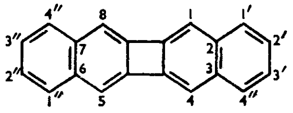
331. *The Synthesis of 2 : 3-6 : 7-Dibenzodiphenylene.*

By R. F. Curtis and G. Viswanath.

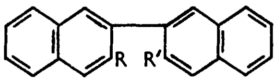
The synthesis of 2 : 3-6 : 7-dibenzodiphenylene (I) from 3-nitro-2-naphthylamine is described. Proof of structure follows from reduction to 2 : 2′-dinaphthyl. 3-Nitro-2-naphthylamine was prepared by dehydrogenation of 6-acetamido-1 : 2 : 3 : 4-tetrahydro-7-nitronaphthalene.

Attempts to prepare the corresponding 1′ : 2′ : 3′ : 4′ : 1″ : 2″ : 3″ : 4″-octahydro-2 : 3-6 : 7-dibenzodiphenylene were unsuccessful; dehydrogenation gave the same 2 : 3-6 : 7-dibenzodiphenylene (I). The preparation of 1′ : 2′ : 3′ : 4′ : 1″ : 2″ : 3″ : 4″-octahydro-2 : 3-6 : 7-dibenzocarbazole (V) and dinaphtho(2′ : 3′-2 : 3)(2″ : 3″-4 : 5)furan (VIII) is also recorded.

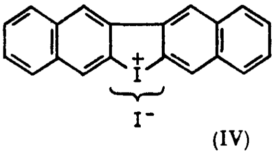
Diphenylene has been extensively investigated,[1] but attempts to synthesise the corresponding naphthalene derivatives, *e.g.*, 2 : 3-6 : 7-dibenzodiphenylene (I) (and three other possible isomers), have failed until recently. Rosenhauer and his co-workers [2] heated 1 : 4-naphthaquinone in anhydrous pyridine and obtained a quinonoid compound which on zinc dust distillation gave a hydrocarbon formulated as (I) but later shown [3] to be trinaphthylene.



(I)



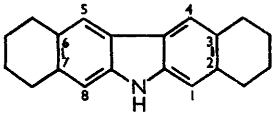
(II); R = R′ = NO_2
(III); R = R′ = NH_2



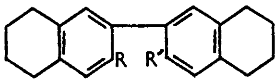
(IV)

Unsuccessful attempts to synthesise the dibenzodiphenylene (I) have been summarised by Bell and Hunter; [4] theoretical calculations have been made by Crawford,[5] and by using L.C.A.O. methods, the bond lengths and light-absorption data were predicted. We have briefly reported [6] the synthesis of 2 : 3-6 : 7-dibenzodiphenylene (I), and several other derivatives of diphenylene have been synthesised by similar methods; *e.g.*, 1 : 2-benzodiphenylene and 1 : 2-7 : 8-dibenzodiphenylene.[7] The latter compound exhibits considerable *cyclo*butadienoid character.

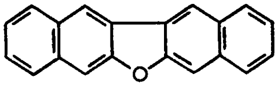
In the work now described 2 : 3-6 : 7-dibenzodiphenylene (I) has been synthesised from 3-nitro-2-naphthylamine, which was converted into 2-iodo-3-nitronaphthalene and thence into the hydrocarbon (I) by the series of reactions (II) ⟶ (III) ⟶ (IV) ⟶ (I).



(V)



(VI); R = R′ = NO_2
(VII); R = R′ = NH_2



(VIII)

3-Nitro-2-naphthylamine has been synthesised by van Rij, Verkade, and Wepster [8]

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[1] Baker, Boarland, and McOmie, *J.*, 1954, 1476 (contains earlier references).

[2] Rosenhauer, Braun, Pummerer, and Reigelbauer, *Ber.*, 1937, **70**, 2281.

[3] Pummerer, Lüttringhaus, Fick, Pfaff, Riegelbauer, and Rosenhauer, *ibid.*, 1938, **71**, 2569.

[4] Bell and Hunter, *J.*, 1950, 2904.

[5] Crawford, *Canad. J. Chem.*, 1952, **30**, 47.

[6] Curtis and Viswanath, *Chem. and Ind.*, 1954, 1174, 1397.

[7] Cava and Stucker, *J. Amer. Chem. Soc.*, 1955, **77**, 6022.

