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4,5:12,13-DIBENZOHEPTAZETHRENE AND 5,6:8,9:14,15:17,18-TETRABENZOHEPTACENE

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Abstract—Terephthalyl chloride and octahydrophenanthrene gave the diketone I which on pyrolysis yielded the tetradecahydro, octahydro, and dihydro-dibenzoheptazethrenes II, III, and IV respectively. The same hydrocarbons were obtained from the isomeric diketone V, involving a rearrangement. Dehydrogenation of the hydro derivatives or pyrolyses of the diketones in presence of copper powder gave the green dibenzoheptazethrene VI. This is a strongly basic hydrocarbon and forms stable salts VII. Oxidation formed the quinone IX. The dihydro compound IV added maleic anhydride twice, to give the dianhydride X, which cyclized in a sodium chloride-zinc chloride melt, to tetrabenzoheptacene XI. This is a fully benzenoid, orange hydrocarbon of very high stability.

TEREPHTHALYL chloride condensed twice with octahydrophenanthrene and aluminium chloride in an analogous way to benzoyl chloride with octahydrophenanthrene.[1] The diketone I was pyrolysed and dehydrogenated with copper powder. Owing to the sensitivity of the resulting dibenzoheptazethrene* the yield was rather poor. Better results were obtained without copper powder. The dihydro compound IV crystallized first from the diluted pyrolysate together with a little octahydro compound III. The tetradecahydro derivative II was obtained from the mother liquor by chromatography. The latter shows the absorption spectrum of a 1,2:5,6-dibenzanthracene derivative, as is demonstrated by comparison with 1,2:5,6-dibenzanthracene in Fig. 1. The absorption spectra of the dihydro and octahydro compounds IV and III respectively, are closely related to the spectrum of 2,3:7,8-dibenzoperinaphthene[1] as shown in Fig. 2. The two former being related to the latter as terephenyl is to diphenyl. These compounds cannot have a 1,2:5,6-dibenzanthracene complex as in II.

These hydro derivatives can be dehydrogenated with palladium charcoal to dibenzoheptazethrene VI. The dihydro compound was also easily dehydrogenated by a simple crystallization from nitrobenzene or with chloranil in boiling trichlorobenzene.

The diketone V obtained from isophthalyl chloride, octahydrophenanthrene, and aluminium chloride, gave the same hydro derivatives by rearrangement of the diketone during the pyrolysis. The rearrangement is always observed when the resulting hydrocarbon would have the 1,2:7,8-dibenzanthracene skeleton. This has never been obtained by the Elbs reaction. Compounds with the 1,2:5,6-dibenzanthracene structure are formed in its place.[2]

The best yield of the dihydro compound IV was recorded when pure octahydrophenanthrene was replaced by an excess of a technical product containing about 30 per cent tetrahydrophenanthrene.

* The name heptazethrene is derived from zethrene as used in E. Clar, *Aromatische Kohlenwasserstoffe* p. 393. Springer Verlag (1952).

[1] E. Clar, *Ber. Dtsch. Chem. Ges.* **76**, 611 (1943).

[2] J. W. Cook, *J. Chem. Soc.* 487 (1931); 1472 (1932); 499 (1931); E. Clar and Fr. John, *Ber. Dtsch. Chem. Ges.* **64**, 981 (1931); E. Clar. Fr. John and R. Avenarius, *Ber. Dtsch. Chem. Ges.* **72**, 2139 (1939); E. Clar, *Ber. Dtsch. Chem. Ges.* **73**, 81 (1940).

