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THE NON-EXISTENCE OF A THREEFOLD AROMATIC CONJUGATION IN LINEAR BENZOLOGUES OF TRIPHENYLENE (STARPHENES)

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Abstract—The synthesis of nonastarphene-(2,3,3)* (IX) and decastarphene-(3.3.3) (XI) is described. The UV and visible absorption spectra of the starphenes (threefold linearly annellated triphenylene benzologues) indicate that the aromatic conjugation involves only two branches of the system the third branch being isolated from the delocalization of the π-electron system of the other two.

The absorption spectra of polycyclic hydrocarbons can be classified according to their annellation effect. The acenes (with linearly annellated rings) give spectra in which all three groups of bands α-, β- and p-bands show regular shifts towards the red with the fusion of each successive ring. In the spectra of the phenes (linearly annellated benzologues of phenanthrene) only the α- and β-bands shift in the same way towards the red, whilst the p-bands show a small shift towards shorter wavelength.[1]

If three branches are annellated to a central ring, radiating linearly from it, benzologues of triphenylene are formed for which we propose the name "Starphenes" (starlike phenes). In this case only two branches are in aromatic conjugation during the time of light absorption. The two longest branches determine the long wave part of the spectrum. This has been shown before in the cases of the 1:2,3:4-dibenzacenes[2] and lin. benzologues of pentaphene.[3]

We are now presenting the extreme asymmetric annellation effect in the series consisting of heptaphene[4] and its benzologues: octastarphene-(1.3.3),† nonastarphene-(2.3.3) (IX) and decastarphene-(3.3.3) (XI). Their absorption spectra are recorded in Fig. 1. The α- and β-bands do not shift towards the red but show small shifts to shorter wavelength. A full aromatic conjugation of the phene type would require a shift of more than 1000 Å towards the red in the case of decastarphene (XI).

Very small shifts of the p-bands are recorded in this series. However, already in the phene series only the longest branch accounts for the p-band shift towards the red. Therefore no further significant changes are observed.

The spectra of the asymmetric hydrocarbons octastarphene-(1.3.3) and nonastarphene-(2.3.3) show β-bands at shorter wavelength and higher intensity than the β-bands. These β′-bands can be explained by an aromatic conjugation between a long and a short branch. There are two possibilities for this in octastarphene- (1.3.3)

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* The numbering system of the starphenes follows the principle introduced by T. H. Goodwin and D. A. Morton-Blake, *Theor. Chim. Acta* Berl. **2**, 75 (1964). The figures give the number of rings in each of the three branches annellated linearly and radiating from a central ring. The total number of rings is therefore the sum of the three figures plus one, as indicated by the name of the starphene.

† Named 7:8-Benzheptaphene in Ref. 5.

and nonastarphene-(2.3.3), whilst there can be only one case of conjugation between the two longest branches. The two β′-bands at 3220 Å and at 3310 Å correspond to the β-bands of 1:2-benzotetracene[6] and hexaphene[7] at 3190 Å and 3580 Å resp.

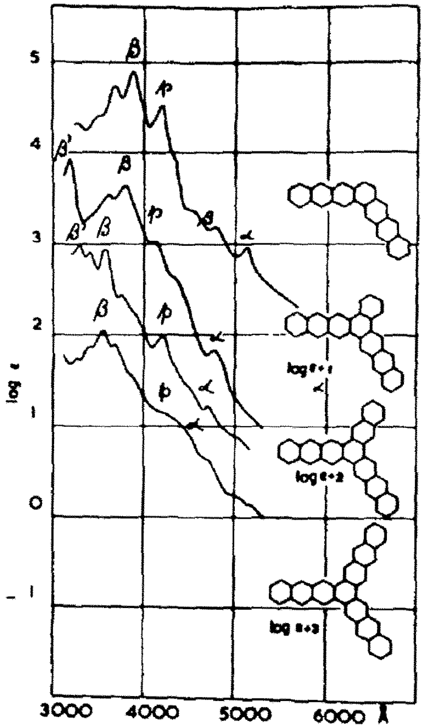

FIG. 1 Absorption spectra in trichlorobenzene with max (Å) and log ε in (parentheses). Heptaphene: α: 5190 (2·94), 4870 (3·16), 4570 (3·34); p: 4220 (4·47); β: 3900 (4·83), 3700 (4·67). Octastarphene-(1,3,3): α: 4850 (2·82); p: 4170 (4·02); β: 3840 (4·60), 3660 (4·49); β′: 3220 (4·88), Nonastarphene-(2,3,3): α: 4·700 (3·22); p: 4200 (3·99); 3760 (4·44); β: 3590 (4·95), 3420 (4·90); β′: 3310 (4·99).
Decastarphene-(3,3,3): α: 4700 (3·66)?; p: 4250 (4·08)?; 3670 (4·89); β: 3540 (5·04), 3380 (4·88).

