726. *Polycyclic Cinnoline Derivatives. Part V.*[1] *Some Unsymmetrical Polycyclic Cinnolines.*

By J. F. Corbett and P. F. Holt.

The preparation of two new cinnoline derivatives by the reduction of dinitrobiaryls is described, together with a study of these and other polycyclic derivatives of cinnoline. Tentative structures have been ascribed to the *N*-oxides and quaternary salts of the unsymmetrical cinnolines. The formation of stable salts is a general property of these cinnolines.

Part II [2] of this series described the preparation and some of the properties of symmetrical polycyclic derivatives of cinnoline. Reduction of *oo'*-dinitrobiaryls was suggested as a general method for their preparation. We have now obtained the compounds (I)—(III) by similar methods. Naphtho[2,1-*c*]cinnoline (II) has been prepared by Badger and Walker by the oxidation of 1-*o*-aminophenyl-2-naphthylamine with permonosulphuric acid.[3]

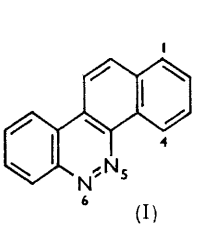
The necessary unsymmetrical *oo'*-dinitrobiaryls were prepared by mixed Ullmann reactions. Whaley *et al.*[4] described the preparation of 1-nitro-2-*o*-nitrophenylnaphthalene by a mixed Ullmann reaction without a solvent; they did not state the yield. Repetition of this method gave variable results, the maximum yield being 15%. Employing an excess of *o*-bromonitrobenzene with 2-bromo-1-nitronaphthalene in dimethylformamide gives yields of up to 30% of the unsymmetrical biaryl. 1',2-Dinitro-1,2'-binaphthyl was prepared by the method of Ward and Pearson [5] and 2-nitro-1-*o*-nitrophenylnaphthalene was obtained by a similar method, the reactions being carried out below 170° in order to avoid the formation of 2,2'-dinitro-1,1'-binaphthyl. The use of dimethylformamide resulted, in each case, in the formation of all three possible products, inseparable by crystallisation or chromatography.

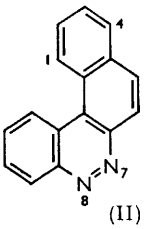
1-Nitro-2- and 2-nitro-1-*o*-nitrophenylnaphthalene, and 1',2-dinitro-1,2'-binaphthyl, are reduced to the cinnolines (I), (II), and (III), respectively, by lithium aluminium hydride or by zinc and potassium hydroxide in aqueous ethanol. Reduction with sodium amalgam in methanol gives the corresponding diaminobiaryls; under similar conditions the cinnolines are also reduced to diamines. It has previously been shown that 1,1'-dinitro-2,2'-binaphthyl and 2,2'-dinitro-1,1'-binaphthyl and the corresponding cinnolines (IV) and (V) give the diaminobinaphthyls under these conditions.[2] On the other hand, 2,2'-dinitrobiphenyl is reduced to *NN'*-dihydrobenzo[*c*]cinnoline with sodium amalgam in methanol,[6] and the reagent has been used to prepare a number of substituted benzo[*c*]-cinnolines.[7] Thus reductive fission of the −N=N− bond occurs more readily with the higher polycyclic derivatives than with benzo[*c*]cinnoline.

The reduction of *oo'*-dinitrobiaryls with sodium sulphide and sodium hydroxide in aqueous ethanol has been shown to give the cinnoline *N*-oxide.[8] 1-Nitro-2-*o*-nitrophenyl-naphthalene and 1',2-dinitro-1,2'-binaphthyl with this reagent give single products which are, in each case, identical with the products of the oxidation of the corresponding cinnoline with peracetic acid. Reduction of 2-nitro-1-*o*-nitrophenylnaphthalene under similar conditions, or oxidation of naphtho[2,1-*c*]cinnoline (II), gives, probably, a mixture of the two isomeric *N*-oxides. It appears that only one of the nitrogen atoms in naphtho-[1,2-*c*]cinnoline and in benzo[*f*]naphtho[1,2-*c*]cinnoline can readily co-ordinate to an

[1] Part IV, preceding paper.
[2] Braithwaite and Holt, *J.*, 1959, 3025.
[3] Badger and Walker, *J.*, 1956, 122.
[4] Whaley, Meadow, and Robinson, *J. Org. Chem.*, 1954, **19**, 973.
[5] Ward and Pearson, *J.*, 1959, 3378.
[6] Tauber, *Ber.*, 1891, **24**, 3081.
[7] Kenner and Stubbins, *J.*, 1921, 593; Meyer, *Ber.*, 1893, **26**, 2238; Braithwaite, Holt, and Hughes, *J.*, 1958, 4073.
[8] (*a*) Ullmann and Dieterle, *Ber.*, 1904, **37**, 23; (*b*) ref. 2.