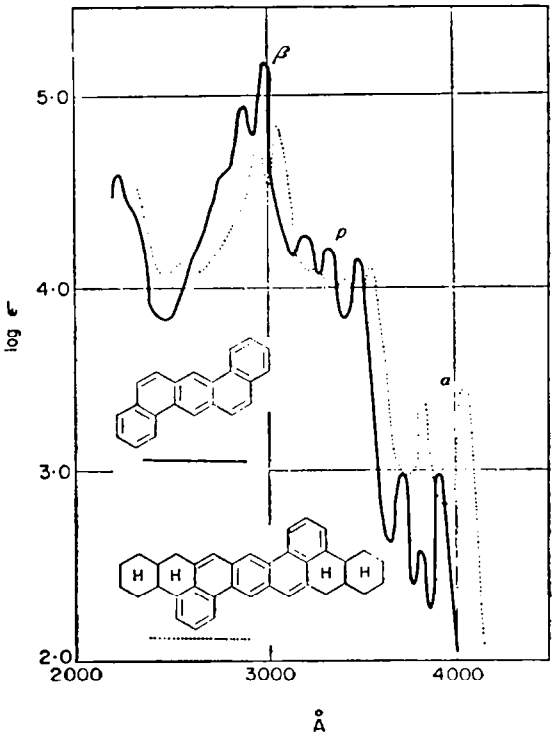


FIG. 1. Absorption max (Å) and log ε (in parentheses) of:
(————) 1:2,5:6-Dibenzoanthracene, in benzene; α, 3950 (3·16), 3850 (2·70), 3730 (3·10); *p*, 3510 (4·24), 3365 (4·21), 3220 (4·32); β, 3000 (5·10), 2900 (4·93), in alcohol 2770 (4·72), 2300 (4·50).
(· · · · ·) Tetradecahydro-4:5,12:13-dibenzoheptazethrene (II) in benzene; α, 4100 (3·64), 3880 (3·60); *p*, 3600 (4·30), 3460 (4·26), 3300 (4·32); β, 3100 (4·98), in cyclohexane, 2970 (4·92), 2350 (4·74).

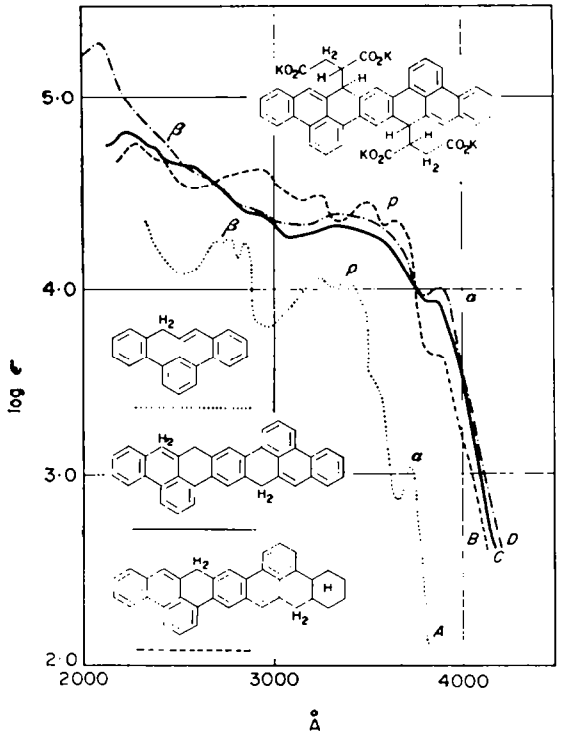
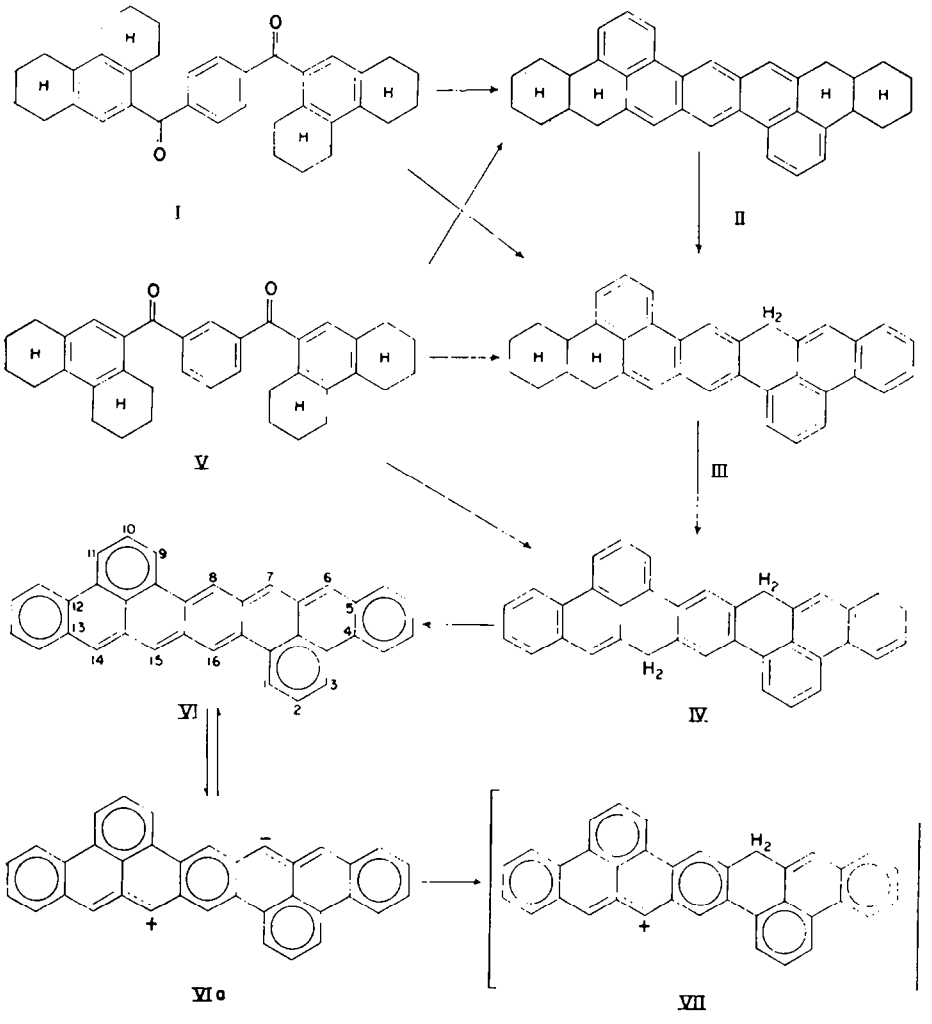


