

NEW BENZENOGENIC DIENE SYNTHESSES

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Abstract—3,8-Diphenylpyrene **5** and 3,10-diphenylpyrene **10** were synthesized from 1,5-dibenzyl-naphthalene and 1,4-diphenyl-naphthalene. Dibenzyl-naphthalenes were dehydrogenated to the quinonoid compounds **2** and **7**, followed by addition of maleic anhydride and dehydrogenation of the adducts to give the aromatic anhydrides **4** and **9**. These were decarboxylated to the corresponding hydrocarbons. By an analogous sequence of reactions 3,9-diphenylanthranthrene and 4,9-diphenyl-1,12-benzoperylene were prepared starting from 3,8-dibenzylpyrene **12** and 3,10-dibenzylpyrene **17** respectively. 1,6-Diphenylcoronene was synthesized by a further benzenogenic diene synthesis starting from 4,9-diphenyl-1,12-benzoperylene.

A benzenogenic diene synthesis involves addition of a compound with a reactive double bond, such as maleic anhydride, to a potential diene, comprising aromatic double bonds, followed by the immediate dehydrogenation of the adduct to an aromatic dicarboxylic anhydride. This is carried out in a single reaction. The best known example of this kind of diene synthesis is the formation of benzperylene-dicarboxylic anhydride from perylene and maleic anhydride in the presence of an dehydrogenating agent.¹

We have now found that dibenzyl compounds which can be dehydrogenated to chinonoid compounds and which have free peri-positions can be used for diene synthesis with maleic anhydride. Thus 1,5-dibenzyl-naphthalene **1** gives diphenylpyrene-tetracarboxylic dianhydride **4** in good yield when boiled with excess maleic anhydride, nitrobenzene and a small amount of iodine. The quinonoid intermediate **2** can be recognized by the transient blueish green colour of the mixture. It is obvious that under the condition the primary addition product **3** which has no sextet in the central complex must be dehydrogenated quickly to the dianhydride **4**. Thus the whole series of reactions 1-4 takes place in a single operation. The decarboxylation to 3,8-diphenylpyrene **5** was carried out with basic copper carbonate in quinoline.

There have been reports of the preparation of 3,8-diphenylpyrene by other methods which are inconclusive about the position of the phenyl groups. Amerer and Zinke² have obtained a hydrocarbon, mp 215°, from the reaction of 3-chloropyrene, benzene and aluminium chloride. The hydrocarbon of Norman, Thompson and Waters³, mp 215°, resulted from the reaction of phenyl radicals with pyrene. The authors present an

absorption spectrum of their hydrocarbon which is almost identical with the one of our 3,8-diphenylpyrene which has mp 225°. Thus it is very likely that both earlier syntheses gave 3,8-diphenylpyrene.

