605. *Polycyclic Cinnoline Derivatives. Part II.* The Symmetrical Dinaphthopyridazines.*

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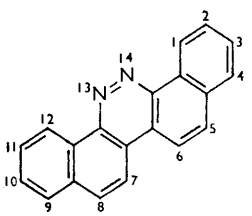
Benzo[*h*]naphtho[1,2-*c*]cinnoline, benzo[*f*]naphtho[2,1-*c*]cinnoline, and 1,2,3,4,9,10,11,12-octahydrobenzo[*g*]naphtho[2,3-*c*]cinnoline have been prepared by reducing dinitrobiaryls. An approach to the chemistry of these cinnolines has been made, in particular, a study of the nitration products of the first two. The product of reduction of 10,10′-dinitro-9,9′-biphenanthryl differs from a substance reported to be dibenzo[*f*,*h*]phenanthro[9,10-*c*]-cinnoline.

Polycyclic cinnoline systems of more than three rings appear not to have been studied systematically, and indeed very few such systems appear to be known. Benzo[*f*]naphtho-[2,1-*c*]cinnoline (III) and its *N*-oxide were prepared [1] incidentally to a study of the reduction of 2-nitronaphthalene, and dibenzo[*f*,*h*]phenanthro[9,10-*c*]cinnoline (IV) was produced by Schönberg and Rosenthal [2] by subliming an epoxide which Zincke [3] had found as an unidentifiable product in the reaction between phenanthraquinone imine and acetic anhydride.

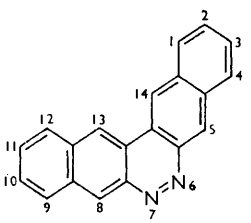
Some of the polycyclic cinnolines are analogues of the carcinogenic hydrocarbons and those in which the azo-group replaces the carbon atoms of the *K*-region would be of particular interest, as the azo-group would increase the electron-density of this region. The theory which relates the electron density of the *K*-region to the carcinogenicity of the compound (see, for example, Schmidt [4]) suggests that these cinnoline analogues will have a very high carcinogenic activity.

One general method which has been applied to the production of the simpler benzo[*c*]-cinnolines involves the formation and subsequent reduction of 2,2′-dinitrobiaryls, and a study of this method has been reported by Braithwaite, Holt, and Hughes.[5] This method has now been applied to the synthesis of higher cinnolines.

An attempt was first made to synthesise and to study the properties of members of the ring systems of the three possible symmetrical dinaphthopyridazines (I)—(III), and the diphenanthropyridazine (IV). As the direct synthesis of benzo[*g*]naphtho[2,3-*c*]cinnoline



(I)



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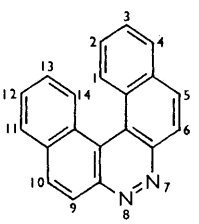

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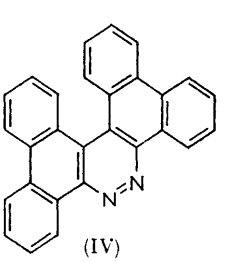

(IV)

(II) requires 2-halogeno-3-nitronaphthalenes as starting materials, which have been prepared only in very small quantities (*e.g.*, by Hodgson and Elliott [6]), the more readily available 1,2,3,4-tetrahydro-6-iodo-7-nitronaphthalene was used to prepare a hydrogenated derivative of (II).

* Part I, *J.*, 1948, 4073.

[1] Meisenheimer and Witte, *Ber.*, 1903, **36**, 4153.
[2] Schönberg and Rosenthal, *Ber.*, 1921, **54**, 1789.
[3] Zincke, *Ber.*, 1879, **12**, 1641.
[4] Schmidt, *Naturwiss.*, 1941, **29**, 146.
[5] Braithwaite, Holt, and Hughes, *J.*, 1958, 4073.
[6] Hodgson and Elliott, *J.*, 1936, 1151.

The obvious route to the more complex dinitrobiaryls is by the Ullmann reaction, but yields are often very low. Dimethylformamide has been found to increase the yield of dinitrobinaphthyl from 1-iodo-2- and 2-iodo-1-nitronaphthalene to 80%, apparently owing to the solvent action of the dimethylformamide in which the copper halide, the reactant, and the products dissolve leaving the copper surface uncoated.

