# 779. Polycyclic Cinnoline Derivatives. Part XIII.[1] The Cyclisation of Azo-compounds and the Ultraviolet Absorption of Benzo[g]naphtho-[1,2-c]cinnoline.

By P. F. Holt and C. W. Went.

2,2′-Azonaphthalene with aluminium chloride in methylene chloride gives high yields of benzo[*f*]naphtho[2,1-*c*]cinnoline. Attempts to cyclise 1,1′-azonaphthalene, 1,2′-azonaphthalene, and 2-phenylazonaphthalene by this method or in aluminium chloride melts were less successful. No cinnoline was produced from some other azo-compounds. In molten aluminium chloride 2,2′-azonaphthalene gives the above cinnoline and a trace of another cinnoline believed, from its absorption spectrum, to be benzo[*g*]naphtho[1,2-*c*]cinnoline.

Polycyclic cinnolines are usually prepared by reducing 2,2′-dinitrobiaryls, but the yield is often very low both in reduction and in the Ullmann reaction by which the dinitrobiaryl is formed. The cyclisation of azobenzene and dimethylaminoazobenzene in aluminium chloride melts has yielded, respectively, benzo[*c*]cinnoline (I)[2] (40—60%) and 2-dimethylaminobenzo[*c*]cinnoline[3] (30%), but with some other azo-compounds the method proved unsuccessful. A search has been made for conditions under which cyclisation could be effected more efficiently, and possible methods for the cyclisation of some phenylazonaphthalenes and azonaphthalenes have been examined.

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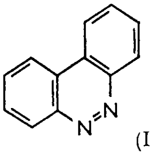
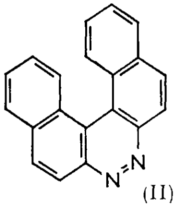
[1] Part XII, Corbett, Holt, and Vickery, *J.*, 1962, 4384.
[2] Wolfram, G.P. 513 206, 1930.
[3] Arcos, Arcos, and Miller, *J. Org. Chem.*, 1956, **21**, 651.

Benzo[*f*]naphtho[2,1-*c*]cinnoline (II), previously made from 1-iodo-2-nitronaphthalene [4] in a yield of 20%, has now been formed in 70% yield by the method used [3] for preparing dimethylaminobenzo[*c*]cinnoline. The optimum yield is obtained by heating 2,2′-azonaphthalene in a eutectic melt of aluminium chloride and sodium chloride at 85—90° for 90 min. By a similar method and heating for 30 min., benzo[*h*]naphtho[1,2-*c*]cinnoline (III) is obtained from 1,1′-azonaphthalene but in only 10% yield. It was previously synthesised from 2-iodo-1-nitronaphthalene in 30% yield. In these examples, the yield of cinnoline is markedly affected by conditions. If the time of heating is short, unchanged azo-compound is recovered; if it is prolonged, or at higher temperatures, much tar is formed.


(I)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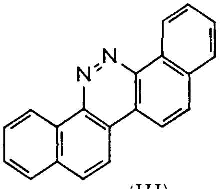
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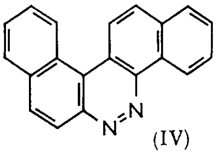
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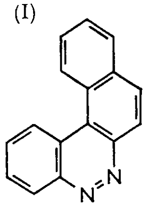
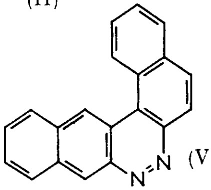
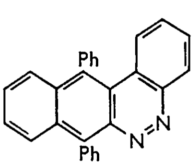



(VI)


(VII)

Even better yields (90%) of the cinnoline (II) have been obtained by heating 2,2′-azonaphthalene under reflux with aluminium chloride in methylene chloride. This method has also yielded, from 1,2′-azonaphthalene, benzo[*f*]naphtho[1,2-*c*]cinnoline (IV) (30%), previously prepared [5] in 9% yield, but 1,1′-azonaphthalene gave only tar.

2-Phenylazonaphthalene gave a low yield of naphtho[2,1-*c*]cinnoline (V), but 1-phenylazonaphthalene did not cyclise. If a substituent (OH or $NH_2$) was adjacent to the azo-group, none of the azonaphthalenes cyclised in solution or in a eutectic melt.

None of the azo-compounds mentioned was cyclised by anhydrous ferric chloride, by stannic chloride or boron trifluoride in methylene chloride or by aluminium chloride in nitrobenzene or nitroethane. Anhydrous aluminium bromide in methylene chloride did not cyclise 2,2′-azonaphthalene and gave only a trace of the cinnoline (II) when used as a eutectic melt.

