519. *Four Higher Annellated Pyrenes with Acene Character.**

By B. BOGGIANO and E. CLAR.

The naphthopentacene (IV) has been synthesised from naphthalene-2 : 3-dicarboxylic anhydride and pyrene, the naphthohexacene (XIII) from anthraquinone-2 : 3-dicarboxylic anhydride and pyrene, and the dinaphthoheptacene (XVIII) from pyromellitic anhydride and pyrene. A benzonaphthotetracene was a by-product in another synthesis of the first product, (IV), from pyrene-3-carboxyl chloride and 6-methyltetralin and has been also prepared by a different route. These annellated pyrenes have been compared with the centrosymmetrically annellated pyrenes of the same number of rings and found to have acene character.

HIGHER, symmetrically annellated pyrenes retain their pyrene character, *i.e.*, they give pyrenequinones and their absorption spectra show the characteristic features of pyrene derivatives.[1] Strongly asymmetric linear annellated pyrenes have now been prepared in order to determine whether the pyrene character is still preserved or an acene character developed.

Naphthalene-2 : 3-dicarboxylic anhydride with pyrene in the presence of aluminium chloride gave the acid (I). Boiling benzoyl chloride and a trace of zinc chloride cyclised this to the quinone (II), which, like pentacenequinone and its angular benzologues, does

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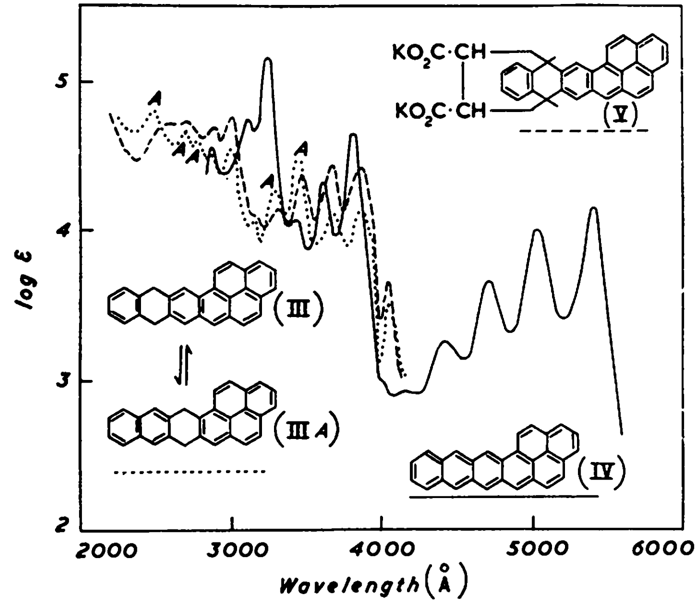
* The term "acene" denotes the series of linear annellated benzene derivatives beginning with anthracene, naphthacene (tetracene), pentacene (cf. Clar, *Ber.*, 1939, **72**, 2137).

[1] Clar, *J.*, 1949, 2013.

not give a vat. The quinone (II) was reduced to the dihydro-compound (III) with pyridine, zinc dust, and acetic acid. However, structure (III), consisting of a 3 : 4-benzopyrene complex linked to a benzene ring by two methylene groups, is not the only form of the dihydro-compound. The absorption bands marked " *A* " in Fig. 1 show clearly that the form (III) is in equilibrium with (III*A*), containing the aromatic complexes of pyrene and naphthalene.

Dehydrogenation of the compound (III) with palladium-charcoal yields the red naphthopentacene (IV; see Fig. 1), which is a rather reactive and photo-oxidisable. It adds maleic anhydride, leading to the formation of (V; see Fig. 1). When compared with that of the dihydro-compound (III $\rightleftharpoons$ III*A*), the absorption spectrum of the adduct (Fig. 1) shows the correctness of the assumed structure (V). The first group of absorption bands of the red hydrocarbon (IV) (Fig. 1) is shifted considerably to the violet, relatively to the first bands of pentacene (5755 Å), as would be expected for an angular annellated benzologue of pentacene.

FIG. 1. *Absorption max.* (Å) *and* log ε (*in parentheses*).



(——) *Naphthopentacene* (IV) *in* C_6H_6, 5410 (4·15), 5040 (4·00), 4720 (3·65), 4430 (3·25), 3820 (4·65), 3630 (4·33), 3440 (4·06), 3250 (5·15), 3110 (4·74), 2890 (4·56).

(– – – –) *Adduct* (V) *in* 50% EtOH, 4050 (3·64), 3870 (4·42), 3670 (4·42), 3470 (4·38), 3310 (4·16), 3010 (4·76), 2890 (4·70), 2720 (4·72), 2610 (4·71).

(. . . .) *Hydrocarbon* (III and III*A*) *in* EtOH, 4050 (3·50), 3880 (4·14), 3680 (4·12), 3440 (4·48), 3290 (4·27), 3150 (4·06), 3000 (4·54), 2870 (4·50), 2790 (4·60), 2680 (4·66), 2480 (2·80).

