ASYMMETRIC AND SYMMETRIC ANNELLATION EFFECTS—III*

BENZOCORONENES

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Abstract—1:2-5:6-Dibenzocoronene (IV) was obtained from 1:2-4:5-8:9-tribenzopyrene (II) via the dianhydride (III). 1:2-4:5-Dibenzopyrene (V) condensed twice with maleic anhydride. The resulting dianhydride (VI) gave 1:2-benzocoronene (VII) on decarboxylation. 1:12-o-Phenyleneperylene (X) was obtained by a zinc dust melt from the quinone (VIII). The annellation effects passing from triphenylene and perylene to the benzocoronenes indicate the presence of a triphenylene complex within the electronic fine structure of coronene.

2:3-8:9-DIBENZOPERYLENE (1) like other benzologues of perylene condenses with maleic anhydride and chloranil to form a new aromatic ring.¹ Giving this hydrocarbon the maximum number of aromatic sextets or benzenoid rings as indicated by the circles, the two central double bonds appear to be fixed. The above reaction might be related to this arrangement of double bonds. If this were the case then 1:2-4:5-8:9-tribenzopyrene (II) should also react with maleic anhydride and chloranil as a dehydrogenating agent. Although condensations of this type involving benzopyrenes have not been reported, tribenzopyrene (II) condensed twice in this way and yielded the dianhydride (III). Decarboxylation gave the pale yellow 1:2-5:6-dibenzocoronene (IV). Its absorption spectrum is recorded in Fig. 1 together with the tetrapotassium salt of the tetracarboxylic acid derived from (III).

An analogous formulation of the 1:2-4:5-dibenzopyrene (V) using aromatic sextets suggests the possibility of the same "benzenogenic" condensation. In accordance with this, dibenzopyrene (V) yielded the dianhydride (VI) from which 1:2-benzocoronene (VII)² was obtained by decarboxylation. The absorption spectra of both compounds (VI) and (VII) are reproduced in Fig. 2. It is remarkable that in these two cases of double benzenogenic condensations the number of benzenoid rings with inherent sextets increases by one and this might be the reason for the double condensation, since it would not be the case with a single condensation. When the crude adduct was examined after a short reaction, no dicarboxylic acid could be found in the absorption spectrum, indicating that the two molecules of maleic anhydride reacted simultaneously. For comparison of the annellation effects leading to the benzecoronene the unknown 1:12-o-phenyleneperylene (X) was needed. It was obtained from the quinone (VIII)³ via the tetrahydro compound (IX)? by a zinc dust meltfollowed by a dehydrogenation. The spectra of (IX) and (X) are in Fig. 3.

^{*} Part II: Tetrahedron 6, 355 (1959).

E. Clar, Ber. Disch. Chem. Ges. 65, 846 (1932); Chem. Ber. 82, 53 (1949); E. Clar and O. Kuhn, Liebigs Ann. 601, 181 (1956); E. Clar, W. Kelly, J. M. Robertson and M. G. Rossmann, J. Chem. Soc. 3878 (1956); E. Clar, and M. Zander, J. Chem. Soc. 4616 (1957); 1861 (1958).

^{*} E. Clar and M. Zander, J. Chem. Soc. 1577 (1958).

³ F. Bergmann, H. E. Eschinazi and M. Nceman, J. Org. Chem. 8, 179 (1943).

Coronene can be considered to be derived from triphenylene by connecting three double bonds to it with the formation of the three "empty" rings 1, 2, 3 in formula (XI). In this formula the central ring would have obtained induced benzenoid character by the reversible transfer of 3 π -electron pairs from the three benzenoid rings.⁴ Another possibility is the hexagonally symmetric arrangement in formula (XII) in which the



3 π -electron pairs are shared between neighbouring rings, thus forming three fused naphthalene systems. The central ring is here empty (E). Both formulae have the same number of inherent sextets in benzenoid rings, i.e. three.

Very significant spectral shifts of the β -bands accompany the connexion of the three double bonds to triphenylene as seen in formula (XI). The spectral shift due to the formation of the rings 1, 2 and 3 are 320, 100 and 30 Å corresponding to 3.06, 0.92 and 0.28 \sqrt{A} . This is exactly contrary to what could be expected from the conventional ideas about aromaticity, namely, that the third double bond completing the external frame of nine conjugated double bonds should bring about the biggest shift. This external frame ought to allow a rotation of electrons through it. This is obviously not the case and neither does the effective π -orbital radius (1.94 Å) as

4 E. Clar, Tetrahedron 5, 98 (1959); 6, 355 (1959).

obtained from the diamagnetic anisotropy measurements support this view.⁵ In accordance with formula (XI) the three non-benzenoid double bonds in rings 1, 2 and 3 can be hydrogenated with the formation of 1:2-5:6-9:10-hexahydrocoronene.⁶

The building up of 1:2-benzocoronene (VII) from 1:12-benzoperylene (XIII) by an o-phenylene complex provides further support for formula (XI) for coronene. Since 1:12-benzoperylene already contains the stable triphenylene skeleton the effect of this annellation is small (170 Å, corresponding to $1.52\sqrt{\AA}$). This shift is well below the maximum value for two contact bonds and the newly formed ring must be empty. The same observation can be made when two o-phenylene radicals are attached to 1:2benzopyrene (XIV) forming (XV) and (IV). The two shifts are similar to the one (XIII \rightarrow VII).



