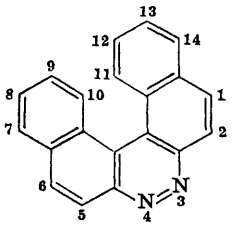
1171. *Polycyclic Cinnoline Derivatives. Part XV.*[1] *Nitration of Benzo[f]naphtho[2,1-c]cinnoline and the Synthesis of Symmetrical Dibromo-derivatives.*

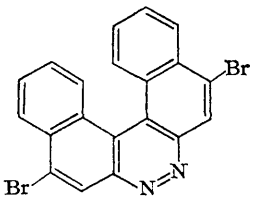
By P. F. Holt and A. E. Smith.

Benzo[*f*]naphtho[2,1-*c*]cinnoline gives the 7,12- and 7,14-dinitro-derivatives on direct nitration. The cyclisation of some new symmetrical dibromoazonaphthalenes to dibromobenzo[*f*]naphtho[2,1-*c*]cinnolines is described. The ultraviolet absorption of all the known derivatives of this cinnoline has been studied.

Braithwaite and Holt[2] isolated two dinitro-derivatives (designated α and β) on nitrating benzo[*f*]naphtho[2,1-*c*]cinnoline (I), but did not determine the positions of the substituent groups. Each was reduced to a diamine and each diamine was converted into the corresponding dibromo-derivative. The protonated azo-group is normally *meta*-directing and substitution would be favoured in the 1,6,7,9,12, and 14-positions. Braithwaite and Holt[2] synthesised 1,6-dibromobenzo[*f*]naphtho[2,1-*c*]cinnoline (II) from 4,4′-dibromo-2,2′-dinitro-1,1′-binaphthyl (III) which was then the only derivative of the cinnoline (I) of known



(I)



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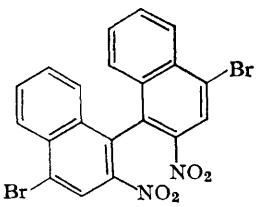

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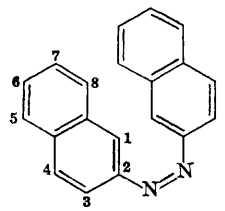

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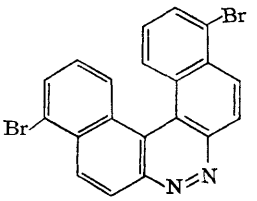

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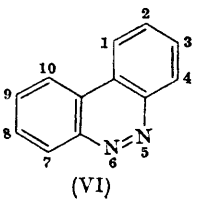

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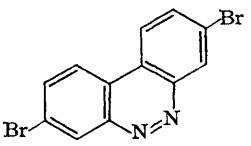

(VII)

orientation, but this product differed from the α- and β-dibromo-compounds. Since substitution in a position *ortho* to the diaza-group is improbable, it seemed likely that the inner rings of the α- and β-derivatives were unsubstituted. This was confirmed by absorption spectra (see below).

Three dibromo-derivatives of the cinnoline (I) have now been prepared by the cyclisation of previously unknown derivatives of 2,2′-azonaphthalene (IV) with aluminium chloride in

[1] Part XIV, P. F. Holt and R. Oakland, preceding paper.
[2] R. S. W. Braithwaite and P. F. Holt, *J.*, 1959, 3025.

methylene chloride, using a modification of the method of Holt and Went.[3] These bromoazonaphthalenes were formed by the reduction of bromonitronaphthalenes with lithium aluminium hydride. Only one other symmetrical dibromo-2,2′-azonaphthalene could be prepared by this method as lithium aluminium hydride removes bromine from positions *ortho* to the nitro-group,[4] and 7-bromo-2-nitronaphthalene is unknown.