FIG. 2. Absorption max (Å) and log ε (in parentheses) of:
(A) (· · · · ·) 2:3:7:8-Dibenzoperinaphthene in alcohol; α, 3720 (3·04); *p*, 3390 (4·02), 3270 (4·04), 3020 (4·84) β, 2850 (4·23), 2760 (4·24), 2690 (4·26).
(B) (– – – – –) Octahydro-(4:5,12:13)-Dibenzoheptazethrene (III) in benzene; α, 3840 (3·58); *p*, 3600 (4·31), 3440 (4·41), 3090 (4·44); in cyclohexane β, 2860 (4·58), 2110 (4·64).
(C) (————) 7,15-Dihydro-(4:5,12:13)-dibenzoheptazethrene (II) in benzene; α, 3900 (4·01); *p*, 3540 (4·32), 3400 (4·36); in cyclohexane α, 2530 (4·68), 2220 (4·84).
(D) (– · – · – · –) Tetrapotassium salt of (X), in 50% alcohol; α, 3860 (3·96); *q*, 3400 (4·40); α, 2100 (5·32).

Dibenzoheptazethrene VI has a green, shining surface and gives violet red, photo-oxidizable solutions. It forms an insoluble, stable, deep violet, hydrochloride, perchlorate and sulphate, giving a salt even with phosphoric acid VII. These basic properties can be explained by the polarized structure VIa, which has one more benzenoid ring (marked with circles) than structure VI, which shows four fixed double bonds in the centre, compared with two in zethrene.[3]



Suspensions of the hydrochloride gave the chloro derivative VIII, on standing in the presence of light and air. The same compound was easily obtained from the dihydro compound IV or dibenzoheptazethrene VI with phosphorus pentachloride in boiling xylene. Dibenzoheptazethrene VI and its chloro derivative VIII, can be readily reduced to the dihydro compound IV with boiling pyridine, acetic acid and zinc dust. Oxidation of dibenzoheptazethrene VI, or its derivative IV, with selenium dioxide in boiling nitrobenzene, gave the yellow quinone IX which does not form a vat with

[3] E. Clar, K. F. Lang and H. Schulz-Kiesow. *Chem. Ber.* **88**, 1520 (1955).

alkaline sodium dithionite solution. The absorption spectrum of dibenzoheptazethrene VI, and its chloro compound are shown in Fig. 3. The spectrum of the quinone IX is recorded in Fig. 4 in comparison with 2,3:7,8-dibenzoperinaphthone.[1]

Dihydrodibenzoheptazethrene IV condensed quantitively with maleic anhydride to the dianhydride X. The absorption spectrum of the corresponding tetracarboxylic acid (Fig. 2) is very closely related to the dihydro compound IV, thus indicating that no change in the aromatic conjugation had taken place.