*Benzo*[g]*naphtho*[1,2-c]*cinnoline*.—The 3-position of 2,2′-azonaphthalene could conceivably be involved in cyclisation, but the high yield of the product (II) indicates that this can occur only to a very small extent; 3,3′-cyclisation in detectable amounts is improbable. A very small quantity of a substance from the melt of 2,2′-azonaphthalene was isolated on a chromatographic column; in acetone it gave a blue fluorescence and in sulphuric acid a red-green dichroic solution. The material from a number of preparations was pooled. Although insufficient of this by-product could be prepared for analysis or study of its properties, the ultraviolet absorption leaves no doubt that it is a polycyclic cinnoline and presumably is the previously unknown benzo[*g*]naphtho[2,1-*c*]cinnoline (VI). It is the first unsubstituted cinnoline to be described which is an anthracene analogue, although 7,12-diphenylnaphtho[2,3-*c*]cinnoline (VII) is known. That it is not formed by isomerisation of compound (II) was proved by heating the latter in an aluminium chloride melt for 3 hr. The cinnoline was recovered, no tar was formed, and a benzene extract of the melt gave a single band on an alumina column.

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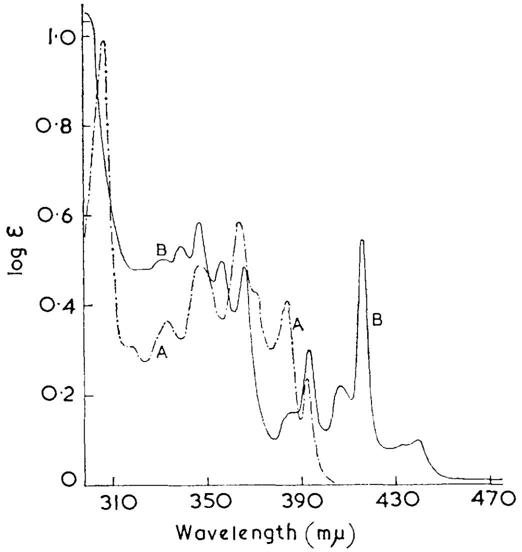
[4] Braithwaite and Holt, *J.*, 1959, 3025.

[5] Corbett and Holt, *J.*, 1960, 3646.

The ultraviolet absorption of this material (VI) is compared with that of 3,4-benzotetraphene, in the Figure. The true analogue, 1,2-benzotetraphene, was unobtainable. The curves are similar. The cinnoline shows the usual three main regions of absorption (groups I, II, and III), together with a characteristic [6,7] band at 415 mμ due to an $n - \pi^*$ transition.

Designating the peaks of longest wavelength in the group I, II, and III bands as $\lambda_{\mathrm{I}}$, $\lambda_{\mathrm{II}}$, and $\lambda_{\mathrm{III}}$, respectively, Corbett, Holt, and Hughes [8] noticed that the ratio $\lambda_{\mathrm{I}}/\lambda_{\mathrm{II}}$ for cinnolines free from ring strain was 0·82 but that it was higher for strained cinnolines, and that the ratio $\lambda_{\mathrm{I}}/\lambda_{\mathrm{III}}$ increases with increasing number of rings for unstrained cinnolines only. Cinnoline (VI) gives the values: $\lambda_{\mathrm{I}}/\lambda_{\mathrm{III}} = 0{\cdot}82$; $\lambda_{\mathrm{II}}/\lambda_{\mathrm{III}} = 0{\cdot}90$ (benzo[*c*]cinnoline, 0·84). Both values indicate an unstrained ring system.



The spectra of (A) 3,4-benzotetraphene and (B) the (supposed) benzo[*g*]naphtho[1,2-*c*]cinnoline, in cyclohexane.

Corbett, Holt, and Hughes did not find a relation, observed by Clar and Stewart [9] for polycyclic hydrocarbons, between the ratio $\lambda_{\mathrm{I}}/\lambda_{\mathrm{III}}$ and the extent of ring strain. The values for the cinnolines previously considered and that for compound (VI) suggest a variation dependent on the number of rings, apparent in the annexed Table.

| Cinnoline | No. of rings | $\lambda_{\mathrm{I}}/\lambda_{\mathrm{III}}$ |
|---|---|---|
| Benzo[*c*] | 3 | 0·69 |
| Dibenzo[*cf*] | 4 | 0·73 |
| Dibenzo[*c,h*] | 4 | 0·72 |
| Benzo[*f*]naphtho[2,1-*c*] | 5 | 0·74 |
| Benzo[*h*]naphtho[1,2-*c*] | 5 | 0·75 |
| Benzo[*f*]naphtho[1,2-*c*] | 5 | 0·75 |
| Benzo[*g*]naphtho[1,2-*c*] | 5 | 0·74 |