oxygen atom. Molecular models and a scale diagram indicate considerable intramolecular overcrowding between an oxygen atom bonded to a nitrogen atom adjacent to the 1-position of a naphthalene nucleus, and the *peri*-hydrogen atom. There is however no such overcrowding if the oxygen is in the alternative position. On this basis we suggest that the *N*-oxides of naphtho[1,2-*c*]cinnoline and benzo[*f*]naphtho[1,2-*c*]cinnoline are the 6-oxides. These results are similar to those of Badger and Lewis, who studied the oxidation of diaryl azo-compounds.[9] Our suggestion is also supported by a study of quaternary salt formation by the polycyclic derivatives of cinnoline. Quaternisation, by refluxing the cinnoline with freshly distilled methyl iodide in nitromethane, was manifested by considerable darkening of the solution. Quaternary salts were given by the cinnolines (I), (II), (III), and (V); a methotri-iodide of the latter has been described,[2] and benzo[*c*]-cinnoline methiodide has been prepared.[10] Benzo[*h*]naphtho[1,2-*c*]cinnoline (IV), in


(I)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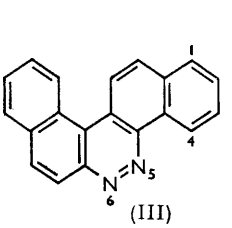
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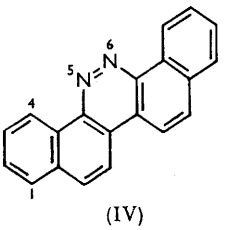

(IV)

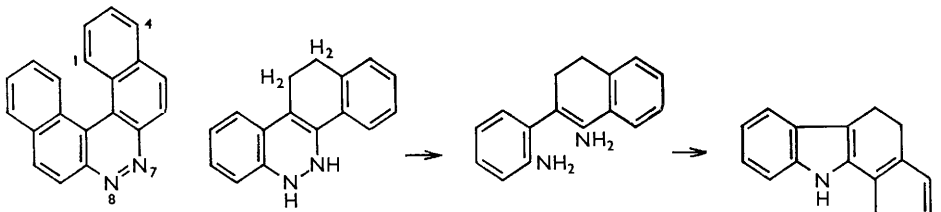
which co-ordination to both nitrogen atoms is hindered, was recovered after 12 hr. under reflux; no darkening of the reaction mixture occurred. Thus, while this cinnoline gives an *N*-oxide on oxidation,[2] the more bulky methyl group cannot be accommodated. This indicates that steric effects are of prime importance in these reactions. The methiodides of naphtho[1,2-*c*]cinnoline (I) and benzo[*f*]naphtho[1,2-*c*]cinnoline (III) are probably quaternised at the 6-nitrogen atom, and the product obtained from naphtho[2,1-*c*]cinnoline (II) is probably a mixture of two isomeric methiodides.

Like the *N*-oxides of the symmetrical polycyclic derivatives of cinnoline,[2] the *N*-oxides of the unsymmetrical derivatives are reduced to the parent cinnolines by lithium aluminium hydride or, less well, by stannous chloride and hydrochloric acid. With excess of either reagent reduction proceeds to the *NN'*-dihydro-cinnoline; this was evident from the formation of a colourless solution, but these dihydro-derivatives are readily oxidised in air to the cinnoline and were not isolated.

Reduction of benzo[*c*]cinnoline with zinc and acetic acid has been shown to give the unstable *NN'*-dihydrobenzo[*c*]cinnoline.[6] Schönberg and Rosenthal reported that dibenzo[*f*,*h*]phenanthro[9,10-*c*]cinnoline was not attacked by this reagent,[11] but it seems likely that the unstable dihydro-derivative was formed but not isolated. Benzo[*h*]naphtho-[1,2-*c*]cinnoline is reduced to dibenzo[*a*,*i*]carbazole by zinc and acetic acid.[2] Meisenheimer and Witte reported the reduction of benzo[*f*]naphtho[2,1-*c*]cinnoline (V) to 2,2'-diamino-1,1'-binaphthyl after $\frac{3}{4}$ hour's refluxing.[12] We have made a systematic study of the reduction of polycyclic cinnoline derivatives with this reagent, and find that reduction to the *NN'*-dihydro-cinnoline is rapid—a sample removed from the reaction mixture 1 min. after the addition of the zinc dust decolorises Methylene Blue solution.[13] Further reduction is slow, between 2 and 6 hr. being necessary. Benzo[*c*]cinnoline and phenanthro-[9,10-*c*]cinnoline were not reduced beyond the *NN'*-dihydrocinnoline after 12 hours' refluxing. Contrary to the results of Meisenheimer and Witte,[12] we recovered benzo[*f*]-naphtho[2,1-*c*]cinnoline after $\frac{3}{4}$ hour's refluxing, but obtained dibenzo[*c*,*g*]carbazole with

[9] Badger and Lewis, *J.*, 1953, 2151.
[10] Wohlfahrt, *J. prakt. Chem.*, 1902, **65**, 295; Ullmann and Dieterle, ref. 8(*a*).
[11] Schönberg and Rosenthal, *Ber.*, 1921, **54**, 1789.
[12] Meisenheimer and Witte, *Ber.*, 1903, **36**, 4153.
[13] Cf. Wittig and Stichnoth, *Ber.*, 1935, **68**, 928.