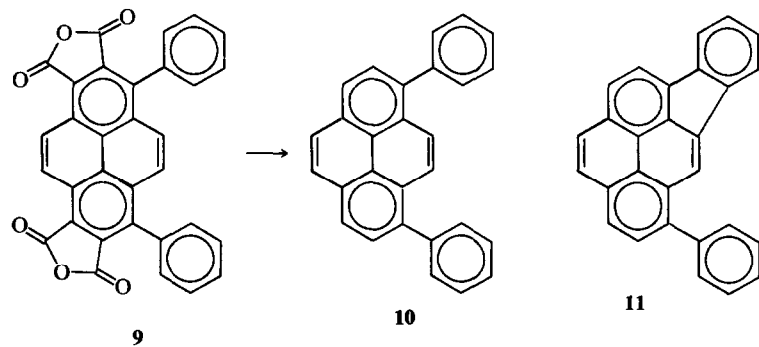
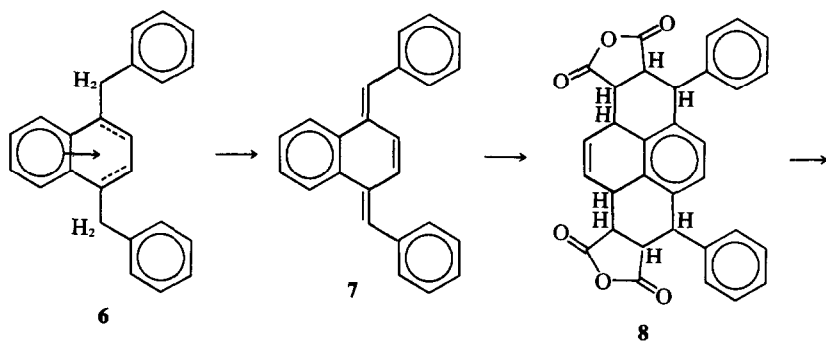
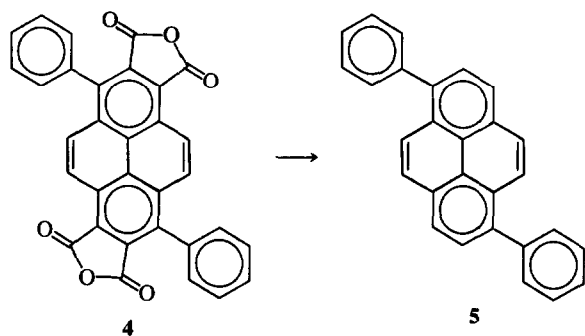
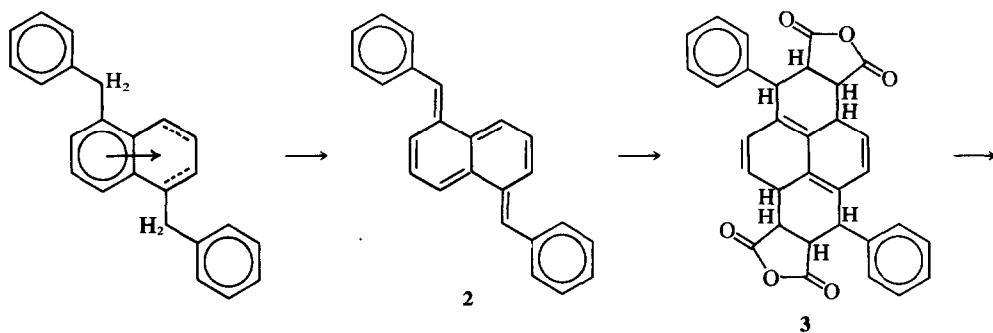
A similar series of reaction can be carried out starting from 1,4-dibenzyl-naphthalene **6**. However the yield of the anhydride **9** is considerable lower than in the first synthesis. This is easily explained by the lower reactivity of the intermediate quinonoid compound **7** which has still one sextet intact in the central naphtho-quinonoid system. It is understandable that its participation in the diene synthesis is less favourable than the compound **2**. The dehydrogenation was again achieved using basic copper carbonate and quinoline. A yellow by-product of the 3,10-diphenylpyrene **10** was observed. It has probably the fluoranthene type constitution **11**, because its spectrum is related to that of 2,3-o-phenylene-pyrene.⁴

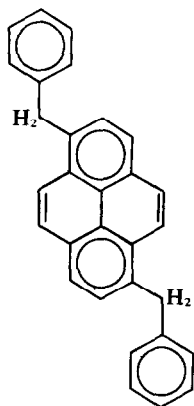
The syntheses of diphenylanthanthrene **16** and diphenylbenzoperylene **21** started from 3,8-dibenzoylpyrene and 3,10-dibenzoylpyrene respectively. These two diketones were obtained in the ratio 2:1 by the reaction of benzoyl chloride, pyrene and aluminium chloride.⁵ Huang-Minlon reduction gave 3,8-dibenzylpyrene **12** and 3,10-dibenzylpyrene **17**.

