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NMR STUDIES OF PERYLENE AND CORONENE DERIVATIVES

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Abstract—3-Methyl-1:12-benzoperylene, 4-methyl-1:12-benzoperylene and 3,10-dimethyl-1:12-benzoperylene have been synthesized. The protons in the ABX systems of perylene have different coupling constants whilst in 1:12-benzoperylene J_{XB}, J_{AB}, J_{BA} and J_{BX} are equal. This is explained by the formulation with aromatic sextets. The NMR spectra of the Me derivatives support this formulation. The comparison of the NMR spectra of coronene and 1:2-benzocoronene with 1:12-benzoperylene and its benzologues indicates a strong ring current in the coronene complex which can be related to "superaromaticity".

THE NMR spectrum of perylene has been recorded at 60 mc/s,[1] Fig. 1 shows the more refined spectrum at 100 mc/s. This consists of an ABX† system with $J_{XB} = 7{\cdot}0$, $J_{XA} = 1{\cdot}2$, $J_{AB} = 8{\cdot}4$, $J_{AX} = 1{\cdot}4$, $J_{BX} = 7{\cdot}6$ and $J_{BA} = 8{\cdot}7$ c/s. From these figures it can be concluded that the bond A–B has a higher degree of double bond character than the bond B–X. Perylene is thus closely related to naphthalene as shown by the sextet formula in Fig. 1.

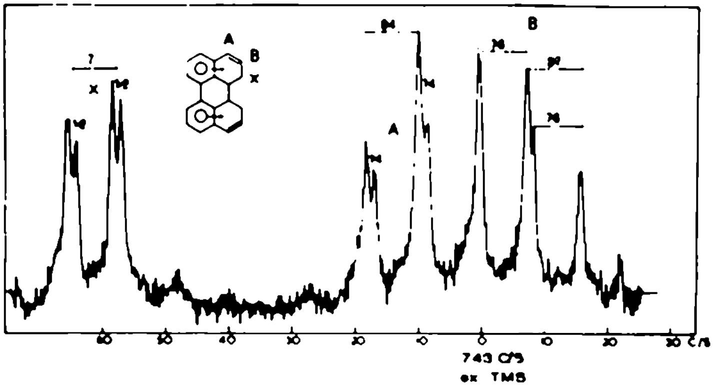


FIG. 1 NMR spectrum of perylene in CS_2 at 100 Mc/s. Protons centred at: A, 756·9; B, 734·9; X, 804·6 c/s ex TMS

Although 1:12-benzoperylene (I, R = R′ = R″ = H) has a lower degree of symmetry than perylene its NMR spectrum (Fig. 2) is considerably simpler than the spectrum of perylene. There is just one coupling constant between the protons ABX.

[*] 3-, and 4-methyl-1:12-benzoperylene were synthesized by M. Zander in the Central Laboratory of Rütgerswerke und Teerverwertung AG. in Castrop-Rauxel.

[†] The marking A B X in different hydrocarbons has been retained for better comparison

The double doublet A has $J_{AB} = 7{\cdot}5$ and $J_{AX} = 1{\cdot}4$ c/s. The double doublet originating from X has $J_{XB} = 7{\cdot}5$ and $J_{XA} = 1{\cdot}4$ c/s, and the triplet B has $J_{BA} = J_{BX} = 7{\cdot}5$ c/s. The sextet in the position 1 and 12 prevents the other two sextets from migrating between the two rings as in perylene. This produces a fixation of the double bonds in the positions 2,3 and 10,11, which can be demonstrated in 3,10-dimethyl-1:12-benzoperylene (I, R = R' = Me, R'' = H). The Me resonance at 286 c/s ex TMS in Fig. 3 is split into a doublet with a separation of 1·0 c/s. The split band at 795·5 c/s

