Tetrahedron. Vol. 28, pp. 1237 to 1240. Pergamon Press 1972. Printed in Great Britain

NAPHTHOPENTACENE AND THE ANNELLATION PRINCIPLE

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(*Received in the UK* 24 *September* 1971; *Accepted for publication* 6 *December* 1971)

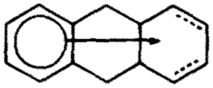
Abstract—Naphthopentacene (III) was synthesized to see whether a new annellation series: anthracene (I), benzotetracene (II) and naphthopentacene (III) can be established in which the character of the electronic spectrum is maintained.

IN THE ACENE SERIES: benzene, naphthalene, anthracene, tetracene and pentacene the ratio of the wavelength of the p-bands to the β-bands is continuously increased from 1·138 to 1·289, 1·489 and 1·915 resp. This causes profound changes in the spectra. Thus the α-bands disappear in the anthracene spectrum behind the more intense p-bands and reappear again in the minimum of the pentacene spectrum.

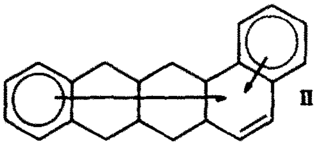
No such changes are observed if one linear and one angular ring are fused to any of the above acenes. Then the whole spectrum shifts towards the red but the type remains the same[1] *i.e.* the ratio of the wavelength of the p-bands to the β-bands is almost constant. This is the case in the series: benzene, phenanthrene, pentaphene, heptaphene and in the series: naphthalene, tetraphene, hexaphene.[1] In this paper the next higher series: anthracene (I), benzotetracene (II) and naphthopentacene (III) is established by synthesis of the latter.

The synthesis of naphthopentacene (III) started from leucoquinizarin (IV) which was condensed with benzophenone-tricarboxylic anhydride (V) to form the acid (VI). Reduction with dil NaOH soln and Zn dust gave a product which still contained two hydroxyls. Their unknown position was inferred by analogy[2] to be as assumed in formula VII. Cyclization with $POCl_3$ yielded the anthrone derivative (VIII). This is so readily oxidizable that it had to be immediately reduced to the tetrahydronaphthopentacene (IX) with pyridine, Zn dust and AcOH. The position of the CH_2 groups in IX can be derived from the UV spectrum which is of the alkylnaphthalene type. Besides compound IX there appears to be a small amount of dihydro-compound X present in the crude product. It could be recognized by the tetraphene type spectrum.

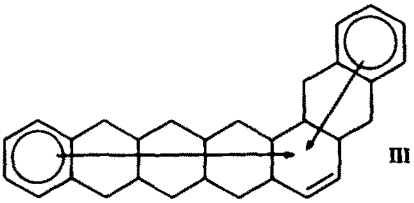
Since the above route gave low yields and contained intermediates of uncertain structure the primary condensation product (VI) was reduced with HI and red phosphorus. This method is known to effect cyclization and reduction simultaneously.[3] Thus the tetrahydro-compound together with a little X was obtained again. Decarboxylation with copper powder at 400° yielded naphthopentacene (III). This purple hydrocarbon is rather readily photooxidized in solution like pentacene. The confrontation in the series: anthracene (I), benzotetracene (II) and naphthopentacene (III) (Fig 1) shows that the latter fits perfectly into the series. The change of the ratio (if any) of the wavelength of the p-bands to the β-bands (1·419 and 1·420