There is no evidence that formally equal protons in triphenylene are different in the NMR spectrum.* This cannot be expected if the twofold conjugation involving different branches switches over quickly enough to give only one NMR record. However, to account for the electronic spectra a twofold conjugation must have a life which is long by comparison with the very short time of light absorption.

Goodwin and Morton-Blake[9] have shown that a satisfactory explanation can be given for the restriction to a twofold conjugation by a simple molecular orbital study.

There must be a compelling reason why the third branch is not in aromatic conjugation with the remaining π-electron system of a starphene. The simplest explanation is the assumption that the pair of π-electrons on the lowest level in the central ring belongs to a double bond. This partly cuts off conjugation as in a crossconjugated

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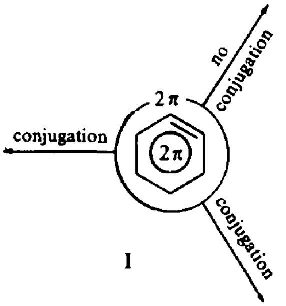
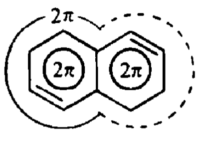
* Our own unpublished spin–spin decoupling experiments at 100 mc/s and Ref. 8.

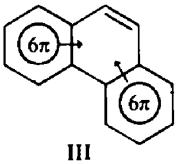
system. The extention of this idea to all benzene rings results in a subdivision of the aromatic sextet in which one pair of π-electrons is located in a double bond, the pair on the next level is delocalized within the ring and the third pair is delocalized on an orbital outside the ring and capable of migrating from one ring to the next. Thus for benzene formula I is obtained in which the double bond is freely mobile. There may be restrictions of this mobility in compounds which show the Mills–Nixon effect.[10]