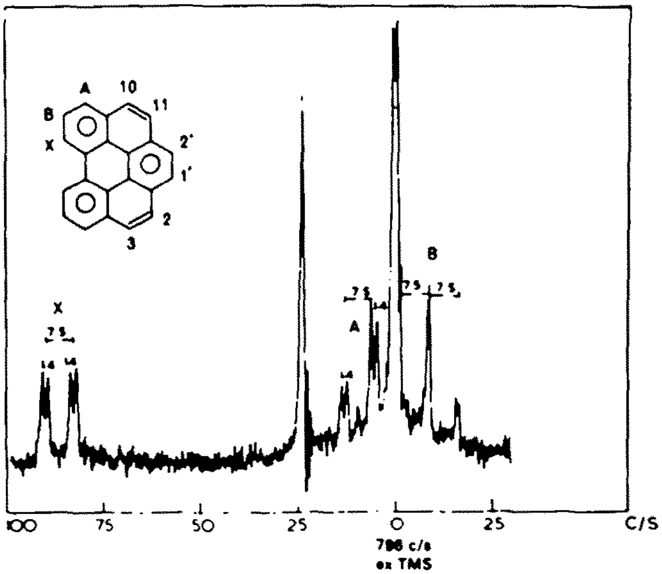


Fig. 2 NMR spectrum of 1:12-benzoperylene in CS_2 at 100 Mc/s Protons centred at: A, 803·0; B, 788·0; X, 881·6; $H_{3,10'}$, 796·0; $H_{2,11'}$, 795·0, $H_{1',2'}$, 819·0 c/s ex TMS

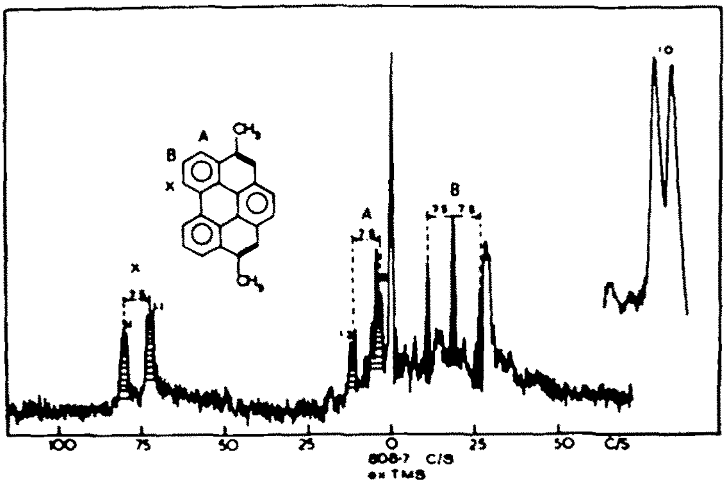


Fig 3 NMR spectrum of 3,10-dimethyl-1:12-benzoperylene in CS_2 at 100 Mc/s. Protons centred at: A, 816·7; B, 790 5; X, 885·3; $H_{2,11}$, 780·6; $H_{1',2'}$, 808·7; H_{Me}, 286 c/s ex TMS.

ex TMS in the spectrum of 1:12-benzoperylene in Fig. 2 which originates from the protons in the positions 2, 3, 10, 11 disappears in dimethylbenzoperylene (Fig. 3) and is replaced by a broad band at 780·6 c/s. This obtains its shape from coupling of the protons at the 2 and 11 positions with the protons of the methyl groups. The other features of the spectrum remain essentially unaltered by comparison with the spectrum of 1:12-benzoperylene (Fig. 2), the coupling constants being: J_{AB} = 7·5, J_{AX} = 1·3, J_{XB} = 7·5, J_{XA} = 1·1 and J_{BA} = J_{BX} = 7·5 c/s.

