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THE SIGNIFICANCE OF BENZENOID RINGS FOR THE STABILITY OF AROMATIC HYDROCARBONS

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Abstract—The hitherto unknown tribenzotetracene(V) was synthesized and fitted into the series: heptacene(I), benzohexacene(II), the dibenzopentacenes III and IV, tribenzotetracene(V) and tetrabenzanthracene (VI). It is obvious that in the series I → VI the stability increases and the absorption bands shift to shorter wavelength with the number of benzenoid rings (marked with circles). In contrast to this the absorption spectra of the benzotetracenes show little change in the annellation series VII → V → VIII because the benzenoid rings were fused to double bond which are already localized.

BENZENOID rings, i.e. rings which can be written with 3 double bonds and which are marked with circles, provide aromatic systems with additional stability.[1] They are also responsible for the localization of aromatic double bonds making these accessible for the addition of maleic anhydride.[2] Benzenoid rings also explain the phenomenon of assymetric annellation.[3]

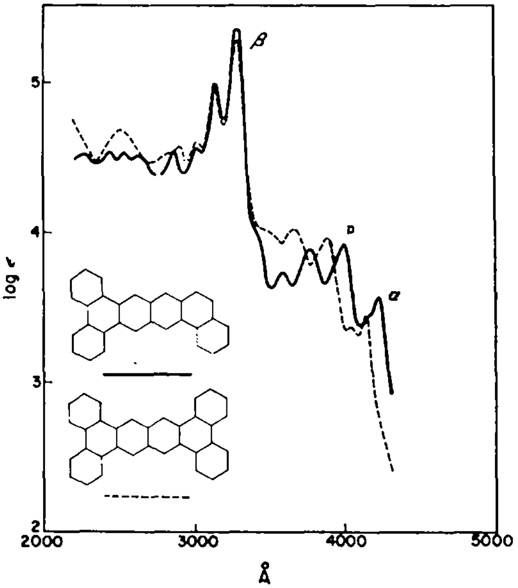

FIG. 1. Absorption max. (Å) and log ε (in parentheses). 1:2,3:4,7:8-Tribenzotetracene V in benzene, α:4230 (3·56); p:4000 (3·92), 3780 (3·89), 3590 (3·73); β:3280 (5·36), 3130 (4·96), 3020 (4·56); 2870 (4·55); in cyclohexane, 2630 (4·50), 2530 (4·52), 2430 (4·52), 2270 (4·53). 1:2,3:4,7:8,9:10-Tetrabenzotetracene in benzene, α:4140 (3·50); p:3900 (3·98), 3680 (4·06); β:3280 (5·30), 3140 (4·90), 3010 (4·60), 2900 (4·58); in heptane, 2530 (4·68).

In the series of the isomeric hydrocarbons $C_{30}H_{18}$ I → VI, there is an increase in the

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[1] T. W. Armit and R. Robinson, *J. Chem. Soc.* 1604 (1925); E. Clar, *Tetrahedron* 5, 98 (1959); 6, 355 (1959).
[2] E. Clar, C. T. Ironside and M. Zander, *Tetrahedron* 6, 358 (1959).
[3] E. Clar, *Tetrahedron* 5, 98 (1959); 6, 355 (1959); 9, 202 (1960).

number of benzenoid rings to the maximum in the fully benzenoid tetrabenzanthracene(VI). Heptacene(I) is a green, most reactive hydrocarbon, which cannot be obtained in a pure state because of its reactivity.[4] It has only one benzenoid ring which is shared among seven rings. 1:2-Benzohexacene(II) is blue-green and because of its two benzenoid rings, somewhat more stable. However, a complete absorption spectrum has not yet been obtained, only the *p*-bands were measured by visual observation.[5] The two dibenzopentacenes III and IV, both having three benzenoid rings are very similar and considerably more stable than pentacene.[6] The small differences between III and IV might be explained by the different relative positions which the benzenoid rings can assume. The hitherto unknown tribenzotetracene(V) is yellow and reacts more slowly with maleic anhydride than most benzotetracenes, except tetrabenzotetracene(VIII).[3] The colourless tetrabenzanthracene(VI)[7] does not react with maleic anhydride. Its absorption spectrum is the most shifted to the short wave among its isomers. Thus tribenzotetracene(V) fits perfectly into the series predicted by the assumption of benzenoid rings within the aromatic system.