4,4′-Dibromo-2,2′-azonaphthalene gave 1,6-dibromobenzo[*f*]naphtho[2,1-*c*]cinnoline (II), confirming the work of Braithwaite and Holt. 7,14-Dibromobenzo[*f*]naphtho[2,1-*c*]-cinnoline (V) was prepared from 5,5′-dibromo-2,2′-azonaphthalene. 8,13-Dibromobenzo[*f*]-naphtho[2,1-*c*]cinnoline was synthesised by a similar route from 6,6′-dibromo-2,2′-azonaphthalene. The dibromo-compound (V) and that derived from the α-dinitro-compound of Braithwaite and Holt were identical as regards m. p., infrared and ultraviolet absorption spectra, and colours in concentrated sulphuric acid. The α-dinitro-compound is therefore 7,14-dinitrobenzo[*f*]naphtho[2,1-*c*]cinnoline. None of the dibromo-compounds was identical with that derived from the β-dinitro-compound.

The infrared absorption spectra (see Table 1) of the 7,14-dinitrobenzo[*f*]naphtho[2,1-*c*]-cinnoline and the corresponding amino- and bromo-derivatives all showed main peaks in the regions 790—803 cm.$^{-1}$ (three adjacent CH groups) and 814—823 cm.$^{-1}$ (two adjacent CH groups). 8,13-Dibromobenzo[*f*]naphtho[2,1-*c*]cinnoline shows a strong peak at 880 cm.$^{-1}$ (lone CH) and four strong peaks in the region 810—855 cm.$^{-1}$ (two types of two adjacent CH groups). The infrared spectra of the substituted azonaphthalenes also conform with the assigned structures.

The structure of the β-dinitro-compound can be deduced from absorption spectra; it is 7,12-dinitrobenzo[*f*]naphtho[2,1-*c*]cinnoline. There are no strong peaks in the region 750—770 cm.$^{-1}$ of the infrared spectra of the β-dinitro-, β-diamino-, or β-dibromo-derivatives (Table 1), indicating that the outer rings of the cinnoline are both substituted. There are

TABLE 1.

Values of $\lambda_{max.}$ (cm.$^{-1}$) for some benzo[*f*]naphtho[2,1-*c*]cinnoline derivatives and 2,2′-azonaphthalene derivatives.

Number of adjacent C–H groups:	4	3	2	1
Region of absorption	747—770	780—820	810—855	860—900
Benzo[*f*]naphtho[2,1-*c*]cinnoline	752s		823s	
Derivatives: Oxide	754s		827s	
1,6-Br_2	757s			855m
8,13-Br_2			810s 823s	880s
			837s 855m	
7,14-$(NO_2)_2$ (α)		795m	818s	(873m)
7,14-$(NH_2)_2$ (α)		803s	823m	
7,14-Br_2 (α)		790m 800m	814s	
7,12-$(NO_2)_2$ (β)		788m 813m	838m 851m	(875m)
7,12-$(NH)_2$ (β)		789m 803m	833m 848m	
7,12-Br_2 (β)		787m 795s	816s 835m	
2,2′-Azonaphthalene	750s		834s	871m
Derivatives: 1,1′-$(NO_2)_2$	758s		828s	(870m)
1,1′-Br_2	747s		820s	
4,4′-Br_2	765s			869m
5,5′-Br_2		783s	827m	885m
				879m
6,6′-Br_2			813s 830s	890s
				900s

s = strong; m = medium.

two strong peaks in the region 816—851 cm.$^{-1}$ (more than one type of paired CH groups). There are two peaks in the region 787—813 cm.$^{-1}$ (three adjacent CH groups) showing substitution in the 7- or 10-position. Substitution in position 10 is unlikely both because this position is de-activated by the diaza-group, which is *meta*-directing, and because of steric hindrance. The hydrogen atoms in the 10- and 11-positions interfere even in the parent cinno-

[3] P. F. Holt and C. Went, *J.*, 1963, 4099.
[4] J. F. Corbett and P. F. Holt, *J.*, 1963, 2385.

line and the molecule is slightly twisted, consequently no strong peak appears in the region 860—880 cm.$^{-1}$ because the lone CH in position 1 is hindered. A substituent in position 10 would result in a degree of twisting sufficient to produce a large shift in the ultraviolet absorption peaks. This is not observed. The ultraviolet absorption curves of the α- and β-derivatives are in fact very similar.