[8] van Rij, Verkade, and Wepster, *Rec. Trav. chim.*, 1951, **70**, 236.

and by Ward [9] in low yield from 6-acetyl-1 : 2 : 3 : 4-tetrahydronaphthalene but preparation from 2-acetamidonaphthalene is simpler. High-pressure hydrogenation [10,11] over Raney nickel (W2) [12] gave 6-acetamido-1 : 2 : 3 : 4-tetrahydronaphthalene; this was nitrated by Schroeter's method [13] to the 7-nitro-compound which with *N*-bromosuccinimide gave a dibromo-derivative. This could not be dehydrobrominated directly, but treatment with methanolic potassium acetate produced a monobromo-derivative. Acid hydrolysis then gave 3-nitro-2-naphthylamine. This dehydrogenation [14] with *N*-bromosuccinimide is not of general application to substituted tetrahydronaphthalenes since it failed with the free amine and the corresponding iodo-compound.

3-Nitro-2-naphthylamine was diazotised and converted into 2-iodo-3-nitronaphthalene [15] which under Ullmann conditions gave 3 : 3′-dinitro-2 : 2′-dinaphthyl (II) but the m. p. did not agree with that recorded for the same compound by Cumming and Howie.[15]

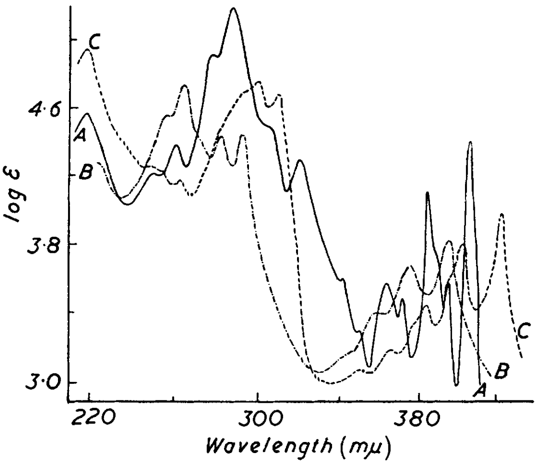

FIG. 1. *Ultraviolet spectra in ethanol solution.* A, 2 : 3-6 : 7-*Dibenzodiphenylene* (I). B, 1 : 2-*Benzodiphenylene.* C, 1 : 2-7 : 8-*Dibenzodiphenylene.*

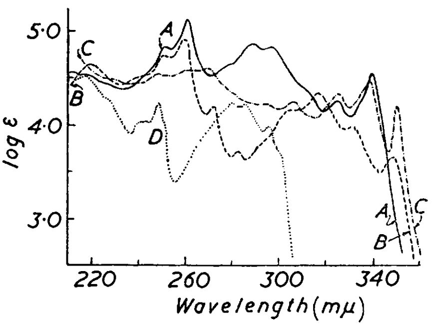

FIG. 2. *Ultraviolet spectra in ethanol solution.* A, *Dinaphtho*(2′ : 3′-2 : 3)(2″ : 3″-4 : 5)-*furan* (VIII). B, *Brazan.* C, *Dinaphtho*-(1′ : 2′-2 : 3)(1″ : 2″-4 : 5)*furan.* D, *Diphenylene oxide.*

Previous attempts to reduce this type of dinitrodinaphthyl chemically have often been unsuccessful,[4,15,16] but catalytic hydrogenation gave 3 : 3′-diamino-2 : 2′-dinaphthyl (III) in good yield. Tetrazotisation and treatment with potassium iodide gave an iodonium iodide (not isolated) which was pyrolysed with cuprous oxide, under vacuum, giving 2 : 3-6 : 7-dibenzodiphenylene (I). The compound has an unusually high m. p. and great stability compared with 1 : 2-benzo- and 1 : 2-7 : 8-dibenzo-diphenylene; it is comparable with tetracene [17] in this respect. Reduction by freshly prepared Raney nickel in ethanolic solution gave 2 : 2′-dinaphthyl.