The yields of biaryls from 4-bromo-1-iodo-2-nitronaphthalene and 1,2,3,4-tetrahydro-6-iodo-7-nitronaphthalene are, however, not improved by dimethylformamide, and the solvent causes halogen to be eliminated without biaryl formation when 9-bromo-10-nitrophenanthrene and 1-chloro-2,6-dinitrobenzene react with copper. In the latter case the absence of biaryl formation is presumably due to steric hindrance, but this cannot apply to the phenanthrene derivative because 1-iodo-2-nitronaphthalene, in which the groups have similar spatial relations, gives a high yield of biaryl. The partly aliphatic nature of the 9,10-bond of phenanthrene is probably relevant; vinyl halides do not undergo the Ullmann reaction.

The dinitrobiaryls were reduced by one or more of the reagents, lithium aluminium hydride, sodium amalgam and methanol, sodium sulphide, and zinc and potassium hydroxide. Conforming to the generalisations made earlier (Braithwaite, Holt, and Hughes [5]) these always gave cinnolines or their oxides, except that sodium amalgam and methanol produced diamines from 2,2′-dinitro-1,1′- and 1,1′-dinitro-2,2′-binaphthyl (confirming the observation by Chudožilov [7]), and zinc and potassium hydroxide produced a dehalogenated cinnoline from 4,4′-dibromo-2,2′-dinitro-1,1′-binaphthyl.

On reduction with lithium aluminium hydride, 10,10′-dinitro-9,9′-biphenanthryl gave a substance (m. p. >360°) that was not identical with the cinnoline (m. p. 290°) assumed to be (IV) by Schönberg and Rosenthal.[2] The yield was so small that a full investigation and analysis was impossible but the new substance appeared to be a cinnoline.

Although 1,1′-dinitro-2,2′-binaphthyl gave benzo[*h*]naphtho[1,2-*c*]cinnoline (I) with lithium aluminium hydride at room temperature, under reflux a dihydrocinnoline was formed which was also formed directly from the cinnoline by a similar reduction process. The dihydro-compound had the yellow colour which is characteristic of cinnolines, formed a red hydrochloride more stable than the hydrochloride of (I), and was readily oxidised by air. It formed a coloured solution in concentrated sulphuric acid, as do all cinnolines. These properties indicate that the new compound contains an unreduced cinnoline ring system. Bohlmann [8] detected a reduction product assumed to be the *NN*′-dihydro-derivative when he treated benzo[*c*]cinnoline with lithium aluminium hydride, though he found the substance too unstable for isolation. In picene, the homocyclic analogue of (I), the 5,6-bond is most easily attacked. By analogy, the new compound appears to be 5,6-dihydrobenzo[*h*]naphtho[1,2-*c*]cinnoline.

Benzo[*h*]naphtho[1,2-*c*]cinnoline *N*-oxide, prepared by reducing 1,1′-dinitro-2,2′-binaphthyl with sodium sulphide, and by oxidation of the cinnoline by hydrogen peroxide, appears to be identical with a substance reported by Cumming and Howie [9] as 1-amino-1′-nitro-2,2′-binaphthyl. Similarly, the compound reported by Cumming and Howie [9] to be 2-amino-2′-nitro-1,1′-binaphthyl appears to be identical with benzo[*f*]naphtho[2,1-*c*]-cinnoline *N*-oxide, previously prepared by Meisenheimer and Witte,[1] the constitution of which we have proved from its oxygen content and its formation by oxidation of the cinnoline. Cumming and Howie gave N = 9·3%. The calculated value for the amino-nitrobiaryl is 8·9% and for the cinnoline *N*-oxide, 9·4%.

