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THE SIGNIFICANCE OF KEKULÉ STRUCTURES FOR THE STABILITY OF AROMATIC SYSTEMS

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Abstract—The attempted synthesis of the hydrocarbons (I), (XXII) and (XXIX) with no Kekulé structures indicates that these hydrocarbons are unstable diradicals that polymerise immediately. Quantum mechanics can not offer a stable arrangement of paired electrons in molecular orbitals in cases where Kekulé structures fail. Perinaphthene (X) and perinaphthone (XIII) show a pronounced tendency to go over into ring systems with an aromatic frame work of alternating double bonds with an odd electron or a positive charge in the centre. Tribenzoperinaphthene (XVI) is oxidised in acid solution with molecular oxygen to salts of the type (XVII), which are not paramagnetic. Combinations of two perinaphthyl radicals, (XVIII) or (XXI), go over either into the stable red hydrocarbon zethrene (XIX) with two fixed double bonds in the centre or into the diradical with no Kekulé structure (XXII). The newly described synthesis of the next higher benzologue (XIX) with no Kekulé structure indicates that the latter is an unstable diradical. All the experimental results support the view that Kekulé structures are of paramount importance for the stability of aromatic systems.

QUANTUM mechanics characterises the aromatic state by the distribution of paired electrons in molecular orbitals (MO) which extend over the whole ring system. This method does not need Kekulé structures. Therefore it would be of considerable interest to synthesise hydrocarbons with no Kekulé structure which might be possibly described by a MO structure. A hydrocarbon of this kind is the symmetric triangulene $C_{22}H_{12}$, which has an even number of carbon and hydrogen atoms. From the standpoint of classical chemistry this hydrocarbon has no Kekulé structure and can be only formulated as a diradical like (I).

From the standpoint of quantum mechanics the structure (II) with the frame of alternating double bonds might be considered a possibility in which the four electrons in the centre could be arranged in pairs in MO's. The recently synthesised methylene-*cyclo*propene (III)[1] shows that such a system is reasonably stable. It should be even more stable when included in an aromatic system like (II), provided Kekulé structures were not essential for the aromatic state. In that case resonance might occur between the three structures as indicated in (III). The synthesis of the colourless hexahydrotriangulene (IV) was carried out by Clar and Stewart.[2] When this hydrocarbon was dehydrogenated by methods that succeeded in the preparation of even the most reactive aromatic hydrocarbons like hexacene, the fundamental hydrocarbon triangulene polymerised immediately and could not be observed even for a short time.

It is obvious that triangulene reacts as a diradical (I). Longuet-Higgins[3] came to the same results by quantum mechanical calculations. This view is further supported by the course of the reduction of the red, stable, triangulenequinone (VI). This gives a deep bluish-green vat with alkaline sodium dithionate solution. That seems to

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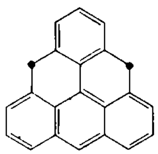
[1] J. T. Cragson, K. W. Greenlee, J. M. Derfer and C. E. Boord, *J. Amer Chem. Soc.* **75**, 3344 (1953).
[2] E. Clar and D. G. Stewart, *J. Amer. Chem. Soc.* **75**, 2667 (1953); **76**, 3504 (1954).
[3] H. C. Longuet-Higgins, *J. Chem. Phys.* **18**, 265 (1950).



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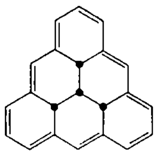

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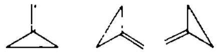

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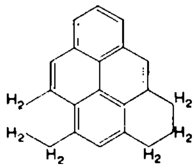

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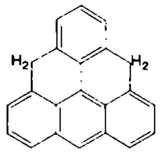

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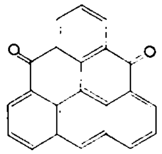

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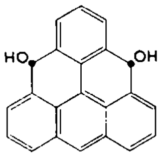

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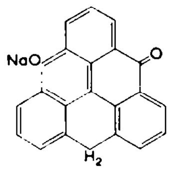

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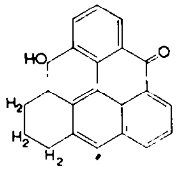

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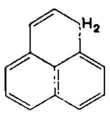

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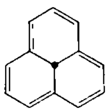

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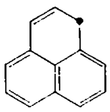

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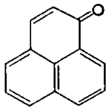

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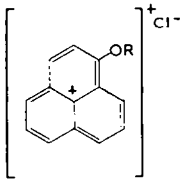

