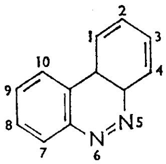
344. *Polycyclic Cinnoline Derivatives. Part X.*[1] *Effect of Substituents on the Ultraviolet Absorption Spectra of Benzo*[c]*cinnoline.*

By J. F. Corbett, P. F. Holt, A. N. Hughes, and Mrs. M. Vickery.

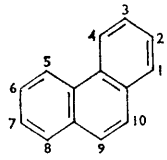
The ultraviolet absorption spectra of some methyl-, bromo-, chloro-, methyl-bromo-, amino-, and nitro-derivatives of benzo[*c*]cinnoline and benzo[*c*]cinnoline *N*-oxide are recorded. The spectral shifts caused by methyl, bromo-, and chloro-substituents are additive and depend on the position of the substituents. The magnitudes of the shifts are in qualitative agreement with those calculated for the corresponding phenanthrene derivatives by the L.C.A.O. molecular-orbital method. Shifts of the n–π^* transitions of benzo[*c*]cinnoline produced by bromine substituents have the same pattern as those for the corresponding chlorocinnolines. The spectra of the nitro-derivatives resemble that of benzo[*c*]cinnoline rather than those of the corresponding nitrophenanthrenes. 1,10-Disubstituted benzo[*c*]cinnolines exhibit spectra which are characteristic of strained ring systems. The spectra of the four aminobenzo[*c*]cinnolines are characteristic of those of amino-derivatives of nitrogen heterocycles. Spectral changes resulting from acidification indicate that the basic centre is one of the hetero-atoms. Shifts of the long-wavelength band resulting from protonation are similar in magnitude to those for the corresponding aminocinnolines.

In an earlier paper[2] we noted similarities between the ultraviolet absorption spectra of a number of unsubstituted polycyclic derivatives of cinnoline and those of their carbocyclic and monoaza-analogues, and spectral features were related to molecular structure. The effect of substituents on the spectrum of benzo[*c*]cinnoline has now been studied to discover (i) any relation between the effect of substituents on the spectrum of benzo[*c*]cinnoline and on that of phenanthrene, (ii) whether the theoretical methods applied to the spectrum of phenanthrene could usefully be extended to the isoelectronic benzo[*c*]cinnoline system, (iii) whether the steric effects observed in the spectra of some aromatic hydrocarbons were also evident in those of their heterocyclic analogues, and (iv) whether the ultraviolet absorption spectra could assist in orienting derivatives produced in studies of the substitution of benzo[*c*]cinnoline and its derivatives.

In the discussion which follows it should be borne in mind that the benzo[*c*]cinnoline (I) and phenanthrene (II) ring systems are numbered differently. In the Tables the numbering is that of the benzo[*c*]cinnoline derivative.



(I)



(II)

Benzo[c]*cinnoline*.—The spectrum of benzo[*c*]cinnoline in n-hexane (Fig. 1) has four distinct bands. Three of these, designated group I ($\lambda_{\max.} \approx 250$ mμ; log ε 4·6), II ($\lambda_{\max.} \approx 300$ mμ; log ε 3·9), and III ($\lambda_{\max.} \approx 350$ mμ; log ε 3·2), are attributed to π–π^* transitions and are related to the β-, *p*-, and α-bands, respectively, in the spectrum of phenanthrene. The fourth band ($\lambda_{\max.} \approx 410$ mμ; log ε 2·6) is attributed to an n–π^* transition, involving the lone pair electrons of the heteroatoms.[3]

It is interesting that the spectra of phenanthrene, phenanthridine, and benzo[*c*]cinnoline show the same spread in both the group II (10—11 mμ) and the group III band

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[1] Part IX, Corbett and Holt, *J.*, 1961, 5029.

[2] Corbett, Holt, and Hughes, *J.*, 1961, 1363.

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

TABLE 1.

(i) Spectra ($\lambda_{\text{max.}}$, in mμ)[a] of benzo[*c*]cinnoline and some isoconjugate compounds in various solvents.