3-Methyl-1:12-benzoperylene (I, R′ = Me, R = R″ = H) shows also a Me doublet at 280 c/s with a separation of 1·1 c/s, as expected, the aromatic part of the spectrum being, of course, more complicated than in Fig. 3 (25 lines). If the Me group is attached to the sextet in position 4 as in 4-methyl-1:12-benzoperylene (I, R″ = Me, R = R′ = H) no splitting of the Me resonance at 274 c/s can be observed. The aromatic part of the spectrum contains 14 lines. A comparison of the sharp singlets of 1:2-benzopyrene (II),[2] 1:12-benzoperylene (III) and coronene (IV) shows that their position cannot be related to Hückels rule 4n + 2. Passing from benzopyrene (II) $C_{20}H_{12}$ to 1:12-benzoperylene (III) $C_{22}H_{12}$ one ethylene bridge is added. This produces small shifts of +15 and +38 c/s, respectively, whilst the second ethylene bridge in going to coronene $C_{24}H_{12}$ causes the big shifts of +76 and +53 c/s respectively. There cannot be any doubt that the sextets in coronene (IV) can migrate through the six external rings, thus producing a ring current which is due to the "superaromaticity" of coronene.

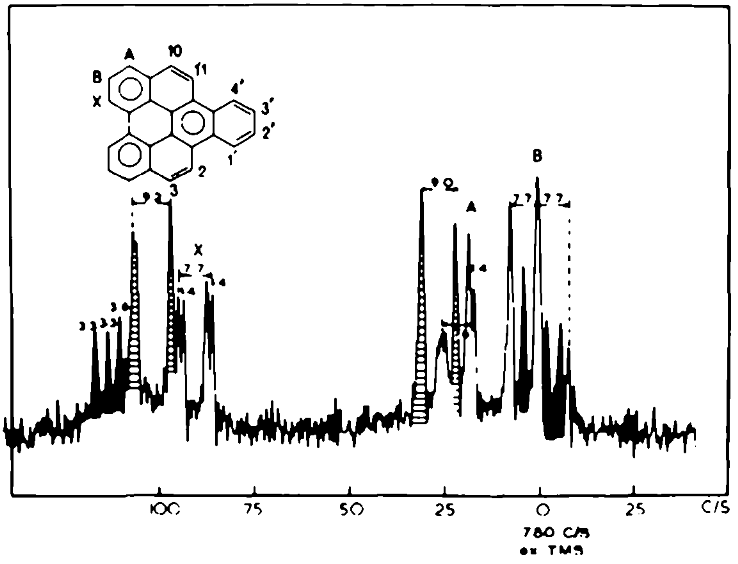


FIG 4 NMR spectrum of 1:12-o-phenylene-perylene in CS_2 at 100 Mc/s Protons centred at: A, 800·5; B, 780·0; X, 871·0; $H_{3,10}$, 807·8; $H_{2,11}$, 882·2; $H_{1',4'}$, 898–888·5; $H_{2',3'}$, 783·5–774·0 c/s ex TMS.

The NMR spectrum of 1:12-[*o*-phenylene] perylene (V)[3] (Fig. 4) belongs to the same type as the one of 1:12-benzoperylene (I, R = R′ = R″ = H), except that there is no singlet. The ABX system has the coupling constants: J_{AB} = 7·6, J_{AX} = 1·4, J_{XB} = 7·7, J_{XA} = 1·4, J_{BA} = J_{BX} = 7·7 c/s. The protons in the positions 2, 3, 10, 11, produce the quartet centred at 807·8 and 882·2 c/s with coupling constant of 9·2 and 9·0 c/s, respectively. The partly hidden systems of the protons in 1′ and 4′ at 888·5–898 c/s and in 2′ and 3′ at 774–783·5 c/s are marked in black.