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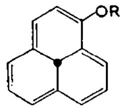

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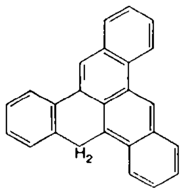

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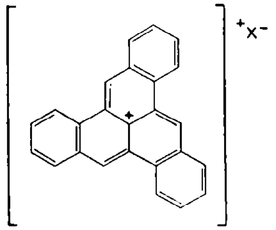

XVII

indicate that the vat was derived from the diradical dihydroxytriangulene (VII). However, it forms only a monosodium salt and must have therefore the structure (VIII). Further reduction gives (IX) and not a derivative of dihydrotriangulene (V), which is a yellow easily oxidisable hydrocarbon. It shares its sensitivity to oxygen with perinaphthene (X).

There is increasing evidence that perinaphthene (X) and perinaphthone (XIII) tend to go over into compounds with a frame of alternating double bonds and an odd electron or a positive charge in the centre.[4] Thus perinaphthene (X) is oxidised in the air to perinaphthone (XIII) via the radical perinaphthyl (XI), whose existence can be proved by paramagnetic measurements[5] and whose lifetime extends over months. The radical formula (XI) has only two Kekulé structures, whilst (XII) has eighteen Kekulé structures. A radical of the type (XII) should have a very short lifetime like the radicals phenyl or naphthyl. The centrosymmetric formula (XI) is therefore a better expression for its stability. This casts some doubt on the current assumption of the equal contribution of Kekulé structures. It is obvious that the two structures (XI) if not the only ones, are strongly preferred.

Perinaphthone (XIII) shows also a strong tendency to form a cyclic polyenic frame. It dissolves in hydrochloric acid to give a yellow salt (XIV) (R = H).[6] It also adds acid chlorides to form (XIV) (R = acetyl or benzoyl), from which the chlorine can be removed with Grignard magnesium. The blue solution probably contains the radical (XV).[7] The preparation of the radical (XI) and one of its trimethyl derivatives has been described by Reid[8] recently. When perinaphthone (XIII) is reduced in alkaline dithionate solution, a red intermediate stage is observed before the pale yellow dihydro stage is reached. In fact, potentiometric measurements indicate the formation of a radical monohydro stage.[9]

The tendency to form a centrosymmetric system is so strongly pronounced that tribenzoperinaphthene (XVI) is oxidised in acetic acid solution by atmospheric oxygen to a blue salt (XVII) (X = CH_3CO_2). Although the blue acetate is not very stable, the corresponding chloride and perchlorate are stable crystalline compounds.[10] These salts are not paramagnetic and show no paramagnetic resonance absorptions.* They have therefore the non-radical structure (XVII).

If two perinaphthyl radicals are combined, the two dibenzotetracenes (XVIII) and (XXI) are formed. If the possibilities of Kekulé structures for the two molecules are disregarded, the two odd electrons could be paired and both should be nonradical non-paramagnetic aromatic hydrocarbons. The centrosymmetric dibenzotetracene (XIX), which was given the name "zethrene"[11] because of its Z-shape, has a similar spectrum to 1:2-7:8-dibenzoperylene.[12] The spectrum is not related to any spectrum of the diarylpolyene type. Therefore it must be concluded that zethrene is a normal aromatic hydrocarbon in spite of the two fixed double bonds in the central region.

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* These measurements were kindly carried out by Prof. J. Weiss and Dr. P. A. Forrester in Newcastle.

[4] E. Clar, *Aromatische Kohlenwasserstoffe* p. 431. Springer-Verlag (1952).

[5] P. B. Sogo, M. A. Nakazaki and M. Calvin, *J. Chem. Phys.* **26**, 1343 (1957).

[6] E. Bamberger and M. Philip, *Liebigs Ann.* **240**, 147 (1887).

[7] E. Clar and D. G. Stewart, see E. Clar.[4]

[8] D. R. Reid, *Chem. & Ind.* 1504 (1956).

[9] P. Beckmann and H. Silerman, *Chem. & Ind.* 1635 (1955).

[10] E. Clar and D. G. Stewart, *J. Chem. Soc.* **23**, (1958).

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

[12] E. Clar, *Chem. Ber.* **82**, 46 (1949).

Moreover, it shows the same annellation effect as perylene. Thus the long-wave absorption bands shift to the violet when passing from zethrene to 4:5-11:12-dibenzozethrene (XX) (Fig. 1) exactly as in passing from perylene to 2:3-8:9-dibenzoperylene.[13] The fixed double bonds in the centre of the two zethrenes do not alter the aromatic character to any appreciable extent.

