)



$\lambda_\beta = 2210 \xrightarrow{290} 2500 \xrightarrow{130} 2630$ Å (in alcohol)

The first shift is equal to the annellation of one ring in the acene series, i.e. from naphthalene to anthracene. The second smaller shift is similar to the one recorded

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[1] E. Clar, *Tetrahedron* **5**, 98 (1959); **6**, 355 (1959); **9**, 202 (1960).

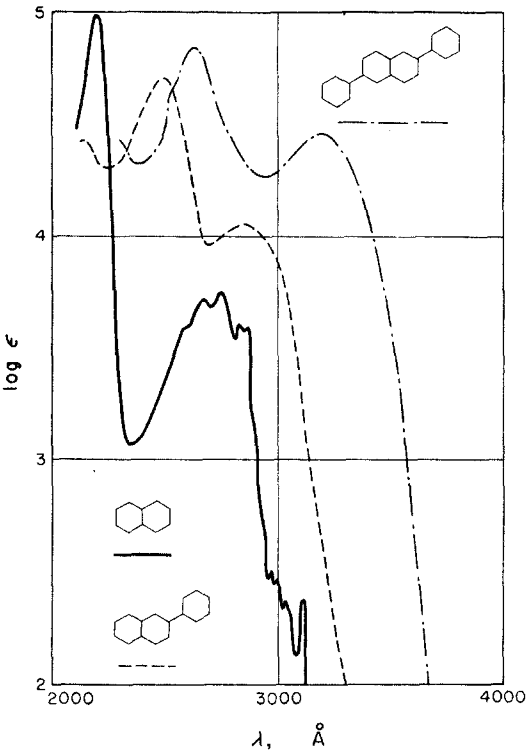
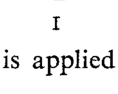
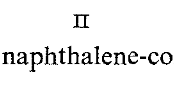


FIG. 1. Absorption max (Å) and log ε (parentheses) of:
——— Naphthalene in alcohol: α, 3110 (2·40), 3040 (2·38), 3010 (2·48), 2970 (2·64); p, 2850(3·60), 2830 (3·60), 2750 (3·75), 2660 (3·70), 2570 (3·60), 2480 (3·30); β, 2210 (5·00).
– – – – 2-Phenylnaphthalene in cyclohexane: p, 2850 (4·05); β, 2,500 (4·70).
–·–·–· 2,6-Diphenlynaphthalene in benzene: p, 3180 (4·44); in alcohol: β, 2630 (4·48).

in the transition from diphenyl to terphenyl. If the experimentally established equal red shift in the acene series originates from the mobility of the two π_α-electrons then a similar process must be assumed for the large shift in passing from naphthalene to 2-phenylnaphthalene. This will be possible if the four positive charges belonging to the two pairs of mobile electrons assume the position as indicated in the formula of phenylnaphthalene. Then the π_α-electrons can partly leave the rings and form an induced quartet as symbolized by the broken circle. It is the analogous process to the formation of an induced sextet, just without the double bond bridge. Benzene was represented by the formula I with four π_β-electrons belonging to the whole ring, one electron being above and the other one below the molecular plane.[2]



I



II

If the same principle is applied to the naphthalene-complex the structure II is obtained.

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[2] E. Clar, *Tetrahedron* **9**, 202 (1960).