Pyrolysis of the ketone (VI), obtained from pyrenecarboxyl chloride and methyltetralin, also yields the red naphthopentacene (IV) together with a yellow hydrocarbon (VII), whose structure was established by synthesis from the ketone (VIII). Since " *cis* "-bis-angular dibenzanthracenes and tetracenes cannot be obtained from the corresponding *ortho*-methylated ketones by pyrolysis, owing to the preceding rearrangement of the ketone,[2] it must be assumed that the ketone (VIII) also rearranges and pyrolyses to the " *trans* "-bis-angular hydrocarbon (VII). The absorption spectrum of the compound (VII)

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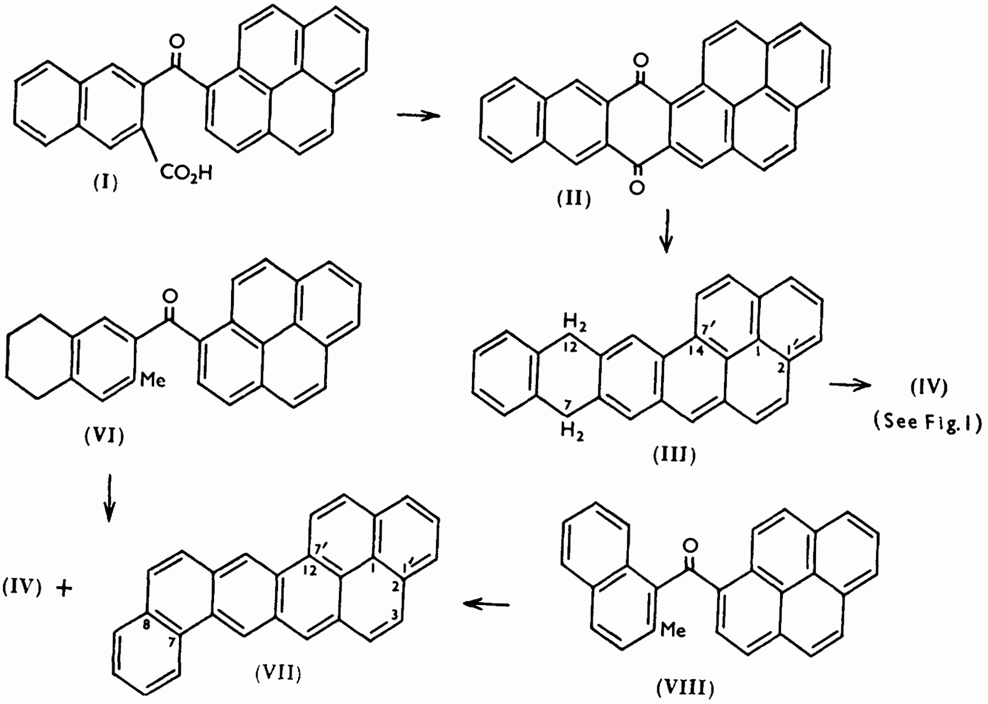
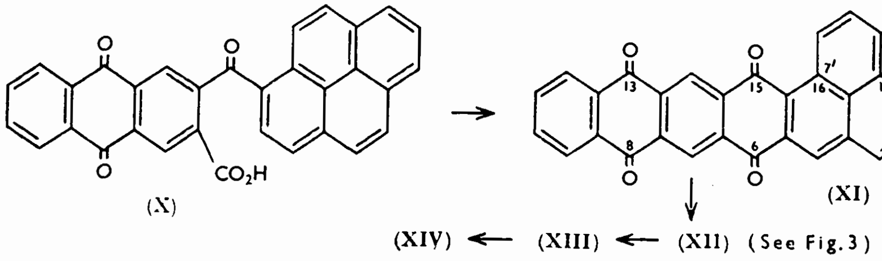
[2] Cook, *J.*, 1931, 499, 478; Clar, John, and Avenarius, *Ber.*, 1939, **72**, 2139; Clar, *Ber.*, 1943, **76**, 149; Nichol, Thorn, Jones, and Sandin, *J. Amer. Chem. Soc.*, 1947, **69**, 376.

is closely related to that of the naphthotetracene (IX; Fig. 2), the fusion of an angular ring to the latter causing a shift to the violet as usual.