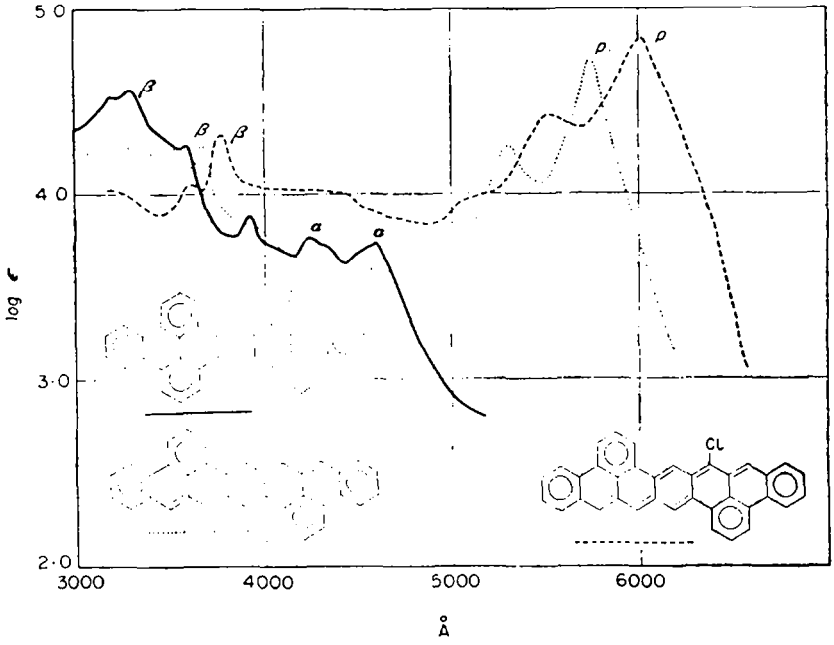


FIG. 3. Absorption max (Å) and log ε (parentheses) of:
(· · · · · ·) 4:5,12:13-Dibenzoheptazethrene (VI) in benzene, (intensities from trichlorobenzene); *p*, 5720 (4·70), 5280 (4·26), 4880 (3·74); *β*, 3640 (4·26).
(– – – –) 7-Chlorodibenzoheptazethrene (VIII) in trichlorobenzene; *p*, 6000 (4·83), 5500 (4·40), 5100 (3·98); *β*, 3780 (4·30).
(————) 5:6,8:9,14:15,17:18-Tetrabenzoheptacene (XI) in benzene (intensities from methyl naphthalene); α, 4610 (3·70), 4260 (3·75); *p*, 3930 (3·86); *β*, 3290 (4·54).

The tetracarboxylic acid (derived from X) cyclized in a sodium chloride-zinc chloride melt, with simultaneous decarboxylation, to tetrabenzoheptacene XI. This is an orange hydrocarbon of high thermal stability, which does not dissolve in concentrated sulphuric acid, and shows a red phosphorescence of long life in solid ethanolic solution at 77°K (see Table 2). It does not react with maleic anhydride and shares these properties with other purely benzenoid hydrocarbons.[4] The chemical inertness of benzenoid hydrocarbons can be related to the fact that their U.V. spectra are the most strongly shifted to the violet among the spectra of the isomeric aromatic hydrocarbons, except for the corresponding polyphenyls with the same number of rings. Confirmation that benzenoid rings are the reason for the high stability and the extreme violet shift in the U.V. spectrum of such hydrocarbons is obtained by the comparison

[4] 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); M. Zander, *Chem. Ber.* **92**, 2744 (1959).

in Fig. 3, where the spectrum of tetrabenzoheptacene XI is shown together with that of dibenzoheptazethrene VI. The spectrum of the fully benzenoid tetrabenzoheptacene XI is strongly shifted to the violet, although the hydrocarbon XI contains two more rings than dibenzoheptazethrene VI which is not fully benzenoid.

The structure XI is based on the assumption that a hydrocarbon with the maximum number of benzenoid rings is usually formed in preference to other ways of cyclization, which would yield hydrocarbons with fewer benzenoid rings. This would be contrary

