# CIRCOBIPHENYL AND THE ATTEMPTED SYNTHESIS OF 1:14, 3:4, 7:8, 10:11-TETRABENZOPEROPYRENE

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Abstract - A reducing condensation of naphthanthrone (2) gave the isomeric dinaphthoperopyrenes 3, 4 and 5, besides circobiphenyl (7). Tetrabenzoperopyrene (1) was not formed. An attempt to synthesize it from 2,5-dimethylterephthalic acid failed.

THE aim of this work was to synthesize terabenzoperopyrene (1). This remarkable hydrocarbon contains an equal number of marked and unmarked C atoms (19 and 19) and ought to be stable in spite of the fact that it cannot be written with a Kekulé structure.<sup>1</sup> However it can be formulated with two para- $\pi$ -bonds as in 1a or with only one para- $\pi$ -bond in the centre.

The most simple starting material appeared to be naphthanthrone 2 which might be condensed under reducing condition to afford 1. A zinc dust melt of naphthanthrone was reported before.<sup>2</sup> It resulted in the formation of dinaphtho-peropyrene (3) and another hydrocarbon which was given the most likely formula 4. We have now carried out this reducing condensation under pressure with zinc dust and a few drops of water in a sealed tube at  $310^{\circ}$ .

The resulting hydrocarbon mixture contained the monomeric reduction products of naphthanthrone (2) i.e. naphthanthrene and 1:10-trimethylene-pyrene.<sup>3</sup> Further chromatographic separation yielded the main constituent the orange dinaphthoperopyrene (3) followed the reddish brown isomer 4. In addition a new bright scarlet hydrocarbon was found which according to its analysis and mass spectrum had the composition  $C_{38}H_{20}$ . This must be a dihydroderivative of a condensation product of unknown structure.

Sublimation of the condensation product, which was almost insoluble in cold xylene, yielded, after removal of the zinc dust, besides smaller amounts of **3** and **4** a purple hydrocarbon. This reacted twice with maleic anhydride. The adduct lost readily 4H atoms and gave the Na salt drived from the dianhydride (6). This showed an absorption spectrum in alkaline solution which was very similar to the starting hydrocarbon (Fig 1) except for a shift towards the red as one would expect for an alkyl-derivative of the parent hydrocarbon.

None of the other condensation products gave a reaction with maleic anhydride and it could be used to remove the purple hydrocarbon from the mixture. This double reaction would fit very well with the formula I or Ia which was also observed with 2:3,4:5,8:9,10:11-tetrabenzoperylene.<sup>4</sup> However, the NMR spectrum was too complicated for a hydrocarbon of such high symmetry as 1. Fig 1 shows the absorption

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spectrum of the purple hydrocarbon together with the spectrum of isoviolanthrene. Both hydrocarbons belong to the same type which indicates that the purple hydrocarbon has the structure **5**. It was found that isoviolanthrene reacted in an analogous way with maleic anhydride. Decarboxylation of the adduct **6** with soda-lime resulted in splitting and in re-forming hydrocarbon **5**.

Sublimation of the condensation product from above  $400^{\circ}/10^{-4}$  mm yielded a greenish-yellow hydrocarbon, which was extremely sparingly soluble, but could be recrystallized from boiling 1-methylnaphthalene. Its analysis and mass spectrum indicated clearly the composition  $C_{38}H_{16}$ . There is just one structure which fits this composition. This is the hydrocarbon 7 for which we propose the name circobiphyl because a biphenyl system is completely surrounded by benzene rings as anthracene in circumanthracene.<sup>5</sup>

Further support for the structure 7 of circobiphenyl comes from the NMR spectrum. Because of the low solubility it had to be carried out in molten hexamethylbenzene at 200°. The "Bay protons" are at extremely low field at 9.92 ppm from TMS. This indicates a very high ring current in the system,<sup>6</sup> indeed the lowest value for any combination of aromatic rings. This is best accounted for by the five sextets which move as indicated by the arrows. The neighbouring protons forming a quartet with the above mentioned protons are at 8.86 ppm. The other protons form a singlet at 8.65 ppm which is near to the value for coronene. Therefore circobiphenyl must have a very high degree of superaromaticity.<sup>7</sup>







CO₂H

11

Dinaphthoperopyrene (3) has also five sextets but these cannot produce superaromaticity through rotation. In accordance with this the bay protons are at higher field, at 9.42 and 9.23 ppm respectively, than in circobiphenyl in spite of the higher degree of overcrowding. Because of the more highly condensed structure of 3 they are at lower field than the bay protons in peropyrene which are at 9.15 ppm. The latter are already at much lower field by comparison with perylene where the bay protons are at 8.05 ppm. This illustrates the importance of the formulation with aromatic sextets. In all peropyrene derivatives there is an inherent sextet in the centre and there is none in perylene. Thus the NMR spectrum of the bay protons proves the existence of an inherent sextet in the centre. The other NMR values of dinaphthoperopyrene (3) are all at higher field by comparison with coronene showing the absence of superaromaticity. It is significant that the fixed double bond near the bay position has J = 9, whilst the bay sextet has J = 7.5 for both bonds.