The acid (X) was prepared from anthraquinone-2 : 3-dicarboxylic anhydride, pyrene, and aluminium chloride. It was cyclised with boiling benzoyl chloride to the diquinone (XI). Reduction in pyridine with zinc dust and acetic acid yielded a dihydro-compound



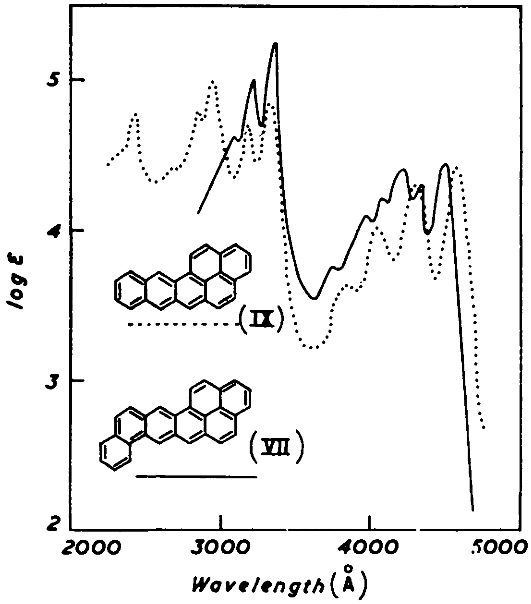
which, like (III $\rightleftharpoons$ III*A*), consisted of an equilibrium mixture of isomers (XII) and (XII*A*) (Fig. 3). The absorption spectrum in Fig. 3 shows that the isomer (XII), containing the aromatic complexes of 3 : 4-benzopyrene and naphthalene, dominates the absorption spectrum, whilst the isomer (XII*A*), with the naphthopyrene (bands marked *A*) and benzene complexes, forms only about 10% of the mixture.



The naphthohexacene (XIII) (in Fig. 3) was obtained from its dihydro-compound by dehydrogenation with palladium–charcoal. Although highly reactive and photo-oxidisable, the green hydrocarbon is more stable than hexacene and a quantitative absorption spectrum can be obtained which shows the expected considerable violet shift compared with hexacene (Fig. 3). The compound adds maleic anhydride immediately, leading to the adduct (XIV) (in Fig. 3), whose structure was established by comparison with the absorption spectrum of (XII $\rightleftharpoons$ XII*A*) (Fig. 3).

Pyromellitic anhydride condensed twice with pyrene in the presence of aluminium chloride, to give the acid (XV) which might possibly contain the isomeric *iso*phthalic acid. Ring closure with benzoyl chloride gave an apparently uniform diquinone for which, in analogy with the formation of 1 : 2-8 : 9-dibenzopentacene-5 : 14-7 : 12-diquinone[3] from pyromellitic anhydride and naphthalene, the "*trans*"-bis-angular structure (XVI) is assumed. It was reduced to a dihydro-compound with zinc dust and acetic acid in pyridine. The absorption spectrum shows that the dihydro-compound, as in the cases described previously, consists of an equilibrium mixture of (XVII $\rightleftharpoons$ XVII*A*) (Fig. 4), the bands of the asymmetric form being marked *A*.

FIG. 2. *Absorption max.* (Å) *and* log ε (*in parentheses*).



(——) *Hydrocarbon* (VII) *in* C_6H_6, 4500 (4·45), 4350 (4·31), 4230 (4·40), 4100 (4·20), 4000 (4·10), 3770 (3·75), 3370 (5·24), 3220 (4·98), 3100 (4·61).

(. . . .) *Hydrocarbon* (IX) *in* C_6H_6, 4580 (4·42), 4310 (4·31), 4060 (4·03), 3850 (3·63), 3350 (4·85), 3200 (4·70), 2970 (5·00), 2860 (4·78); *in* EtOH, 2460 (4·79).

Dehydrogenation of the dihydro-compound with palladium–charcoal gave the deep green dinaphthoheptacene (XVIII) (Fig. 4). This is the first fully aromatic benzologue of heptacene obtained pure. It is highly reactive and photo-oxidisable but considerably more stable than heptacene. Contrary to a claim by Baily and Liao[4] we have been unable to obtain pure heptacene by dehydrogenation of its hydro-compounds: the deep green crude heptacene always contained hydro-derivatives which could not be removed by sublimation or extraction; the very sensitive heptacene became even less pure during these operations until the green colour disappeared completely. Baily and Liao did not measure the purity of their heptacene by an absorption spectrum.

Dinaphthoheptacene adds maleic anhydride in solution, to form an endocyclic adduct. From the absorption spectrum the derived salt has the symmetrical structure (XIX) (Fig. 4).

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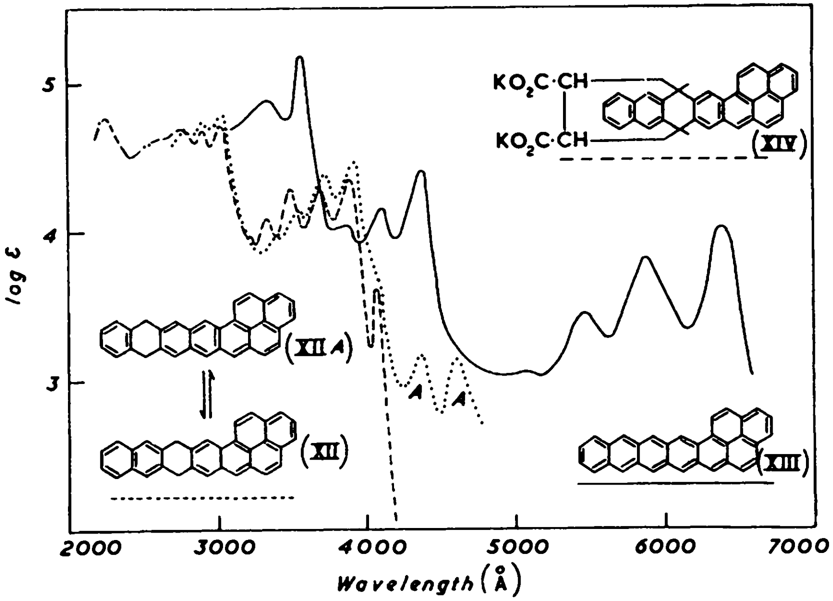
[3] Clar, *Ber.*, 1943, **76**, 257.