A correlation was also observed between the number of rings in polycyclic cinnolines and the bathochromic shift in $\lambda_{\mathrm{I}}$, $\lambda_{\mathrm{II}}$, and $\lambda_{\mathrm{III}}$ measured against the values for benzo[*c*]cinnoline—the so-called " annelation shift." The structure (VI) is formed by adding to (I) one ring at a 1,2-face and one at a 2,3-face. Among the examples previously considered (none had a ring added to a 2,3-face), two rings added to benzo[*c*]cinnoline resulted

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[6] Halverson and Hirt, *J. Chem. Phys.*, 1951, **19**, 711.
[7] Badger and Walker, *J.*, 1956, 122.
[8] Corbett, Holt, and Hughes, *J.*, 1961, 1363.
[9] Clar and Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 6235.

in a shift of $\lambda_{II}$ of about 40 mμ; compound (VI) gives a shift of 62 mμ. The shift in $\lambda_{III}$ approximated to 9 mμ per additional ring fused at a 3,4-face and 26 mμ at a 1,2-face; compound (VI) gives 45 mμ. If 26 mμ corresponds to annelation at the 1,2-face, the shift due to annelation at the 2,3-face for the cinnoline must be 19 mμ. The shift in $\lambda_{I}$ is 52 mμ, comparable with values previously found for 5-ring cinnolines (47—54 mμ).

## EXPERIMENTAL

*Cyclisation in Aluminium Chloride Melts.*—2,2′-Azonaphthalene (1 g.) was added in small quantities to a stirred melt of anhydrous aluminium chloride (32 g.), sodium chloride (4 g.), and sodium fluoride (0·5 g.). The mixture was stirred occasionally and its temperature kept at 85—90° for 90 min. Slight variations in temperature or reaction time decreased the yield and sometimes caused tar formation. The mixture was then poured into ice–water. The whole was boiled for a few minutes, then filtered. The precipitate was separated, washed with sodium carbonate and distilled water, dried, and extracted with benzene. The combined extracts were concentrated and fractionated on alumina (neutral; 100—200 mesh; Brockmann activity 1), the bands being developed with benzene and ethyl acetate (9 : 1 v/v). The distinct bands were not due to pure materials, however, and each was further purified by chromatography with a higher proportion of ethyl acetate.

The main product was benzo[*f*]naphtho[2,1-*c*]cinnoline (II) (0·7 g.), yellow needles (from acetone), m. p. 269°. A fraction from another slower-moving band gave a yellow-blue fluorescence in acetone and a red-green dichroic solution in concentrated sulphuric acid. This was shown by its ultraviolet spectrum to be benzo[*g*]naphtho[2,1-*c*]cinnoline.

By a similar method 1,1′-azonaphthalene (1 g.) gave, in optimum yield after 30 minutes' heating, benzo[*h*]naphtho[1,2-*c*]cinnoline (III) (0·1 g.), m. p. 265°, giving a red-green dichroic solution in acetone, as yellow needles from acetone. At higher temperatures or with prolonged heating, a tar was formed which, after extraction with concentrated hydrochloric acid, was soluble in acetone, from which solution it was recovered as a black, amorphous powder, possibly a polyazo-compound.

*Cyclisation in Aluminium Chloride–Methylene Chloride Complex.*—2,2′-Azonaphthalene (1 g.) in methylene chloride (300 ml.) was added to anhydrous aluminium chloride (5 g.) in methylene chloride (300 ml.). The solution was boiled under reflux for 60 min., then cooled, and shaken with several changes of water. The organic layer was separated and the solvent removed by evaporation. The residue was extracted with acetone, the solution was passed through alumina (neutral; 100—200 mesh; Brockmann activity 1), then allowed to evaporate at room temperature. Benzo[*f*]naphtho[2,1-*c*]cinnoline (II) (0·9 g.), m. p. 270° (lit.,[4] m. p. 270°), crystallised.

1,2′-Azonaphthalene (0·5 g.) in methylene chloride (150 ml.) and aluminium chloride (5 g.) in methylene chloride (150 ml.), when boiled together under reflux (70 min.), then treated as above, yielded a material which required chromatography on alumina from solution in chloroform. The yellow band, when eluted with chloroform, gave a solution from which benzo[*f*]-naphtho[1,2-*c*]cinnoline (IV) (0·15 g.), m. p. 184° (lit.,[5] m. p. 184—185°), crystallised.

2-Phenylazonaphthalene (1 g.), similarly treated, yielded naphtho[2,1-*c*]cinnoline (V) (0·1 g.), m. p. 157° (lit.,[10] m. p. 157°).

The following compounds yielded only tar, together with unchanged starting material: 1,1′-azonaphthalene, 1-phenylazonaphthalene, 2-hydroxy-1,1′-azonaphthalene, 2-hydroxy-1,2′-azonaphthalene, 1-amino-2,2′-azonaphthalene, and 1′-amino-1,2′-azonaphthalene.

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[10] Badger and Walker, *J.*, 1956, 122.