Little of the chemistry of the polycyclic cinnolines has been described. Of the simple derivatives, picrates have been derived from two such cinnolines.[2,10,11] We have produced

[7] Chudožilov, *Chem. Listy*, 1925, **19**, 187.
[8] Bohlmann, *Ber.*, 1952, **85**, 390.
[9] Cumming and Howie, *J.*, 1932, 528.
[10] Sandin and Cairns, *J. Amer. Chem. Soc.*, 1936, **58**, 2019.
[11] Slack and Slack, *Nature*, 1947, **160**, 437.

a monopicrate from compound (III) and a hemipicrate from compound (I), but have not succeeded in producing addition products with 1,3,5-trinitrobenzene from the latter base.

Benzo[*c*]cinnoline is known to form a methiodide and an ethiodide [12] from which the tertiary base is regenerated by ammonia.[13] We find that a methotri-iodide is given when our base (III) is treated with methyl iodide. Since ammonia or sodium carbonate regenerates the original base, and no iodine is produced when the tri-iodide is heated, nuclear substitution by iodine and adsorption of free iodine are both excluded: the salt must contain the tri-iodide ion. Wohlfahrt [12] reported that benzo[*c*]cinnoline methiodide combined with iodine when shaken with ethanolic iodine. No quaternary compound could be isolated from a mixture of compound (I) with methyl iodide; a transitory colour change suggested that a methiodide may be formed but that it is too unstable to be separated.

Different cinnolines vary in their reaction to reducing agents. Benzo[*c*]cinnoline is unaffected by sodium amalgam in methanol but it gives an unstable dihydro-derivative with zinc dust and either hydrochloric acid [14] or potassium hydroxide,[15] and with lithium aluminium hydride.[8] A dihydro-derivative is also formed when compound (III) is reduced with stannous chloride.[1] The compound (III) is reduced to the diaminobinaphthyl [1] by zinc and acetic acid, but the heptacyclic analogue (IV) is unaffected.[2]

We find that both benzonaphthocinnolines (I) and (III) give good yields of the diaminobinaphthyls with sodium amalgam, and that the former gives the corresponding carbazole with zinc and acetic acid and a dihydro-derivative with lithium aluminium hydride.

Benzo[*c*]cinnoline *N*-oxide and its derivatives have been reduced by stannous chloride to the corresponding cinnolines.[13,16–18] The *N*-oxide of compound (I) gave the parent cinnoline with stannous chloride, and that of its analogue (III) a colourless solution probably of the dihydro-derivative, which gave the parent base (III) in good yield on addition of alkali. It appears that cinnoline oxides generally are reduced to cinnolines or their unstable dihydro-derivatives by stannous chloride.

Lithium aluminium hydride, with which Badger, Seidler, and Thomson [19] reduced benzo[*c*]cinnoline *N*-oxide to the cinnoline, also reduces the *N*-oxides of our compounds (I) and (III) to the cinnolines. Coloured intermediates are formed similar to those observed in the reduction of the corresponding dinitrobinaphthyls.

The only reports on the oxidation of polycyclic cinnolines appear to be those of Tauber [20] who obtained pyridazine-1,2,3,4-tetracarboxylic acid by treating benzo[*c*]-cinnoline with alkaline permanganate, and Schönberg and Rosenthal [2] who observed that compound (IV) is unaffected by alkaline permanganate but obtained phenanthraquinone with chromium trioxide. We found that peracetic acid converts benzo[*c*]cinnoline and compounds (I) and (III) into the cinnoline *N*-oxides. Alkaline permanganate and chromium trioxide in acetic acid do not affect either of the last two bases, the rings adjacent to the pyridazine ring being protected by the additional rings.

The only reports of the nitration of a polycyclic cinnoline refer to benzo[*c*]cinnoline and its *N*-oxide. After several days a concentrated solution of compound (III) in fuming nitric acid at room temperature yields two isomeric dinitro-derivatives. The compound (I) also yields a dinitro-derivative when nitrated by a similar method. The determination of the orientation of these dinitro-compounds will be difficult because very few reference compounds are known. However, preliminary investigations were made by reducing the dinitro-compounds derived from base (III) without affecting the azo-group and converting