reaction times of 2—6 hr. Naphtho[2,1-*c*]cinnoline (II) and benzo[*f*]naphtho[1,2-*c*]-cinnoline (III) give benzo[*c*]carbazole and dibenzo[*a*,*g*]carbazole respectively. Naphtho-[1,2-*c*]cinnoline (I) is not readily reduced beyond the *NN'*-dihydro-cinnoline, but after 12 hours' refluxing with zinc and acetic acid we obtained impure 5,6-dihydrobenzo[*a*]-carbazole (VIII), m. p. 151—153°; the m. p. was not raised to that of authentic 5,6-di-hydrobenzo[*a*]carbazole (VIII), m. p. 163—164°, after repeated recrystallisation and



(V) (VI) (VII) (VIII)

chromatography on alumina. However, the mixed m. p. with the authentic sample was 156—158°, and the m. p.s of the picrate and the tetrachlorophthalic anhydride addition compound of the two samples were in close agreement. The ultraviolet absorption spectra of authentic 5,6-dihydrobenzo[*a*]carbazole ($\lambda_{max.}$ 242, 248, 305, 316, 327, and 342 mμ) and of the sample obtained from the reduction of the cinnoline ($\lambda_{max.}$ 242, 248, 276, 305, 316, 327, and 342 mμ) support the assignment of this structure. The additional peak, at 276 mμ, in the spectrum of the impure sample indicates that the impurity may be benzo[*a*]-carbazole which absorbs strongly in this region.[15] It seems likely that the reduction takes place in four stages, *via* 5,6-dihydronaphtho[1,2-*c*]cinnoline, 5,6,11,12-tetrahydronaphtho-[1,2-*c*]cinnoline (VI), and 2-*o*-aminophenyl-3,4-dihydro-1-naphthylamine (VII), which is then deaminated to 5,6-dihydrobenzo[*a*]carbazole (VIII). In support, we find that benzo[*a*]carbazole is not reduced by zinc and acetic acid. The suggested intermediate (VI) is, on the basis of Robinson and Robinson's mechanism for the Fischer indole synthesis,[16] the intermediate in the synthesis of 5,6-dihydrobenzo[*a*]carbazole from α-tetralone and phenylhydrazine. The dihydrocarbazole gives the carbazole when refluxed with chloranil in xylene.

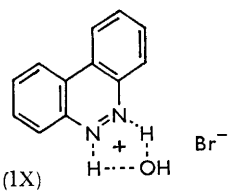
It is noteworthy that, of the polycyclic derivatives of cinnoline which we have investigated, only those in which at least one of the nitrogen atoms is attached to a naphthalene ring system can be reduced beyond the *NN'*-dihydrocinnoline stage. The resistance to reductive fission, in non-acidic media, of the $-N=N-$ bond in benzo[*c*]cinnoline has been noted above. Reduction of *oo'*-dinitrobiaryls, in which at least one of the aryl groups is naphthyl, with zinc and acetic acid gives the corresponding carbazole. 2,2'-Dinitro-biphenyl gives 2,2'-diaminobiphenyl under similar conditions. This indicates that amino-groups attached to a naphthalene nucleus are more readily removed than those attached to a benzene nucleus. McNae, using ^{15}N-labelled 1-nitro-2-*o*-nitrophenylnaphthalene, has shown that the nitrogen atom attached to the naphthalene nucleus is eliminated in carbazole formation under the conditions used by us.[17]

The tetrachlorophthalic anhydride addition compounds of the carbazoles, which have been recommended as superior to picrates as derivatives,[18] are described.

The formation of simple salts of unsubstituted polycyclic cinnolines has not previously been reported. We find that these cinnolines readily give perchlorates, sulphates, hydro-chlorides, and hydrobromides. The salts are stable in air and to moderate heat (up to 150°); they are hydrolysed slowly in cold water and rapidly in hot water. The sulphates

[14] Rogers and Corson, *Org. Synth.*, 1950, **30**, 91.
[15] Clemo and Felton, *J.*, 1952, 1658.
[16] Robinson and Robinson, *J.*, 1924, **125**, 827.
[17] McNae, unpublished work.
[18] Büu-Hoi and Jacquignon, *Compt. rend.*, 1952, **234**, 1056.

contain one molecule of the cinnoline to one of sulphuric acid. The perchlorates have well-defined melting points but the other salts decompose slowly below their melting points. The salts can be used for the determination of the equivalent weights of cinnolines by hydrolysis of the salt in boiling water and titration of the liberated acid with sodium hydroxide; the perchlorates are the most suitable salt for this purpose. The hydrochlorides and hydrobromides are precipitated from acetone solutions of the cinnoline as monohydrates, probably as the result of the formation of the resonance-stabilised cinnolineoxonium ion (IX). The anhydrous salts are precipitated from solutions of the cinnoline in carbon tetrachloride. The perchlorates and sulphates are not hydrated.



(IX)

The ease of salt formation of the cinnolines gives a useful method of separating them from non-basic and weakly basic compounds, in particular from azo-compounds which often occur as by-products in cinnoline synthesis. For the latter purpose the hydrochlorides and hydrobromides are the most useful since azo-compounds form perchlorates.[19] Using salt-precipitation we have obtained yields of up to 43% in the preparation of naphtho[2,1-*c*]cinnoline (II) from 1-*o*-aminophenyl-2-naphthylamine by the method of Badger and Walker, who isolated only 12%.[3] As a result of this, the oxidation of the diamine appears to be the method of choice for the preparation of this cinnoline.