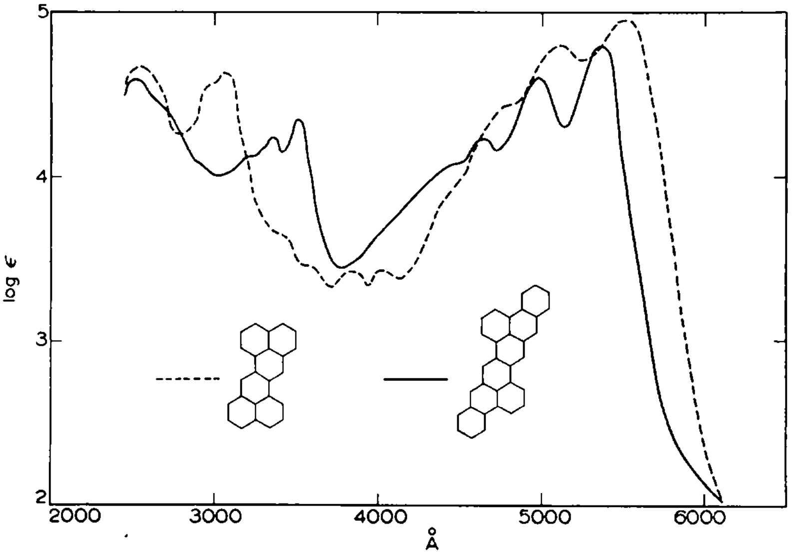

FIG. 1.

(———) 4:5-7:8-Dibenzozethrene (XX). E. Clar and H. Schulz-Kiesow, unpublished results. Absorption maxima (Å) and log ε (in parenthesis): 5350 (4·80), 4975 (4·60), 4650 (4·25), 3525 (4·36), 3360 (4·25) in trichlorobenzene, 2540 (4·58) in dioxan. (- - - -) Zethrene (XIX), see Clar *et al.*

Contrary to this result 1:12-10:11-dibenzotetracene (XXII) does not seem to be a stable aromatic hydrocarbon. Its attempted synthesis is described in this paper for the first time. It begins with the di-(1-dinaphthyl) carbinol[13] (XXIV), which after transformation into the chloride was condensed with magnesio-malonic ester. The dinaphthyl malonic ester (XXV) was so obtained in good yield and in a simpler way than recently described by Newman and Lednicer.[14] Unexpectedly the ring closure to (XXIII) proved extremely difficult, owing to the fact that (XXV) tends to split into naphthalene and perinaphthone when the standard methods are applied. Only phosphorus pentoxide in boiling nitrobenzene gave a very small yield of the orange quinone (XXIII). Since it does not give a vat with alkaline dithionate solution, this quinone does not seem to be a true quinone but rather a diketone. The amount of (XXIII) available was not enough to carry on with the synthesis of dibenzotetracene (XXII).

The prospects of synthesising dibenzopentacene (XXIX) seemed more promising than the synthesis of dibenzotetracene (XXII) and would serve the same purpose of testing the possibilities for the preparation of a similar hydrocarbon with no Kekulé structure. The diketone (XXVI) was obtained from dichloro*iso*phthaloyl dichloride,

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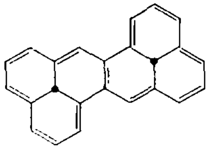
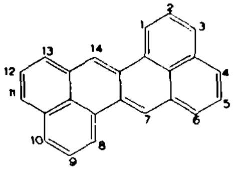
[13] J. Schmidlin and P. Massini, *Ber. Dtsch. Chem.Ges.* **42**, 2377 (1909).

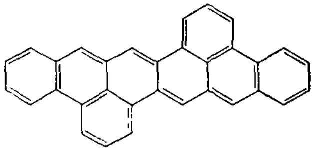
[14] M. S. Newman and D. Lednicer, *J. Amer. Chem. Soc.* **78**, 4765 (1956).