The ultraviolet absorption spectrum of 2 : 3-6 : 7-dibenzodiphenylene (Fig. 1) is complex and exhibits nine major and four minor maxima, being similar in this respect to 1 : 2-benzodiphenylene and 1 : 2-7 : 8-dibenzodiphenylene [7] and, although showing the expected bathochromic shift, similar in general form to that of diphenylene.[1] Maxima are recorded in Table 1: there is fair agreement with those predicted by Crawford.[5]

The infrared spectrum is relatively simple and shows several features of interest,

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[9] Ward and Coulson, *J.*, 1954, 4545.
[10] B.P. 276,571.
[11] Casella and Co., G.P. 479,401; *Chem. Zentr.*, 1929, II, 3186.
[12] *Org. Synth.*, 1955, Coll. Vol. III, p. 181.
[13] Schroeter, *Annalen*, 1922, **426**, 65.
[14] Barnes, *J. Amer. Chem. Soc.*, 1948, **70**, 145.
[15] Cumming and Howie, *J.*, 1931, 3176.
[16] Huisberg and Sorge, *Annalen*, 1950, **566**, 162.
[17] Clar, " Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1952, Vol. II, p. 232.

especially in relation to that of 1 : 2-benzo*cyclo*butene.[18] It has been pointed out [18] that, whereas xylene and tetralin both show a single intense band at 13·5 μ characteristic of *ortho*-disubstituted benzenes,[19] yet indane (a more strained molecule) exhibits two bands slightly separated at 13·30 and 13·55 μ. 4 : 5-Benzindane shows similar separation, with peaks at 13·10 and 13·57 μ.[20] 2 : 3-6 : 7-Dibenzodiphenylene possesses a very strong absorption at 13·45 μ and a partially separated double peak of medium intensity at 13·20 and 13·28 μ. All the other maxima show good correlation with the values suggested for substituted naphthalene derivatives by Hawkins, Ward, and Whiffen.[21]

For comparison we have recorded the infrared spectrum of diphenylene. This also exhibits the split peak at 13·34 and 13·63 μ, the latter being a very strong absorption. There does not appear to be any characteristic absorption by these two hydrocarbons which corresponds to the stretching of the four-membered ring. This may be due to the essential symmetry of the molecules.

The reduction of 3 : 3′-dinitro-2 : 2′-dinaphthyl (II) was difficult to control. With catalysts of high activity or at higher temperatures two other products were obtained in different experiments. On hydrogenation at 100° a compound $C_{20}H_{21}N$ probably 1′ : 2′ : 3′ : 4′ : 1″ : 2″ : 3″ : 4″-octahydro-2 : 3-6 : 7-dibenzocarbazole (V), was produced Comparison of the ultraviolet spectrum with that of carbazole [22] showed a similarity which would not be expected if the hydrogenated rings were adjacent to the pyrrole nucleus, since such a compound should show predominantly benzenoid absorption. In the infrared spectrum the NH stretching, NH deformation, and CN stretching frequencies occur at 2·94, 6·78, and 7·57 μ respectively (cf. carbazole, under the same conditions, 2·93, 6·69, and 7·54 μ).

Additional evidence that the outer rings in (V) were hydrogenated is that hydrogenation of 3 : 3′-dinitro-2 : 2′-dinaphthyl (II) with active catalysts at room temperature gave the diaminodinaphthyl (VII), also prepared by reduction of 5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-octahydro-3 : 3′-dinitro-2 : 2′-dinaphthyl (VI)

An attempt was made to prepare 1′ : 2′ : 3′ : 4′ : 1″ : 2″ : 3″ : 4″-octahydro-2 : 3-6 : 7-dibenzodiphenylene from 6-acetamido-1 : 2 : 3 : 4-tetrahydro-7-nitronaphthalene.[13] This was hydrolysed to the amine [13] and then converted into 1 : 2 : 3 : 4-tetrahydro-6-iodonaphthalene as described by Cumming and Howie.[15] Ullmann condensation gave 5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-octahydro-3 : 3′-dinitro-2 : 2′-dinaphthyl (VI) [15] and catalytic hydrogenation furnished the 3 : 3′-diamino-compound (VII), which was converted into the iodonium iodide and pyrolysed with cuprous oxide. In several experiments the fully aromatic 2 : 3-6 : 7-dibenzodiphenylene was obtained, but results depended very much upon unknown factors connected with the cuprous oxide (cf. Cava and Stucker [7]), since 2 : 2′-dinaphthyl was sometimes isolated as the sole product. This has been confirmed by Ward [23] who has, however, isolated the octahydrodibenzodiphenylene in one experiment.