FIG 2. Absorption spectra max (Å) and log ε in parentheses
Circobiphenyl in 1,2,4-trichlorobenzene: α, 4810 (2:45), 4590 (2:72), 4530 (2:73): p, 4190 (4:60), 3970 (4:58), 3840 (4:72): β, 3640 (5:36), 3450 (4:92).
Coronene in benzene: α, 4280 (2:15), 4200 (2:12), 4100 (2:75), 4020 (2:65), 3965 (2:23), 3880 (2:75), 3815 (2:67), 3780 (2:63), 3685 (2:67), 3475 (4:15): p, 3415 (4:85), 3255 (4:45), 3195 (4:60), 3165 (4:70): β, 3050 (5:50), in ethanol: 2900 (5:10), 2520 (3:88), 2280 (4:08).

The absorption spectrum of circobiphenyl is given in Fig 2 together with the spectrum of coronene. Although both hydrocarbons have a similar type of spectrum the red shift for circobiphenyl is rather small for the condensation effect of 14 C atoms to coronene. This is again explained by the large number of sextets and by the superaromaticity. Circobiphenyl in solid 1,2,4-trichlorobenzene solution in liquid  $N_2$ shows a strong orange red phosphorescence of very long life after irradiation. This must be expected from its superaromaticity.

In another attempt to synthesize tetrabenzoperopyrene (1) the diol (9) was obtained from 2,5-dimethylterephthaloyl chloride with o-tolyllithium. Oxidation with dil nitric acid under pressure at 210° gave the dilactone-tetracarboxylic acid (10). Reduction with dil KOH and zinc dust yielded the hexacarboxylic acid 11. The cyclization to the the triquinone even under the most drastic condition was unsuccessful. Other attempts to use partly cyclized products for cyclization after reduction were equally abortive.

## EXPERIMENTAL\*

Naphthanthrone (2).<sup>8</sup> This was prepared by a simplified method. Glycerol (159 ml), water (372 ml) and cone  $H_2SO_4$  (1346 ml) were mixed and the temp raised to 100°. A soln of pyrene (100 g) in nitrobenzene (100 9 ml) was heated to 100° and added gradually under stirring to the first soln. The temp was maintained between 100-110° for 4 hr. The mixture was poured into water, the ppt filtered off and, washed with water and dried (139 9 g). The crude material was dissolved in hot xylene, the residue filtered off and washed with benzene. The solvents were distilled off and the residue distilled in vacuum. The crystallized distillate (39 g) was recrystallized from xylene, yellow needles, m.p. 243°.

Zinc dust condensation of naphthanthrone. Naphthanthrone (3 g) was powdered intimately with Zn dust (15 g) and heated with 2-3 drops of water in a sealed tube at 310° for 50 hr. The dark red-purple solid mixture from 4 such tubes was broken up and finely powdered.

The light petroleum extract. The crude dried material was extracted with 3 l. of boiling light petroleum (100  $\cdot$ 120°), the soln filtered and the residue worked up as described below. The petrol soln was dried with anhyd Na<sub>2</sub>SO<sub>4</sub>, concentrated and chromatographed over Grade I neutral alumina. Eluting with light petroleum gave a colourless solution with a blue fluorescence which on concentration yielded leaflets of trimethylenepyrene identified by the UV spectrum. Further clution with benzene gave an orange yellow soln which was united with a similar soln obtained from the following chromatogram using xylene. This was rechromatographed over Grade I neutral alumina and eluted with cyclohexane-benzene. The first fraction gave a further portion of trimethylenepyrene and a trace of naphthanthrene recognized from the UV spectrum, further fraction yielded orange red needles of dinaphtho-(7',1':1,13),(1'',7'':6,8)-peropyrene<sup>2</sup> (3, 150 mg), and bright scarlet platelets of a new hydrocarbon (50 mg). After recrystallization from cyclohexane the latter formed thin bright scarlet prisms. m.p. 277-279° (dec), M.S. molecular ion m/e = 476; calc. M.W. 476 for C<sub>38</sub>H<sub>20</sub>. The hydrocarbon dissolved in conc. H<sub>2</sub>SO<sub>4</sub> forming a greenish-blue soln. The benzene solution had max (Å) at: 4760 (4·37), 4465 (4·21), 4215 (4·30), 3980 (4·15), 3580 (4·67), 3400 (4·57) 3180 (4·55), 2995 (4·50), 2775 (4·48). (Found: C, 95·30: H, 4·77. C<sub>38</sub>H<sub>20</sub> requires: C, 95·80: H, 4·20°/.).