XVIII



XIX



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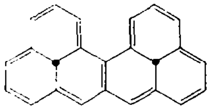
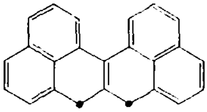


XXI



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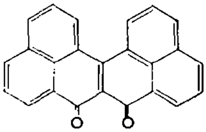

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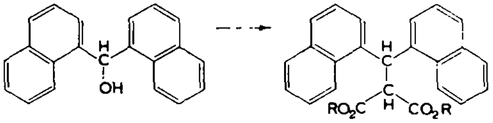
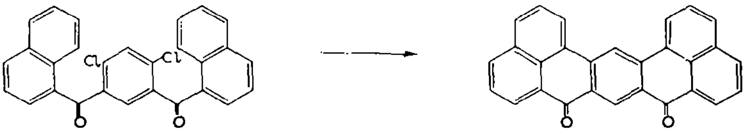


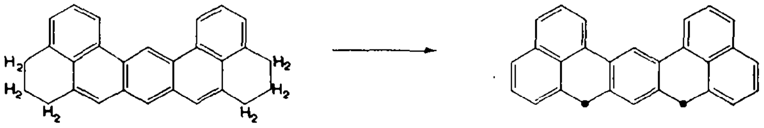
XXIV

XXV



XXVI

XXVII



XXVIII

XXIX

naphthalene and aluminium chloride. Ring closure to (XXVII) was effected by potassium hydroxide in boiling quinoline under carefully controlled conditions. The quinone (XXVII) tends to split with excess of potassium hydroxide into a dicarboxylic acid.

The quinone or rather diketone (XXVII) also forms no vat like (XXIII) and can be reduced to the hexahydro compound (XXVIII) by hydroiodic acid and red phosphorus. This hydrocarbon has a similar absorption as its centrosymmetric isomer hexahydroheptazethrene, as shown by the comparison in Fig. 2. As in the case of hexahydrotriangulene (IV), this hexahydro derivative (XXVIII) was dehydrogenated with palladium charcoal under conditions suitable for the preparation of the most sensitive aromatic hydrocarbons. Here again the dehydrogenation and complete polymerisation took place simultaneously. It must be therefore concluded that 1:14-11:12-dibenzopentacene (XXIX) is an unstable diradical. The unsuccessful attempts to prepare aromatic hydrocarbons with no Kekulé structure support the view that Kekulé structures are of paramount importance for the stablity of aromatic ring systems.

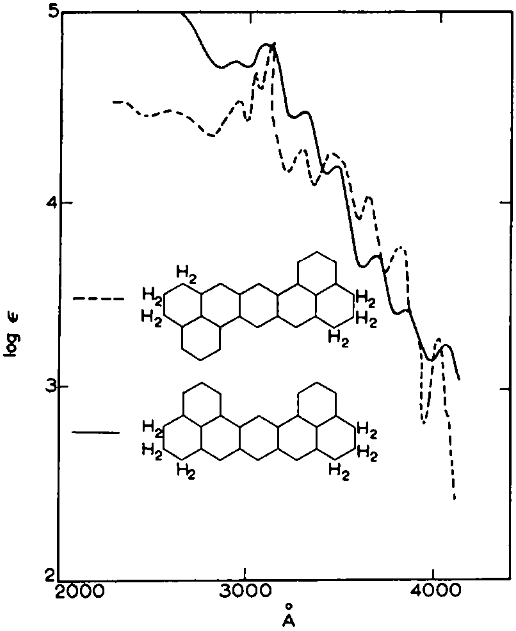


FIG. 2.

(———) 1:14-11:12-Dibenzo 2:3:4:8:9:10-hexahydro-pentacene (XXVIII) in alcohol. Absorption maxima (Å) and log ε (in parentheses): 4050 (3·27), 3860 (3·41), 3660 (3·70), 3460 (4·18), 3300 (4·48), 3090 (4·84), 2940 (4·75). (– – – –) 4:5:6:12:13:14-Hexahydroheptazethrene in alcohol, see Clar[4] (p. 394).

EXPERIMENTAL*

Di-(1-naphthyl)methylmalonic acid (XXV)

Di-(1-naphthyl)chloromethane (30 g) in 400 ml of dry benzene was added to a solution of magnesio-malonic ester in benzene (200 ml), which was prepared according to the method of Lund[15] from 7·5 g of magnesium.

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

[1] H. Lund, *Ber. Dtsch. Chem. Ges.* **67**, 935 (1934).

The mixture was heated under reflux for 30 hr and then cooled, and excess of magnesio-malonic ester was destroyed by shaking with 500 ml of dilute sulphuric acid. The benzene solution was then shaken with dilute sodium carbonate solution, washed with water and dried over magnesium sulphate; the benzene was distilled off to leave a semi-crystalline mass, which consisted mainly of di-(1-naphthyl)methylmalonic ester. Recrystallisation from ethanol gave ivory needles, m.p. 113° (Newman and Lednicer[14] give 113–114·2°) (Found: C, 78·77; H, 5·76. $C_{28}H_{26}O_4$ requires C, 78·85; H, 6·15 per cent).