The condensation of 3,8-dibenzylpyrene **12** with maleic anhydride in nitrobenzene and a small amount of iodine yielded the di-anhydride **15** in one reaction, the intermediate being the quinonoid compound **13** and the octahydro derivative **14**. Decarboxylation attempts with copper carbonate in quinoline resulted in the reductive splitting of the dianhydride **15** and the recovery of 3,8-dibenzylpyrene **12**. This could be prevented if nitrobenzene was added to the mixture. Thus 3,9-diphenylanthanthrene **16** was obtained.

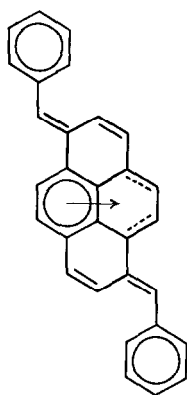
An analogous series of reactions using 3,10-

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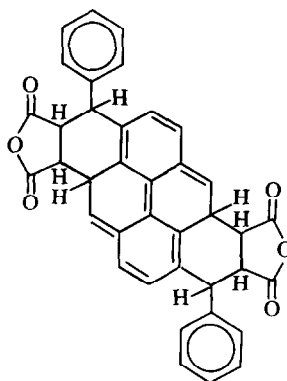




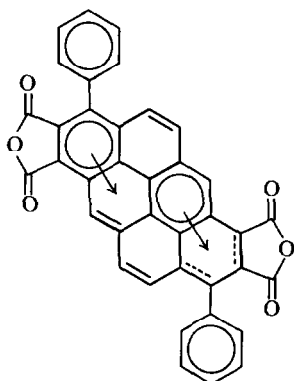
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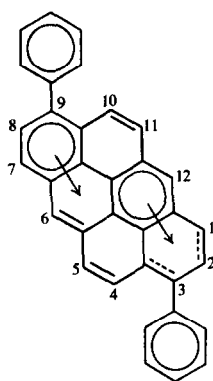
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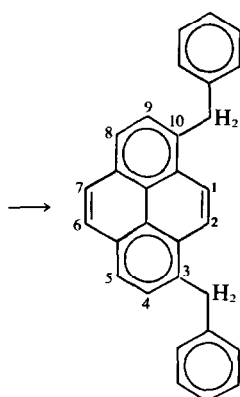
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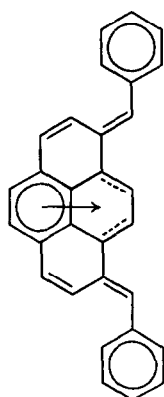
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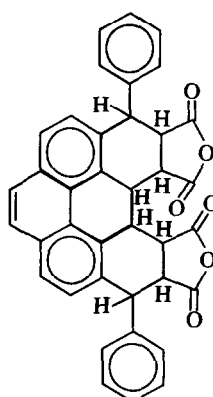
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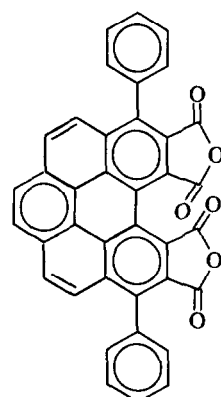
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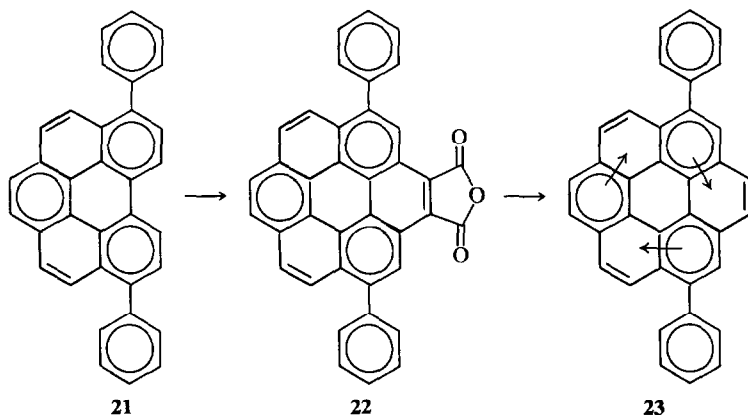
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20