[4] Baily and Chien-Wei Liao, *J. Amer. Chem. Soc.*, 1955, **77**, 992.

FIG. 3. *Absorption max.* (Å) *and* log ε (*in parentheses*).

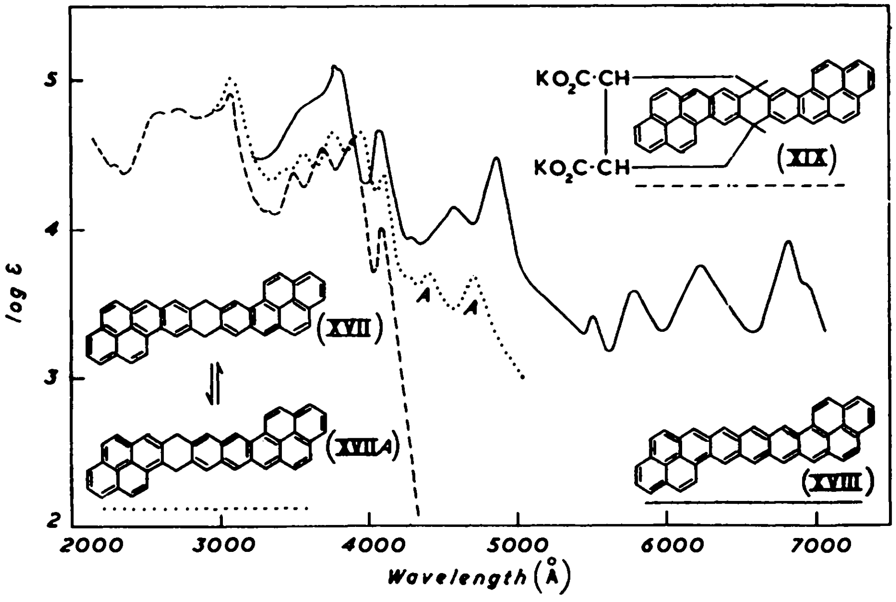


(——) *Naphthohexacene* (XIII) *in* $C_6H_3Cl_3$, 6390 (4·02), 5860 (3·82), 5460 (3·44), 4360 (4·40), 4100 (4·14), 3870 (4·04), 3580 (5·16), 3360 (4·87).

(– – – –) *Adduct* (XIV) *in* 50% EtOH, 4050 (3·59), 3880 (4·34), 3675 (4·28), 3490 (4·27), 3300 (4·06), 3020 (4·70), 2900 (4·68), 2740 (4·70), 2590 (4·62), 2230 (4·76).

(. . . .) *Hydrocarbon* (XII *and* XII*A*) *in* C_6H_6, 4600 (3·15), 4260 (3·18), 3920 (4·47), 3720 (4·40), 3530 (4·14), 3020 (4·80), 2900 (4·74), 2770 (3·68).

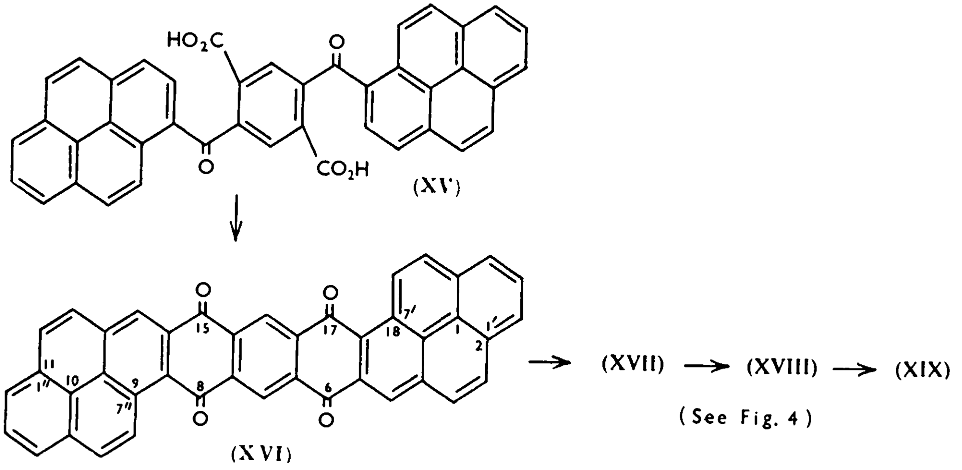
FIG. 4. *Absorption max.* (Å) *and* log ε (*in parentheses*).