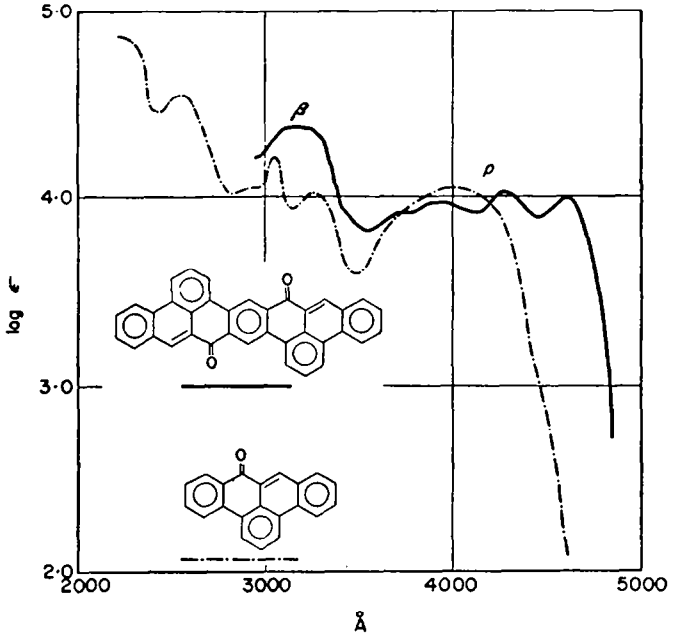


FIG. 4. Absorption max in (Å) and log ε (in parentheses) of:
(————) 4:5,12:13-Dibenzoheptazethrene-7,15-quinone (IX) in trichlorobenzene; *p*, 4770 (4·00), 4550 (4·24); β 3400 (4·60).
(– · – · – · –) 2:3,7:8-Dibenzoperinaphthenone in alcohol; *p*, 4000 (4·06), 3270 (4·02), 3030, (4·22); β, 2570 (4·58).

to experience.[5] The molecular weight of the hydrocarbon was estimated* by the mass spectroscopic method to be 510 ± 5 (Calc. 526). This shows that two rings have in fact been added to the dihydro hydrocarbon IV.

Confirmation that structure XI is correct, was obtained by comparison of the infrared spectra of the benzenoid hydrocarbons, given in Table 1. Groenwege[6] has shown that the γ-vibrations of the C—H bonds (735–900 cm^{-1}), can be used to establish the structure of polycyclic hydrocarbons. Recently Zander[7] applied this method to tetrabenzopentacene XII, the synthesis of which from two molecules of triphenylene in an aluminium chloride melt was not unambiguous. The Table shows that tetrabenzopentacene XII, as well as tetrabenzoheptacene XI, have "solo" C—H vibrations which are lacking in 1,2:6,7-dibenzopyrene XIV, which is also fully benzenoid.

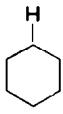
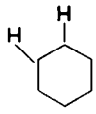
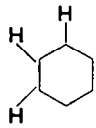
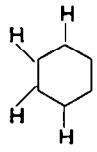
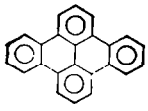
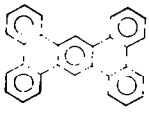
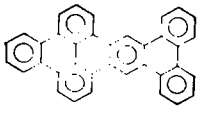
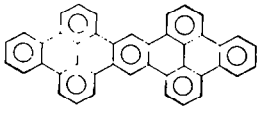
* The molecular weight was kindly measured by Dr. R. I. Reed of this department.

[5] E. Clar, *Ber. Dtsch. Chem. Ges.* **76**, 611 (1943); **81**, 520 (1948).
[6] M. P. Groenwege, *Colloquium Spectroscopicum Internationale VI Amsterdam* p. 579. Pergamon Press, London (1956).
[7] M. Zander, *Chem. Ber.* **92**, 2744 (1959).

Moreover, the resemblance of the infra-red spectra of tetrabenzoanthracene XIII, tetrabenzopentacene XII, and tetrabenzoheptacene XI is very striking.

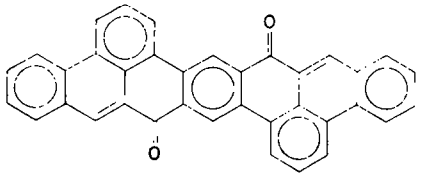
Further evidence that the hydrocarbon has structure XI is supplied by the comparison of the phosphorescence spectra of tetrabenzoanthracene XIII, tetrabenzopentacene XII, and tetrabenzoheptacene XI. The principal phosphorescence

TABLE 1. INFRA-RED SPECTRA

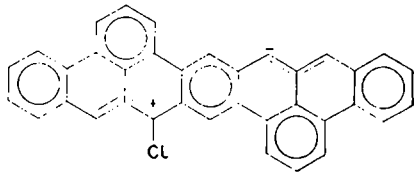
Hydrocarbon		C—H Vibrations (cm^{-1})*			
		solo  900–860 cm^{-1}	duo  860–800 cm^{-1}	trio  810–750 cm^{-1}	quartet  770–735 cm^{-1}
	XIV	—	—	801	744
	XIII	870	—	—	749
	XII	871 863	—	795	746
	XI	867	—	792	745