[12] Wohlfahrt, *J. prakt. Chem.*, 1902, **65**, 295.
[13] Ullmann and Dieterle, *Ber.*, 1904, **37**, 23.
[14] Täuber, *Ber.*, 1891, **24**, 197.
[15] Duval, *Bull. Soc. chim. France*, 1910, **7**, 485.
[16] King and King, *J.*, 1945, 824.
[17] Ross and Kuntz, *J. Amer. Chem. Soc.*, 1952, **74**, 1297.
[18] Arcos and Miller, *J. Org. Chem.*, 1956, **21**, 652.
[19] Badger, Seidler, and Thomson, *J.*, 1951, 3207.
[20] Täuber, *Ber.*, 1895, **28**, 451.

the resulting diamines into dibromo-derivatives. Neither was identical with 5,10-dibromobenzo[*f*]naphtho[2,1-*c*]cinnoline which was synthesised unambiguously by the reduction of 4,4′-dibromo-2,2′-dinitro-1,1′-binaphthyl. As the protonated azo-group is *meta*-directing, it is unlikely that the nitro-groups are in the 6,9-positions; presumably they are in the outer rings, the protonated azo-group having deactivated the rings adjacent to the pyridazine ring. The complete determination of the orientation must await the synthesis of relevant derivatives in the binaphthyl series.

These and other polycyclic cinnolines give intense colours with concentrated sulphuric acid. Progressive dilution of the coloured solution with water first changes the colour, then precipitates the original cinnoline. For example, compound (III) gives a purple solution in concentrated sulphuric acid but a yellow solution in aqueous sulphuric acid.

Experimental

Halogenonitroarenes.—These compounds were prepared by the Sandmeyer procedure according to published methods, except for the following details: 6-halogeno-1,2,3,4-tetrahydro-7-nitronaphthalenes are prepared in better yield if the amines are diazotised in hydrochloric rather than sulphuric acid.

6-*Chloro*-1,2,3,4-*tetrahydro*-7-*nitronaphthalene* (0·18 g.) is precipitated when the diazonium salt from 6-amino-1,2,3,4-tetrahydro-7-nitronaphthalene (0·2 g.) in 1 : 1 hydrochloric acid (30 ml.) is added to cuprous chloride (1 g.) in concentrated hydrochloric acid (20 ml.). Purified by chromatography from acetone on alumina, it gives pale yellow needles (from acetone), m. p. 54·5° (Found: C, 57·2; H, 4·5; N, 6·1. $C_{10}H_{10}O_2NCl$ requires C, 56·8; H, 4·7; N, 6·6%).

1-*Iodo*-2-*nitronaphthalene*. 1-Acetamidonaphthalene (80 g.) was nitrated and partially hydrolysed [21] to 1-amino-4-nitronaphthalene, which is partially precipitated, and 1-acetamido-2-nitronaphthalene. The published method of separating the latter is unsatisfactory. It was easily separated and hydrolysed as follows. Water was added to the filtered solution. The precipitate was separated, dried at 70°, and dissolved in hot acetone. The filtered solution yielded 1-acetamido-2-nitronaphthalene (20 g.), m. p. 198—200° (lit., m. p. 199°), on cooling. To 1-acetamido-2-nitronaphthalene (39 g.) in boiling ethanol (1300 ml.) was added hydrochloric acid (800 ml.). After 12 hours' refluxing, hydrochloric acid (200 ml.) and ethanol (200 ml.) were added and refluxing was continued for 6 hr. The solution precipitated 1-amino-2-nitronaphthalene (30 g.) on cooling, which was converted into 1-iodo-2-nitronaphthalene.[22]

Dinitrobiaryls.—Activated copper bronze was added to an equal weight of the halogenonitro-compound in boiling dimethylformamide. After 4 hr. more copper bronze was added and refluxing continued. After a further 2 hr. the mixture was filtered, the residue was extracted with ethanol, benzene, or dimethylformamide, and the extract boiled with charcoal and filtered. The filtrate was concentrated to give a crystalline product. By this means the following biaryls were prepared: 2,2′-dinitro-1,1′-binaphthyl (8·9 g.), m. p. 177°, from 1-iodo-2-nitronaphthalene (20 g.); 1,1′-dinitro-2,2′-binaphthyl (9 g.), m. p. 285° (lit.,[8] m. p. 284°), from 2-iodo-1-nitronaphthalene (20 g.), and 5,6,7,8,5′,6′,7′,8′-octahydro-3,3′-dinitro-2,2′-binaphthyl (20 mg.), m. p. 195° (lit., m. p. 201°), from 1,2,3,4-tetrahydro-6-iodo-7-nitronaphthalene (150 mg.).