Benzo[*c*]cinnoline forms a dipicrate,[20] benzo[*f*]naphtho[2,1-*c*]cinnoline (V) a monopicrate and benzo[*h*]naphtho[1,2-*c*]cinnoline (IV) a hemipicrate.[2] The three unsymmetrical cinnoline derivatives described in this paper form monopicrates. The picrates are the normal intermolecular addition compounds rather than salts and appear to be more stable than the picrates either of polycyclic aromatic hydrocarbons or of carbazoles, which decompose in moist air.

Experimental

Halogenonitroarenes.—These compounds were prepared from the corresponding aminonitroarenes by the Sandmeyer procedure according to published methods.

Symmetrical oo′-*Dinitrobiaryls.*—2,2′-Dinitrobiphenyl was prepared by Kornblum and Kendall's method.[21] 1,1′-Dinitro-2,2′- and 2,2′-dinitro-1,1′-binaphthyl were prepared by Braithwaite and Holt's methods.[2]

Symmetrical Polycyclic Derivatives of Cinnoline.—Benzo[*c*]cinnoline, m. p. 156° (lit., m. p. 156°), was prepared by the method of Badger, Seidler, and Thomson.[22] Benzo[*f*]naphtho[2,1-*c*]-cinnoline and benzo[*h*]naphtho[1,2-*c*]cinnoline were prepared by reduction of the corresponding dinitrobiaryls with lithium aluminium hydride according to Braithwaite and Holt's method.[2]

Oxidation of 1-o-*Aminophenyl-2-naphthylamine with Permonosulphuric Acid.*—The reaction was carried out according to the method of Badger and Walker.[3] The precipitate, obtained by pouring the reaction mixture into water, was washed with water, dried, and dissolved in acetone. Hydrogen bromide was passed into the solution to precipitate the cinnoline hydrobromide which was filtered off and hydrolysed by recrystallisation from aqueous ethanol. Recrystallisation from benzene–hexane gave naphtho[2,1-*c*]cinnoline (43%), m. p. 157° (lit., m. p. 156·5—157·5°).

1-*Nitro*-2-o-*nitrophenylnaphthalene.*—Copper bronze (6 g.) was added to a solution of 2-bromo-1-nitronaphthalene (5 g.) and *o*-bromonitrobenzene (6 g.) in dimethylformamide (80 ml.). The mixture was heated under reflux for 6 hr., then filtered from remaining copper while still hot, and the copper was extracted with hot dimethylformamide (25 ml.). The combined filtrate and extract were poured into water (800 ml.), and the precipitate was filtered off, dried, and extracted with hot ethanol (500 ml.). The alcoholic extract was concentrated to half-bulk and allowed to cool; crude 1-nitro-2-*o*-nitrophenylnaphthalene separated and crystallised from ethanol–ethyl acetate (2 : 1 v/v) as buff crystals (1·5 g.), m. p. 183—185° (lit.,[4]

[19] Hoffmann, Metzler, and Hobold, *Ber.*, 1910, **43**, 1080.
[20] Sandin and Cairns, *J. Amer. Chem. Soc.*, 1936, **58**, 2019; Slack and Slack, *Nature*, 1947, **160**, 437.
[21] Kornblum and Kendall, *J. Amer. Chem. Soc.*, 1952, **74**, 5782.
[22] Badger, Seidler, and Thomson, *J.*, 1951, 3207.

m. p. 185—186°). Extraction of the ethanol-insoluble residue with benzene gave 1,1′-dinitro-2,2′-binaphthyl (0·9 g.), m. p. and mixed m. p. 285°. The alcoholic mother-liquor gave, on further concentration, 2,2′-dinitrobiphenyl (0·95 g.), m. p. and mixed m. p. 122°.

2-*Nitro*-1-o-*nitrophenylnaphthalene*.—Copper bronze (4·5 g.) was added portionwise, with constant stirring, in ¾ hr., to a molten mixture of 1-iodo-2-nitronaphthalene (3 g.) and *o*-iodonitrobenzene (3 g.) at 165°. The temperature was then raised to 200° and heating continued for a further ½ hr. The mixture was cooled and extracted with ethanol. The extract was evaporated to low bulk and set aside to cool; 2-*nitro*-1-o-*nitrophenylnaphthalene* separated as yellow prisms (0·38 g.), m. p. 98° (Found: C, 65·4; H, 3·4; N, 9·8. $C_{16}H_{10}N_2O_4$ requires C, 65·4; H, 3·4; N, 9·5%). Further concentration of the mother-liquor gave mainly 2,2′-dinitrobiphenyl.

2,1′-*Dinitro*-1,2′-*binaphthyl*.—This compound was prepared by the method of Ward and Pearson.[5] The cooled mixture was extracted with boiling ethanol. The extract was evaporated to low bulk, and the crude biaryl recrystallised from 1 : 1 (v/v) ethanol–ethyl acetate to give orange-yellow rhombs, m. p. 175—178° (lit.,[5] m. p. 174—176°).