I

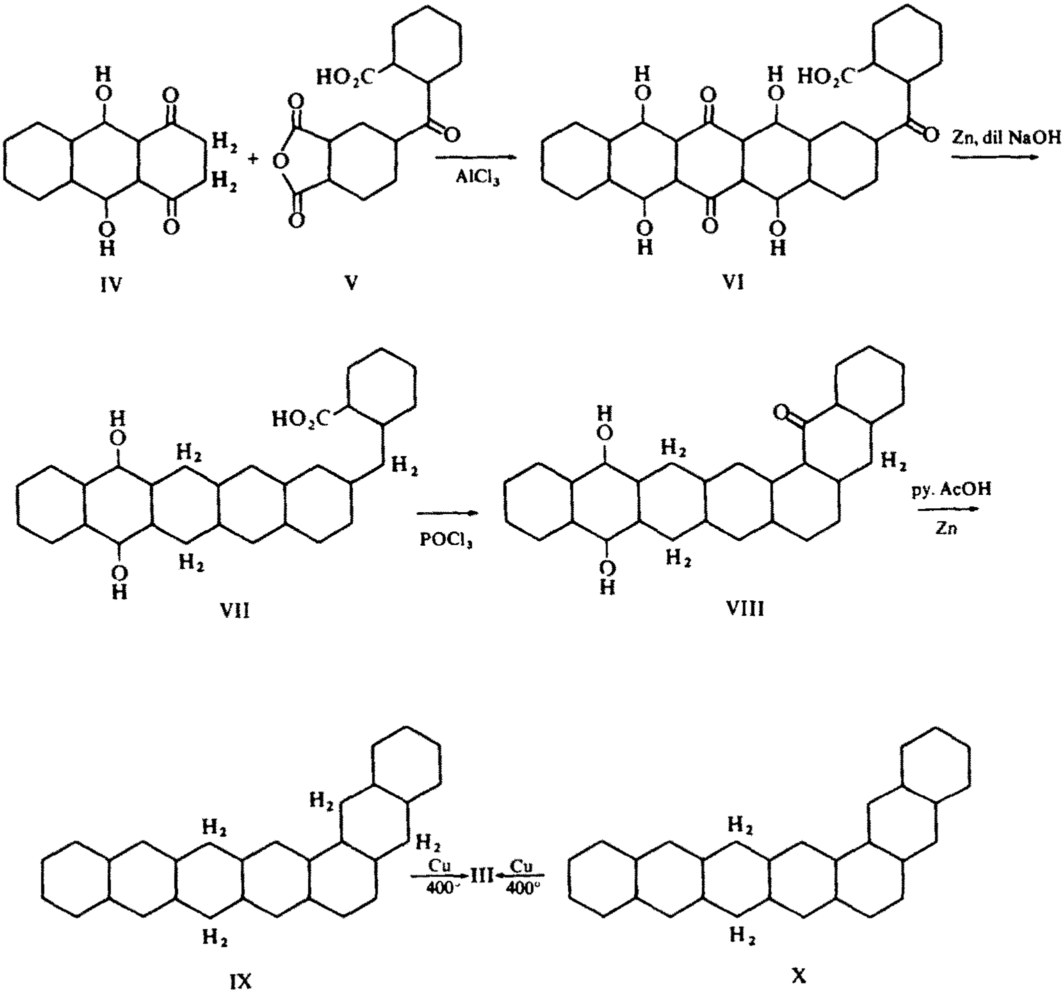


II



III

$p = 3745$	4525	5420 Å
$\beta = 2515$	3190	3815 Å
$\beta = 1{\cdot}489$	1·419	1·420



Note for the presentation of the formulae: Double bonds are not marked in the synthetic route. Rings not carrying H_2 are aromatic rings.

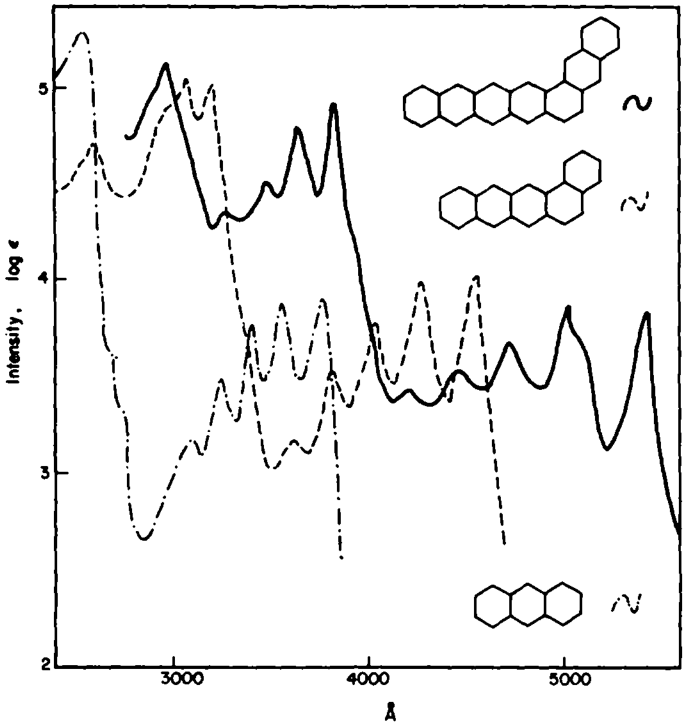


FIG 1. Absorption spectra with max (Å) and $\log \varepsilon$ in parentheses. ——— Naphtho-(2′:3′,1,2)-pentacene in benzene: p, 5420 (3·80), 5025 (3·83), 4705 (3·67), 4450 (3·51), 4215 (3·41): β, 3815 (4·89), 3630 (4·77), 3460 (3·50), 3260 (4·34); β′, 2945 (5·11). ----- 1,2-Benzotetracene in benzene: p, 4525 (4·00), 4250) (3·97), 4010 (3·80), 3800 (3·50), 3620 (3·16); β, 3190 (4·98), 3060 (5·01); in EtOH: β′, 2580 (4·72). -·-·- Anthracene (EtOH): p, 3745 (3·87), 3545 (3·86), 3380 (3·75), 3230 (3·47), 3080 (3·15); β, 2515 (5·29)

respectively) is so small that it is far within the limit of the experimental error. It had been assumed for some time that the molecular axes are responsible for the type and character of the spectrum of an angular kata-annellated hydrocarbon.[4] The establishment of the three annellation series shows. however, that only the geometry *i.e.* the number of rings of the two branches of rings are really relevant for the spectra. The molecular axes vary in the members of the three series.