1-Chloro-2,6-dinitrobenzene (3 g.), gave *m*-dinitrobenzene (1·5 g.), m. p. 87°; and 9-bromo-10-nitrophenanthrene (2 g.) gave 9-nitrophenanthrene (1·2 g.), m. p. 115° (lit., m. p. 116°) [picrate, m. p. 98—99° (lit., m. p. 98—99°)]. In the absence of copper powder, 9-bromo-10-nitrophenanthrene was recovered unchanged.

In two other cases better yields were obtained without dimethylformamide, as follows. Activated copper bronze (3 g.) was added in small portions to the heated (150—160°) 4-bromo-1-iodo-2-nitronaphthalene [23] (2 g.) during 40 min. The cooled mass was repeatedly extracted with ethanol and the extracts were boiled with charcoal, filtered, and concentrated to give 4,4′-*dibromo*-2,2′-*dinitro*-1,1′-*binaphthyl* (0·1 g.), yellow rhombs (from acetone), m. p. 241° (Found: C, 47·8; H, 2·0; N, 5·65; Br, 31·9. $C_{20}H_{10}ON_2Br_2$ requires C, 47·8; H, 2·0; N, 5·58; Br, 31·9%).

[21] Hodgson and Walker, *J.*, 1933, 1205.
[22] *Idem*, *J.*, 1933, 1620.
[23] Meldola and Desch, *J.*, 1892, **61**, 765.

9-Bromo-10-nitrophenanthrene [24] (2 g.) was similarly treated, but in this case the temperature was slowly raised to 200°. From an extract in toluene was obtained 10,10′-*dinitro*-9,9′-*biphenanthryl* (80 mg.), pale brown crystals (from toluene solution filtered through alumina), m. p. 345° (decomp.) (Found: C, 75·8; H, 4·1; N, 6·1. $C_{28}H_{16}O_4N_2$ requires C, 75·8; H, 3·6; N, 6·3%).

Reduction of Dinitrobiaryls with Lithium Aluminium Hydride.—2,2′-*Dinitro*-1,1′-*binaphthyl.* Lithium aluminium hydride (2 g.) in ether (200 ml.) was added dropwise to 2,2′-dinitro-1,1′-binaphthyl (3 g.) in ether (500 ml.). After 45 min. water was added. The resulting precipitate was filtered off and extracted with ether. The extract and filtrate were concentrated to 200 ml., then extracted with 1 : 1 hydrochloric acid. The extract was made alkaline, and the resulting precipitate was washed with ether and recrystallised from acetone, to give compound (III) (0·6 g.), m. p. 270° (lit., m. p. 267—268°). A red tar is also produced which appears to be a complex mixture of azo-compounds. The base (III) is soluble in organic liquids and in acids. From acid solution it is reprecipitated by alkali. It forms a colourless solution when boiled with zinc dust and hydrochloric acid but the product is readily oxidised to the original substance. With saturated picric acid in ethanol, compound (III) gave *benzo*[f]*naphtho*[2,1-c]-*cinnoline monopicrate*, m. p. 182° (Found: C, 60·7; H, 3·15; N, 13·0. $C_{26}H_{15}O_7N_5$ requires C, 61·4; H, 2·95; N, 13·8%).

4,4′-Dibromo-2,2′-dinitro-1,1′-dinaphthyl (70 mg.) was reduced by a similar procedure; the product, purified chromatographically on alumina, gave 5,10-*dibromobenzo*[f]*naphtho*[2,1-c]-*cinnoline* (11 mg.), yellow needles (from acetone), m. p. 277° (Found: C, 54·2; H, 1·9. $C_{20}H_{10}NBr_2$ requires C, 54·8; H, 2·3%).