Naphtho[1,2-c]*cinnoline*.—1-Nitro-2-*o*-nitrophenylnaphthalene (1 g.) in 1 : 1 (v/v) dry benzene–ether (300 ml.) was treated with lithium aluminium hydride (1·7 g.) in dry ether (100 ml.), left at room temperature for 6 hr., then warmed on a water bath for ½ hr., and allowed to cool. Excess of hydride was decomposed by water, and the solids were filtered off and extracted with hot benzene. The combined filtrate and extract was evaporated to low bulk and the crude cinnoline precipitated by addition of light petroleum (b. p. 60—80°). Recrystallisation from ethanol gave *naphtho*[1,2-c]*cinnoline* (2·4 g.) as yellow needles, m. p. 190° (Found: C, 83·3; H, 4·5; N, 12·2. $C_{16}H_{10}N_2$ requires C, 83·4; H, 4·4; N, 12·2%), giving an orange-green dichroic solution in concentrated sulphuric acid. *Naphtho*[1,2-c]*cinnoline monopicrate* separates from ethanol as bright yellow needles, m. p. 216° (decomp.) (Found: C, 57·7; H, 3·0; N, 15·9. $C_{22}H_{13}N_5O_7$ requires C, 57·5; H, 2·8; N, 15·3%). The *perchlorate*, m. p. 250—252° (decomp.), was obtained as yellow needles by warming a solution of the cinnoline in acetic acid with 65% (w/v) aqueous perchloric acid and cooling (Found: C, 57·9; H, 3·5; Cl, 10·8. $C_{16}H_{10}N_2,HClO_4$ requires C, 58·0; H, 3·3; Cl, 10·7%). The hydrochloride and hydrobromide were obtained by passing the relevant gas into a solution of the cinnoline in acetone; the *hydrochloride hydrate* forms yellowish-green needles, decomp. >160° (Found: *M*, 283·0. $C_{16}H_{13}ClN_2O$ requires *M*, 284·5); the *hydrobromide hydrate* formed yellow needles, decomp. >200° (Found: C, 58·8; H, 4·2; N, 8·5; Br, 24·1. $C_{16}H_{13}BrN_2O$ requires C, 58·4; H, 4·0; N, 8·5; Br, 24.2%). The *sulphate* was precipitated by the addition of concentrated sulphuric acid to a solution of the cinnoline in acetone and had m. p. 290° (decomp.) (Found: *M*, 330·5. $C_{16}H_{12}N_2O_4S$ requires *M*, 328·0).

Naphtho[2,1-c]*cinnoline*.—2-Nitro-1-*o*-nitrophenylnaphthalene (0·25 g.) in 1 : 1 (v/v) benzene–ether was reduced with lithium aluminium hydride as described above. The crude product recrystallised from 1 : 1 (v/v) benzene–hexane as yellow leaflets (0·13 g.), m. p. 157° (lit.,[3] m. p. 156·5—157·5°); mixed with a sample, prepared by the method of Badger and Walker, it had m. p. 156°. This cinnoline gives a deep brown solution in concentrated sulphuric acid. *Naphtho*[2,1-c]*cinnoline monopicrate* forms yellow feathery needles from ethanol, m. p. 188° (decomp.) (Found: C, 57·7; H, 2·8; N, 15·4%). The *hydrochloride hydrate* decomposes above 180° (Found: *M*, 286·7). The *hydrobromide hydrate* decomposes above 200° (Found: *M*, 328·5. $C_{16}H_{13}BrN_2O$ requires *M*, 329·0). The *perchlorate* forms yellow needles, m. p. 240° (Found: C, 57·9; H, 3·4; Cl, 10·6%).

Benzo[f]*naphtho*[1,2-c]*cinnoline*.—2,1′-Dinitro-1,2′-binaphthyl (0·34 g.) in 1 : 1 (v/v) benzene–ether was reduced with lithium aluminium hydride as described above. *Benzo*[f]*naphtho*-[1,2-c]*cinnoline* crystallised as yellow needles (0·15 g.) (from ethanol), m. p. 184—185° (Found: C, 85·6; H, 4·2; N, 9·9. $C_{20}H_{12}N_2$ requires C, 85·7; H, 4·3; N, 10·0%). It gives a purple solution in concentrated sulphuric acid: the solution in benzene exhibits a blue fluorescence. *Benzo*[f]*naphtho*[1,2-c]*cinnoline monopicrate* forms yellow needles (from ethanol), m. p. 236° (decomp.) (Found: C, 61·0; H, 2·8; N, 13·7. $C_{26}H_{15}N_5O_6$ requires C, 61·4; H, 2·9; N, 13·8%). Micro-scale experiments indicated that this cinnoline forms salts similar to those described above for the naphthocinnolines.

Reduction of oo′-*Dinitrobiaryls with Zinc and Potassium Hydroxide*.—The biaryl (0·25 g.) in ethanol (150 ml.) and 40% w/v aqueous potassium hydroxide (15 ml.) was heated under reflux with zinc dust (7 g.) for 6 hr. The solid residue was filtered off and the filtrate was boiled with

charcoal, evaporated to low bulk, and poured into water to precipitate the cinnoline. 1-Nitro-2-*o*-nitrophenylnaphthalene gave naphtho[1,2-*c*]cinnoline (0·105 g.) as yellow needles (from ethanol), m. p. and mixed m. p. 190°. 2-Nitro-1-*o*-nitrophenylnaphthalene gave naphtho[2,1-*c*]-cinnoline (0·09 g.), m. p. and mixed m. p. 156°. 2,1′-Dinitro-1,2′-binaphthyl gave benzo[*f*]-naphtho[1,2-*c*]cinnoline as yellow needles (from ethanol), m. p. and mixed m. p. 185°.