The xylene extract. The residue from the light petroleum extract was extracted with 41 of boiling xylene, filtered and the insoluble part used for the isolation of circobiphenyl s.b. The solution was concentrated to 800 ml and on standing yielded a dark reddish-purple deposit which was filtered off and dried (1.8 g). The solution was further concentrated to 150 ml and prior to chromatographing a further ppt was filtered off (2.5 g).

The remaining soln was chromatographed over Grade I neutral alumina. Elution with cyclohexane gave a colourless soln yielding a further quantity of trimethylenepyrene. The following yellow-orange fraction was united with the above petroleum extract.

Further elution with benzene-xylene gave an orange band which was developed with xylene. Concentration yielded orange red needles (1.8 g), m.p.  $338-339^{\circ}$ , of dinaphtho-(7',1':1,13),(1'',7'':6,8)-peropyrene<sup>2</sup> (3). Elution with boiling xylene produced a mixture of dinaphtho-peropyrene (4) and a new hydrocarbon with absorption bands at 568, 525 and 489 nm. The fractions containing this hydrocarbon were rose-red with an orange fluorescence. Concentration gave dark purple needles (2 mg) of 5. The last fraction from the column gave almost pure dinaphtho-(7',1':1,13):(1'',7'':9,11)-peropyrene (4, 26 mg), m.p.  $358-360^{\circ}.^2$ 

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

A further portion of the new hydrocarbon 5 was obtained by sublimation of the above ppt (1.8 + 2.5 g) from the xylene extract before chromatography. In a vacuum of  $10^{-4}$  most of the dinaphtho-peropyrene (3) sublimed below 330°. Further heating to 350° yielded a mixture of mainly 5 with a little of 4. Recrystallization of this fraction (45 mg) from mesytylene gave pure purple dinaphtho(1',7':2,4),(1'',7'':9,11)-peropyrene (dibenzoisoviolanthrene) (5, 12 mg), m.p. 427-430°, which dissolved in conc H<sub>2</sub>SO<sub>4</sub> on warming with a violet colour. M.S. molecular ion m/e 474: cale. M.W. 474 for C<sub>38</sub>H<sub>18</sub>. The absorption spectrum see Fig 1. (Found: C, 96·11: H, 3·84. C<sub>38</sub>H<sub>18</sub> requires: C, 96·18: H, 3·82%).

Maleic anhydride adduct 6. A mixture of the three hydrocarbons 3, 4 and 5 (5.2 mg) was refluxed for 20 min with pure maleic anhydride (30 mg). The purple red soln was poured into water and the residue thoroughly washed with hot water. The residue was extracted with NaOH in 50% EtOH and the purple mixture cooled and filtered. The spectroscopic examination of the residue (4.4 g) showed that almost all the hydrocarbon 5 had reacted leaving 3 and 4. The clear deep purple soln was acidified with cone HCl and the ppt separated by centrifugation and washed. The dark purple solid (500 mg), m.p. > 500°, dissolved in cone H<sub>2</sub>SO<sub>4</sub> forming an olive green soln. The analysis showed that drying caused partly anhydrization. The tetracarboxylic acid was therefore finely powdered and refluxed with excess Ac<sub>2</sub>O for 40 min. The cooled mixture was filtered, thoroughly washed with benzene and dried under vacuum. (Found: C, 82·34: H, 3·44. C<sub>46</sub>H<sub>22</sub>O<sub>6</sub> requires: C, 82·40: H, 3·29%). The electronic spectrum is similar to 5 with max.: p, 5810 (4·29), 5430 (4·36), 5730 (4·24):  $\beta$ , 3800 (4·60), 3670 (4·66) Å. This spectrum agrees with structure 6, whilst the C,H determination point rather to an addition product with 4H more. However the small differences allow no decision.