Ultraviolet Absorption Spectra.—Ultraviolet absorption spectra of the azonaphthalene derivatives and derived cinnolines in chloroform were determined. Shifts in the several bands of the spectra were examined by comparing corresponding peaks; in the group III band there were usually several corresponding peaks and the average shift was determined. In other groups only the peaks of highest intensity could be correlated.

(a) *Nitro-derivatives.* The positions of the peaks in the spectra of nitro-derivatives of benzo[*c*]cinnoline (VI) are little affected[5] by the introduction of the nitro-group. The effect of nitro-groups on the spectra of compound (I) and its oxide are shown in Table 2. Notably there are very small shifts in the group III bands. The hypsochromic shifts in the group I band are larger and similar for both nitro-derivatives but in the group II band the shift is bathochromic for the 7,14- and hypsochromic for the 7,12-dinitro-derivative both for the cinnoline and its oxide. In every case, *N*-oxidation decreases the intensity of the group I and II bands and increases that of the group III band, as is the case with benzo[*c*]cinnoline derivatives, and the group III band suffers a bathochromic shift of about 20 mμ.

(b) *Amino-derivatives.* Substitution of an amino-group in benzo[*c*]cinnoline was observed[5] to eliminate fine structure in the ultraviolet spectra. This is also observed in the spectra of amino-derivatives of the cinnoline (I); in ethanol particularly each band is reduced to a single peak. Very large shifts were recorded[5] in the spectra of aminobenzo[*c*]cinnoline on monoprotonation. Neglecting that of 1,10-diaminobenzo[*c*]cinnoline in which the amino-groups mutually interfere, the spectra of monoamines of benzo[*c*]cinnoline in 5N-hydrochloric acid and diamines in 80% sulphuric acid revert almost to that of the parent cinnoline in 2N-hydrochloric acid; groups I and III are in identical positions. The diamines of the cinnoline (I) in 80% sulphuric acid also have almost identical spectra and, again, these are almost identical with that of the parent cinnoline in 2N-hydrochloric acid. The spectra of the mono-cations (0·1N-hydrochloric acid) are also similar. There are shifts to shorter wavelengths in both groups I and II; the group III band does not appear as the absorption gradually tails off to zero.

(c) *Bromo-derivatives.* The shifts caused by a substituent bromine atom are recorded in Table 2. The three symmetrical derivatives all show shifts of about 3 mμ in the group I band; the unsymmetrical bromo-derivative shows double this value. 1,6-Dibromobenzo[*f*]-naphtho[2,1-*c*]cinnoline (II) is derived from 3,8-dibromobenzo[*c*]cinnoline (VII) by the annelation of two rings. In each case, when their absorption spectra are compared with those of the parent cinnoline very large shifts in the group III bands are observed (31 and 18 mμ respectively.)

(d) *2,2′-Azonaphthalenes and corresponding cinnolines.* The ultraviolet absorption spectrum of 2,2′-azonaphthalene shows bands corresponding to the groups I, II, and III bands of the cinnoline (cf. Tables 2 and 4). Group I band[6] has been called IA, the group II band[7] *K*, and the group III band[7] *R*. We shall use the cinnoline nomenclature.

Substitution in the 6 and 6′ positions of 2,2′-azonaphthalene by bromine produces much larger shifts in group I and II bands than substitution in the other positions. In the spectra of the unsubstituted azo-compound and the 4,4′- and 5,5′-dibromo-derivatives the group I bands show a bathochromic shift of about 16 mμ as compared with the corresponding cinnoline; the 6,6′-dibromo-compound has only half this value. The 6,6′-compound also shows a much larger shift in the group II band.