The substance (III) (125 mg.) in ethanol (150 ml.) when refluxed with methyl iodide (40 ml.) for 7 hr. yielded *benzo*[f]*naphtho*[2,1-c]*cinnoline methotri-iodide* (210 mg.) as red blades with a copper lustre (from acetone), m. p. 207° (Found: C, 37·0; H, 2·4; N, 4·05; I, 56·8. $C_{21}H_{15}N_2I_3$ requires C, 37·3; H, 2·2; N, 4·1; I, 56·3%).

Reduction of compound (III) (44 mg.) with sodium amalgam in methanol gave 2,2′-diamino-1,1′-binaphthyl (31 mg.), m. p. 184°, mixed with 2,2′-diamino-1,1′-binaphthyl (m. p. 191°) m. p. 191°.

1,1′-*Dinitro*-2,2′-*binaphthyl.*—Dinitrobinaphthyl (3 g.) and benzene (500 ml.) were dried by distillation until about 150 ml. of benzene were removed. Lithium aluminium hydride (3 g.) in ether (200 ml.) was added and the mixture was refluxed for 15 min., then stirred at room temperature during 4 hr. Water was added and the solution filtered. The filtrate was concentrated to give crystals, which were recrystallised from acetic acid, of *benzo*[h]*naphtho*[1,2-c]*cinnoline* (I), yellow needles (from acetone), m. p. 266°. A red-green dichroic solution was given in concentrated sulphuric acid (Found: C, 85·3; H, 4·0; N, 9·1. $C_{20}H_{12}N_2$ requires C, 85·7; H, 4·3; N, 10·0%). It gave a *hemipicrate*, m. p. 245° (decomp.) (Found: C, 69·8; H, 3·5; N, 12·8. $C_{46}H_{27}O_7N_7$ requires C, 70·0; H, 3·4; N, 12·4%).

Reduction of compound (I) (24 mg.) with sodium amalgam in methanol gave 1,1′-diamino-2,2′-binaphthyl (14 m.g), m. p. 273°, mixed m. p. 273°. Reduced with zinc dust in acetic acid, the base (I) (33 mg.) gave dibenz[*a*,*i*]carbazole (16 mg.), m. p. 211° [lit., m. p. 216°; picrate, m. p. 237° (lit., m. p. 238°)]. Reduced with lithium aluminium hydride, the base (I) (36 mg.) gave a dihydrobenzo[*h*]naphtho[1,2-*c*]cinnoline (14 mg.), m. p. 186°.

When the reduction of 1,1′-dinitro-2,2′-binaphthyl was continued under reflux for 18 hr. the addition of water and filtration gave a pale green fluorescent filtrate which, with hydrochloric acid (1 ml.) yielded a red precipitate. The separated solid was washed with benzene and boiled with aqueous ammonia· It gave 5(?),6(?)-*dihydrobenzo*[h]*naphtho*[1,2-c]*cinnoline* (0·5 g.) as yellow rhombs (from acetone), m. p. 186—187° (Found: C, 84·6; H, 4·8; N, 9·0. $C_{20}H_{14}N_2$ requires C, 85·1; H, 5·0; N, 9·9%). The compound, *e.g.*, in acetone, was oxidised in air to the parent cinnoline.

5,6,7,8,5′,6′,7′,8′-*Octahydro*-3,3′-*dinitro*-2,2′-*binaphthyl.*—The binaphthyl (21 mg.), reduced by a similar method, gave a product which after chromatography on alumina yielded yellow needles (from benzene) of 2,3,4,5,9,10,11,12-*octahydrobenzo*[g]*naphtho*[2,3-c]*cinnoline* (8 mg.), m. p. 264° (Found: C, 82·8; C, 6·75. $C_{20}H_{20}N_2$ requires C, 83·3; H, 6·95%).

10,10′-Dinitro-9,9′-biphenanthryl (30 mg.), reduced similarly, gave a yellow substance which did not melt at 360° and was different from the compound reported [2] as being (IV), m. p. 290°. Insufficient material was obtained for analysis.

[24] Callow and Gulland, *J.*, 1929, 2424.