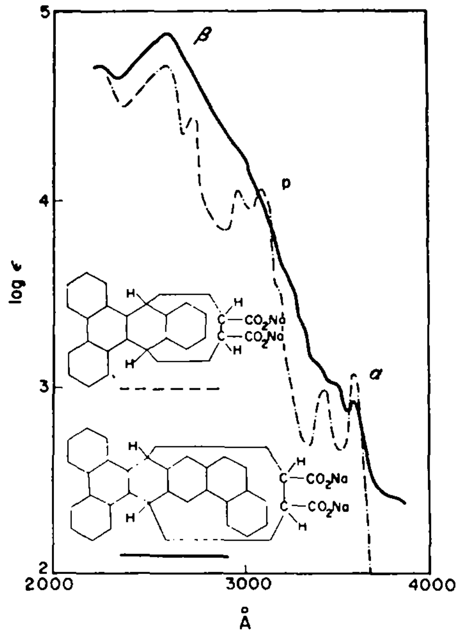

FIG. 2. Absorption max (Å) and log ε (in parentheses). Disodium salt derived from X in water, p :3580 (2·92); β :2610 (4·89). Disodium salt of the adduct of 1:2,3:4-dibenzanthracene and maleic anhydride [E. Clar, *Ber. Dtsch. Chem. Ges.* **65**, 507 (1932)] in water, α :3590 (3·08), 3420 (2·98); p :3100 (4·06), 2·980 (4·05), 2740 (4·44); β :2600 (4·70).

If 1:2,7:8-dibenzotetracene(VII) is given the maximum number of benzenoid rings, the two terminal double bonds in the central tetracene system appear to be fixed. Accordingly, annellation to these double bonds produces only a small shift of the β-bands in passing to tribenzotetracene(V) and tetrabenzotetracene(VIII). The red

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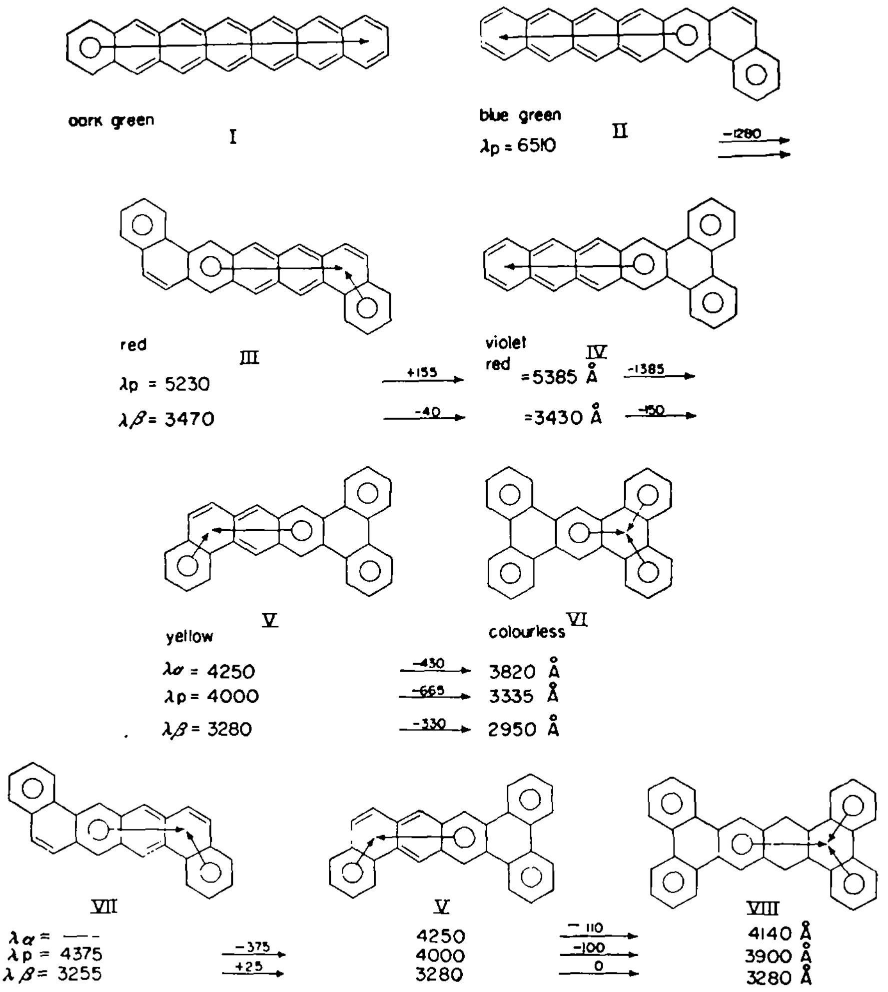
[4] B. Boggiano and E. Clar, *J. Chem. Soc.* 2683 (1957).

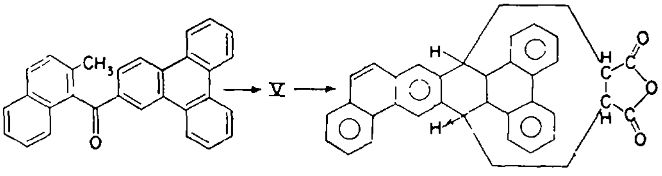
[5] E. Clar, and Ch. Marschalk, *Bull. Soc. Chim.* 444 (1950).

