ASYMMETRIC ANNELLATION EFFECTS-II

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Abstract—The comparison of the U.V. absorption spectra of acenes, 1:2-3:4-dibenzacenes and tetrabenzacenes shows a strong asymmetric annellation effect. This is explained on the basic assumption that an aromatic sextet or benzenoid ring can transfer only two electrons to another ring. Three benzenoid rings can thus produce an induced aromatic sextet in an included ring of the type of the central ring in triphenylene.

The synthesis of tetrabenzotetracene is described.

In the preceding communication¹ strong asymmetric annellation effects were reported in the series benzene I, triphenylene II and tetrabenzanthracene III. These were recorded in Å or better in \sqrt{A} the latter being a scale for reciprocal nuclear charges.² In order to eliminate the influence of the external benzene rings the second difference II \rightarrow III was deducted from the β -band of triphenylene and it was found that the aromatic system of the central benzene ring was extended to a naphthalene system during the first annellation and that the second annellation produced an empty ring "E" only. From these facts it was deduced that a benzenoid ring containing three double bonds and six π -electrons and symbolised by a circle can transfer two electrons only to another ring as indicated by the arrows. Therefore only one induced benzenoid ring "Bz" can be formed.

If this interpretation is correct then the same principle should apply to the central acene system in a higher tetrabenzacene, without regard to the number of rings. There is only one benzenoid ring with an aromatic sextet in an acene independent of its length and accordingly only two transferable electrons. In order to prove this view the hitherto unknown tetrabenzotetracene VI was synthesised as described below. The annellation series napthalene IV, dibenzanthracene V³ and tetrabenzotetracene VI also shows strong asymmetric shifts. The deduction of the second shift $(3.57\sqrt{\text{Å}})$ from the β -band of dibenzanthracene V (53·48 \sqrt{A}) gives 49·91 \sqrt{A} or 2491 Å which is almost identical with the wavelength of the β -band of anthracene at 2515 Å as found in alcoholic solution or calculated by the annellation principle (2493 Å).²

The conclusion is obvious that in the first annellation the aromatic structure of the central naphthalene system is extended to an anthracene system, whilst the second annellation produced an empty ring "E".

In the next higher series all three hydrocarbons, VII, VIII and IX⁴ are known. The deduction of the second shift (2.87 \sqrt{A}) from the β -band of 1:2-3:4-dibenzotetracene⁵ VIII (55.95 \sqrt{A}) yields a β -band at 53.08 \sqrt{A} or 2818 Å. The β -band of tetracene is at 2740 Å in heptane solution. The calculation by the annellation principle² gives a β -band at 2802 Å. This comparison again indicates that in the first annellation the

¹ Part I: Tetrahedron 5, 98 (1959).

² E. Clar, Aromatische Kohlenwasserstoffe p. 29. Springer Verlag (1952).

 ³ E. Clar, Ber. Disch. Chem. Ges. 62, 350, 1574 (1929).
⁴ E. Clar, W. Kelly and W. G. Niven, J. Chem. Soc. 1833 (1956).

⁸ E. Clar, Ber. Disch. Chem. Ges. 81, 68 (1948).

aromatic system of anthracene is extended to a tetracene system as indicated by the arrows.

The idea of two π -electrons per aromatic sextet and benzenoid ring, capable of migrating through an acene system whilst the other π -electrons are confined to their rings is different from the quantum mechanical view of free movement of all π -electrons in molecular orbitals throughout the whole system. But it is in good agreement with the measurement of the diamagnetic anisotropy of the acenes which points to a high



degree of localisation of π -electrons in their rings. According to Akamatu and Matsunaga⁶ this localisation increases with the number of linearly condensed rings. The average π -orbital radius (i.e. 1.71 Å for pentacene) is therefore much smaller than the length of the acene (about 12.14 Å for pentacene) would require, and increases to 1.94 Å for coronene and to 2.12 Å for ovalene.⁶ The latter are systems with 3 and 4 benzenoid rings respectively and contain a triphenylene system with an induced benzenoid ring.¹

The two transferable π -electrons are probably responsible for the addition of protons and for the different degree of basicity of aromatic hydrocarbons which reaches its extreme value in the azulenes.

Tetrabenzotetracene was synthesised from triphenylene-2-carboxylic acid,⁹ the chloride of which was condensed with 9-methylphenanthrene⁷ and aluminium chloride. The ketone XII was smoothly pyrolysed at 400° to tetrabenzotetracene VI.

⁶ H. Akamatu and Y. Matsunaga, Bull. Chem. Soc. Japan 29, 800 (1956).

⁷ O. Kruber and A. Marx, Ber. Disch. Chem. Ges. 71, 2478 (1938).

It has the lowest reactivity of all benzologues of tetracene. It reacts very slowly with boiling maleic anhydride to form a colourless adduct and does not dissolve in concentrated sulphuric acid. Unlike the other benzologues of tetracene it shows a yellow phosphorescence of considerable life in solid dioxan solution at -170° . In these properties it closely resembles the fully benzenoid hydrocarbons.⁸ Its absorption spectrum is recorded in Fig. 1.



FIG. 1. Absorption max. (Å) and log ϵ (in parentheses). 1:2-3:4-8:9-10:11-Tetrabenzotetracene VI in trichlorobenzene, α : 4190 (3.50); p: 3960 (3.98), 3740 (4.06); β : 3340 (5.30), 3190 (4.90). In heptane, β : 3255 (5.30), 3120 (4.90), 2980 (4.60), 2880 (4.58); β' : 2530 (4.68).

EXPERIMENTAL*

1:2-3:4-8:9-10:11-Tetrabenzotetracene VI. The acid chloride (from 5.5 g of triphenylene-2carboxylic acid⁹ and thionyl chloride) was finely powdered and suspended in 200 ml of chlorobenzene. 9-Methylphenanthrene² (4 g) and aluminium chloride (3 g) were added and the mixture stirred at room temp for 4 hr. After heating at 50° for $\frac{1}{2}$ hr the double compound was decomposed with ice and hydrochloric acid and the chlorobenzene removed by steam distillation. The ketone could not be obtained in a pure state from the yellow residue probably because of the formation of isomers which however could not cyclise in the following reaction. The ketone was dissolved in hot xylene, the solution dried, filtered and the xylene distilled off.

The ketone was pyrolysed at 400°. After $\frac{1}{2}$ hr the elimination of water was complete and the residue was submitted to a vacuum sublimation at 400°/1 mm in a current of carbon dioxide. The first fraction yielded some triphenylene followed by yellow leaflets of *tetrabenzo* tetracene. This was twice recrystallised from 1:2:4-trichlorobenzene and formed yellow leaflets, m.p. 452-455° which did not dissolve in concentrated sulphuric acid but became green on the surface. The dilute solution in dioxan showed a phosphorescence of considerably long life after irradiation with a quartz lamp at -170° . (Found: C, 95'1; H, 4'8. C₃₄H₂₀ requires: C, 95'3; H, 4'7).

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- ⁸ E. Clar and M. Zander, J. Chem. Soc. 1861 (1958); E. Clar and C. T. Ironside, Proc. Chem. Soc. 150 (1958); E. Clar, M. Zander and C. T. Ironside, J. Chem. Soc. 142 (1959).
- ⁹ J. W. Cook and C. L. Hewett, J. Chem. Soc. 401 (1933).