* All spectra in KBr

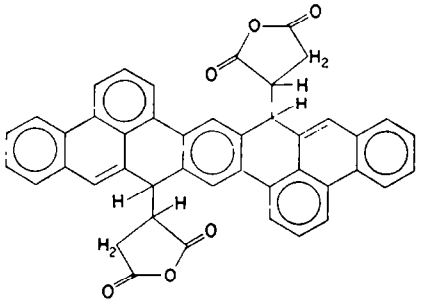
maxima are given in Table 2. The differences between the first phosphorescence bands of these hydrocarbons are so small (235 Å and 115 Å respectively), that they can result only from the annellation of fully benzenoid rings, for which such minimum shifts are typical. Contrary to this, the differences of phosphorescence bands in the acene series where there is only one benzenoid ring are the largest recorded and are



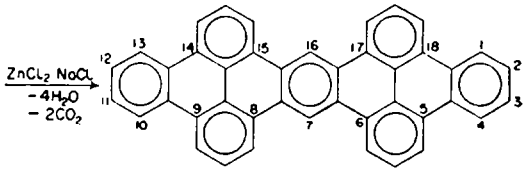
IX



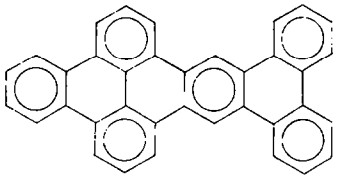
VIII



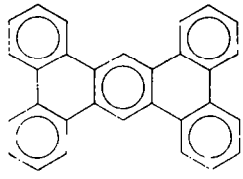
X



XI



XII



XIII

in the order of thousands of Ångstroms. Other series of hydrocarbons show shifts of intermediate magnitude.[8]

EXPERIMENTAL*

1,4-*Di-(octahydrophenanthroyl-9)-benzene* I

Finely powdered terephthalyl chloride (75 g) was mixed with excess of technical octahydrophenanthrene (405 g), and benzene (500 ml). Powdered aluminium chloride (130 g) was added in portions. When the vigorous evolution of hydrochloric acid had ceased, the mixture was decomposed with ice and dil hydrochloric acid. The crude ketone was filtered off, dissolved in xylene, and combined with the benzene mother liquor. This mixture was washed very thoroughly with hot water and dil ammonia. Removal of the xylene–benzene mixture left the crude ketone (200 g), which was used directly for the pyrolysis. Repeated crystallization of a portion of ketone from xylene gave small, pale yellow needles m.p. 201–202°. The solution in conc sulphuric acid was brown at first, later turning orange. (Found: C, 85·9; H, 7·5. $C_{36}H_{38}O_2$ requires: C, 86·0; H, 7·6%).

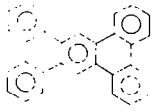
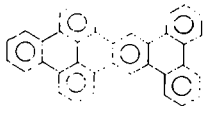
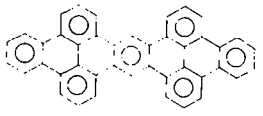
Pyrolyses of 1,4-*di-(octahydrophenanthroyl-9)-benzene* I

The crude ketone (100 g) was melted and the temp raised gradually to 400°; water was evolved and the brownish colour lightened to pale orange with a strong yellow fluorescence. When no more water appeared (½–¾ hr), heating was stopped and the mixture was cooled, with the exclusion of air.

* Melting points are uncorrected and were taken in evacuated capillaries. Microanalyses by Mr. J. M. L. Cameron and his staff of this department.

[8] E. Clar and M. Zander, *Chem. Ber.* **89**, 749 (1956).

TABLE 2. PHOSPHORESCENCE SPECTRA*

Hydrocarbon		Phosphorescence maxima (A)
	XIII	4865 (weak, 5300 (strong), 5730 (medium)
	XII	5100 (medium), 5545 (strong), 5990 (weak)
	XI	5215 (strong), 5685 (strong), 5930 (weak)

* In solid ethanolic solution at 77IK.

Hot xylene (150 ml) was added and on cooling a red solid (5 g) was deposited. Further portions (2–3 g) were later obtained from the mother liquor. This crystalline pyrolysate consisted of a mixture of hydrogenated hydrocarbons, mainly the dihydro IV, with some octahydro III and a trace of the fully aromatic dibenzoheptazethrene VI. This crystalline mixture was used directly for subsequent reactions. The mixture dissolved slowly in conc sulphuric acid and gave a violet colour at first which changed to purple.

Tetradecahydro-4,5:12,13-*dibenzoheptazethrene* II

The filtrate from the above reaction was chromatographed on alumina. Elution with petroleum ether (60–80°) and then benzene, gave several fractions. The major portion was a viscous oil which could not be characterized. Later fractions gave a small amount (50 mg) of a yellow crystalline hydrocarbon m.p. 438–440° which gave yellow solutions in conc sulphuric acid. (Found: C, 92·1; H, 7·5. $C_{36}H_{34}$ requires: C, 92·6; H, 7·4%).