1:2-Benzopyrene (XIV) also contains the triphenylene complex, so the double annellation produces two empty rings (E) and four contact bonds. If the triphenylene complex in 1:2-5:6-dibenzocoronene (IV) was free to rotate or oscillate through the coronene system the maximum number of five benzenoid rings would be reduced to three (formula IVa). Considering the extreme stability of hydrocarbons consisting exclusively of benzenoid rings this possibility seems remote. But this does not exclude an oscillation or rotation of the triphenylene complex in coronene itself.

⁵ H. Akamatu and Y. Matsunaga, Bull. Chem. Soc. Japan 29, 800 (1956).

⁶ H. Fromherz, L. Thaler and G. Wolf, Z. Elektrochem. 49, 387 (1943).

A strikingly different result is obtained when 1:2-7:8-dibenzocoronene (XVII) is built up from perylene in an analogous way. The first phenylene complex forms the triphenylene complex in (X). The shift related to it is far beyond the value for any pair of contact bonds (595 Å, corresponding to $5.63\sqrt{\AA}$). This process is therefore a benzenogenic annellation (Bz). The second phenylene complex in (XVII) produces two contact bonds (173 Å, corresponding to $1.55\sqrt{\AA}$) and an empty ring (E). The two naphthalene complexes forming the central perylene system have each, like any other acene, one pair of transferable π -electrons according to their definition given recently.⁴ If an aromatic sextet is induced into the central ring of the triphenylene complex as indicated by the arrows in (XVII) then this process cannot be repeated simultaneously for the triphenylene system including the ring (E).

If the shift for the second annellation $(1.55\sqrt{\text{\AA}})$ is deducted from the β -band of 1.12-o-phenyleneperylene (X) a β -band at $54.18\sqrt{\text{\AA}}$ corresponding to 2936 Å is obtained. The β -band of 1.12-benzoperylene (XIII) is at 3030 Å for benzene solution. Although the agreement is not so close as in the case of the benzacenes described in the preceding paper it shows in the same way that the first annellation is a benzenogenic one (Bz) whilst the second produces an empty ring (E).

EXPERIMENTAL*

1:2-4:5-8:9-Tribenzopyrene (11). The method described by Zincke, Ott and Schuster⁷ was modified in that stannic chloride was added. No unreacted picene was then recovered.

Picene (25 g), aluminium chloride (50 g) and stannic chloride (150 g) in benzene (250 ml) were refluxed for $2\frac{1}{2}$ hr. The mixture was first blue and finally became violet red. After decomposition with hydrochloric acid and ice the tribenzopyrene (31 g) separated from the benzene layer and was filtered off. Vacuum sublimation yielded long needles (11.1 g).

1:2-5:6-Dibenzocoronene-7:8-11:12-tetracarboxylic dianhydride (III). Tribenzopyrene (II) (2.0 g), maleic anhydride (20 g) and chloranil (7.0 g) were refluxed for 1½ hr. The mixture was diluted with hot xylene, and the dianhydride (0.42 g) filtered off at room temp. A further 0.96 g dianhydride was obtained on concentration of the mother liquor. Dec. pt. >500°. An analytical sample was prepared by reprecipitation from alkali solution and refluxing with acetic anhydride. (Found: C, 77.0; H, 2.6. $C_{38}H_{14}O_7$ requires: C, 77.4; H, 2.5. $C_{38}H_{12}O_8$ requires: C, 80.0; H, 2.2%). The analysis fits the monoanhydride dicarboxylic acid rather than the dianhydride.

1:2-5:6-*D*:*benzocoronene* (IV). The dianhydride (II) (4.0 g), potassium hydroxide (30 g) and water (100 ml) were heated in an autoclave for 18 hr at 350°. The crude product was washed with water and sublimed at 400°/0.05 mm. The sublimate crystallised from trichlorobenzene in long pale yellow needles (0.5 g). These had m.p. 327-328°C. and did not dissolve in concentrated sulphuric acid. (Found: C, 96.0; H, 4.1. C₃₂H₁₈ requires: C, 96.0; H, 4.0%). The spectra of (IV) and of the tetra-carboxylic acid derived from (III) are shown in Fig.1.