Substance	Solvent	Group I	Group II	Group III
Phenanthrene	EtOH [b]	251	282, 293	314, 322, 329, 337, 345
Phenanthridine	EtOH [c]	247	290, *296*	— — 330, — 346
,,	n-Hexane [b]	250	286, 296	312, 321, 327, 335, 343
,,	Acid [c]	247	*316*, 322	— — 357, — *365*
Benzo[*c*]cinnoline	n-Hexane	245, 250	294, 305	331, *340*, 345, 354, 361
,,	CCl_4	—	296, 308	331, — 347, — 362
,,	EtOH	251	308	— — 354, — *363*
,,	2N-HCl	250	356	— — — — *420*

(ii) Spectra of benzo[*c*]cinnoline *N*-oxide.

Solvent	Group I	*x*-Band	Group II	Group III
n-Hexane	251, *264*	286, 297	329, 337	344, *354*, 361, 370, 380
CCl_4	—	287, 299	331, 339	345, *354*, 363, *372*, 382
EtOH	252	*300*	330	*344*, — 365, — 384
80% H_2SO_4	253	— —	348	— — — — 405

[a] Values in italics relate to shoulders or inflexions in this and other Tables. [b] Friedel and Orchin, "Ultra-violet Spectra of Aromatic Compounds," John Wiley & Sons, New York, 1951. [c] Osborn, Schofield, and Short, *J.*, 1956, 4191.

(30—31 mμ), and all show similar fine structure which becomes progressively less marked with the introduction of heteroatoms (Table 1). The spectrum of benzo[*c*]cinnoline in carbon tetrachloride shows less fine structure, and the group III band has only three maxima which are less well defined than those in the spectrum in n-hexane. The group II and III bands are at slightly longer wavelengths. The fine structure is lost when the benzo[*c*]cinnoline is in ethanol; the group I and the group II band each have single maxima, and the group III band is a broad shoulder with a slight central maximum. The loss of fine structure and the absence of a feature ascribable to an *n*–π* transition is probably due to hydrogen bonding between the solvent molecules and the heteroatoms. Such interaction would increase the number of vibrational states and the energy of the *n*–π* transition, so that the relevant feature in the spectrum would suffer a blue shift to become masked by the group III band.

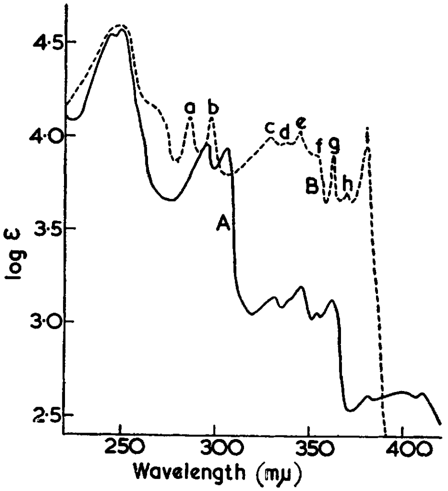

FIG. 1. The spectra of benzo[*c*]cinnoline (A) and its *N*-oxide (B) in n-hexane.

The spectrum of benzo[*c*]cinnoline in 2N-hydrochloric acid shows changes similar to those resulting from protonation of other nitrogen heterocycles.[4] Thus, while the group I

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[4] Osborn, Schofield, and Short, *J.*, 1956, 4191.

band remains at 250 mμ, the group II and III bands undergo large red shifts; the shift of the group II band of benzo[*c*]cinnoline is about double that resulting from the protonation of phenanthridine (Table 1).