1,3-*di*-(*octahydrophenanthroyl*-9)-*benzene* V

Procedure as for ketone I. Crystallization from benzene and petroleum ether (100–120°) gave white needles m.p. 172–173° which dissolved in conc sulphuric acid to give a brown solution which later turned orange. (Found: C, 86·0; H, 7·9. $C_{34}H_{38}O_2$ requires: C, 86·0; H, 7·6%).

Pyrolyses of 1,3-*di*-(*octahydrophenanthroyl*-9)-*benzene* V

Conditions were the same as for ketone I. The crude ketone (100 g) gave the mixed hydrogenated hydrocarbons (6 g).

4,5:12,13-*Dibenzoheptazethrene* VI

(i) *Dehydrogenation with palladium charcoal.* The crystalline pyrolysate (500 mg) was sublimed, in a current of air free carbon dioxide, over 15% palladium charcoal at 300–320°/0·1 mm. Shining green needles (450 mg) of the fully aromatic hydrocarbon VI were formed, dec pt above 400°. Solutions of the hydrocarbon VI in organic solvents were violet-red with a strong red fluorescence. The dibenzo heptazethrene VI dissolved immediately in conc sulphuric acid to give a deep purple solution which showed absorption bands in the visible region at 550 mμ, and 512 mμ. (Found: C, 95·2; H, 4·7. $C_{36}H_{20}$ requires C, 95·55; H, 4·46%).

(ii) *Dehydrogenation with nitrobenzene.* The pyrolysate (1 g) was suspended in nitrobenzene (15 ml), and refluxed for 2–3 min. The brownish red solution turned deep purple with a strong red fluorescence and on cooling glistening green needles (300 mg) were deposited.

(iii) *Dehydrogenation using chloranil in trichlorobenzene.* The pyrolysate (1 g) was suspended in trichlorobenzene (20 ml) and excess chloranil (1 g) added. The mixture was boiled for 2–3 min and on cooling crystals (200 mg) of the hydrocarbon XI were formed.

Salts of 4,5:12,13-*dibenzoheptazethrene* VII

(i) *Hydrochloride.* Solutions of the hydrocarbon VI in trichlorobenzene were shaken with conc hydrochloric acid. The organic layer was completely decolourized and a violet salt formed. The salt could also be formed by the passage of hydrochloric acid gas. A solution of hydrocarbon VI (100 mg) in trichlorobenzene (500 ml), was saturated with hydrochloric acid gas. The flocculant violet precipitate was filtered off, washed with dry benzene, and dried *in vacuo.* (Found: C, 88·0; H, 4·3; Cl, 6·8. $C_{36}H_{21}Cl$ requires: C, 88·4; H, 4·3; Cl, 7·3%).

The hydrochloride decomposed on standing, turning black, with loss of hydrochloric acid. If a suspension of the salt in trichlorobenzene was allowed to stand for several days a solution with the absorption bands (600, 500mμ) of the chlorodibenzozethrene VIII resulted. The hydrochloride appeared insoluble in most organic solvents. When a suspension of the salt in pyridine was boiled green crystals of the parent hydrocarbon VI were formed. The salt gave purple solutions in conc sulphuric acid which had bands at 550 mμ and 512 mμ.

(ii) *Sulphate.* Solutions of dibenzoheptazethrene VI were completely decolourized on shaking with 80% sulphuric acid. The violet sulphate being formed. Dibenzoheptazethrene VI gave solutions in conc sulphuric acid which showed absorption bands at 550 mμ, and 512 mμ, compared to the hydrocarbon VI in trichlorobenzene solution where the bands were at 572 mμ and 528 mμ. This shift is indicative of salt formation.

(iii) *Perchlorate and phosphate.* Solutions of dibenzoheptazethrene in trichlorobenzene were also decolourized when shaken with perchloric or phosphoric acid, the violet salts being precipitated.

7-*Chloro*-4,5-*dibenzoheptazethrene* VIII

An excess of phosphorus pentachloride (500 mg) was added to a suspension of the crystalline pyrolysate (300 mg) in boiling xylene. The reddish-brown solution turned a deep blue with a strong red fluorescence and on cooling the dark blue chlorohydrocarbon VIII (250 mg) was deposited. Recrystallization from trichlorobenzene gave the pure chlorohydrocarbon, dec pt above 450°, which dissolved in conc sulphuric acid to give a deep purple solution. (Found: Cl, 7·3. $C_{36}H_{19}Cl$ requires: Cl, 7·5%).