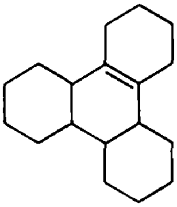
I



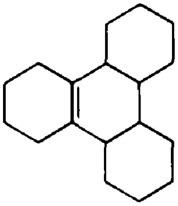
II



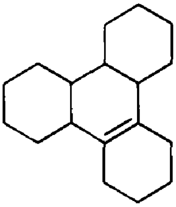
III



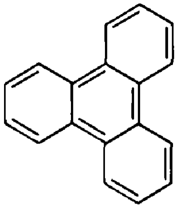
IVa



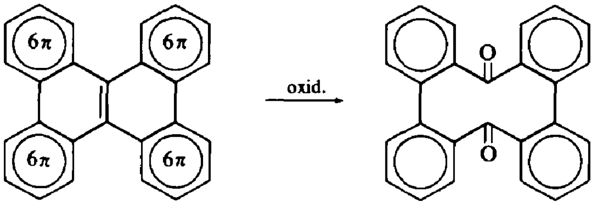
IVb



IVc



IVd

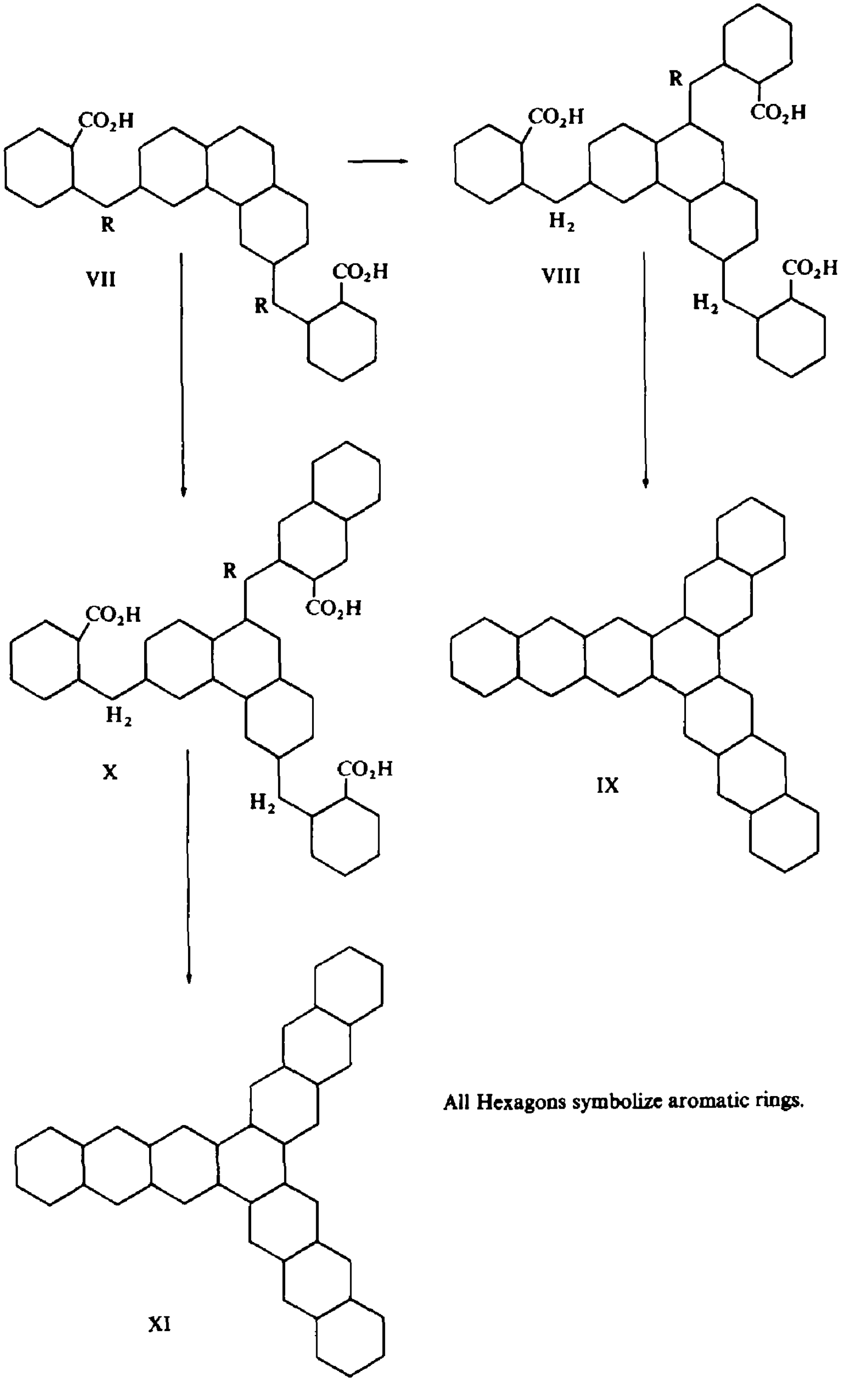


V VI

There are also restrictions in naphthalene (II) where the double bonds are localized between any α–β-position. Complete localization of one double bond is expected in phenanthrene as indicated in formula III. This can be shown by the NMR spectra of methylphenanthrenes.[11]

The double bond in the central ring of triphenylene can be in three positions IVa, IVb, IVc (the other double bonds are not marked). The double bond between two rings always excludes one ring from aromatic conjugation. Structure IVd appears unacceptable, since it has only one aromatic sextet, which is in the central ring.

Localization of a double bond between two rings is completely restricted to 1:2,7:8-dibenzochrysene (V) and some of its derivatives.[12] This becomes obvious in the very exceptional oxidation of this central double bond to the diketone VI.



All Hexagons symbolize aromatic rings.

The arrangement of the π-electrons outlined above has the advantage that their distribution in each ring obeys strictly the Pauli principle and that the different degree of localization of only *one* double bond does not impair the aromaticity of the system as a whole but accounts well for the observed reactivities.

The synthesis of the new starphenes started from the dicarboxylic acid VII (R = H_2) which was prepared by a drastic condensation of phenanthrene with phthalic anhydride and aluminium chloride.[4] This gave the dicarboxylic acid VII (R = O) which was reduced to the acid VII (R = H_2). A condensation of the latter with phthalic anhydride gave the acid VIII (R = O). Reduction yielded the acid VIII (R = H_2). The threefold cyclization to nonastarphene-(2.3.3) IX was achieved by a melt with sodium chloride–zinc chloride and zinc dust.

An analogous reaction of the acid VII (R = H_2) with naphthalene-2,3-dicarboxylic anhydride gave the acid X(R = O). After reduction to X(R = H_2) a threefold cyclization yielded decastarphene-(3,3,3) XI.

EXPERIMENTAL*

3,6-*Di-*o*-carboxybenzyl-phenanthrene* (VII, R = H_2). The dicarboxylic acid (7 g)[4] was dissolved in dil KOHaq (2000 ml, 5%) and a crystal of $CuSO_4$ added. The surface of the mixture was covered with amyl alcohol (50 ml) to avoid frothing. Zn dust (20 g) was added and the mixture heated under reflux for 24 hr. Further portions of Zn dust (20 g) were added at intervals of 24 hr and the mixture with a total of 100 g Zn dust was heated under reflux for a total of one week. The amyl alcohol was distilled off, and the soln filtered. The residue with the Zn dust was thoroughly washed with hot water until acidification with HCl gave no more ppt. The suspension was boiled, filtered and washed with hot water, yield 6 g. A further small portion was obtained by dissolving the Zn in conc HCl. The crude product was recrystallized four times from acetic acid, m.p. 241° and dissolved in conc H_2SO_4 to give an orange yellow soln which turned green on heating. The NMR spectrum confirmed the symmetrical structures of the molecule. (Found: C, 80·7; H, 5·0. $C_{30}H_{22}O_4$ requires: C, 80·7; H, 5·0%).