Reduction with Sodium Amalgam and Methanol.—*2,2′-Dinitro-1,1′-binaphthyl.* Sodium amalgam (2%; 100 g.) was added to the binaphthyl (1 g.) in methanol (300 ml.). After 12 hr. the mixture was concentrated. The precipitate formed when the solution cooled was identified as 2,2′-diamino-1,1′-binaphthyl (0·7 g.), colourless crystals (from benzene–light petroleum), m. p. 190° (lit., m. p. 187°) [acetyl derivative, m. p. 228° (lit., m. p. 235—236°)]. 1,1′-Dinitro-2,2′-binaphthyl in benzene (400 ml.), reduced similarly, gave 1,1′-diamino-2,2′-binaphthyl (0·5 g.), m. p. 273° (lit., m. p. 281°) [acetyl derivative, m. p. 227° (lit., m. p. 229—230°)].

Reduction with Sodium Sulphide.—2,2′-Dinitro-1,1′-binaphthyl (1·4 g.) in ethanol (200 ml.) with hydrated sodium sulphide (2 g.), sodium hydroxide (0·5 g.), and water (20 ml.) was refluxed for 3 hr., concentrated to 100 ml., and poured into water. The resulting precipitate recrystallised from acetone as yellow needles (0·85 g.), identified as benzo[*f*]naphtho[2,1-*c*]cinnoline *N*-oxide, m. p. 252° [lit., m. p. 247—248° (decomp.)] (Found: O, 5·4. $C_{20}H_{12}ON_2$ requires O, 5·4%). Reduction of the oxide with stannous chloride or with lithium aluminium hydride gave base (III).

1,1′-Dinitro-2,2′-dinaphthyl (1 g.) was dissolved in benzene (400 ml.), then reduced with sodium sulphide as above after addition of ethanol (400 ml.). The product gave yellow needles (from acetone) of benzo[*h*]naphtho[1,2-*c*]cinnoline *N*-oxide (0·22 g.), m. p. 255—257°, mixed with specimen formed from the cinnoline (see below) m. p. 258°. Reduction of the oxide with stannous chloride or lithium aluminium hydride gave base (I).

Reduction with Zinc Dust and Potassium Hydroxide.—To 2,2′-dinitro-1,1′-binaphthyl (2 g.) in ethanol (600 ml.) was added potassium hydroxide solution, then zinc dust (25 g.). After refluxing for 30 min. the solution, when concentrated, yielded benzo[*f*]naphtho[2,1-*c*]cinnoline (1·2 g.), m. p. 258—260° (lit., m. p. 267—268°), which gave a purple colour with sulphuric acid (*d* 1·84). With less zinc (10 g.), benzo[*f*]naphtho[2,1-*c*]cinnoline *N*-oxide (0·6 g.), m. p. 246° (lit., m. p. 247—248°), was obtained, which gave a brown colour with sulphuric acid.

By a similar method (large excess of zinc) 4,4′-dibromo-2,2′-dinitro-1,1′-binaphthyl gave benzo[*f*]naphtho[2,1-*c*]cinnoline (7·5 mg.), m. p. and mixed m. p. 261° (lit., m. p. 267°) {mixed with 5,10-dibromobenzo[*f*]naphtho[2,1-*c*]cinnoline, m. p. 220—230°}.

1,1′-Dinitro-2,2′-dinaphthyl (1 g.) required refluxing for 4 hr. to give benzo[*h*]naphtho[1,2-*c*]-cinnoline (0·34 g.), m. p. 263—265°, which gave a red-green dichroic solution in sulphuric acid. 10,10′-Dinitro-9,9′-diphenanthryl required a reduction time of 14 hr. The precipitate was separated and extracted with ethanol (which removed unchanged diphenanthryl), then with chloroform. The chloroform solution gave yellow needles which did not melt at 360°, in too small a yield for analysis. The product gave a deep blue colour with sulphuric acid.