Naphtho[1,2-c]*cinnoline* 6-*Oxide*.—1-Nitro-2-*o*-nitrophenylnaphthalene (0·5 g.) was dissolved in boiling ethanol (100 ml.), and a solution of hydrated sodium sulphide (1 g.) and sodium hydroxide (0·25 g.) in water (10 ml.) was added. The mixture was heated under reflux for 3 hr. After concentration, the mixture was poured into water, and the precipitate was filtered off and dissolved in ethanol. The solution was boiled with charcoal, filtered, and concentrated; on cooling, *naphtho*[1,2-c]*cinnoline* 6-*oxide* (0·19 g.) separated as yellow needles, m. p. 232° (Found: C, 77·8; H, 3·9; N, 11·5. $C_{16}H_{10}N_2O$ requires C, 78·0; H, 4·1; N, 11·4%); it gives a yellow solution in concentrated sulphuric acid.

Mixed Naphtho[2,1-c]*cinnoline* N-*Oxides*.—2-Nitro-1-*o*-nitrophenylnaphthalene (0·1 g.) reduced with sodium sulphide, as described above, gave a yellow mixture of the two naphtho-[2,1-*c*]cinnoline *N*-oxides, m. p. 130—140° (Found: C, 78·1; H, 4·2; N, 11·3%). The mixture gives a yellow solution in concentrated sulphuric acid.

Benzo[f]*naphtho*[1,2-c]*cinnoline* 6-*Oxide*.—2,1′-Dinitro-1,2′-binaphthyl (0·5 g.) was reduced with sodium sulphide as described above. *Benzo*[f]*naphtho*[1,2-c]*cinnoline* 6-*oxide* crystallises from ethanol as yellow needles, m. p. 210° (Found: C, 81·1; H, 4·0; N, 9·2. $C_{20}H_{12}N_2O$ requires C, 81·0; H, 4·1; N, 9·5%), giving a red-brown solution in concentrated sulphuric acid.

Oxidation of Cinnolines with Peracetic Acid.—The cinnoline (0·1 g.) in acetic acid (5 ml.) was treated with 80% w/v aqueous hydrogen peroxide (0·5 ml.) and left at room temperature for 5 hr., then poured into water. The precipitate was filtered off, dried, and recrystallised from ethanol. Naphtho[1,2-*c*]cinnoline and benzo[*f*]naphtho[1,2-*c*]cinnoline gave products identical with their 6-oxides. Naphtho[2,1-*c*]cinnoline gave mixed *N*-oxides, m. p. 132—145°. The yields were 75—85%.

Reduction of the Cinnoline N-*Oxides*.—The *N*-oxides were reduced to the corresponding cinnolines by lithium aluminium hydride in benzene–ether [22] or by stannous chloride in hydrochloric acid.[12] The former method gave the better yields, 90—95% compared with 40—55%.

Reduction of oo′-*Dinitrobiaryls with Sodium Amalgam in Methanol*.—The biaryl (0·2 g.) in methanol (40 ml.) was shaken with 5% w/w sodium amalgam (20 g.) for 3 hr. The solution was decanted from residual mercury and evaporated to low bulk. The diamine separated on cooling. 1-Nitro-2-*o*-nitrophenylnaphthalene gave 2-*o*-aminophenyl-1-naphthylamine (0·08 g.), m. p. 118—120° (lit.,[4] m. p. 118—119°), identified by conversion into benzo[*a*]carbazole (by refluxing acetic acid), m. p. 266° (lit.,[23] m. p. 266°). 2-Nitro-1-*o*-nitrophenylnaphthalene gave 1-*o*-amino-phenyl-2-naphthylamine (0·05 g.), m. p. and mixed m. p. 154° (lit.,[24] m. p. 156°). 2,1′-Dinitro-1,2′-binaphthyl gave 2,1′-diamino-1,2′-binaphthyl (0·04 g.), m. p. 146—147° (lit.,[25] 150—151°); the mixed m. p. with an authentic sample prepared by reduction of 1,2′-azonaphthalene and rearrangement of the hydrazo-compound, was 149°.[5] The corresponding cinnolines were reduced under similar conditions to the expected diaminobiaryls.

Reduction of oo′-*Dinitrobiaryls with Zinc and Acetic Acid*.—The biaryl (0·1 g.) in acetic acid (10 ml.) was heated under reflux with zinc dust (1 g.) for 2 hr. Excess of zinc was filtered off, and the filtrate was concentrated and poured into water. The precipitate was filtered off, dried, and recrystallised from aqueous acetic acid. 2,2′-Dinitrobiphenyl gave 2,2′-diaminobiphenyl (0·02 g.), m. p. 79° [(lit., m. p. 81°; diacetyl derivative, m. p. 161° (lit.,[26] m. p. 161°)]. 1-Nitro-2-*o*-nitrophenylnaphthalene gave benzo[*a*]carbazole (0·04 g.), m. p. 224° (lit.,[23] m. p. 226°) [picrate, m. p. 185° (lit.,[23] m. p. 185°)]; the *benzo*[a]*carbazole–tetrachlorophthalic anhydride addition compound* forms vermilion needles, m. p. 206—207°, from acetic acid (Found: C, 57·4; H, 2·0; Cl, 28·2. $C_{24}H_{11}Cl_4NO_3$ requires C, 57·3; H, 2·2; Cl, 28·2%). 2-Nitro-1-*o*-nitro-phenylnaphthalene gave benzo[*c*]carbazole (0·025 g.), m. p. 135° (lit.,[24] m. p. 135°) [picrate, red needles (from benzene), m. p. 174° (lit.,[24] m. p. 174—175°); *benzo*[c]*carbazole–tetrachlorophthalic anhydride addition compound*, orange needles, m. p. 202° (Found: C, 57·3; H, 2·1; Cl, 28·4%)].