3,6-*Dicarboxybenzyl-9-*o*-carboxybenzoylphenanthrene* (VIII, R = O). The above acid (1 g) was powdered with phthalic anhydride (1·5 g) and suspended in tetrachloroethane (10 ml). The mixture was shaken for 10 min and $AlCl_3$ (5 g) added. The brown mixture was gently heated before shaken for 3 hr. After standing for 18 hr it was decomposed with dil HCl and the tetrachloroethane distilled off with steam. The residue was repeatedly extracted with boiling water to ensure that excess phthalic anhydride was removed. The acid was dissolved in dil ammonia leaving a small amount on insoluble material. Acidification first with AcOH and then with dil HCl gave the acid (0·98 g) which after repeated recrystallization from AcOH had m.p. 274–275°. It dissolved in conc H_2SO_4 to give a violet soln which changed to yellow on heating. (Found: C, 76·6; H, 4·4. $C_{38}H_{26}O_7$ requires: C, 76·8; H, 4·1%).

3,6,9-*Tri-*o*-carboxybenzylphenanthrene* (VIII, R = H_2). This acid was obtained from VIII (R = O) in the manner described for the preparation of VII (R = H_2). The yield was 0·4 g from 0·5 g starting material. The acid was recrystallized three times from AcOH, m.p. 287° and dissolved in conc H_2SO_4 to form a bright red soln which became yellowish-brown at 50°. (Found: C, 78·4; H, 4·8; $C_{38}H_{28}O_7$ requires: C, 78·6; H, 4·9%).

Nonastarphene-(2.3.3) (IX). The above acid (0·1 g) was thoroughly powdered with Zn dust (2 g) and then mixed with NaCl (2 g) and cryst. $ZnCl_2$ (10 g). The mixture was heated with stirring to 380° and kept at this temp for 2 min. After cooling the melt was dissolved in dil AcOH and the residue treated with conc. HCl. The insoluble part was filtered off and washed with hot water and then with dil ammonia. The crude dried hydrocarbon (0·023 g) was powdered with sodalime (0·5 g) and heated under N_2 to 310° until all traces of humidity were removed. The press was then reduced to 3×10^{-3} mm. Sublimation up to 420° yielded the orange yellow hydrocarbon which after crystallization from xylene gave dark yellow clustered needles, m.p. 310–315°, which dissolved in conc H_2SO_4 to give a dark brown soln which changed to yellowish-brown on standing. (Found: C, 95·4; H, 4·6. $C_{38}H_{22}$ requires: C, 95·4; H, 4·4%); mol. wt. mass spectrographic $m/e = 478$; calc. 478·5).

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* M.ps are uncorrected and were taken in evacuated capillaries.

3,6-Di-o-carboxybenzyl-9-(3′-carboxy-2′-naphthyl)-phenanthrene (X, R = O). This acid was prepared in a way analogous to the synthesis of VIII (R = O), the phthalic anhydride being replaced by naphthalene-2,3-dicarboxylic anhydride. The yield was 1·02 g from 1 g starting material (VII, R = H_2). The crude acid was recrystallized three times from AcOH, m.p. 261° and dissolved in conc H_2SO_4 to give a leaf green soln which turned to violet on standing. (Found: C, 78·5; H, 4·5. $C_{42}H_{28}O_7$ requires: C, 78·3; H, 4·4%).

3,6-Di-o-carboxybenzyl-9-(3′-carboxylic-2′-naphthylmethyl)-phenanthrene (X, R = H_2). This acid was prepared as described for VII (R = H_2). The yield was 1·4 g from 1·9 g of X (R = O). The crude product had m.p. 280° which rose to 295° after three crystallizations from nitrobenzene. The acid dissolved in conc H_2SO_4 to form a wine red soln which became red on heating. (Found: C, 80·0; H, 4·7. $C_{42}H_{30}O_6$ requires: C, 80·0; H, 4·8%).

Decastarphene (XI). The Zn dust melt was carried out in the way as described for IX. The sublimation of the crude hydrocarbon (0·072 g from 0·1 g of X, R = H_2) yielded decastarphene in orange red needles. The sublimate was first extracted with boiling xylene and the insoluble part recrystallized from 1,2,4-trichlorobenzene. It formed flat dark yellow needles dec. > 500°, which dissolved in conc H_2SO_4 to give a violet soln which became yellowish brown on standing. (Found: C, 95·3; H, 4·6. $C_{42}H_{24}$ requires: C, 95·4; H, 4·6%); mol. wt. Found: $m/e = 529$. Cal.: 528·6).

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