A product of other experiments was considered, on comparison [24-26] of its ultraviolet absorption spectrum (Fig. 2), to be dinaphtho(2′ : 3′-2 : 3)(2″ : 3″-4 : 5)furan (VIII). This structure was supported by the infrared spectrum which was more complex than that of 2 : 3-6 : 7-dibenzodiphenylene and possessed a sharp peak at 9·35 μ (cf. peak at 9·49 μ in brazan [27] and 9·5 μ in 4 : 5-benzocoumaran [28]) which probably represents the antisymmetric

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[18] Cava and Napier, *J. Amer. Chem. Soc.*, 1958, **80**, 2255.
[19] Bellamy, " The Infra-red Spectra of Complex Molecules," Methuen and Co., London, 1958, p. 77.
[20] Dannenberg and Rahman, *Ber.*, 1955, **88**, 1405.
[21] Hawkins, Ward, and Whiffen, *Spectrochim. Acta*, 1957, **10**, 105.
[22] Friedel and Orchin, " Ultraviolet Spectra of Aromatic Compounds," John Wiley and Sons Inc., N.Y., 1951, no. 338.
[23] Ward and Pearson, personal communication.
[24] Friedel and Orchin, *op. cit.*, no. 337.
[25] *Idem, op. cit.*, no. 435.
[26] *Idem, op. cit.*, no. 540.
[27] Chatterjee, *J. Indian Chem. Soc.*, 1956, **33**, 447.
[28] Cagniant and Cagniant, *Bull. Soc. chim. France*, 1955, 931.

ether C–O–C frequency for the five-membered ring.[29,30] The origin of the oxygen function is interesting, but Tauber and Halberstadt [31] have recorded the formation of diphenylene oxide from the tetrazonium salt of 2 : 2′-diaminodiphenyl by boiling with water.

TABLE 1. *Ultraviolet absorption spectra.* (*All in ethanol solution*; *wavelengths recorded in* mμ.)

(I) $\lambda_{max.}$	217	250	257	278	288	301	322	341	349	362	370	380	394	406
log $\varepsilon_{max.}$	4·56	4·23	4·41	4·93	5·23	4·47	4·31	3·61	3·56	3·63	3·57	4·15	3·63	4·43
(VIII) $\lambda_{max.}$	212	252	261	278	288	297	324	340	360	370	380	394	406	
log $\varepsilon_{max.}$	4·61	4·89	5·19	4·62	4·86	4·85	4·26	4·55	3·18	3·07	3·61	3·21	3·81	
(V) $\lambda_{max.}$	222	235	242	252	270	288	300	310	336					
log $\varepsilon_{max.}$	4·54	4·55	4·54	4·39	4·45	4·31	4·40	4·33	3·90					

EXPERIMENTAL

6-*Acetamido*-1 : 2 : 3 : 4-*tetrahydronaphthalene.*—To 2-acetamidonaphthalene (150 g.) suspended in decalin (distilled from Raney nickel) (250 ml.), Raney nickel (W2, 15 g.) in decalin suspension was added. The mixture was hydrogenated, with shaking, at 800 lb./sq. in. Reaction commenced at *ca.* 175° and was complete in 30 min. at 200°. This process was repeated with more (150 g.) material and the combined products were filtered (Filter-cel) and steam-distilled to remove decalin.

The residue, hydrochloric acid (*d* 1·2; 200 ml.), and ethanol (50 ml.) were boiled for 12 hr., cooled, and made alkaline with aqueous sodium hydroxide (25% w/v). After further cooling an oily layer separated and was collected. The aqueous layer was extracted with ether (2 × 100 ml.), which was combined with the oil, and dried ($MgSO_4$).

Distillation (14″ Vigreux column) gave a fore-run, b. p. up to 148°/19 mm. (14·0 g.), and 6-amino-1 : 2 : 3 : 4-tetrahydronaphthalene (165 g., 69%), b. p. 148—156°/19 mm., m. p. 38°. Schroeter [13] gives m. p. 38—39°. Acetylation gave 6-acetamido-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 106° (from aqueous ethanol), in quantitative yield. Ward [9] gives m. p. 106°.

6-*Acetamido*-1 : 2 : 3 : 4-*tetrahydro*-7-*nitronaphthalene.*—The preceding compound was nitrated as described by Schroeter.[13] Satisfactory yields were obtained on the 75 g. scale provided that adequate cooling was maintained after the initial induction of nitration. Nitration at 40—42° gave optimum yields, and 6-acetamido-1 : 2 : 3 : 4-tetrahydro-7-nitronaphthalene was obtained as dark yellow needles (from ethanol), m. p. 134—135° (Verkade [8] gives m. p. 134—135°).