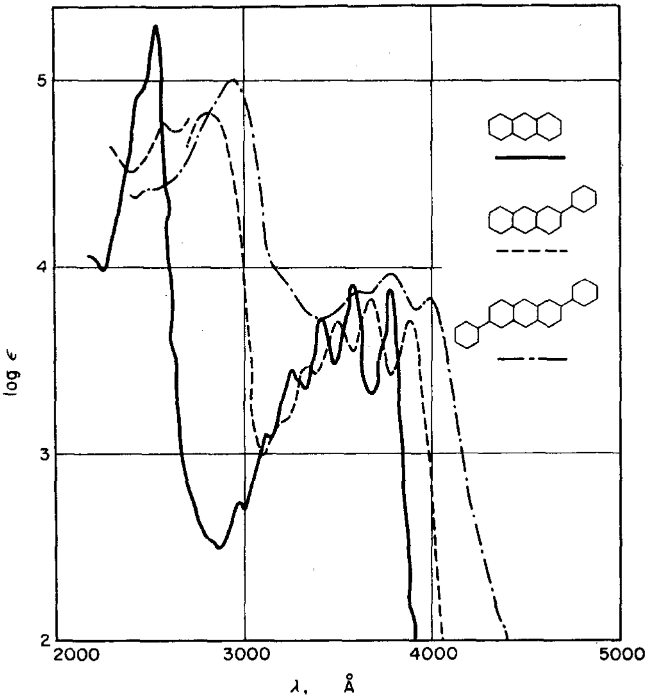
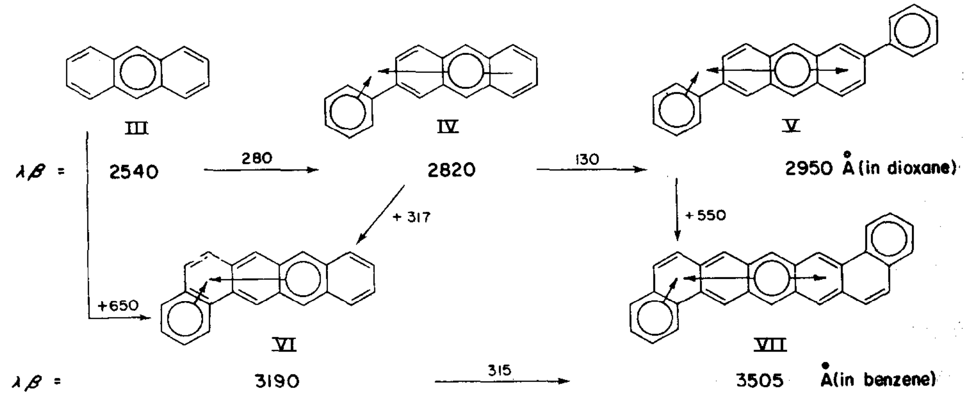


FIG. 2. Absorption max (Å) and log ε (parentheses) of:
——— Anthracene in dioxane: p, 3780 (3·88), 3580 (3·90), 3420 (3·73), 3260 (3·45), 3120 (3·10), 2970 (2·74); β, 2540 (5·30).
- - - - 2-Phenylanthracene in benzene: p, 3880 (3·71), 3680 (3·83), 3500 (3·72), 3350 (3·47); β, 2820 (4·82); from 2760 Å in alcohol.
—·—·· 2,6-Diphenylanthracene in benzene: p, 3990 (3·84), 3775 (3·96), 3600 (3·87); β, 2950 in alcohol. (5·00); from 2800 Å in alcohol

The transfer to two π_α-electrons from the phenyl-group cannot be repeated a second time in an anthracene-complex, because a third pair of π_α-electrons from the second phenyl group would not have the four positive charges available to form another quartet. In accordance with this, another asymmetric annellation series is formed with anthracene III, 2-phenylanthracene IV and 2,6-diphenylanthracene V (Fig. 2):



The connection of the first phenyl-group to anthracene shifts the β-band to the position of the β-band of tetracene. The second phenyl-group in going to V has again little effect. The introduction of the ethylene bridges in passing from IV to VI and from V to VII produces the annellation series III → VI → VII and brings the shift deduction rule[2] into operation. They also transform the quartet into a sextet.

It is obvious that the replacement of two mobile π_α-electrons by four π_α-electrons must strongly affect the p-bands. It has been known for a considerable time that angular annellation produces a shift of the p-bands to shorter wavelength. However, this shift is much bigger than apparent in the electronic transition, because the p-bands change their class from p-bands to $p_{II}(p_\beta)$-bands. Without this discrimination which was explained in detail recently,[3] there would be no asymmetric annellation effect for the p-bands and the 1,2-benzacenes would have the same p-bands as the acenes with the same number of rings.

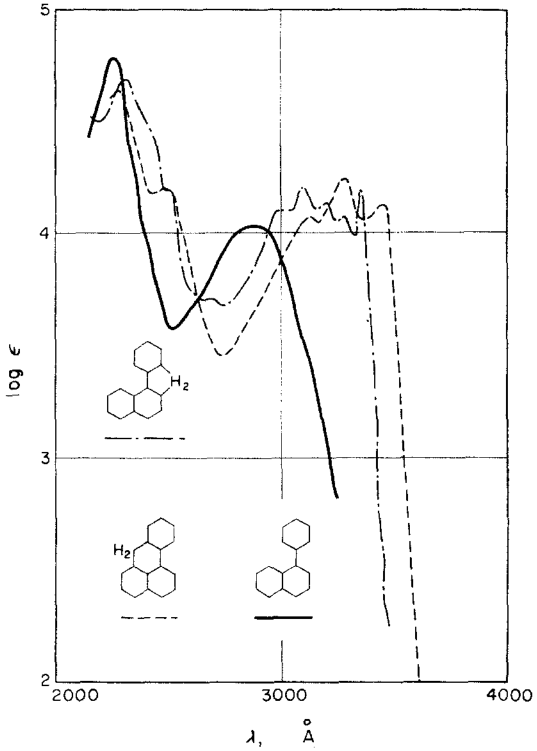


FIG. 3. Absorption max (Å) and log ε (parentheses) of:

——— 1-Phenylnaphthalene in cyclohexane: p, 2900 (4·04); β, 2260 (4·80).