1:2-Benzocoronene-3:4-7:8-tetracarboxylic dianhydride (VI). 1:2-4:5-Dibenzopyrene⁸ (V) (30.2 g), chloranil (130 g) and maleic anhydride (200 g) were refluxed for 7 hr. Hot xylene (400 ml) was added and the precipitated dianhydride (18.7 g) filtered from the hot solution and washed with xylene and ether. Dec. pt. 460°. An analytical sample was prepared by reprecipitation and refluxing with acetic anhydride. (Found: C, 78.1; H, 2.4; C₃₂H₁₀O₆ requires: C, 78.4; H, 2.1%).

1:2-Benzocoronene (VII). The dianhydride (12·3 g), potassium hydroxide (35 g) and water (80 ml) were heated in an autoclave for 15 hr. The crude hydrocarbon was washed with water and sublimed at 300°/0.05 mm. Recrystallisation of the sublimate from xylene gave pale yellow needles (1·2 g).

* Melting points are uncorrected and were taken in evacuated capillaries.

⁷ E. Clar, J. Chem. Soc. 2168 (1949); A. Zinke, R. Ott and O. Schuster, Monat. 83, 1100, 1497 (1952).

 ⁸ E. Clar, Ber. Disch. Chem. Ges. 73, 609 (1943); I. G. Farbenindustrie A. G., French Patent 795447 (1935);
B. Schiedt, Ber. Disch. Chem. Ges. 71, 1248 (1938); A. Zinke and W. Zimmer, Monat, 81, 783 (1950); A. Zinke and W. Zimmer, Monat, 82, 348, 946 (1951).



FIG. 1. Absorption max. (Å) and log ϵ (in parentheses). 1:2-5:6-Dibenzocoronene (IV) in C₈H₈Cl₉, α : 4335 (2·25), 4180 (2·66), 4100 (2·75); p: 3790 (4·38), 3600 (4·31), 3490 (4·45); β : 3280 (5·06), 3140 (4·72). 1:2-5:6-Dibenzocoronene-7:8-11:12-tetracarboxylic acid tetrapotassium salt in H₂O, α : 4470 (3·26), 4190 (3·43); p: 3850 (4·28), 3670 (4·39); β : 3345 (5·02).



FIG. 2. Absorption max. (Å) and log ϵ (in parentheses). 1:2-Benzocoronene (VII) in C_8H_8 , α : 4320 (2·50), 4140 (2·91), 4080 (2·85); p: 3760 (4·30), 3580 (4·30), 3430 (4·29); β : 3200 (5·15), 3080 (4·90). From 3000 Å in alcohol. 1:2-Benzocoronene-3:4-7:8-tetracarboxylic acid tetrapotassium salt in H₈O, α : 4190 (3·34); p: 3825 (4·06), 3650 (4·17), 3470 (4·26); β : 3260 (4·87). The 1:2-benzocoronene had m.p. $292-294 \cdot 5^{\circ}$. and gave no depression when mixed with the benzocoronene described recently.^a The spectra of this hydrocarbon and of the tetracarboxylic acid from (VI) are shown in Fig. 2.

1:12-o-Phenyleneperylene (X). The quinone³ (VIII) (0.6 g) was ground up with zinc dust (1.5 g) and sodium chloride (1.5 g) and melted with zinc chloride (7.5 g) and a few drops of water, with constant stirring. When the foaming subsided the temp was raised to 310° at which it was kept for 10 min. The colour changed to bright yellow. On extraction with benzene some crystals of (X) were



FIG. 3. Absorption max. (Å) and $\log \epsilon$ (in parentheses). 1:12-o-Phenyleneperylene (X) in C₆H₆, p: 4180 (4·47), 3940 (4·31), 3730 (3·98), 3530 (3·58); β : 3105 (4·96), 2975 (4·74); in cyclohexane, 2720 (4·40), β ': 2490 (4·56). Tetrahydro-compound (IX)? in cyclohexane, p: 2940 (4·26), 2840 (4·26).

obtained; however, when chromatographed on alumina, the mother liquor gave a trace of perylene identified spectroscopically and white plates of (IX)? The spectrum of this compound suggested a naphthalene derivative such as the *tetrahydro-compound* (IX) m.p. 148-149°C. though the analysis agreed better for a dihydro-compound. (Found: C, 94.6; H, 5.5. $C_{16}H_{18}$ requires: C, 94.5; H, 5.5. $C_{26}H_{19}$ requires: C, 93.9; H, 6.1%).

This hydro-compound which was quite stable, was dehydrogenated by passing over palladium charcoal at 350° to give 1:12-o-phenyleneperylene (X), which crystallised from benzene in long yellow needles, m.p. 268-270° (Found: C, 95.9; H, 4.3. C₁₀H₁₄ requires: C, 95.7; H, 4.3%). The spectra of (IX) and (X) are shown in Fig. 3. The hydro-compound (IX) showed strong yellow phosphorescence at -80° K in solid alcoholic cyclohexane solution.

Phenyleneperylene, in accordance with the structure (X), reacted readily in the 6:7 position with boiling maleic anhydride and chloranil to form a red-brown anhydride, the spectrum of which showed it to be a derivative of 1:2 benzocoronene.

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