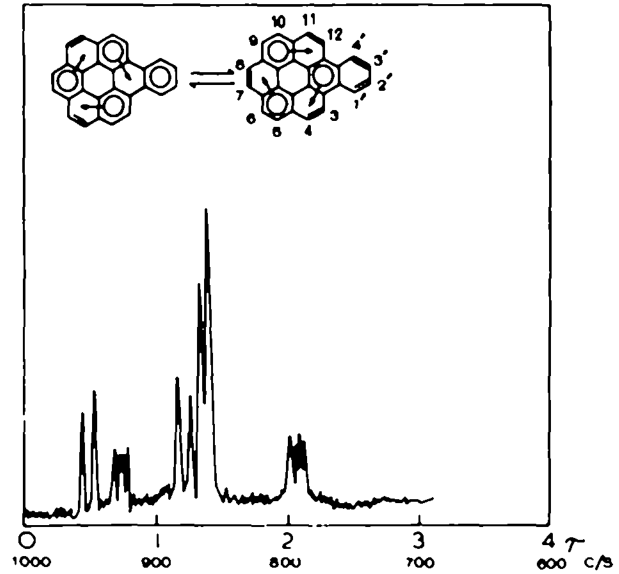
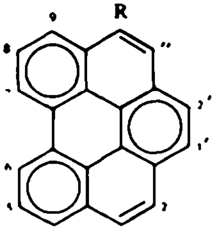


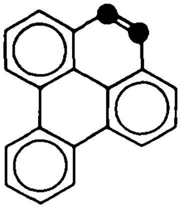
Fig. 5 NMR spectrum of 1:2-benzocoronene in CS_2 at 100 Mc/s. Protons centred at. $H_{5,6,9,10}$, 871·0; $H_{7,8}$, 876·5; $H_{4,11}$, 887·3; $H_{3,12}$, 958·7; $H_{1',4'}$, 929·5 939·5; $H_{2',3'}$, 795·5 805·5 c/s ex TMS.

The NMR spectrum of 1:2-benzocoronene (VI)[4] Fig. 5 shows a singlet at 876·5 c/s and another singlet of double this intensity at 871 c/s which originate from the position 7,8 and 5,6,9,10, respectively. The protons in the positions 3,12 and 4,11 produce the quartet centred at 958·7 and 887·3 c/s with $J_{34} = J_{11\cdot12} = 9$. The protons in 1′ and 4′ cause the group of bands at 929·5–939·5 and the protons in 2′ and 3′ the group at 795·5–805·5 c/s. A comparison of the singlets in 1:2-benzocoronene (VI) with the marked protons in 1:12-o-phenylene-perylene (V), 1:12,4:5-dibenzoperylene (VII)[5] and 1:12,2:3-dibenzoperylene (VIII)[6] shows that the former in (VI) are at much lower field than the marked protons in the hydrocarbons V, VII and VIII. The differences are about the same as in the series 1:2-benzopyrene (II), 1:12-benzoperylene (III) and coronene (IV). In both cases coronene and the coronene complex in 1:2-benzocoronene (VI) must have a high degree of "superaromaticity". A comparison of the β-bands of the UV spectra demonstrates that the β-band of coronene is about halfway between the β-bands of the hydrocarbons V, VII and VIII. This indicates that the annellation effect of benzocoronene results from the combined effects of the annellation of the benzo ring to a sextet as in V and VII and to a fixed double bond as in VIII.

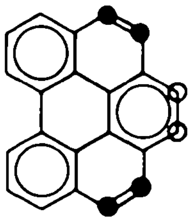
This as well as the same result of the comparison in the series of the naphtho-1:12-benzoperylenes with naphthocoronene[7] shows clearly that the coronene complex constitutes a separate "superaromatic" entity. 3-Methyl-1:12-benzoperylene (I,



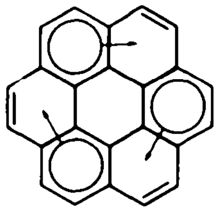
R″ R′ I



II



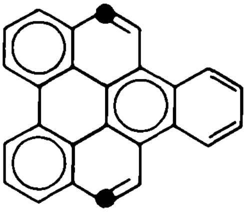
III



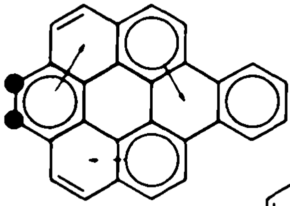
IV

Protons marked ● 781 $\xrightarrow{+15}$ 796 $\xrightarrow{+76}$ 872 c/s ex TMS

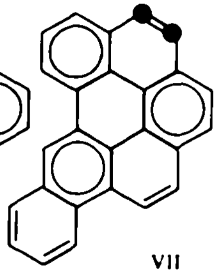
Protons marked ○ $\xrightarrow{+38}$ 819 $\xrightarrow{+53}$ in CS_2