dibenzylpyrene 17 gave diphenylbenzoperylene 21 through the non-isolated intermediates 18 and 19. It is remarkable that the decarboxylation of the dianhydride 20 with copper carbonate in quinoline did not require the addition of nitrobenzene. Like 1,12-benzoperylene,⁶ diphenylbenzoperylene 21 reacts with maleic anhydride and chloranil to give

the anhydride 22. Decarboxylation with copper carbonate in quinoline yielded 1,6-diphenylcoronene 23. Its NMR spectrum is displaced so much to lower field by comparison with diphenylbenzoperylene 21 that superaromaticity, as indicated by the arrows in 23, must be assumed as in coronene itself.⁷



There are interesting features in the electronic spectra of the phenyl derivatives described in this paper. All are like those of the parent hydrocarbons but with considerably broadened bands. This is typical for phenyl derivatives. 3,8-diphenylpyrene **5** and 3,10-diphenylpyrene **10** have very similar spectra. However, the spectra of diphenylanthranthrene **16** and diphenylbenzoperylene **21** are very different. The spectrum of diphenylanthranthrene (dominated by the central complex which has only 2 aromatic sextets) is shifted more towards the red by comparison with the spectrum of diphenylbenzoperylene the central complex of which has 3 aromatic sextets. This must be expected if Robinson's aromatic sextet is applied in a strict and logical sense. None of the spectra shows the exceptional strong red shift which is found in 2-phenylnaphthalene and 2-phenylanthracene and their derivatives⁸ and which is restricted to β -phenyl derivatives. Thus one must conclude that the conjugation between the phenyl groups and the central aromatic complexes of the hydrocarbons described in this paper does not go beyond the electronic interaction produced by the single bond of the diphenyl type.

EXPERIMENTAL*

1,5-Dibenzoynaphthalene. This was prepared following the description in I. G. Farbenindustrie A. G., Brit. Pats. 279506 and 291347. Aluminium chloride (200 g) was added slowly to a melt of naphthalene (128 g) and benzoyl chloride (210 g). The reaction was violent at room temperature. After cooling in ice, another portion of benzoyl chloride (210 g), and powdered aluminium chloride (200 g), were added. The mixture was heated to 100°. A slow reaction took place. The red mixture became solid on cooling and was decomposed with ice and dil HCl. After washing with water, xylene was added, the aqueous layer was removed and the xylene layer washed with hot water. After concentration of the soln, 1,5-

dibenzoynaphthalene (49 g) crystallized out. After recrystallisation it had mp 188°. Another product was isolated from the mother liquor but not investigated.

1,5-Dibenzynaphthalene 1. 1,5-Dibenzynaphthalene (25 g) was dissolved in diethylene glycol (250 ml) and hydrazine hydrate (15 ml, 80%) added. The mixture was boiled to remove water and refluxed at 180–200° for 3 h. After cooling to 100° NaOH (10 g) was added slowly and then refluxed for 3 h. On cooling long needles (21 g) crystallized which were recrystallized from light petrol 60–80°. Colourless needles were obtained which had mp 132°.

3,8-Diphenylpyrene-4,5,9,10-tetracarboxylic dianhydride 4. Nitrobenzene (75 ml) and maleic anhydride (75 g) were boiled and water removed. 1,5-Dibenzynaphthalene (15 g) and a few iodine crystals were added and the mixture refluxed for 4 h. 25 ml solvent was distilled from the mixture under vacuum. After cooling, acetic acid was added. Fine brown leaflets crystallized which were filtered off (15 g) and washed with acetic acid and ether. Sublimation at 240°/0.04 mm gave a compound which had mp 363°. (Found: C, 77.9; H, 2.8; C₃₂H₁₄O₆ requires: C, 77.7; H, 2.9%).