(——) *Dinaphthoheptacene* (XVIII) *in* $C_6H_3Cl_3$, 6830 (3·90), 6240 (3·72), 5770 (3·56), 5500 (3·40), 4860 (4·48), 4570 (4·14), 4070 (4·66), 3780 (5·10).

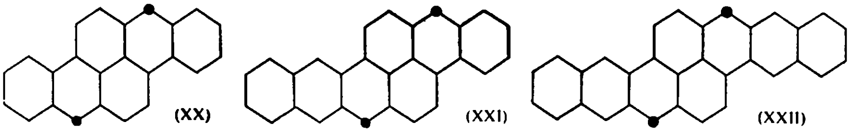
(– – – –) *Adduct* (XIX) *in* 50% EtOH, 4070 (4·00), 3900 (4·60), 3690 (4·54), 3480 (4·34), 3320 (4·12), 3060 (4·90), 2940 (4·78), 2700 (4·81), 2590 (4·78), 2240 (4·42).

(. . . .) *Hydrocarbon* (XVII *and* XVII*A*) *in* $C_6H_3Cl_3$, 4675 (3·70), 4390 (3·70), 4090 (4·36), 3950 (3·70), 3750 (4·64), 3550 (4·52), 3080 (5·04).

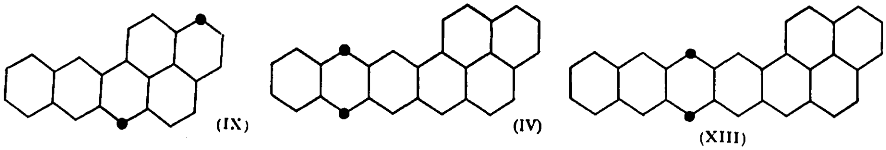


The differences between acenes and pyrenes are best illustrated by the following comparison of centrosymmetric annellated pyrenes and naphtho-acenes.

The pyrenes (XX, XXI, XXII) form pyrenequinones, on oxidation, in the positions marked with dots. The differences (4·79, 4·67, and 4·07) in $\sqrt{\text{Å}}$ in this annellation series



	(XX)	(XXI)	(XXII)
Wavelength of 1st band (Å) in benzene (log ε in parentheses)	4510 (4·60)	5160 (4·15)	5760 (4·45)
$\sqrt{\text{Å}}$	$\xrightarrow{4·79}$ 67·16	$\xrightarrow{+4·67}$ 71·83	$\xrightarrow{+4·07}$ 75·90



	(IX)	(IV)	(XIII)
Wavelength of 1st band (Å) in benzene (log ε in parentheses)	4580 (4·42)	5410 (4·15)	6330 (4·02)
$\sqrt{\text{Å}}$	$\xrightarrow{5·31}$ 67·68	$\xrightarrow{+5·87}$ 73·55	$\xrightarrow{+6·01}$ 79·56

(beginning with 3 : 4-benzopyrene) are much smaller than in the acene series [5] (7·7 $\sqrt{\text{Å}}$) and not constant but decreasing. Contrary to this, the differences in the naphtho-acene series (IX, IV, XIII) are much larger and increasing (5·31, 5·87, and 6·01 $\sqrt{\text{Å}}$). If this series were extended the differences might well increase to the value 7·7 $\sqrt{\text{Å}}$ which is typical of the acene series.[5]

The high intensity (log ε 4·42) of the first band and the fact that oxidation of naphthopyrene (IX) gives a mixture of quinones [6] indicates that it still has pyrene character. The absorption spectrum of the closely related hydrocarbon (VII) (Fig. 2), however, shows a

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[5] Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1952, p. 27.
[6] Cook and Hewett, *J.*, 1933, 403.

second group of bands (4350, 4100 Å) superimposed on the *para*-bands, which originates from another transition, probably to an excited acenoid structure.

The wavelength of the first *p*-bands of the later naphtho-acenes (IV and XIII) deviate more and more from the corresponding pyrenes (XXI and XXII) and their intensities decrease to the value (log ε about 4) which is characteristic for acenes. The reactivity, in particular the addition of maleic anhydride, and the ease of photo-oxidation in the marked positions increase with increasing acene character.

EXPERIMENTAL

M. p.s were taken in evacuated capillaries and corrected. Microanalyses are by Mr. J. M. L. Cameron and Miss M. W. Christie.