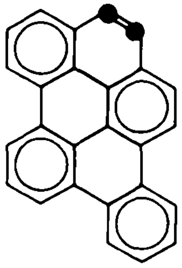
V



VI



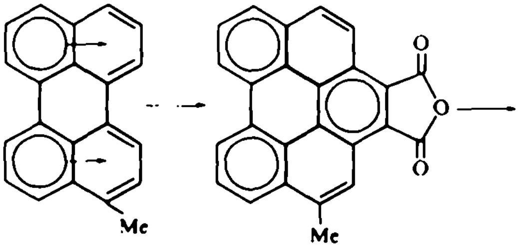
VII



VIII

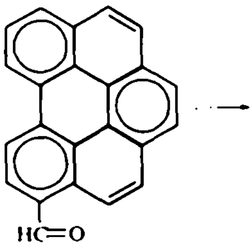
Protons marked ● 808 $\xrightarrow{+69}$ 877 $\xleftarrow{+77}$ 800 (in $AsBr_3$) 812 (in $AsBr_3$) c/s ex TMS

UV β = 3105 3200 3300 3095 Å



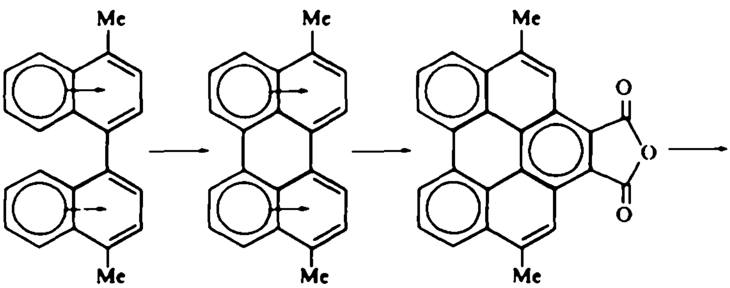
IX X

I: R = R″ = H
R′ = Me



XI

I: R = R′ = I
R″ = Me



XII XIII XIV

I: R = R′ = Me
R″ = H

R = Me, R′ = R″ = H) was prepared from the known 3-methylperylene (IX)[8] which was condensed with maleic anhydride and chloranil to form the anhydride X. The decarboxylation with cupric acetate and copper powder in quinoline gave mainly the desired 3-methyl-1:12-benzoperylene and only a smaller amount of 4-methyl-1:12-benzoperylene. The condensation must have resulted in the formation of X as main product.

A Rieche synthesis of 1:12-benzoperylene[9] with dichloromethyl-n-butyl ether and titanium tetrachloride gave only the aldehyde XI, the reduction of which with hydrazine hydrate and potassium hydroxide yielded 4-methyl-1:12-benzoperylene (I, R″ = Me, R = R′ = H).

4,4′-Dimethyl-1:1-dinaphthyl (XII) was obtained from 4-methyl-1-naphthyl magnesium bromide and cuprous chloride. The cyclization in a sodium chloride–aluminium chloride melt gave 3,10-dimethylperylene (XIII) which was identical with a hydrocarbon obtained by two successive aldehyde synthesis both followed by reduction to Me derivatives.[9] The 3,10-dimethylperylene (XIII) reacted with maleic anhydride and chloranil with the formation of the anhydride XIV. Decarboxylation with soda lime yielded 3,10-dimethyl-1:12-benzoperylene (I, R = R′ = Me, R″ = H).