The crude ester was then hydrolysed by boiling for 6 hr with 500 ml of 15% alcoholic potassium hydroxide solution, after which most of the alcohol was removed by distillation. Then 400 ml of water was added and the remainder of the alcohol was distilled off azeotropically. The resulting aqueous solution was diluted to 1 l., filtered, cooled and acidified with concentrated hydrochloric acid, thus precipitating white needles of the required dicarboxylic acid (XXV), which was then filtered off, washed with water and dried. Yield, 32 g or 84 per cent of theoretical.

The acid was recrystallised from glacial acetic acid, as white needles, m.p. 238°, containing one molecule of water of crystallisation (Found: C, 74·30; H, 5·35. $C_{24}H_{18}O_4.H_2O$ requires C, 74·21; H, 5·19 per cent).

The dicarboxylic acid dissolved slowly in concentrated sulphuric acid to give a bluish-green solution, which on warming to 80° became yellow and at 100° changed to red.

The attempted cyclisation of di-(1*-naphthyl*)*methylmalonic acid* (XXV)

(*a*) Liquid hydrogen fluoride did not alter the acid within 24 hr.

(*b*) Polyphosphoric acid did not achieve ring closure at 100°. At 170° cyclisation and partial splitting occurred. The only product isolated by recrystallisation from benzene and light petroleum was a small amount of perinaphthone, m.p. 142°, identified by mixed melting point with an authentic sample.

(*c*) A melt of the acid with sodium chloride and aluminium chloride at 160° for 3 min yielded a dark condensation product, which was mostly insoluble in benzene and could not be purified by chromatography. A similar result was obtained when zinc dust was added to the melt.

(*d*) A cyclisation and reduction with 55% hydriodic acid and red phosphorus in a sealed tube at 200° for 4 hr gave a solid material, which after extraction with ether and washing of the extract with water and sodium carbonate, was distilled at 10^{-2} mm. The first fraction consisted of colourless crystals with the characteristic odour of naphthalene. The following oily fraction, which did not crystallise, was dehydrogenated with palladium–charcoal. A sticky yellow solid distilled off the catalyst, which showed the characteristic absorption bands at 4440 and 4160 Å (in benzene) of peropyrene. Peropyrene is a condensation product obtained by reduction of perinaphthone.[16]

(*e*) A dark-green insoluble solid was obtained when the acid (XXV) was first transformed into the chloride and then treated with aluminium chloride in nitrobenzene. When benzene was used as a solvent, a small amount of perinaphthone was isolated.

(*f*) The cyclisation of the acid (XXV) with boiling benzoyl chloride and a few drops of sulphuric acid in nitrobenzene gave an insoluble dark condensation product.

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[16] E. Clar, *Ber. Dtsch. Chem. Ges.* **76**, 458 (1943).

1:12-10:11-*Dibenzotetracene*-4:5-*quinone* (XXIII)

The dicarboxylic acid (XXV) (5 g) was dissolved in nitrobenzene (50 ml) at 130° and phosphorus pentoxide (15 g) was added with stirring. The colour of the solution changed to green, then violet and then brown within 10 min. The mixture was treated with water (100 ml) and the nitrobenzene was removed by steam-distillation. The dark residue was filtered off, boiled with dilute ammonia solution, filtered off and dried (4·1 g). Recrystallisation from xylene gave red-brown needles, m.p. 270–280° (dec.) (Found: C, 86·8; H, 3·7. $C_{24}H_{12}O_2$ requires C, 86·7; H, 3·6 per cent). The quinone dissolved in concentrated sulphuric acid to give a red-violet solution; it also dissolved in concentrated hydrochloric acid to give a similar red-violet solution.

The above-described procedure sometimes yielded an isomeric compound without any apparent reason. This compound had m.p. 270–280° (dec.) and dissolved in concentrated sulphuric acid to give a green solution but it did not dissolve in concentrated hydrochloric acid (Found: C, 87·0; H, 4·1. $C_{24}H_{12}O_2$ requires C, 86·7; H, 3·6 per cent). It gave no vat with alkaline sodium dithionate.