6-*Acetamido*-x : y-*dibromo*-1 : 2 : 3 : 4-*tetrahydro*-7-*nitronaphthalene.*—The acetamide (20 g.), *N*-bromosuccinimide (30·4 g., 2 mol.), and benzoyl peroxide (0·5 g.) in carbon tetrachloride (200 ml.) were heated under reflux over a 250-w infrared lamp, the lamp and flask being enclosed with aluminium foil. After the initial vigorous reaction, the solution was heated for a further 20 min. (longer heating resulted in lower yield). The red mixture was filtered hot and then concentrated (to *ca.* 100 ml.) in a current of nitrogen. After 1 hr. at 0°, 6-*acetamido*-x : y-*dibromo*-1 : 2 : 3 : 4-*tetrahydro*-7-*nitronaphthalene* was collected as thin yellow needles (26·6 g., 81%), m. p. 134° (after crystallisation from carbon tetrachloride) (Found: C, 36·5; H, 3·3; Br, 37·0. $C_{12}H_{12}O_3N_2Br_2$ requires C, 36·75; H, 3·1; Br, 40·8%).

6-*Acetamido*-x-*bromo*-x : y-*dihydro*-7-*nitronaphthalene.*—The dibromo-compound (16·2 g.) was added rapidly to a boiling solution of potassium acetate (15 g.; fused) in dry methanol (150 ml.), and the solution boiled for 5 min. Potassium bromide separated and the product was then poured into water and chopped ice (2 l.). After 12 hr. at 0° the very pale yellow solid was collected (13·2 g., quantitative yield), m. p. 154—156° (decomp.). One crystallisation from methanol gave the *monobromo-compound* as pale cream needles, m. p. (rapid heating) 172° (decomp.) (Found: C, 45·55; H, 3·4; Br, 22·1. $C_{12}H_{11}O_3N_2Br$ requires C, 46·3; H, 3·6; Br, 25·7%). Both mono- and di-bromides were difficult to analyse for bromine.

3-*Nitro*-2-*naphthylamine.*—The monobromo-compound (13·0 g.), ethanol (100 ml.), hydrochloric acid (*d* 1·2, 50 ml.), and water (10 ml.) were boiled for 1 hr. and then poured into excess of dilute aqueous ammonia. After the mixture had been kept at 0° overnight, the precipitate

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[29] Bellamy, *op. cit.*, p. 114.

[30] Barrow and Searles, *J. Amer. Chem. Soc.*, 1953, **75**, 1175.

[31] Tauber and Halberstadt, *Ber.*, 1892, **25**, 2745.

was collected and dried (6·53 g., 83%). One crystallisation from light petroleum (b. p. 60—80°) gave 3-nitro-2-naphthylamine as deep red needles, m. p. 115—116°. Ward [9] gives m. p. 115—116° (Found: C, 63·7; H, 3·9; N, 14·9. Calc. for $C_{10}H_8O_2N_2$: C, 63·8; H, 4·3; N, 14·9%).

2-*Iodo*-3-*nitronaphthalene*.—Sodium nitrite (4·7 g.) in sulphuric acid (*d* 1·84; 30 ml.) at 0° was heated to 70° and then cooled to 10°. This solution was used to diazotise 3-nitro-2-naphthylamine (12·8 g.) in acetic acid (150 ml.) and sulphuric acid (*d* 1·84; 2 ml.) by dropwise addition below 20°. The solution was stored for 30 min. at room temperature and then poured into potassium iodide (30 g.) in water (80 ml.). After 24 hr. at 0°, the solid was collected, dried, dissolved in benzene, and passed through alumina (acid washed, activated at 110° for 12 hr.). Evaporation of the eluate and crystallisation from aqueous ethanol gave 2-iodo-3-nitronaphthalene as deep yellow needles (8·5 g., 47%), m. p. 89—90°. Cumming and Howie [15] give m. p. 89° (Found: C, 40·6; H, 2·0; I, 42·2. Calc. for $C_{10}H_6O_2NI$: C, 40·2; H, 2·0; I, 42·4%).