EXPERIMENTAL[*]

3-*Methyl*-1:12-*benzoperylene*-1′,2′-*dicarboxylic anhydride* (X). Compound IX[8] (11 g), maleic anhydride (110 g) and chloranil (22 g) were refluxed for 5 min. Xylene (660 ml) was added to the hot mixture and the ppt (13·5 g) filtered off at 70°. Sublimation at 330°/0·001 mm gave 2·65 g of an anhydride mixture which consisted mainly of the isomer X. (Found: C, 83·2; H, 3·4. $C_{25}H_{12}O_3$ requires: C, 83·3; H, 3·4%.)

3-*Methyl*-1:12-benzoperylene (I, R = Me, R′ = R″ = H). The above anhydride (2·65 g), Cu powder (0·9 g), cupric acetate (0·9 g), AcOH (50%, 0·45 g) and quinoline (105 ml) were refluxed under N_2 for 46 hr. The mixture was filtered and the filtrate boiled with dil HCl. The ppt (2·4 g) was filtered off, dissolved in hot xylene and chromatographed on alumina. The first fractions (1·1 g) formed a mixture of two hydrocarbons. The mother liquors gave a further portion (0·16 g) containing the 4-Me derivative m.p. 147–149°. The first fraction (1·1 g) was dissolved in xylene (65 ml) and picric acid (3·9 g) added. The crystallized picrate (1·5 g) was recrystallized from xylene under addition of picric acid. Decomposition of the picrate with dilute ammonia and recrystallization from xylene yielded the 3-Me derivative (0·39 g) m.p. 186–188°. The mother liquors of the picrate gave another 0·17 g of 3-Me derivative. These portions were united and recrystallized four times from benzene. Pure 3-methyl-1:12-benzoperylene (0·23 g) formed yellow needles, m.p. 200·5–202°, which dissolved in conc. H_2SO_4 with a green colour. (Found: C, 95·0; H, 5·1. $C_{23}H_{14}$ requires: C, 95·1; H, 4·9%.)

1:12-*Benzoperylene-4-aldehyde* (XI). Dichloromethyl-n-butyl ether (10 g) and titanium tetrachloride (150 ml) were added to a soln of 1:12-benzoperylene (4 g) in CS_2 (600 ml) at room temp. The mixture was stirred for 20 hr and then decomposed with ice and dil HCl. The crude aldehyde (1·7 g) was filtered off and washed with dil HCl, water and ammonia. Concentration of the mother liquors yielded another portion of the aldehyde (2·3 g). Repeated recrystallization from xylene gave yellow needles, m.p. 204–206°, which dissolved in conc. H_2SO_4 to give a violet soln. (Found: C, 90·7; H, 4·2. $C_{23}H_{12}O$ requires: C, 90·8; H, 4·0%.)

4-*Methyl*-1:12-*benzoperylene* (I, R″ = Me, R = R′ = H). Benzoperylene-aldehyde (2·8 g) was dissolved in pyridine (43 ml), hydrazine hydrate (80%, 7 ml) and water (7 ml) added. The mixture was boiled, filtered hot and the filtrate diluted with water (43 ml). The precipitated hydrazone (2·6 g), diethylene glycol (68 ml), KOH (9 g) and hydrazine hydrate (80%, 6 ml) were heated under N_2 at 230–240° for 3 hr. The water which was formed during the reaction was distilled off. After cooling to 120° the mixture was diluted with water and the hydrocarbon (2·2 g) filtered off. Sublimation at 220°/0·001 mm followed by recrystallization from benzene and formation of the picrate (1·9 g) with picric acid (5 g) in xylene (83 ml) and

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

recrystallization from xylene gave a purified picrate (1·5 g). This was decomposed with dilute ammonia and recrystallized from xylene. The hydrocarbon formed yellow needles, m.p. 152–153°, which dissolved in conc. H_2SO_4 to give an olive green soln. Further purification by chromatography did not increase the m.p. (Found: C, 94·9; H, 5·0. $C_{23}H_{14}$ requires: C, 95·1; H, 4·9%.) Picrate: brown needles, m.p. 225–228° dec. (Found: N, 8·3. $C_{29}H_{17}O_7$ requires: N, 8·1%.)