1:3-*Dichloro*-4:6-*di*-(*-naphthoyl*)*benzene* (XXVI)

The acid chloride (from 50 g of 4:6-dichloro*iso*phthalic acid[17] treated with 90 g of phosphorus pentachloride) was dissolved in methylene dichloride (150 ml) with naphthalene (55 g), and anhydrous aluminium chloride (60 g) was added over 1½ hr. During the vigorous reaction the solution changed from brown to red. The mixture was shaken overnight, poured into ice and hydrochloric acid, and the solvent and excess of naphthalene were removed by steam-distillation, to leave a brown oil, which solidified on cooling and could be ground in a mortar (58 g of crude product).

A sample was recrystallised from benzene–ethanol–water (2:4:1) as white needles, m.p. 157° (Found: C, 73·92; H, 3·69; Cl, 15·74. $C_{28}H_{16}O_2Cl_2$ requires C, 73·86; H, 3·54; Cl, 15·57 per cent).

The colour in concentrated sulphuric acid was orange and, on heating, yellow.

1:14-11:12-*Dibenzopentacene*-5:7-*quinone* (XXVII)

(a) *With potassium hydroxide in quinoline.* The crude diketone (XXVI) (10 g) was heated under reflux in quinoline (50 ml) with potassium hydroxide pellets (2·5 g) for 8 hr and then poured into dilute hydrochloric acid (400 ml). The aqueous liquors were decanted off, and the tarry mass was boiled with water (300 ml) and then with dilute ammonia solution (300 ml), the aqueous solutions again being removed by decantation. On cooling, the dark tar solidified and was ground in a mortar with ethanol (10 ml). Yield (crude) 8·5 g.

Chromatography on alumina, with benzene and chloroform (1:1) as eluant, gave brown needles, which were sublimed twice at 300° and 10^{-2} mm pressure. This gave orange needles of the *quinone* (XXVII), softening at 280°, m.p. 342° (Found: C, 87·83, H, 3·87. $C_{28}H_{14}O_2$ requires C, 87·94; H, 3·69 per cent). The colour in concentrated sulphuric acid was red, with very faint orange fluorescence. It did not form a vat in alkaline sodium dithionate solution.

(*b*) *With potassium hydroxide in alcohol.* Strong alcoholic potassium hydroxide solution was prepared by evaporation of a 10% solution till the boiling point rose to 140°.

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[17] A. Claus and H. Burstert, *J. Prakt. Chem.* **41**, 552 (1890).

The diketone (XXVI) (5 g) was added to this and heated for ½ min at 140°. The mixture was cooled and poured into water. The insoluble material (0·5 g of crude) was the quinone (XXVII) and could be washed with water and purified as described above under (*a*). The alkaline solution was acidified with hydrochloric acid and the resulting white solid was filtered off and recrystallised twice from aqueous acetic acid (1:1). White needles of a *dinaphthylbenzenedicarboxylic acid*, m.p. 153° (Found: C, 76·74; H, 4·85·$C_{28}H_{18}O_4.H_2O$ requires C, 77·05; H, 4·62 per cent). The colour in concentrated sulphuric acid was violet, fading rapidly to brown and, on heating becoming pale red.

1:14-11:12-*Dibenzo*-2:3:4:8:9:10-*hexahydropentacene* (XXVIII)

The quinone (XXVII) (1g) was ground with red phosphorus (0·34 g) and added to constant-boiling hydriodic acid (10 ml) in a large sealed tube. This was heated at 200° for 8 hr. The contents were extracted with benzene, and the benzene solution well washed with water and sodium dithionate solution and dried. Chromatography on alumina, with light petroleum (boiling range 60–80°) containing 30 per cent of benzene as eluant, gave yellow needles of the *hexahydro derivative* (XXVIII), softening at 197°, m.p. 215° (Found: C, 93·85; H, 6·23. $C_{28}H_{22}$ requires C, 93·81; H, 6·19 per cent). In concentrated sulphuric acid it dissolved very slowly to give a brown-green solution with red fluorescence, which, on heating, became olive green with red fluorescence.

Dehydrogenation of 1:14-11:12-*dibenzo*-2:3:4:8:9:10-*hexahydropentacene* (XXVIII)

The hexahydro derivative (XXVIII) (30 mg) was sublimed in a current of air-free carbon dioxide into the palladised charcoal catalyst at 310° and 10^{-3} mm pressure, but was completely absorbed in it. The temperature was raised to 500°, but no sublimate was obtained from the catalyst.

The efficiency of the catalyst was tested both before and after this experiment by the dehydrogenation of 9:10-dihydroganthracene to anthracene in good yield.

The complete testing of the catalyst and dehydrogenation of the hexahydro derivative (XXVIII) was repeated several times with identical results.

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