3 : 3′-*Dinitro*-2 : 2′-*dinaphthyl* (II).—2-Iodo-3-nitronaphthalene (1·97 g.) was heated with copper-bronze powder (5·0 g.) in a wide test-tube immersed in an oil-bath at 130—135° for 40 min. Stirring was maintained and a few crystals of iodine were added occasionally. The product was extracted with hot benzene (3 × 100 ml.), and the extract concentrated (to *ca.* 10 ml.) before being passed through alumina. Evaporation of the eluate gave 3 : 3′-dinitro-2 : 2′-dinaphthyl (II) as yellow needles (0·35 g.), m. p. 270—271°. Recrystallisation from benzene gave m. p. 275° (Found: C, 69·7; H, 3·4. Calc. for $C_{20}H_{12}O_4N_2$: C, 69·8; H, 3·5%). Cumming and Howie record m. p. 257°.

3 : 3′-*Diamino*-2 : 2′-*dinaphthyl* (III).—The dinitro-compound (II) (1·36 g.) suspended in ethanol (50 ml.) and acetic acid (10 ml.) was shaken with Raney nickel (W2, which had been kept under ethanol for 2 weeks; *ca.* 3 g.) under hydrogen at 40 lb./sq. in. in a glass bottle until the solution was colourless (approx. 2 hr.). The product was filtered (Filter-cel), diluted with water (200 ml.), saturated with hydrogen, and kept at 0° for 24 hr. The precipitate was collected and crystallised from ethanol (charcoal), giving 3 : 3′-*diamino*-2 : 2′-*dinaphthyl* as needles (0·75 g., 67%), m. p. 215—220°. Recrystallisation gave m. p. 220° (decomp.), darkening rapidly in air. The *diacetyl* derivative, long, stout, needles from acetic acid, had m. p. 164—165° (Found: C, 77·9; H, 5·4; N, 7·2. $C_{24}H_{20}O_2N_2$ requires C, 78·2; H, 5·5; N, 7·6%).

2 : 3-6 : 7-*Dibenzodiphenylene* (I).—The diamine (III) (0·70 g.) in 6N-hydrochloric acid (15 ml.) was treated dropwise with a solution of sodium nitrite (0·51 g.) in water (1 ml.) with rapid stirring at 5°. The mixture was stirred for 30 min., and then treated with potassium iodide (2 g.) in water (5 ml.). Nitrogen was rapidly evolved and a dark brown amorphous solid separated. The mixture was set aside for 30 min., saturated sodium sulphite solution (10 ml.) added, and the solid collected. This was washed with sodium sulphite solution, then cold methanol (7 ml.), and dried, giving the iodonium iodide as a brown powder (1·03 g.).

This powder (350 mg.) was intimately mixed with cuprous oxide (3·5 g.) and pyrolysed under partial vacuum (*ca.* 30 mm.) in a cold-finger sublimation apparatus immersed in a metal-bath at 350°; a yellow semi-solid rapidly sublimed. This process was repeated on two further portions, and the combined solid was collected in hot benzene (20 ml.), filtered (charcoal), and concentrated (to *ca.* 2 ml.). The crystalline solid was collected and sublimed three times at 390°/10 mm. (bath temp.), giving 2 : 3-6 : 7-*dibenzodiphenylene* (I) as thin, twinned, rectangular plates (15 mg., approx. 3%), m. p. (sealed tube) 376° ± 2° (corr.). Crystallisation from benzene gave discrete, very pale yellow plates (Found: C, 95·3, 95·1; H, 4·9, 5·0. $C_{20}H_{12}$ requires C, 95·2; H, 4·8%). (The molecular weight could not be determined by the Kofler technique since the compound was insoluble in the usual solvents.) The hydrocarbon sublimes rapidly without melting at 340—345° on the Kofler block. Its dilute solution in benzene exhibits a strong blue fluorescence.

The infrared spectrum was determined in a potassium bromide disc; the maxima (μ) were: 6·05 (w), 6·20 (w), 6·66 (w), 6·89 (w), 7·91 (w), 8·07 (w), 8·51 (w), 8·78 (w), 8·84 (w), 9·76 (w), 10·50 (m), 11·39 (v.s.), 13·2 (m), 13·28 (m), 13·45 (s). The infrared spectrum of diphenylene under the same conditions showed maxima at 6·94 (m), 7·06 (m), 7·50 (w), 7·96 (m), 8·58 (w), 8·70 (m), 8·85 (m), 9·02 (w), 10·44 (s), 10·86 (m), 11·29 (m), 12·63 (w), 13·34 (m), 13·52 (s), 13·63 (s) μ.