3,8-Diphenylpyrene 5. The anhydride **4** (5 g) was suspended in boiling quinoline (70 ml) and basic copper carbonate (3 g) was added. The mixture was refluxed under N₂ for 48 h. After cooling the mixture was boiled with dil HCl, the ppt filtered off, and washed with water. The solid was dissolved in hot xylene and the soln dried and chromatographed on alumina Grade I. The first colourless fraction contained 3,8-diphenylpyrene (3 g) which crystallized in pale prisms, mp 225°. The soln in cyclohexane had max λ_{\max} (nm) log ϵ in parantheses: ρ , 354 (4.48); β , 285 (4.58); 274 (4.41); β' , 249 (4.58). NMR (CS₂): τ H_{2,7} = 8.07, H_{1,6} 7.9; H_{4,9} 8.06; H_{5,10} = 7.83; H_{phenyl} 7.42 (multiplet) ppm, J_{1,2} = J_{6,7} = 9.5 Hz, J_{4,5} = J_{9,10} = 8 Hz. (Found: C, 94.8; H, 5.2. C₂₈H₁₈ requires: C, 94.9; H, 5.1%).

1-Benzyl-4-benzoynaphthalene. Aluminium chloride (20 g) was added slowly to a mixture of 1-benzyl-naphthalene (30 g) and benzoyl chloride (20 g) in CS₂ (50 ml). During the reaction the mixture was cooled with ice. After standing at room temperature for 1 h the complex was decomposed with ice and dil HCl. After separation of the aqueous layer the CS₂ was removed and the residue distilled in vacuum. The fraction at 250°/0.1 mm contained the ketone (17 g) which had m.p. 112°.

1,4-Dibenzynaphthalene 6. The reduction of the above

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

ketone was carried out as described for 1,5-dibenzoylnaphthalene. Yield 20 g.

3,10-Diphenyl-4,5,8,9-tetra carboxylic dianhydride 9. This reaction was carried out as described for 4. However, it was necessary to remove most of the nitrobenzene and excess maleic anhydride in vacuum before acetic acid was added. The dianhydride (9) formed fine red crystals which were recrystallized from acetic anhydride and had mp 343°. It was sublimed at 250°/0.04 mm. (Found: C, 77.9; H, 2.6. C₃₂H₁₄O₆ requires: C, 77.7; H, 2.8%).

3,10-Diphenylpyrene 10. The decarboxylation was carried out in the same way as with the dianhydride 4. The colourless fraction of the chromatogram yielded 3,10-diphenylpyrene (2 g) which was recrystallized from light petrol 60–80° and gave pale yellow prisms mp 138°. The compound in cyclohexane had λ_{\max} (nm), log ϵ in parentheses: α , 357 (4.48); β , 285 (4.58), 275 (4.61); 250 (4.85). (Found: C, 94.7; H, 5.3. C₂₈H₁₈ requires: C, 94.9; H, 5.1%).

10-Phenyl-2,3-o-phenylenepylene 11. The following yellow fraction of the above chromatogram yielded yellow needles which were recrystallized from light petrol 100–120° and had mp 180°. The soln in cyclohexane had λ_{\max} (nm) with log ϵ in parentheses: 414 (3.73), 384 (4.08), 366 (4.02); 318 (4.17), 307 (4.43) 282 (4.27), 255 (4.57). (Found: C, 95.2; H, 4.7. C₂₈H₁₆ requires: C, 95.5; H, 4.5%).

3,8-Dibenzylpyrene 12. 3,8-Dibenzoylpyrene⁵ (30 g) and hydrazone hydrate (100%, 18 ml) were refluxed in diethylene glycol (300 ml) for 3 h. The water formed was removed from the condenser at regular intervals. The mixture was allowed to cool to 100° and NaOH (12 g) added. After refluxing for a further 3 h the mixture was cooled and diluted with an equal volume of water. Colourless needles separated which were filtered off and washed with hot water. Yield quantitative. Recrystallisation from xylene gave long needles which had mp 193–194°. (Found: C, 94.3; H, 5.8. C₃₀H₂₂ requires: C, 94.2; H, 5.8%).