7,15-*Dihydro*-4,5:12,13-*dibenzoheptazethrene* IV

Although this substance is the main product of the pyrolysis the best method of obtaining it pure was by reduction of dibenzoheptazethrene VI, or chlorodibenzheptazethrene VIII. Dibenzoheptazethrene VI (500 mgs) or chlorodibenzheptazethrene VIII (500 mgs), was ground together with zinc dust (2 g). This mixture was suspended in pyridine (100 ml) and refluxed. Acetic acid (80%, 10 ml) was added slowly over 3 hr. The violet solution, decolourized immediately becoming a pale yellow with a strong blue fluorescence. After cooling the solution was filtered into water and boiled. The pale yellow dihydro-dibenzoheptazethrene was filtered off, dried and sublimed, m.p. 395–400° (dec). The colour in conc sulphuric acid was violet. (Found: C, 94·6; H, 5·4. $C_{36}H_{22}$ requires: C, 95·1; H, 4·9%). This hydrocarbon could not be recrystallized since it was too easily dehydrogenated.

4,5:12,13-*Dibenzoheptazethrene*-7,15-*quinone* IX

The crystalline pyrolysate (300 mg) and selenium dioxide (100 mg) were refluxed in nitrobenzene (10 ml) for 20 min. The red solution turned purple and then dark brown. On cooling the product was filtered off, washed with nitrobenzene and methanol, followed by hot water to remove excess selenium dioxide. The dark brown product (400 mg) was purified by sublimation. Brown needles of the quinone (200 mg) sublimed at 400°/0·1 mm, dec pt. above 450°. The colour in conc sulphuric acid was green. (Found: C, 89·5; H, 4·3. $C_{36}H_{18}O_2$ requires: C, 89·6; H, 3·8%).

Maleic anhydride adduct X *from* 7,15-*dihydro*-4,5-*dibenzoheptazethrene* IV

The pyrolysate (5 g) was added to molten maleic anhydride and boiled for 15 min. After cooling, the mixture was poured into water and digested. The crude light brown anhydride X was filtered off, and dissolved in 15–20% caustic potash solution, giving a pale yellow colour with blue fluorescence. Zinc dust was added to prevent aerial oxidation and after filtration the solution was acidified. The brown acid was dried (6·5 g). A portion was crystallized from acetic anhydride, m.p. 250–255° (dec). (Found: C, 78·8; H, 4·8. $C_{44}H_{28}O_7$; (semi-anhydride) requires: C, 79·0; H, 4·3). The solution in conc sulphuric acid was steel blue at first, later turning reddish.

Octahydro-4,5:12,13-*dibenzoheptazethrene* III

When the above condensation was carried out for a shorter time there was an alkali insoluble residue (200 mg). Recrystallization from benzene gave small white needles, m.p. 318–320°. This hydrocarbon III could not be dehydrogenated by means of chloranil in trichlorobenzene, but sublimation over 15% palladium charcoal at 300–320° gave a dibenzoheptazethrene VI in quantitative yield. The octahydro hydrocarbon III gave a blue solution in conc sulphuric acid. (Found: C, 93·5; H, 6·3. $C_{36}H_{28}$ requires; C, 93·9: H, 6·1%).

5,6:8,9:14,15:17,18-*Tetrabenzoheptacene* XI

The tetracarboxylic acid, derived from X, (5 g) was ground together with zinc dust (5 g). Zinc chloride (50 g), sodium chloride (5 g) and a little water (2 ml) were added and the temp of the mixture was raised, with constant stirring, to 300–320° for 10 min. After cooling the mixture was digested with dil acetic acid and the zinc dust dissolved in dil hydrochloric acid. The crude product (2 g) was extracted with ether and xylene, to remove impurities of low molecular weight. Repeated sublimation (400–450°/0·1 mm), followed by recrystallization from methyl naphthalene gave yellow needles (300 mg) of tetrabenzoheptacene, m.p. 480–490° (sublim). Tetrabenzoheptacene does not dissolve in conc sulphuric acid although the surface of the crystals turns black. The hydrocarbon has a long life phosphorescence in solid ethanolic solution at 77 K°. (Found: C, 95·5; H, 4·5. $C_{42}H_{28}$ requires: C, 95·8; H, 4·2%). The molecular weight was found to be 510 ± 5, $C_{42}H_{28}$ requires 526.