EXPERIMENTAL*

Leucoquinizarin. To a boiling soln of Na_2CO_3 (16 g) in water (1500 ml) was added finely ground quinizarin (12 g); the mixture was vigorously stirred until all quinizarin had dissolved. To the deep violet soln was added $Na_2S_2O_4$ (4 × 5 g) until all the leucoquinizarin precipitated out. Additional $Na_2S_2O_4$ (3 g) was added to complete the reduction, shown by the red-orange colour of the soln. The ppt was filtered and washed with dil AcOH until alkali-free. It was dried at 75–80°; m.p. 150–153 (lit. m.p. 155°).[5] Yield 11·5 g.

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

2-(o-*Carboxybenzoyl*)-*5,7,12,14-tetrahydroxy-pentacene-6,13-quinone* (VI). A finely ground mixture of leucoquinizarin (IV, 10 g), benzophenone-2′,3,4-tricarboxylic acid-3,4-anhydride (V, 10 g)[6] and powdered $AlCl_3$ (2 g) were heated in a metal-bath at 280° for 30 min. The powdered cooled melt was extracted with dil HCl and then with hot alkaline $Na_2S_2O_4$ soln, dil AcOH and water. The dried residue was extracted with boiling $PhNO_2$ to remove soluble impurities and washed thoroughly with EtOH. The condensation product (14.5 g) was a purple-brown powder, m.p. > 500°, which dissolved in conc H_2SO_4 with a royal-blue colour. The soln in NaOH was purple. The rose-red soln in benzene had absorption max at 5645, 5530, 5250 and 4900 Å. (Found: C, 69·4; H, 3·6. $C_{30}H_{16}O_9$ requires: C, 69·2; H, 3·1%).

2-(o-*Carboxybenzyl*)-*7,12-dihydroxy-6,13-dihydropentacene* (VII). The above acid (5·2 g) in NaOH (5%, 1500 ml) was reduced with Cu-activated Zn dust (5 × 3 g) added at 24 hr intervals. The purple suspension became reddish-brown over 5 days refluxing. The hot soln was acidified with conc HCl. The brown ppt filtered off, washed and dried at 100°. After trituration with ether it was crystallized from AcOH as golden-yellow needles, m.p. 248–250° which dissolved in conc H_2SO_4 with a blue colour which turned to violet-red on standing. The benzene soln had max at 4085 (3·67), 4000 (3·68), 3045 (4·70), 2410 (4·14), 2315 (4·12) Å. (Found: C, 80·6; H, 5·1. $C_{30}H_{22}O_4$ requires: C, 80·7; H, 5·0%).

4′-Oxo-1′,4′-dihydro-naphtho-(2′:3′,1:2)-7,12-dihydroxy-6,13-dihydropentacene (VIII). The reduced acid (VII, 1g) was refluxed with $POCl_3$ (25 ml) for 1 hr, the soln developing a red-orange colour. Xylene (50 ml) was added and the mixture distilled until the temperature reached 140°. The ppt could not be recrystallized from $PhNO_2$ because of oxidation and darkening.

1′,4′-Dihydro-naphtho-(2′:3′,1:2)-6,13-dihydropentacene (IX). The above crude product (0·72 g) was suspended in pyridine (75 ml) and Zn dust (5g) added. AcOH (80%, 10 ml) was added dropwise over 1 hr and the mixture refluxed for 5 hr. The hot pyridine soln was filtered into dil HCl (1500 ml) and refluxed to coagulate the ppt which was washed with water, dil NH_4OH and water. The ppt was sublimed (200–210°/0·05 mm) to give yellow sublimate (23 mg), m.p. 219–223°. This hydrocarbon had the same spectrum as the one obtained by the improved procedure now described.

A finely ground mixture of the condensation product (VI, 1g) and red phosphorus (0·67 g) together with HI (45%, 10 ml) were heated in a sealed tube at 240° for 3 days. The solid was filtered from the soln and extracted with xylene (1500 ml). The filtered soln was extracted with alkaline $Na_2S_2O_4$ to remove unreduced products. The soln was concentrated and chromatographed on Neutral Alumina Grade I. Elution with benzene gave a pale yellow soln which on concentration yielded yellow prisms, m.p. 224–227° which dissolved in conc H_2SO_4 to form a reddish-brown soln. Yield from 8 tubes 528 mg. UV spectrum: 3340 (3·57), 3250 (3·60); 3050 (4·16), 2945 (4·20), 2835 (4·08); 2695 (5·15), 2420 (5·29) Å. (Found: C, 94·0; H, 5·5. $C_{30}H_{22}$ requires: C, 94·2; H, 5·8%).

Naphtho-(2′:3′,1,2)-pentacene (III). The above tetrahydro-compound (500 mg) was covered in a boat with copper bronze and sublimed rapidly in vacuum at 400°. A yellow sublimate, followed by a reddish-purple sublimate at higher temperature was obtained. Refluxing with benzene removed the yellow compound. The residue was resublimed at 300–310°/0·01 mm and yielded deep red pyramids (8 mg), m.p. 391–394°, which dissolved in conc H_2SO_4 to give a green soln which turned to orange-brown. (Found: C, 94·9; H, 4·5. $C_{30}H_{18}$ requires C, 95·2; H, 4·8%).

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