The group III band in the spectrum of the azo-compound has a different form from that

[5] J. F. Corbett, P. F. Holt, A. N. Hughes, and M. Vickery, *J.*, 1962, 1812.
[6] G. M. Badger and R. G. Buttery, *J.*, 1953, 2156.
[7] A. Burawoy, *J.*, 1937, 1865.

TABLE 2.

Values of $\lambda_{max.}$ (mμ) and (log ε) for some benzo[*f*]naphtho[2,1-*c*]cinnoline derivatives in chloroform.

Subst.	Group I	δλ	Group II	δλ	Group III	δλ
None	272s 297 309s (4·32) (4·36) (4·49)	0	328 345 (4·20) (3·87)	0	377 399s 421 (3·32) (3·37) (3·40)	0
1,6-Br_2	279 — 313 (4·15) (4·38)	+4	339 368 (4·19) (3·68)	+11	407 430 455 (3·12) (3·26) (3·24)	+31
7,14-Br_2	269 277 313 (4·29) (4·30) (4·41)	+4	333 — (4·14)	+5	383s 405s 429s (3·21) (3·27) (3·33)	+7
8,13-Br_2	261 282 312s (4·35) (4·39) (4·47)	+3	326 350 (4·15) (3·89)	−2	396s 420 445 (3·35) (3·31) (2·61)	+21
7,12-Br_2	270 279 317 (4·20) (4·25) (4·29)	+8	334 — (4·01)	+6	383 406s 429 (3·22) (3·29) (3·30)	+7
7,14-$(NO_2)_2$(α)	— 287s 300 (4·08) (4·37)	−9	— 347 (4·05)	+2	— 397 421 (3·42) (3·22)	−1
7,12-$(NO_2)_2$(β)	261 285 301 (4·41) (4·41) (4·43)	−8	322 — (4·31)	−6	— 397 420s (3·49) (3·39)	−1
	N-Oxides					
None	286 309 302 (4·22) (4·19) (4·21)	0	335 356 374 (4·17) (4·01) (3·75)	0	396 419s 444 (3·35) (3·53) (3·64)	0
7,14-$(NO_2)_2$	285 309 — (4·10) (4·12)	+1	342 — — (4·14)	+7	395 421 446 (3·47) (3·46) (3·50)	+1
7,12-$(NO_2)_2$	267 (?) (4·41)	?	334 — 371 (4·33) (4·12)	−2	— 422s 447 (3·61) (3·63)	+3

TABLE 3.

Values of $\lambda_{max.}$ (mμ) and (log ε) for some diaminobenzo[*f*]naphtho[2,1-*c*]cinnolines in various solvents.

Amino-groups	Solvent	Group I	Group II	Group III
None	Ethanol	229 236s 257 272 295s (4·57) (4·51) (4·34) (4·34) (4·40)	308 326 346 (4·55) (4·24) (3·88)	375 400 423 (3·43) (3·37) (3·37)
	2N-HCl	221 241s 268 282 297s (4·56) (4·58) (4·06) (4·08) (4·15)	327 (4·43)	397 (3·83)
7,14-Di-amino-(α)	Ethanol	260 (4·47)	330 (4·20)	461 (3·56)
	0·1N-HCl	222 230s 276 (4·50) (4·49) (4·14)	310 323s (4·27) (4·20)	—
	80% H_2SO_4	222 238s 269 281 (4·57) (4·52) (4·19) (4·19)	327 (4·41)	390 (3·85)
7,12-Di-amino-(β)	Ethanol	257 (4·58)	339s (4·19)	460 (3·46)
	0·1N-HCl	223 234s 275 (4·58) (4·50) (4·20)	310 323s (4·30) (4·20)	—
	80% H_2SO_4	222 237s 267 280 (4·64) (4·54) (4·18) (4·16)	327 (4·39)	390 (3·85)

s = shoulder.

TABLE 4.

Values of $\lambda_{max.}$ (mμ) and ($\varepsilon \times 10^{-4}$) for some 2,2′-azonaphthalenes in chloroform.