[6] E. Clar, *Ber. Dtsch. Chem. Ges.* **76**, 257 (1943); E. Clar and H. Frömmel, *Chem. Ber.* **81**, 163 (1948).

[7] P. Lambert and H. Martin, *Bull. Soc. Chim. Belg.* **61**, 124 (1952).



All wavelengths were measured in benzene except II which is in 1-methylnaphthalene



IX X

shift, due to the addition of the 4π-electrons per ring, is compensated by the violet shift, due to the formation of a new aromatic sextet.[8] The movement of the sextet through the central tetracene system is not restricted in the series VII, V and VIII in contrast to the increasing restriction imposed in the series I → VI as indicated by the arrows.

Tribenzotetracene was obtained by pyrolysis of the ketone IX which was prepared from 2-methyl-1-naphthoyl chloride, triphenylene and aluminium chloride. The reaction proceeded analogous to the condensation of triphenylene[9] with other acid chlorides which gave only substitution in the β-positions. However, another condensation product which does not react with maleic anhydride was observed in the pyrolysis. The adduct of maleic anhydride with tribenzotetracene(X) showed an absorption spectrum (Fig. 2) which indicated the presence of a 9,10-substituted phenanthrene complex. Therefore the addition must have taken place in position 5 and 12. The adduct was readily decomposed by sublimation with soda lime and yielded pure tribenzotetracene (V).

EXPERIMENTAL*

2-*Methyl*-1-*naphthoyl*-2′-*triphenylenyl*-*ketone*(IX). To triphenylene (7 g) and 2-methyl-1-naphthoyl chloride[10] (7 g) in chlorobenzene (20 ml) or in benzene (50 ml) powdered aluminium chloride (12 g) was added. After a slight warming the reaction began and the triphenylene went into solution. The dark reddish-yellow mixture was heated to 50° for a few min until the evolution of HCl ceased. After decomposition with dil HCl the solvent was removed by steam distillation. The resinous residue crystallized when treated with ether. The *ketone*(IX) was recrystallized first from xylene and then from acetic acid. It formed very pale yellow needles, m.p. 214–216°, which dissolved in conc H_2SO_4 forming a red solution. (Found: C, 90·6; H, 4·9. $C_{30}H_{20}O$ requires: C, 90·9, H, 5·1%).

1:2,3:4,7:8-*Tribenzotetracene*(V). The ketone (10 g) was heated to 400–420° under the protection of a current of carbon dioxide. The formation of water was completed after ½ hr. The residue was sublimed at 270°/1 mm. Triphenylene (0·77 g) was first obtained, followed by the yellow hydrocarbon at 350°/1 mm. The crude hydrocarbon was recrystallized from xylene and was found not to be uniform (1·97 g). For further purification it was transformed into the adduct X with boiling maleic anhydride. The excess of maleic anhydride was removed with boiling water and the residue several times extracted with sodium hydroxide in aqueous alcoholic solution. This left a colourless by-product undissolved which was filtered off. The united filtrates were acidified with HCl and the white precipitate (1·1 g) washed with water and dried.

The adduct was mixed with soda lime (1·5 g) and sublimed at 300°/0·1 mm. The *tribenzotetracene* which formed yellow needles was repeatedly recrystallized from xylene. When the solution was quickly cooled it yielded yellow wart-like conglomerates and on slow crystallization long needles. The hydrocarbon dissolved in conc H_2SO_4 with a blue colour (absorption band about 6200 Å) which soon changed to green and then to yellow. Both forms have m.p. 277–278°. (Found: C, 95·3; H, 4·5. $C_{30}H_{18}$ requires: C, 95·2; H, 4·8%).

1:2,3:4,7:8-*Tribenzotetracene-maleic anhydride adduct*(X). This adduct was obtained by boiling pure tribenzotetracene with excess maleic anhydride. After removing the excess maleic anhydride the adduct was dissolved in aqueous-alcoholic sodium hydroxide filtered and the *free acid* precipitated with HCl. It formed a white powder which decomposed at 190–192°. (Found: C, 82·6; H, 4·8. $C_{34}H_{22}O_4$ requires: C, 82·6; H, 4·5%).

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* Melting points are uncorrected and were taken in evacuated capillaries. Microanalyses by J. M. L. Cameron and his staff, Glasgow University.

[8] E. Clar, *Tetrahedron* in press.

[9] E. Clar, *Chem. Ber.* **81**, 68 (1948); *J. Chem. Soc.* 2440 (1949).

[10] R. Adams and L. O. Binder, *J. Amer. Chem. Soc.* **63**, 2774 (1941).