Benzo[c]*cinnoline* N-*Oxide.*—The spectrum of benzo[*c*]cinnoline *N*-oxide (Table 1, Fig. 1) has been reported previously.[2] *N*-Oxidation produces a large red shift of the group II and III bands and a considerable increase in the intensity of the group III band. In addition, a new band, which we have called the *x*-band, appears between the group I and the group II band. This feature, which consists of two maxima (a and b in Fig. 1), is probably due to transitions involving the lone pair of electrons of the oxygen atom that is conjugated with the nucleus. As with benzo[*c*]cinnoline, the group II and group III bands are at slightly longer wavelengths when the *N*-oxide is in carbon tetrachloride than when in n-hexane. The effects of substituents on the spectrum of benzo[*c*]cinnoline *N*-oxide (see below) suggest that the feature " e " (Fig. 1) is part of the group III band and not, as previously assumed,[2] part of the group II band; on this basis we suggest that the group II band comprises features c and d, and the group III band, the features e, f, g, h, and i. The general shape of the group III band of benzo[*c*]cinnoline is retained in the spectrum of the *N*-oxide, but the band is spread over 36 mμ, compared with 30 mμ.

The spectrum of protonated benzo[*c*]cinnoline *N*-oxide, in 80% aqueous sulphuric acid (Table 1) is similar in form to that of the benzo[*c*]cinnolinium ion, except that the group II and III bands are at slightly shorter wavelengths. The similarity between these spectra, and the disappearance of the *x*-band, suggest that the oxygen atom, rather than the unsubstituted nitrogen atom, is protonated. If the nitrogen were protonated, the oxygen atom should produce a red shift of the group II and III bands, relative to those of the benzo[*c*]cinnolinium ion.

General Discussion of Substituent Effects.—Friedel and Orchin stated that there is no relation between spectral shifts in the spectra of polycyclic hydrocarbons and their derivatives and the number and position of the substituents.[5] However, it has been reported that the shifts of the *p*-band of phenanthrene caused by alkyl substituents are independent of the nature of the alkyl groups, and are additive in the spectra of polyalkylphenanthrenes.[6] From the data in the literature for 58 alkyl- and polyalkyl-phenanthrenes, we confirm this result and find that the shifts of the β- and α-bands are also additive, within ±1 mμ.

Benzo[*c*]cinnoline and phenanthrene are iso-electronic and, as is generally observed,[7] the introduction of nitrogen atoms in place of methine groups has only a small effect on the spectrum (Table 1). Further, the molecular orbitals employed to describe the π-electron system of phenanthrene should, with minor modifications, also apply to benzo[*c*]cinnoline.

Peters employed the Hückel L.C.A.O. theory in calculating the shifts to be expected from the introduction of substituents into alternant hydrocarbons.[8] The equation for the *p*-band which is considered to involve a transition from the highest bonding molecular orbital to the lowest non-bonding molecular orbital, is:

$$\delta\lambda = 475 c_{\mathrm{ar}}^{2}(\beta_{\mathrm{rs}}/\beta)^{2}\frac{1}{\varepsilon_{\mathrm{i}}(\varepsilon_{\mathrm{i}}^{2}-\alpha^{2})}\ \mathrm{m}\mu, \qquad (1)$$

where ε_i is the energy of the highest bonding molecular orbital of the unsubstituted hydrocarbon, c_{ar} the atomic-orbital coefficient at the substituted carbon atom, β_{rs} is the resonance integral of the bond between the carbon atom r and the substituent, β the carbon–carbon resonance integral, and α the coulomb integral for a single *p*-orbital of the substituent.

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[5] Friedel and Orchin, " Ultra-violet Spectra of Aromatic Compounds," John Wiley & Sons, New York, 1951.

[6] Ochiai, Okamoto, Sakai, and Natsume, *Pharm. Bull.* (*Japan*), 1957, **5**, 133.

[7] Badger, Pearce, and Pettit, *J.*, 1951, 3199.

[8] Peters, *J.*, 1957, 646, 1993, 4182.

ε_i and α are expressed in units of β. For phenanthrene, the values of c_{ar}^2 for the atoms in the outer rings are: 1-, 0·115; 2-, 0·00; 3-, 0·098; and 4-, 0·054; and the value of ε_i is −0·605β. For methyl substituents, which are regarded as modified vinyl groups, β_{rs}/β = 0·51 and α = 2·5, while for bromine or chlorine β_{rs}/β = 0·2 and α = 1·0.