3-(*3-Carboxy-2-naphthoyl*)*pyrene* (I).—Naphthalene-2 : 3-dicarboxylic anhydride (2·0 g.) and aluminium chloride (2·5 g.) were mixed and added to tetrachloroethane (12 ml.). Powdered pyrene (2·5 g.) was then added, causing a violet-red coloration and a vigorous reaction, with complete dissolution. The solution was kept at 40° for 2 hr., then the complex was decomposed with dilute hydrochloric acid. The tetrachloroethane was distilled with steam, leaving pale yellow crystals which were filtered off and washed with benzene to remove excess of pyrene. The *acid* (4·0 g.; theor., 4·04 g.) crystallised from acetic acid as buff-coloured prisms, m. p. 259—260° (Found: C, 84·3; H, 4·3. $C_{28}H_{16}O_3$ requires C, 84·0; H, 4·0%). The colour in concentrated sulphuric acid changed from red, violet, blue to green-blue.

Naphtho(1′ : 7′-2 : 14)*pentacene-6 : 13-quinone* (II).—3-(3-Carboxy-2-naphthoyl)pyrene (1 g.) was dissolved by heat in benzoyl chloride (1 ml.) and α-chloronaphthalene (3 ml.). The solution was boiled for 35 min., cooled, and filtered. The *quinone* (0·85 g.) was washed with benzene, then recrystallised from nitrobenzene as orange plates, m. p. 340—341° (Found: C, 87·7; H, 4·1. $C_{28}H_{14}O_2$ requires C, 87·9; H, 3·7%). The colour in cold concentrated sulphuric acid was leaf-green. No vat could be obtained.

6 : 13(+7 : 12)-*Dihydronaphtho*(1′ : 7′-2 : 14)*pentacene* (III and III*A*).—The foregoing quinone (0·7 g.) was dissolved in pyridine (9 ml.), and zinc dust (4 g.) was added. The mixture was refluxed, and acetic acid (10 ml.) added during 4½ hr. The colour change in solution was orange, brown, cherry-red, and yellow. The solution was poured into hydrochloric acid, and the pink precipitate washed, finally with dilute aqueous ammonia, and dried. The pale pink powder (650 mg.) was distilled *in vacuo*, yielding a pink glass (0·5 g.). The red colour was due to a small amount of (IV) which was removed by chromatography in benzene–light petroleum on alumina. The *dihydronaphthopentacene* was obtained as very pale yellow, feathery crystals (400 mg.), m. p. 238—240°, by crytallisation from light petroleum (Found: C, 94·7; H, 5·0. $C_{28}H_{18}$ requires C, 94·9; H, 5·1%).

Naphtho(1′ : 7′-2 : 14)*pentacene* (IV).—The dihydro-compound (150 mg.) was sublimed at 300°/0·01 mm. over palladium–charcoal, giving red crystals (135 mg.), m. p. 348—350°, of the aromatic *hydrocarbon* (Found: C, 95·5; H, 4·7. $C_{28}H_{16}$ requires C, 95·4; H, 4·6%). The colour in cold concentrated sulphuric acid changed from blue, violet, green, brown to red-brown.

Maleic Anhydride Adduct of (IV).—The preceding naphthopentacene (50 mg.) was heated with maleic anhydride (100 mg.) and xylene (2 ml.). After a few minutes a clear yellow solution was obtained which deposited the *adduct*, yellow prisms, on cooling. These were filtered off, washed with xylene, and dried at 200° *in vacuo*. They decomposed above 220° (Found: C, 85·8; H, 3·8. $C_{32}H_{18}O_3$ requires C, 85·3; H, 4·0%).

3-(5 : 6 : 7 : 8-*Tetrahydro-3-methyl-2-naphthoyl*)*pyrene* (VI).—Pyrene-3-carboxyl chloride [7] (5·1 g.) and aluminium chloride (6 g.) were powdered together and added to methylene chloride (100 ml.). 6-Methyltetralin (3·65 g.) was added and the orange solution was refluxed for 2 hr. The complex was decomposed with dilute hydrochloric acid, and the methylene chloride distilled off, leaving a gum. This was treated successively with dilute hydrochloric acid, water, and dilute sodium hydroxide solution, whereupon the gum hardened. It was then filtered off, washed, and dried *in vacuo* (4·9 g.; theor., 7·48 g.). The product could not be obtained crystalline.

Naphtho(1′ : 7′-2 : 14)*pentacene* (IV) *and* 7 : 8-*Benzonaphtho*(1′ : 7′-2 : 12)*tetracene* (VII).—The above product was heated to 390° during 10 min. and copper bronze (*ca.* 0·5 g.) was added.

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[7] Vollmann, Becker, Corell, and Streeck, *Annalen*, 1937, **531**, 110.

During the next 15 min. the temperature was raised to 410°, steam and hydrogen being evolved. The melt, on cooling, solidified to a black glass which was powdered and sublimed at 300°/0·01 mm. The semicrystalline sublimate (*ca.* 1 g.) was crystallised from benzene, then chromatographed in benzene–light petroleum on alumina in an inert atmosphere. The naphthopentacene (IV) was obtained as red leaflets, m. p. 348—350°, and the benzonaphthotetracene (VII) (*ca.* 50 mg.) as deep yellow leaflets, m. p. 332—333°.