4,4′-*Dimethyl*-1,1′-*dinaphthyl* (XII). 4-Methyl-1-naphthyl magnesium bromide was prepared in the usual manner from 1-methyl-4-bromonaphthalene[10] (200 g) and Mg (22 g) in dry ether (600 ml) and dry benzene (600 ml). The Grignard reagent was cooled and anhydrous $CuCl_2$ (280 g) (prepared from $CuCl_2 \cdot 2H_2O$ and $SOCl_2$) was added slowly in one portion.[11] After stirring and refluxing for 3 hr, the reaction mixture was decomposed with ice and HCl, the organic layer was washed with water and dried over $CaCl_2$; the benzene and ether were removed and the product fractionally distilled at 282–288°/15–16 mm. Crude 4,4′-dimethyl-1,1′-dinaphthyl was obtained (42 g) and crystallized from acetone as colourless rods, m.p. 146–146·5° (Found: C, 93·88; H, 6·22. $C_{22}H_{18}$ requires: C, 93·58; H, 6·42%.)

3,10-*Dimethylperylene* (XIII). 4,4′-Dimethyl-1,1′-dinaphthyl (30 g) was heated with $AlCl_3$ (300 g) and NaCl (60 g) at 140° for 30 min. After decomposition with ice and HCl, the yellow-brown ppt was filtered off and washed with dil HCl, aqueous ammonia and then with water, dissolved in benzene and chromatographed on alumina. Elution yielded (20 g) of a mixture of starting material and dimethylperylene which was used directly in the next stage since separation proved to be very wasteful.

A portion of crude product (3 g) was re-chromatographed on alumina, the eluate obtained was concentrated and treated with excess picric acid to form the picrate which recrystallized from benzene 3 times as brown plates (0·7 g), m.p. 208–210° (Found: N, 8·29. $C_{28}H_{19}O_7N_3$ requires: N, 8·25%.) After decomposition of the picrate, the hydrocarbon was recrystallized from xylene as yellow platelets (46 mg), m.p. 198–199° (lit. 202°). (Found: C, 94·36; H, 5·49. $C_{22}H_{16}$ requires: C, 94·25; H, 5·75%.)

3,10-*Dimethyl*-1:12-*benzoperylene*-1′,2′-*dicarboxylic anhydride* (XIV). The above crude hydrocarbon mixture (14 g), maleic anhydride (30 g) and chloranil (5 g) were boiled for 1–2 min. AcOH was added and the dark red–brown ppt was filtered off and washed with AcOH, benzene and ether (yield 8·8 g). The crude product (0·8 g) was twice sublimed at 350°/0·6 mm, yielding bright red crystals of the anhydride XIV (70 mg). (Found: C, 83·39; H, 4·06. $C_{26}H_{14}O_3$ requires: C, 83·41; H, 3·79%.)

3,10-*Dimethyl*-1:12-*benzoperylene* (I, R = R′ = Me, R″ = H). The anhydride (6 g) and soda-lime (20 g) were ground together and heated to 330° under N_2 for 45 min, then sublimed at 380°/0·6 mm; the sublimate was recrystallized from xylene and resublimed at 210°/0·6 mm, yielding pale yellow needles (80 mg) m.p. 198–199° (Found: C, 94·48; H, 5·50. $C_{24}H_{16}$ requires: C, 94·70, H, 5·30%.)

In another improved experiment 3,10-dimethyl-1:12-benzoperylene (50 mg) was converted into the picrate (30 mg) which formed reddish-brown rectangular plates, m.p. 223–225° (Found: N, 7·89. $C_{30}H_{19}O_7N_3$ requires: N, 7·88%.) After decomposition of the picrate, the resulting hydrocarbon was recrystallized from xylene (5 mg) and had m.p. 219–220°.

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