3,9-Diphenylanthranthrene-1,2-7,8-tetracarboxylic dianhydride 15. 3,8-Dibenzylpyrene (25 g), maleic anhydride (97.5 g), nitrobenzene (65 mg) and a few crystals of iodine were refluxed together for 2 h. The colour of the mixture changed from yellow to brown and dark violet. The water and fumaric acid formed during the reaction were removed from the condenser. 20 ml solvent were distilled off from the mixture. Purplish violet crystals crystallized out. They were filtered off and washed with acetic acid and ether. Yield 9.75 g. Concentration of the mother liquors gave a further 2.3 g. Sublimation at 390–395°/0.03 mm gave dark purple prismatic crystals which had mp about 420–440°. Absorption spectrum in dil alic. NaOH with λ_{\max} (nm) and log ϵ in parentheses: α , 463 (4.61), 435 (4.46), 413 (4.14); β , 330 (4.78), 316 (4.60); 283 (4.52); 260 (4.82). (Found: C, 80.3; H, 2.9. C₃₈H₁₆O₆ requires: C, 80.1; H, 3.0%).

3,9-Diphenylanthranthrene (16). The above dianhydride (2 g), quinoline (20 ml), nitrobenzene (10 ml) and basic copper carbonate $\frac{1}{2}$ g were refluxed under dry nitrogen for 24 h. Light brown yellow crystals separated on cooling. These were filtered off and washed with hot dil HCl and water. The product was extracted with methanolic NaOH, filtered, and washed with water. It was dissolved in xylene, the soln dried, and chromatographed on Grade 1 neutral alumina (10 g). The yellow eluate yielded orange plates on concentration (1.1 g) which had mp 369–370° and dissolved in conc H₂SO₄ with a violet colour. The absorption spectrum in benzene had λ_{\max} (nm) and log ϵ in parenthesis: α , 453 (4.69), 425 (4.48), 406 (4.150); β , 324

(4.84), 315 (4.56); in cyclohexane: β , 275 (4.53), 260 (4.64), 252 (4.84). (Found: C, 95.3; H, 4.7. C₃₄H₂₀ requires: C, 95.3; H, 4.8%).

If the above decarboxylation was carried out without nitrobenzene splitting of the dianhydride (15) occurred and only 3,8-dibenzylpyrene could be isolated.

3,10-Dibenzylpyrene 17. 3,10-Dibenzoylpyrene⁵ was reduced as described for 3,8-dibenzoylpyrene. The yield was quantitative. The hydrocarbon crystallized from xylene as long needles, mp 188–189°. (Found: C, 94.3; H, 5.7. C₃₀H₂₂ requires: C, 94.2; H, 5.8%).

4,9-Diphenyl-1,12-benzopyerylene-5,6-7,8-tetracarboxylic dianhydride 20. 3,10-Dibenzylpyrene 17 (16.74 g), nitrobenzene (75 ml) and maleic anhydride (75 g) were refluxed and a small amount of iodine added to the yellow solution. The mixture which became dark brown was refluxed for 2½ h. Water and fumaric acid formed during the reaction were removed from the condenser. 20 ml solvent were distilled off from the mixture. On cooling long golden brown needles crystallized out. These were filtered off and washed with hot acetic acid and ether. Yield 14.1 g. Sublimation at 340–360°/0.03 mm yielded brick red needles, mp 404–410°. Absorption spectrum in dil methanolic NaOH with λ_{\max} (nm) and log ϵ in parentheses: α , 433 (2.64); β , 414 (4.48), 392 (4.44); 347 (3.58); β , 321 (4.62), 306 (4.62), 290 (4.50). (Found: C, 80.3; H, 2.9. C₃₄H₁₆O₆ requires: C, 80.3; H, 2.9%).