Oxidation of Cinnolines with Hydrogen Peroxide.—Hydrogen peroxide (80%; 2 ml.) was added to compound (III) (67 mg.) in acetic acid (20 ml.) at 0°. After 18 hr. and on concentration, benzo[*f*]naphtho[2,1-*c*]cinnoline *N*-oxide (47 mg.), m. p. and mixed m. p. 252·5°, was precipitated. By a similar process benzo[*c*]cinnoline (75 mg.) gave its *N*-oxide (35 mg.), m. p. 140° (lit., m. p. 139°). Compound (I) (0·16 g.) gave *benzo*[h]*naphtho*[1,2-c]*cinnoline* N-*oxide* (0·11 g.), yellow needles (from ethanol or acetone), m. p. 259° (Found: C, 80·8; H, 4·4; N, 9·6. $C_{20}H_{12}ON_2$ requires C, 81·0; H, 4·1; N, 9·45%).

Nitration of Compound (III).—The compound (III) (1 g.) was nitrated at 18° with nitric acid (*d* 1·5; 5 ml.) for 2 days. w,x-*Dinitrobenzo*[f]*naphtho*[2,1-c]*cinnoline* (0·24 g.) separated, giving yellow rhombs (from nitrobenzene), m. p. 337° (Found: C, 64·2; H, 2·9; N, 14·5. $C_{20}H_{10}O_4N_4$ requires C, 64·8; H, 2·7; N, 15·1%). With stannous chloride (1 g.) in hydrochloric acid (50 ml.) at 100°, the dinitro-compound (0·24 g.) gave impure *w,x*-diaminobenzo[*f*]naphtho[2,1-*c*]-cinnoline hemihydrate (62 mg.) as dark red needles (from aqueous dimethylformamide), m. p. 360° [Found: C, 74·2; H, 4·7. Calc. for $C_{20}H_{10}N_2(NH_2)_2,\frac{1}{2}H_2O$: C, 75·2; H, 4·7. Calc. for $C_{20}H_{10}N_2(NH_2)_2$: C, 77·5; H, 4·5. Calc. for $C_{20}H_{10}N_2(NH_2)\cdot NO_2$: C, 70·7; H, 3·55%). The tetrazotised diamine (60 mg.), when treated with cuprous bromide in hydrobromic acid, gave w,x-*dibromobenzo*[f]*naphtho*[2,1-c]*cinnoline* (11 mg.) as yellow plates (from acetone–ethanol), m. p. 293—297° {mixed m. p. with 5,10-dibromobenzo[*f*]naphtho[2,1-*c*]cinnoline (m. p. 277°) 230—245°} (Found: C, 52·7; H, 2·3; N, 6·2; Br, 35·5. $C_{20}H_{10}N_2Br_2$ requires C, 54·8; H, 2·3; N, 6·4; Br, 36·6%).

The filtrate from the nitration of compound (III) was left at 18° for 2 days. y,z-*Dinitrobenzo*[f]*naphtho*[2,1-c]*cinnoline* (0·22 g.) separated as pale yellow needles (from nitrobenzene), m. p. 324° {mixed with *w,x*-dinitrobenzo[*f*]naphtho[2,1-*c*]cinnoline, m. p. 280—290°} (Found: C, 65·7; H, 2·6; N, 14·8. $C_{20}H_{10}O_4N_2$ requires C, 64·8; H, 2·7; N, 15·1%). With stannous

chloride (0·5 g.) in hydrochloric acid the dinitro-compound (30 mg.) was reduced and the solution gave a red powder with excess of alkali; this product was passed in solution in ethanol through an alumina column. The diluted eluate gave y,z-*diaminobenzo*[f]*naphtho*[2,1-c]*cinnoline hemihydrate*, m. p. 296° [Found: C, 75·6; H, 5·1. $C_{20}H_{10}N_2(NH_2)_2,\frac{1}{2}H_2O$ requires C, 75·2; H, 4·7%).

Nitration of Compound (I).—To the base (0·1 g.) was added nitric acid (*d* 1·5; 1·5 ml.) at 0°. The mixture was kept 6 days at 18°. The resulting x,y-*dinitrobenzo*[h]*naphtho*[1,2-c]*cinnoline* (90 mg.) was filtered off, and formed yellow crystals (from nitrobenzene), m. p. 345° (Found: C, 64·3; H, 2·84; N, 14·3%).

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