Attempted decarboxylation. The tetracarboxylic acid (50 mg) was heated at  $200^{\circ}/10^{-4}$  mm. A pale yellow product sublimed. The temp was raised to  $380^{\circ}$  and a purple sublimate began to appear. The temp was held at  $380-410^{\circ}$  for 2 hr. The purple sublimate was removed extracted with dil alcoholic NaOH and recrystallized from xylene. The hydrocarbon (2 mg) had the same spectrum as 5.

Circobiphenyl (7). The residue left after extraction of the crude reaction product with light petrol and xylene was boiled with cone HCl to destroy the Zn dust. The remaining organic product was filtered, washed with dil ammonia and water (6.2 g). Sublimation at  $310^{\circ}/10^{-4}$  yielded first dinaphthoperopyrene (3) and at 400° the isomer 4 and another hydrocarbon. The latter sublimed alone at temperatures above 400° in bright olive-yellow blades. This fraction was extracted with hot xylene and then recrystallized from boiling 1-methylnaphthalene under CO<sub>2</sub>. Circobiphenyl (7) formed fine greenish-yellow needles, m.p. 480-483°, M.s. molecular ion m/e 472: calc. M.W. 472 for C<sub>38</sub>H<sub>16</sub>. The hydrocarbon dissolved slowly in warm cone H<sub>2</sub>SO<sub>4</sub> forming a reddish-brown soln. The electronic spectrum is shown in Fig 2. (Found: C, 96·32: H, 3·63. C<sub>38</sub>H<sub>16</sub> requires C, 96·59: H, 3·41%).

2,5-(0,0'-Dimethyldiphenylhydroxymethyl)-1,4-dimethylbenzene (9). A soln of o-tolyllithium was prepared in the conventional way from Li (8 g), o-bromotoluene (95 g) and dry ether (500 ml) under N<sub>2</sub>. After the Li had dissolved a soln of 2,5-dimethyl-terephthalyl chloride<sup>9</sup> (17 g) in ether (100 ml) was added dropwise under stirring. The mixture was refluxed for 1 hr. The brown-red soln was filtered through glass wool into a mixture of ice and dil AcOH. The ether layer was washed with water and evaporated. The light brown residue crystallized after trituration with light petrol. The colourless powder (9 g) was recrystallized from light petrol (100-120°) or from benzene and yielded colourless prisms, m.p. 249-251°, which dissolved in conc H<sub>2</sub>SO<sub>4</sub> to give a deep magenta soln. (Found: C, 86-39: H, 7-38. C<sub>38</sub>H<sub>38</sub>O<sub>2</sub> requires: C, 86-66: H, 7-28%).

Di-2,5-(0,0'-dicarboxydiphenylhydroxymethyl)-terephthalic acid dilactone (10). The diol (1 g) and HNO<sub>3</sub> (20%, 20 ml) were heated in a sealed tube at 210° for 16 hr. The mixture was diluted with water and the yellow-green amorphous solid filtered washed with water, dried and powdered (0.65 g). Recrystallization from little dil AcOH gave a colourless powder, m.p. 220-225° dec which dissolved in conc H<sub>2</sub>SO<sub>4</sub> to give a yellow solution  $v_{c=0} = 1720 \text{ cm}^{-1}$ ,  $v_{c=0} = 1780 \text{ cm}^{-1}$ . (Found: C, 68.04; H, 3.28. C<sub>38</sub>H<sub>22</sub>O<sub>12</sub> requires: C, 67.73; H, 3.14%).

Di-2,5-(0,0'-dicarboxydiphenylmethyl)-terephthalic acid (11). The dilactone (0.6 g) was dissolved in 20% ethanolic KOH (8 ml) and a few drops of water were added. Cu activated Zn dust (2.5 g) was added in portions and the mixture refluxed for 96 hr. The initial green colour of the mixture became reddish-brown. After cooling water (10 ml) was added and the Zn dust filtered off. The soln was boiled to remove the EtOH and then acidified with conc HCl. The ppt was boiled, filtered off and washed with water (180 mg). It was dissolved in a little Ac<sub>2</sub>O and xylene added. Concentration of this soln gave a powder, m.p. 195-205°, which dissolved in con H<sub>2</sub>SO<sub>4</sub> to form a brown soln. (Found: C, 67.63; H, 3.94. C<sub>38</sub>H<sub>26</sub>O<sub>12</sub> requires: C, 67.65; H, 3.86%).

The cyclization with  $H_2SO_4$ . Oleum with  $P_2O_5$  or pyrophosphoric acid proved to be unsuccessful. The product remained soluble in alkali or decomposed under more drastic conditions. Cyclization in steps reducing the intermediates also failed.

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