Reduction of 2 : 3-6 : 7-*Dibenzodiphenylene* (I).—2 : 3-6 : 7-Dibenzodiphenylene (26·5 mg.) in ethanol (35 ml.) at 50° was shaken with freshly prepared Raney nickel (*ca.* 1 g.) for 5 min., the faint blue fluorescence then having disappeared. The filtered solution was concentrated (to 10 ml.) and on cooling yielded plates, m. p. 180—183°. Sublimation at 150°/13 mm. and crystallisation from ethanol gave 2 : 2′-dinaphthyl (8 mg.), m. p. 184° undepressed when mixed with authentic material, and showing an identical infrared curve.

Anomalous Reductions of 3 : 3′-*Dinitro*-2 : 2′-*dinaphthyl* (II).—(*a*) The dinitro-compound (II) (0·3 g.) in ethanol (20 ml.) and acetic acid (5 ml.) was hydrogenated over Raney nickel under hydrogen (150 lb./sq. in.) at 110° for 1 hr. The solution was cooled and filtered, and on addition of water (200 ml.) yielded a pale green solid. This was collected, dried, and recrystallised from benzene (intensely fluorescent solution) to give 1′ : 2′ : 3′ : 4′ : 1″ : 2″ : 3″ : 4″-*octahydro*-2 : 3-6 : 7-*dibenzocarbazole* (V) as pale green-yellow plates (0·08 g.), m. p. 275° (Found: C, 87·5; H, 7·2; N, 5·2. $C_{20}H_{21}N$ requires C, 87·2; H, 7·7; N, 5·1%). The infrared spectrum in potassium bromide showed maxima (μ) at 2·94 (s), 3·32 (w), 3·41 (s), 3·50 (m), 6·16 (m), 6·78 (s), 6·93 (m), 7·12 (w), 7·47 (m), 7·78 (w), 8·06 (s), 8·59 (w), 8·82 (w), 9·28 (w), 10·42 (w), 10·55 (w), 10·97 (m), 11·75 (s), 12·28 (w), 13·35 (m), 13·47 (m).

(*b*) The dinitro-compound (II) (4·0 g.) suspended in ethanol (150 ml.) and acetic acid (30 ml.) was shaken with freshly prepared Raney nickel (W2; *ca.* 4 g.) under hydrogen at 40 lb./sq. in. until colourless. The solution was filtered, diluted with water (500 ml.), and kept under hydrogen for 24 hr. at 0°. The precipitate was collected and dried. Recrystallisation from benzene (charcoal) gave 3 : 3′-*diamino*-5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-*octahydro*-2 : 2′-*dinaphthyl* as prisms (2·1 g.), m. p. 191—192° (Found: C, 82·1; H, 8·3; N, 9·6. $C_{20}H_{24}N_2$ requires C, 82·15; H, 8·3; N, 9·6%).

6-*Amino*-1 : 2 : 3 : 4-*tetrahydro*-7-*nitronaphthalene*.—This compound was prepared by acid hydrolysis of the acetamido-compound substantially as described by Ward [9]; it had m. p. 125—127°.

1 : 2 : 3 : 4-*Tetrahydro*-6-*iodo*-7-*nitronaphthalene*.—Sodium nitrite (10 g.) in sulphuric acid (*d* 1·84; 70 ml.) was heated to 70° and then cooled to 10°. This solution was used to diazotise the foregoing amine (25·4 g.) in acetic acid (300 ml.) and sulphuric acid (*d* 1·84; 3 ml.), at 10—15°. After 30 min. the solution was added to potassium iodide (60 g.) in water (100 ml.) and vigorously stirred. After 24 hr. at 0°, the solid was collected, washed with aqueous sodium sulphite, and crystallised from ethanol, forming pale orange needles (19·0 g., 47%), m. p. 76°. Cumming and Howie [15] give m. p. 76° for this compound prepared in very low yield.