Subst.	Group I (region IA)	δλ	Group II (*K* band)	δλ	Group III	δλ
None	266s 281 293 (2·22) (1·73) (1·33)	0	342 (2·36)	0	375 (1·69)	0
1,1′-Br_2	272 279 289 301s (1·79) (1·84) (1·89) (1·52)	8	350 (2·44)	8	397 (1·92)	22
4,4′-Br_2	279 289 298 (1·97) (2·10) (1·87)	6	336 (1·56)	−6	382s 394 (1·08) (1·12)	19
5,5′-Br_2	280 288 298 (2·11) (2·31) (1·97)	6	338 (1·90)	−4	378 (1·02)	3
6,6′-Br_2	260 267 291 305 (1·69) (1·63) (1·61) (1·95)	11	324 355 (1·15) (1·63)	13	395 (1·22)	20

of the cinnoline. In the former it is a single peak or shoulder; in the latter there are three distinct peaks. The *cis*-forms of the azo-compounds would be more relevant in a comparison with cinnolines but these have very short half-lives.

There is considerable uniformity in the heights of the main peaks in the spectra of the 2,2′-azonaphthalenes. For this reason values of $\varepsilon \times 10^{-4}$ have been recorded in Table 4 rather than $\log \varepsilon$ which always has a value between 4·00 and 4·35.

Experimental

Nitration of Benzo[f]*naphtho*[2,1-c]*cinnoline* (I).—Benzo[*f*]naphtho[2,1-*c*]cinnoline (2 g.) was nitrated in fuming nitric acid as described by Braithwaite and Holt.[2] The α-dinitrobenzo[*f*]naphtho[2,1-*c*]cinnoline, m. p. 337° (lit.,[2] 337°) (0·54 g.), crystallised pure, but the β-dinitro-derivative was contaminated by the α-isomer. The isomers were adsorbed from hot chloroform solution on to alumina. The α-isomer was eluted by benzene, followed by the β-dinitrobenzo[*f*]naphtho[2,1-*c*]-cinnoline (0·50 g.), m. p. 222° (lit.,[2] 224°).

Preparation of Azo-compounds.—To the bromonitronaphthalene (1 g.) suspended in dry diethyl ether (50 ml.) was added an excess of powdered lithium aluminium hydride. The solution became brown, then transient pea-green (nitroso-compound), and finally orange. The solution stood for 1 hr., then water was added. The liquid was filtered, then the residue was dried and extracted several times with acetone. The mixed extracts and filtrate were evaporated to dryness. The residue was dissolved in chloroform, chromatographed on alumina, and eluted with chloroform, the first band being collected. On evaporation crystals of the azo-compound were deposited. Only 4-bromo-2-nitronaphthalene gave, as well as the azo-compound, 1,6-dibromobenzo[*f*]naphtho[2,1-*c*]cinnoline (II). By this method 4-bromo-2-nitronaphthalene (2 g.) gave *4,4′-dibromo-2,2′-azonaphthalene* (0·3 g.) as yellow plates, m. p. 273°, purple in sulphuric acid, magenta then yellow on dilution (Found: C, 54·2; H, 2·8; Br, 35·5; N, 6·2. $C_{20}H_{12}Br_2N_2$ requires C, 54·5; H, 2·7; Br, 36·4; N, 6·4%), and 1,6-dibromobenzo[*f*]naphtho[2,1-*c*]cinnoline (40 mg.), identical (ultraviolet and infrared spectra) with a specimen prepared by Braithwaite and Holt.[2]

5-Bromo-2-nitronaphthalene (2 g.) gave *5,5′-dibromo-2,2′-azonaphthalene* (0·5 g.) as orange plates, m. p. 180°, blue in concentrated sulphuric acid turning orange on dilution (Found: C, 54·7; H, 2·65; Br, 36·6; N, 5·9%). 6-Bromo-2-nitronaphthalene (2 g.) gave *6,6′-dibromo-2,2′-azonaphthalene* (0·4 g.) as orange-brown plates, m. p. 233°, purple in sulphuric acid turning orange-yellow on dilution (Found: C, 54·4; H, 2·6; Br, 36·3; N, 6·7%).