3-(2-*Methyl*-1-*naphthoyl*)*pyrene* (VIII).—Pyrene-3-carboxyl chloride [7] (14 g.) and aluminium chloride (15 g.) were ground together and added to dry nitrobenzene (150 ml.). 2-Methylnaphthalene (8·75 g.) was added in a little nitrobenzene. The mixture, which had developed a purple colour, was stirred at 60—70° for 2 hr. The complex was decomposed with dilute hydrochloric acid, and the nitrobenzene layer washed with warm dilute hydrochloric acid, then with water. Steam-distillation gave a semisolid residue which was dissolved in benzene and extracted with warm dilute alkali. Pyrenecarboxylic acid (6·7 g.) was recovered by acidification of the alkaline extracts. The benzene was distilled off and the gummy residue (8·7 g.) recrystallised from alcohol, then from benzene, giving the *ketone* as yellow prisms, m. p. 194—195° (Found: C, 90·9; H, 4·6. $C_{28}H_{18}O$ requires C, 90·8; H, 4·9%).

7 : 8-*Benzonaphtho*(1′ : 7′-2 : 12)*tetracene* (VII).—The preceding ketone (6·7 g.) was heated to 390°, then the temperature was allowed to rise to 410° during 15 min. The almost quiescent melt was cooled and heated in a sublimation apparatus at 300°/0·01 mm. An orange glass was obtained which crystallised when treated with benzene. Chromatography in benzene–light petroleum gave, first, an oil and then the hydrocarbon (500 mg.), which recrystallised from benzene as yellow leaflets, m. p. (and mixed m. p. with product from earlier synthesis) 332—333° (Found: C, 95·3; H, 4·6. $C_{28}H_{16}$ requires C, 95·4; H, 4·6%).

3-(*Pyrene*-3-*carbonyl*)*anthraquinone*-2-*carboxylic Acid* (X).—Anthraquinone-2 : 3-dicarboxylic anhydride (22·4 g.) was ground with aluminium chloride (22·5 g.) and suspended in nitrobenzene (600 ml.) at 55°. Pyrene (20 g.) was added and the mixture was stirred at this temperature for 3½ hr., then treated with water (500 ml.) and concentrated hydrochloric acid (150 ml.). Steam-distillation removed the nitrobenzene, and the solid product was filtered off, extracted with dilute hydrochloric acid, washed with water, dried, and washed with benzene to remove excess of pyrene from the brownish-yellow powder (34 g.). Extraction with boiling ammonia solution and acidification of the extracts yielded the pure *acid* as a yellow precipitate, which crystallised from acetic acid as orange needles, m. p. 317—319° (Found: C, 79·7; H, 3·5. $C_{32}H_{16}O_5$ requires C, 80·0; H, 3·4%). The colour in concentrated sulphuric acid changed from red violet to violet and blue.

Naphtho(1′ : 7′-2 : 16)*hexacene*-6 : 15-8 : 13-*diquinone* (XI).—The *recrystallised* acid (1·7 g.) was dissolved in boiling benzoyl chloride (40 ml.) to give an orange solution, rapidly becoming brown. Addition of a trace of zinc chloride quickly changed the colour to blue-green and then to brown and deep red. The solution was cooled and allowed to crystallise. The deep red-maroon *diquinone* (1·15 g.) was filtered off, washed with benzoyl chloride, acetic acid, and ether, and recrystallised from nitrobenzene as red-maroon leaflets, m. p. 418—419° (Found: C, 82·8; H, 3·2. $C_{32}H_{14}O_4$ requires C, 83·1; H, 3·0%). With alkaline sodium dithionite it formed a two-stage vat, first a greenish-brown, then a reddish-brown one. The colour in cold concentrated sulphuric acid was green.

8 : 13(+7 : 14)-*Dihydronaphtho*(1′ : 7′-2 : 16)*hexacene* (XII and XII*A*).—The diquinone (1·6 g.) was dissolved in pyridine (160 ml.), zinc dust (10 g.) added, and the mixture refluxed while 80% acetic acid was added dropwise. The initial deep red colour of the solution changed quickly to blue-green, then back to pale red, and finally to canary-yellow. The mixture was refluxed for 17 hr. while a total of 90 ml. of acetic acid was added, then poured into much dilute hydrochloric acid, and the precipitated, incompletely reduced material (1·4 g.) washed, dried, and further reduced in 70 ml. of pyridine, with 30 ml. of acetic acid, for 11 hr. The solution was again poured into hydrochloric acid and the precipitate filtered off, washed, and dried (1·3 g.). The product was extracted with boiling xylene and repeated crystallisation of the extracted material gave the *dihydro-compound* (250 mg.) as yellow needles, m. p. 314—316° (Found: C, 95·0; H, 4·9. $C_{32}H_{20}$ requires C, 95·0; H, 5·0%).