[23] Ghigi, *Gazzetta*, 1931, **61**, 45.
[24] Fuchs and Nizel, *Ber.*, 1927, **60**, 209.
[25] Cook, Hewett, Kennaway, and Kennaway, *Amer. J. Cancer*, 1940, **40**, 62.
[26] Tauber, *Ber.*, 1891, **24**, 198.

2,2′-Dinitro-1,1′-binaphthyl gave dibenzo[*c*,*g*]carbazole (0·02 g.), m. p. 158° (lit.,[27] m. p. 158°), which gave a black picrate, m. p. 219° (lit.,[27] m. p. 219°), and *tetrachlorophthalic anhydride addition compound*, red needles (from acetic acid), m. p. 207° (Found: C, 60·3; H, 2·1; N, 2·7; Cl, 25·7. $C_{28}H_{13}Cl_4NO_3$ requires C, 60·7; H, 2·3; N, 2·5; Cl, 25·7%). 2,1′-Dinitro-1,2′-binaphthyl gave dibenzo[*a*,*g*]carbazole (0·05 g.) m. p. 230—231° (lit.,[28] 231°) [*tetrachlorophthalic anhydride addition compound*, vermilion needles (from acetic acid), m. p. 248° (Found: C, 60·9; H, 2·2; N, 2·5; Cl, 25·4%)].

Reduction of Cinnolines with Zinc and Acetic Acid.—The cinnoline (0·1 g.) in acetic acid (15 ml.) was heated under reflux with zinc dust (1 g.) for 2—12 hr. A sample withdrawn after 2 min. decolorised a solution of Methylene Blue in acetic acid; the reaction was considered to be complete when a sample no longer decolorised this reagent. The mixture was filtered hot and the filtrate poured into water to precipitate the product which was recrystallised from aqueous acetic acid. Benzo[*c*]cinnoline, m. p. and mixed m. p. 154° (lit.,[22] 156°), and phenanthro[9,10-*c*]cinnoline, m. p. and mixed m. p. 220—223° (lit.,[2] 224°), were recovered after 12 hr. at reflux temperature. Naphtho[2,1-*c*]cinnoline gave benzo[*c*]carbazole (0·04 g.), m. p. and mixed m. p. 133°. After 2 hours' refluxing benzo[*f*]naphtho[2,1-*c*]cinnoline gave dibenzo[*c*,*g*]carbazole (0·03 g.), m. p. and mixed m. p. 156°. Benzo[*f*]naphtho[1,2-*c*]cinnoline (4 hr.) gave dibenzo[*a*,*g*]carbazole (0·04 g.), m. p. and mixed m. p. 230°. Naphtho[1,2-*c*]cinnoline (12 hr.) gave a white powder, m. p. 151—153°, giving an analysis corresponding to a dihydrobenzo[*a*]carbazole (Found: C, 88·0; H, 5·9; N, 6·4. Calc. for $C_{16}H_{13}N_2$: C, 87·7; H, 5·9; N, 6·4%). The picrate crystallised from benzene as black needles, m. p. 143—144°; the addition compound with tetrachlorophthalic anhydride forms deep-red needles (from benzene), m. p. 165°. The mixed m. p. with authentic 5,6-dihydrobenzo[*a*]carbazole [14] (m. p. 163—164°) was 156—158°. 5,6-*Dihydrobenzo*[a]*carbazole picrate* forms black needles, m. p. 147—148° (Found: C, 59·1; H, 3·65; N, 12·2. $C_{22}H_{16}N_4O_7$ requires C, 59·0; H, 3·6; N, 12·5%); the *tetrachlorophthalic anhydride addition compound* forms red needles, m. p. 168° (Found: C, 58·0; H, 2·5; N, 2·6; Cl, 28·0. $C_{24}H_{13}Cl_4NO_3$ requires C, 58·05; H, 2·6; N, 2·75; Cl, 28·15%). The ultraviolet absorption spectra of the two samples of 5,6-dihydrobenzo[*a*]carbazole were determined in n-hexane (B.D.H., spectroscopy grade) with a Unicam S.P. 500 spectrophotometer.

Dehydrogenation of 5,6-*Dihydrobenzo*[a]*carbazole.*—The dihydro-compound (20 mg.) and chloranil (35 mg.) in xylene (10 ml.) were refluxed for 24 hr. The solution was washed with 10% w/v aqueous sodium hydroxide and with water. The xylene solution was dried ($CaCl_2$) and concentrated. On cooling, benzo[*a*]carbazole (18 mg.) separated as needles, m. p. and mixed m. p. 223°.