5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-*Octahydro*-3 : 3′-*dinitro*-2 : 2′-*dinaphthyl* (VI).—This compound was prepared as described by Cumming and Howie [15] from the foregoing iodo-compound by using copper powder. Control of temperature at 110—120° to avoid violent decomposition was important, but even in these circumstances it was difficult to obtain a yield as high as that claimed.[15] After purification by chromatography over alumina, the m. p. of the product could not be raised to that stated (201°).[15] Recrystallisation from acetic acid gave yellow needles, m. p. 192° (Found: C, 68·1; H, 5·3; N, 8·5. Calc. for $C_{20}H_{20}O_4N_2$: C, 68·2; H, 5·7; N, 7·95%).

3 : 3′-*Diamino*-5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-*octahydro*-2 : 2′-*dinaphthyl* (VII).—The dinitro-compound (XV) (0·5 g.) in ethanol (25 ml.) and acetic acid (2·5 ml.) was reduced over Raney nickel (W2, *ca.* 0·5 g.) as described above for (III). When worked up in the usual way, the diamine was obtained as microcrystalline prisms (from benzene) (0·35 g.), m. p. (and mixed m. p. with material prepared as above) 192°.

2 : 3-6 : 7-*Dibenzodiphenylene from* 3 : 3′-*Diamino*-5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 8′-*octahydro*-2 : 2′-*dinaphthyl* (VII).—The diamine (1·6 g.) in hydrochloric acid (*d* 1·2; 17 ml.) and water (17 ml.) was treated with sodium nitrite (1·2 g.) in water (3 ml.) at 5°, with vigorous stirring. After 30 min., the solution was poured into potassium iodide (5 g.) in water (10 ml.). The solid was collected, washed with aqueous sodium sulphite and ice-cold methanol (2 ml.), and dried (2·1 g.).

Pyrolysis of this salt (0·35 g.) with cuprous oxide (3·5 g.) (Baker's " Analysed " grade) under the same conditions as for 2 : 3-6 : 7-dibenzodiphenylene gave a product which was combined with those from four similar runs. The combined material gave 2 : 3-6 : 7-dibenzodiphenylene from benzene as pale yellow plates (0·26 g.), m. p. (sealed tube) 357° (uncorr.), showing no depression with the sample prepared from the fully aromatic precursor.

Anomalous Pyrolysis of 3 : 3′-*Diamino*-5 : 6 : 7 : 8 : 5′ : 6′ : 7′ : 9′-*octahydro*-2 : 2′-*dinaphthyl* (VII).—*Dinaphtho*(2′ : 3′-2 : 3)(2″ : 3″-4 : 5)*furan* (VIII). The diamine (VII) (1·45 g.) was tetrazotised in the usual way, giving the iodonium iodide (2·45 g.). This was pyrolysed, in seven portions (0·35 g.), with cuprous oxide (3·5 g.), exactly as described above. The combined products yielded the *dinaphthofuran* (VIII) from benzene as pale yellow plates (70 mg.), m. p. 260°. Recrystallisation gave m. p. 266° (subliming at the m. p.) [Found: C, 88·7, 89·7; H, 4·55, 4·3%; *M* (Rast), 272. $C_{20}H_{12}O$ requires C, 89·5; H, 4·5%; *M*, 268]. Its 2 : 4 : 7-*trinitrofluorenone complex* (prepared in benzene solution) formed deep purple-brown needles (from benzene), m. p. 244—246° (decomp.) (Found: C, 68·4; H, 3·0; N, 6·9. $C_{20}H_{12}O,C_{13}H_5O_7N_3$ requires C, 67·9; H, 2·9; N, 7·2%).

The infrared spectrum of the furan in potassium bromide showed maxima (μ) at 6·18 (w), 6·28 (w), 6·69 (w), 6·84 (w), 7·24 (w), 7·50 (m), 7·86 (w), 8·29 (w), 8·39 (m), 8·81 (w), 9·35 (m-s), 9·69 (w), 9·85 (w), 10·45 (m), 11·41 (v.s.), 11·85 (w), 13·04 (w), 13·32 (m-s), 13·54 (vs).

Microanalyses were by Mr. J. Walter, the Johns Hopkins University, and Dr. F. Pascher, Mikroanalytische Laboratorium, Bonn. Infrared spectra were determined by Dr. Lester Kuhn, Aberdeen Proving Grounds, Aberdeen, Maryland, U.S.A., and by Mr. D. Jones of this Department (Swansea). We thank Dr. H. E. Hallam for advice on infrared spectra; one of us (G. V.) thanks Andhra University, Waltair, India, for study leave.

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