1,1′-Dibromo-2,2′-azonaphthalene.—2,2′-Azonaphthalene (5 g.) was dissolved in hot chloroform (100 ml.) and bromine (3 g.) was added slowly. The solution was left for 30 min. and it was allowed to evaporate to dryness without further heating. 1,1′-Dibromo-2,2′-azonaphthalene (6 g.) separated as red rosettes, m. p. 250° after recrystallisation from toluene (lit.,[4] m. p. 252°), identical (ultraviolet and infrared spectra and mixed m. p.) with a specimen prepared from 1-bromo-2-naphthylamine.[8] This compound gives a blue colour in concentrated sulphuric acid going to red on dilution. It is different from that said to be 1,1′-dibromo-2,2′-azonaphthalene, which was prepared by Hodgson, Habeshaw, and Murti,[9] from 1 bromo-2-naphthylamine. Their compound, m. p. 193—195°, gave a Bordeaux-colour in concentrated sulphuric acid changing to scarlet on dilution.

Cyclisation of Azo-compounds.—A method similar except in detail to that described by Holt and Went[3] was used. Powdered aluminium chloride (10 g.) was added to the azo-compound (1 g.) dissolved or suspended in dry methylene chloride (200 ml.) and the mixture was boiled under reflux for 1 hr. The suspension was filtered and water was added to the filtrate. The residue was extracted with hot water then with methylene chloride, the latter extract being added to that from the first filtration. This solution was evaporated to dryness, the residue was dissolved in chloroform, and the solution chromatographed on alumina (Spence, type H). The main yellow band was removed in chloroform and the eluate set aside to crystallise.

By this method 2,2′-azonaphthalene (5 g.) gave benzo[*f*]naphtho[2,1-*c*]cinnoline (4 g.), m. p. 269° (lit.,[3] 269°). 6,6′-Dibromo-2,2′-azonaphthalene (0·8 g.) gave *8,13-dibromobenzo*[f]*naphtho*-[2,1-c]*cinnoline* (0·2 g.), m. p. 304°, as yellow needles giving a purple solution in concentrated sulphuric acid, which turns red then yellow with water (Found: C, 52·5; H, 2·6; Br, 33·1; N, 6·3. $C_{20}H_{10}Br_2N_2$ requires C, 54·9; H, 2·3; Br, 36·5; N, 6·4%).

[8] B. M. Bogoslowskii and Z. S. Kazakova, *Zhur. obshchei. Khim.*, 1952, **22**, 1183.
[9] H. H. Hodgson, J. Habeshaw, and P. B. R. Murti, *J.*, 1947, 1390.

5,5′-Dibromo-2,2′-azonaphthalene (0·52 g.) gave 7,14-*dibromobenzo*[*f*]*naphtho*[2,1-*c*]*cinnoline* (80 mg.), yellow needles from dimethylformamide, m. p. 299°, mixed with α-dibromobenzo[*f*]-naphtho[2,1-*c*]cinnoline, m. p. 299° (Found: C, 54·5; H, 2·5; Br, 33·9; N, 6·1%).

4,4′-Dibromo-2,2′-azonaphthalene (0·25 g.) gave 1,6-dibromobenzo[*f*]naphtho[2,1-*c*]cinnoline (50 mg.), yellow needles from dimethylformamide, m. p. 277° (lit.,[2] 277°). The ultraviolet absorption spectrum of this material was identical with that of a specimen provided by Dr. R. S. W. Braithwaite. 1,1′-Dibromo-2,2′-azonaphthalene gave only tar by this procedure.

Spectra.—Ultraviolet spectra were determined with an Optica Spectrophotometer model C.F.4 and infrared spectra with an Infracord model 137.

One of the authors (A. E. S.) received a grant from the D.S.I.R.

THE UNIVERSITY, READING, BERKSHIRE. [*Received, September 17th,* 1964.]