Methiodides of Polycyclic Cinnoline Derivatives.—The cinnoline (0·1 g.) in nitromethane (8 ml.) was heated under reflux with freshly distilled methyl iodide (5 ml.) for 4 hr. The solution was evaporated to about 2 ml. and allowed to cool, whereupon the pure dark red methiodide separated, was filtered off, and washed with acetone, and dried. *Naphtho*[1,2-c]*cinnoline methiodide* had m. p. 215° (decomp.) (Found: C, 54·9; H, 3·5; N, 7·8; I, 35·2. $C_{17}H_{13}N_2I$ requires C, 54·7; H, 3·5; N, 7·5; I, 34·4%). Naphtho[2,1-*c*]cinnoline methiodide, probably a mixture of the two isomeric methiodides, forms needles, m. p. 208—213°, after three recrystallisations from acetone (Found: C, 54·7; H, 3·4; N, 7·5; I, 34·9%). *Benzo*[f]*naphtho*[1,2-c]*cinnoline methiodide* forms dark red needles, m. p. 195° (Found: I, 30·2. $C_{21}H_{15}N_2I$ requires I, 30·8%). *Benzo*[f]*naphtho*[2,1-c]*cinnoline methiodide* forms needles, m. p. 256° (decomp.) (Found: I, 30·6%). Benzo[*h*]naphtho[1,2-*c*]cinnoline, m. p. and mixed m. p. 266° (lit.,[2] m. p. 266°), was recovered, and no darkening was observed during the refluxing.

Salts of Symmetrical Polycyclic Cinnoline Derivatives.—(a) *Perchlorates.* The cinnoline (25 mg.) in acetic acid (2·5 ml.) was warmed with 60% w/v aqueous perchloric acid (0·5 ml.) on a water-bath. On cooling, the perchlorate separated as yellow or olive-green needles. *Benzo*[c]*cinnoline perchlorate* had m. p. 215—216·5° (Found: C, 51·5; H, 3·3; N, 10·2; Cl, 12·5. $C_{12}H_9ClN_2O_4$ requires C, 51·3; H, 3·2; N, 10·0; Cl, 12·7%). *Benzo*[f]*naphtho*[2,1-c]*cinnoline perchlorate* had m. p. 288° (Found: Cl, 9·45. $C_{20}H_{13}ClN_2O_4$ requires Cl, 9·4%). *Benzo*[h]*naphtho*[1,2-c]*cinnoline perchlorate* had m. p. 258° (Found: Cl, 9·3%).

(b) *Sulphates.* A solution of the cinnoline in acetone (0·025 g. in 5 ml.) was treated with 1 drop of concentrated sulphuric acid; the salt separated immediately, was filtered off, washed with acetone, and dried. *Benzo*[c]*cinnoline sulphate* had m. p. 216° (decomp.) (Found: C, 52·1;

[27] Cumming and Howie, *J.*, 1932, 528.
[28] Japp and Maitland, *J.*, 1903, **83**. 274.

H, 3·6; N, 10·05; S, 11·6. $C_{12}H_8N_2,H_2SO_4$ requires C, 51·9; H, 3·6; N, 10·1; S, 11·5%). *Benzo*[f]*naphtho*[2,1-c]*cinnoline sulphate* decomposed above 240° (Found: *M*, 370. $C_{20}H_{12}N_2,H_2SO_4$ requires *M*, 378).

(c) *Hydrochlorides.* Hydrogen chloride was passed into a solution of the cinnoline in acetone (25 mg. in 5 ml.). The salt was precipitated; it recrystallised from acetone. *Benzo*[c]*cinnoline hydrochloride hydrate* decomposed above 154° (Found: C, 61·35; H, 4·7; N, 12·15; Cl, 15·5. $C_{12}H_9ClN_2,H_2O$ requires C, 61·5; H, 4·7; N, 12·0; Cl, 15·2%).

(d) *Hydrobromides.* Hydrogen bromide was passed into a solution of the cinnoline in acetone (25 mg. in 5 ml.). The salt separated and was recrystallised from acetone. *Benzo*[c]-*cinnoline hydrobromide hydrate* decomposed above 220° (Found: C, 51·6; H, 4·1; N, 10·0; Br, 28·5. $C_{12}H_9BrN_2,H_2O$ requires C, 51·6; H, 3·95; N, 10·0; Br, 28·5%). An anhydrous *benzo*[c]*cinnoline hydrobromide*, obtained when dry hydrogen bromide was passed into a solution of the cinnoline in carbon tetrachloride, decomposed above 200° (Found: N, 10·9; Br, 31·4. $C_{12}H_9BrN_2$ requires N, 10·9; Br, 30·7%). *Benzo*[f]*naphtho*[2,1-c]*cinnoline hydrobromide hydrate* decomposed above 240° (Found: *M*, 382. $C_{20}H_{13}N_2Br,H_2O$ requires *M*, 379).

(e) *Molecular weights.* The cinnoline salt (*ca.* 10 mg.) was boiled with water (10 ml.) for 15 min. It was hydrolysed and the cinnoline did not go into solution. The hydrolysate was titrated with 0·01N-sodium hydroxide to Methyl Orange.

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