– – – – Benzanthrene in alcohol: p, 3440 (4·13), 3290 (4·25), 3120 (4·08); 2500 (4·20); β, 2280 (4·66).

–·–·– 3,4-Benzofluorene in alcohol: p, 3350 (4·20), 3280 (4·08), 3200 (4·14), 3100 (4·14), 3000 (4·10), 2500 (4·29); β, 2310 (4·70).

The transfer of a pair of π_α-electrons from a phenyl-group to form a quartet is possible only in β-positions. But it does not take place in α-positions. Thus the

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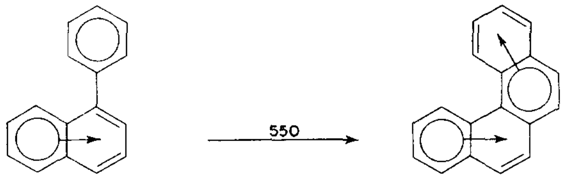
[3] *IVth Symposium on Molecular Spectroscopy.* Pergamon Press, London (1960).

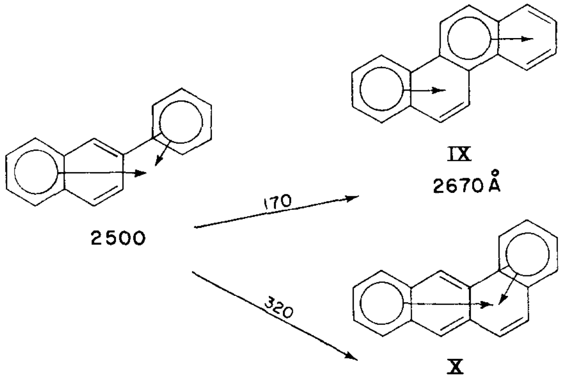
β-band of naphthalene (2210 Å) shifts little in passing to 1-phenylnaphthalene (2260 Å). One can argue that the phenyl-group is not uniplanar with the naphthalene-complex, so preventing the transfer of π_α-electrons. But this does not apply to benzanthrene (β-band at 2280 Å) and 3,4-benzofluorene (β-band at 2310 Å) (Fig. 3). The shifts in the two latter cases are as small as would be expected for a substitution with methylene-groups. There is no difference to account for a π_α-electron transfer. One could rather say that 1-phenylnaphthalene is not planar because little energy, if any, could be gained by forcing the phenyl-group into a planar arrangement.

A new situation is created by fusing a ring between phenyl- and naphthalene-complex, as in 3,4-benzophenanthrene VIII. Although this hydrocarbon is not planar a strong shift of the β-band by comparison with 1-phenylnaphthalene is recorded. The shift of 550 Å is much bigger than the one observed in passing from 2-phenylnaphthalene to chrysene IX or tetraphene X which amounts to 170 Å and 370 Å respectively.



λ_β = 2260

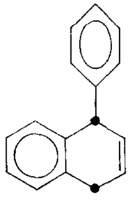
VIII
2810 Å (in alcohol)



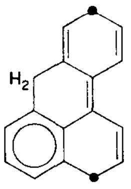
2500

IX
2670 Å

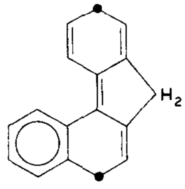
X
2870 Å (in alcohol)



XI



XII



XIII

It is obvious that the two central rings in VIII can assume naphthalene structure, thus providing electron transport as indicated by the arrows, in formula VIII which is analogous to the structure IX for chrysene. The difference in $\lambda\beta$ in comparison with chrysene is accounted for by the planar arrangement of the rings in IX and the non-planarity in VIII. The shift in going from 2-phenylnaphthalene to chrysene IX is smaller than in passing to tetraphene X. The former has more benzenoid character because the two sextets forming a diphenyl-system can move simultaneously into the other two rings giving them a share of benzenoidity.

Although the β-bands of the hydrocarbon in Fig. 3 are in a very narrow region, the p-bands of benzanthrene and 3,4-benzofluoranthene are considerably advanced in comparison with 1-phenylnaphthalene. In the excited state of 1-phenylnaphthalene XI two π-electrons are located in the naphthalene-complex, whilst in the excited state of benzanthrene XII and 3,4-benzofluorene XIII both the phenyl- and the naphthalene-complex are involved and a double bond is formed between them. The gain of this double bond makes the transition energy smaller just as in diphenyl compared with benzene. This produces a red shift of the p-bands.