4,9-Diphenyl-1,12-benzopyerylene 21. The above dianhydride 20 (2 g), quinoline (16 ml), nitrobenzene (8 ml) and basic copper carbonate (0.5 g) were refluxed under nitrogen for 24 h. The dark mixture was poured into dil HCl and the nitrobenzene removed by steam distillation. The residue was filtered off and treated with a dil soln of NaOH in methanol. The undissolved dark product was filtered off washed with water and dissolved in hot xylene and dried. The soln was chromatographed on Grade 1 neutral alumina (10 g). The eluate yielded 4,9-diphenyl-1,12-benzopyerylene (0.21 g) which crystallized from xylene in large yellow plates, mp 277–278°, which dissolved in conc H₂SO₄ to give a deep purple soln. Absorption spectrum in cyclohexane with λ_{\max} (nm) and log ϵ in parentheses: α , 422 (2.68); β , 403 (4.54), 384 (4.49); 340 (3.60); β , 310 (4.68), 296 (4.68), 285 (4.60). NMR (CS₂) at 100 MHz: H_{1,12} 8.94; H_{2,11} 7.88; H_{4,9} 7.97; H_{5,8} 8.12; H_{6,7} 8.23; H_{phenyl} 7.40–7.70 ppm; J_{1,2} = J_{11,12} = 7.8; J_{4,5} = J_{8,9} = 9.0 Hz. (Found: C, 95.0; H, 5.0. C₃₄H₂₀ requires: C, 95.3; H, 4.7%). No splitting was observed when nitrobenzene was omitted.

2,9-Diphenylcoronene-11,12-dicarboxylic anhydride 22. 4,9-Diphenyl-1,12-benzopyerylene 21 (3 g) and maleic anhydride (17 g) were refluxed and all water from the condenser removed. Chloranil (9 g) was added and refluxing continued for 5 h. Brown needles crystallized out. The solution was diluted and boiled with acetic acid and the crystals were filtered off and washed with hot acetic acid and ether. They were then boiled with xylene to extract any unreacted hydrocarbon. The undissolved needles (2.4 g) were filtered off, washed with ether, and sublimed at 350–365°/0.3 mm. They had m.p. 414–416°. Absorption spectrum of the anhydride 22 in dil ethanol-water solution of NaOH with λ_{\max} (nm) and log ϵ in parentheses: α , 446 (2.15), 438 (2.19), 431 (2.55), 422 (2.50), 419 (2.73), 414 (2.85), 408 (2.80), 403 (2.85), 387 (2.92); β , 366 (4.15), 351 (4.50) 337 (2.32); β , 316 (5.45). (Found: C, 87.2; H, 3.7. C₃₈H₁₈O₃ requires: C, 87.3; H, 3.5%).

2,9-Diphenylcoronene 23. The above anhydride (2 g), quinoline (20 ml) nitrobenzene (12 ml) and basic copper

carbonate were refluxed under nitrogen for 48 h. The nitrobenzene was removed by steam distillation and the residue treated with a dil soln of methanolic NaOH to remove unreacted anhydride. The residue was dissolved in xylene, dried and chromatographed on Grade 1 neutral alumina (10 g). The eluate yielded on concentration 2,9-diphenylcoronene in yellow prisms (4 g). Sublimation at 290–305°/0.02 mm gave yellow prisms, mp 307–309° which dissolved in conc H₂SO₄ to give a green solution. Absorption spectrum in cyclohexane with λ_{\max} (nm) log Σ in parentheses: α , 441 (2.10), 436 (2.13), 427 (2.52), 415 (2.70), 408 (2.80), 404 (2.75), 399 (2.78), 282 (2.90); β , 361 (4.13), 346 (4.47), 331 (4.26); β , 311 (5.41), 300 (4.90). NMR (CS₂) at 100 MHz: H_{1,10} 8.74; H_{3,8} 8.86, H_{4,7} 8.82; H_{5,6,11,12} 8.7; H_{phenyl} 7.50–7.90 ppm. J_{3,4} = J_{7,8} = 9 Hz. (Found: C, 95.3; H, 4.3. C₃₆H₂₀ requires: C, 95.6; H, 4.5%).

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