Naphtho(1′ : 7′-2 : 16)*hexacene* (XIII).—The preceding dihydro-compound (100 mg.) was sublimed at 300°/0·01 mm. into closely-packed lumps of palladium–charcoal. The green deposit of naphthohexacene was sublimed from the charcoal at 350°. Extraction with boiling xylene removed unchanged dihydro-compound. Resublimation of the *hydrocarbon* gave clusters of blue-green leaflets (70 mg.), m. p. 384—386° (Found : C, 95·5; H, 4·4. $C_{32}H_{18}$ requires C, 95·5; H, 4·5%). The colour in cold concentrated sulphuric acid changed from violet to brown and green.

The *maleic anhydride adduct* was obtained by dissolving the naphthohexacene in molten maleic anhydride. Dilution of the melt with xylene and recrystallisation of the precipitate from xylene yielded yellow needles, decomp. >200° (Found : C, 85·0; H, 3·7. $C_{36}H_{20}O_3$ requires C, 86·4; H, 4·0%).

2 : 5-*Di*(*pyrene*-3-*carbonyl*)*terephthalic Acid* (XV).—Pyromellitic anhydride (9·7 g.) and anhydrous aluminium chloride (30 g.) were ground together and added at room temperature to a stirred solution of pyrene (25 g.) in benzene (80 ml.). On gentle heating, exothermic reaction occurred. After being kept at room temperature for 2 days the complex was decomposed with dilute hydrochloric acid. The benzene was boiled off and the solid product was filtered off and washed with dilute hydrochloric acid, then with water. The *acid* was extracted from the crude product as its sparingly soluble ammonium salt from which it was obtained by acidification (12·5 g.). It recrystallised from acetic acid in yellow needles, m. p. 334—336° (Found : C, 80·0; H, 3·5. $C_{42}H_{22}O_6$ requires C, 81·0; H, 3·5%). The colour in sulphuric acid was violet red.

Dinaphtho(1′ : 7′-2 : 18)(7″ : 1″-9 : 11)*heptacene*-6 : 17-8 : 15-*diquinone* (XVI).—The acid (3 g.) was dissolved in boiling benzoyl chloride (45 ml.) containing a trace of zinc chloride. The solution developed a greenish-yellow colour which changed to violet-red. After the solution had been refluxed for 15 min. the *quinone* began to crystallise. It was filtered off, washed with benzoyl chloride, acetic acid, and ether (yield 0·7 g.), and sublimed *in vacuo* (0·005 mm.) at 420° in violet-red plates, m. p. 500—502° (Found : C, 85·8; H, 3·4. $C_{42}H_{18}O_4$ requires C, 86·0; H, 3·1%).

8 : 15(+7 : 16)-*Dihydrodinaphtho*(1′ : 7′-2 : 18)(7″ : 1″-9 : 10)*heptacene* (XVII).—The preceding diquinone (1 g.) was powdered with zinc dust (10 g.) and added to pyridine (40 ml.). Acetic acid (80% ; 50 ml.) was added to the refluxing mixture during 15 hr., and the amount of zinc was renewed twice. The colour of the solution changed from violet-brown to yellow-brown, then to yellow. The supernatant hot pyridine solution was poured into water (200 ml.). The yellow precipitate was filtered off, washed with hot dilute hydrochloric acid, then with water, and dried (780 mg.). The zinc residues were dissolved in concentrated hydrochloric acid. The diluted solution was filtered and the residue washed with water and dried (yield, 115 mg. of pale yellow-brown material). The combined product was extracted with boiling xylene (2 × 50 ml.) (residue : 660 mg.), the xylene solution evaporated to dryness, and the residue sublimed at 360°/0·01 mm. It gave a yellow crystalline sublimate which, when recrystallised from xylene, yielded the *dihydro-compound* as yellow-brown needles (120 mg.), m. p. 413—414° (Found : C, 95·2; H, 4·5. $C_{42}H_{24}$ requires C, 95·4; H, 4·6%).

Dinaphtho(1′ : 7′-2 : 18)(7″ : 1″-9 : 11)-*heptacene* (XVIII).—The preceding compound (50 mg.) was sublimed into closely-packed palladium–charcoal lumps at 375°/0·001 mm. during several hours. The temperature was raised to 415° and after about 16 hr. 25 mg. of the aromatic *hydrocarbon* had sublimed as deep green-black needles, m. p. 461—462°. It dissolved very slowly in concentrated sulphuric acid with a brown violet colour (Found : C, 95·7; H, 4·3. $C_{42}H_{22}$ requires C, 95·8; H, 4·2%).

The *maleic anhydride adduct* crystallised from a solution of dinaphthoheptacene in molten maleic anhydride when the melt was diluted with xylene. Recrystallised from xylene it formed yellowish prisms, decomp. >200° (Found : C, 88·8; H, 3·7. $C_{46}H_{24}O_3$ requires C, 88·4; H, 3·9).

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