The coefficient of the carbon $2p\pi$-atomic orbitals in the relevant molecular orbitals will have the same relative values in benzo[*c*]cinnoline as in phenanthrene, so that the equation (1) is a rough guide to substituent effects in the heterocycle. As to the value of ε_i, the energies of the highest bonding and lowest non-bonding molecular orbitals are symmetrical about an arbitrary zero for both phenanthrene and benzo[*c*]cinnoline. It has been noted that the group II band is at longer wavelengths in the spectrum of benzo[*c*]-cinnoline than in that of phenanthrene, *i.e.*, the energy of the transition is smaller for benzo[*c*]cinnoline. It follows, since the value of ε_i for the highest bonding orbital is taken as half of the *p*-band transition energy, that it will be absolutely greater but numerically smaller for benzo[*c*]cinnolines than for phenanthrene.

The equation shows that the numerical decrease of ε_i results in an increase of $\delta\lambda$, thus for a particular substituent, the shift for a substituted benzo[*c*]cinnoline should be greater than that for the corresponding phenanthrene derivatives.

Steric effects in the spectra of 1,10-disubstituted benzo[*c*]cinnolines include loss of fine structure and a large red shift of the group II band. Similar effects have been observed in the spectrum of 4,5-dimethylphenanthrene.[9] That a red shift of this band should result from steric strain which is relieved about the 4a–4b bond through which the highest bonding molecular orbital has a node, has recently been explained on the basis of the L.C.A.O. theory.[10]

The Spectra of Methylbenzo[c]*cinnolines*.—The spectra of the methyl derivatives of benzo[*c*]cinnoline are similar in form to that of the parent compound (Table 2). The shifts of the three π–π^* bands, resulting from methyl substitution, depend on the number and position of the substituents. For 3-methyl- and 3,8-dimethyl-benzo[*c*]cinnoline the shifts are additive within ±1 mμ.

TABLE 2.

$\lambda_{max.}$ (mμ) for some methyl- and substituted methyl-benzo[*c*]cinnolines in n-hexane.

	Group I		Group II		Group III	
Benzo[*c*]cinnoline	$\lambda_{max.}$	Shift	$\lambda_{max.}$	Shift	$\lambda_{max.}$	Shift
—	245, 250	0	294, 305	0	331, *340*, 345, 354, 361	0
1-Methyl	— 249	−1	300, 311	6	334, *340*, 347, 357, 363	2·5
1,10-Dimethyl	— 252	2	314, 325	20	— — 362, — *375*	15
1,10-(HO·CH$_2$)$_2$	— 253	3	— 326	21	— — — — *370*	9
1,10-(CH$_2$(Cl)$_2$	— 252	2	313, 324	19	— — 360, — *375*	14
1,10-CH$_2$·O·CH$_2$	— 255	5	304, 315	10	336, — 350, *359*, 367	5
3-Methyl	— 253	3	293, 305	0	338, *345*, 351, 361, 367	6
3,8-Dimethyl	*253*, 258	8	296, 306	1·5	343, *353*, 358, 368, 374	13
2,9-Dimethyl	249, 255	4·5	300, 311	6	*328*, 339, 343, *355*, 359	−2

The observed shifts for benzo[*c*]cinnoline derivatives and the observed and calculated values for the phenanthrene analogues are given in Table 3. As predicted, the shifts of the group II band are greater for the benzo[*c*]cinnoline derivatives than for the phenanthrene analogues, while the magnitude of the shifts associated with the different positions of substitution are in the order, 1- > 2- > 3- in both series. Similarly, the shifts in the group I band for the cinnoline derivatives are greater than, and the order 3- > 2- > 1- is the same as, that for the phenanthrene derivatives. The agreement between the observed and the calculated values is best for the group II band, for which the calculations are most rigorous; the high value of the shift for the 1-methyl compound

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[9] Johnson, *J. Org. Chem.*, 1959, **24**, 833.
[10] Cromartie and Murrell, *J.*, 1961, 2063.

TABLE 3.

Comparison of the observed shifts for monomethyl substitution of benzo[*c*]cinnoline and the calculated and observed shifts for substitution in the analogous positions of phenanthrene.

	Group I			Group II			Group III		
	Cinn.	Phen.		Cinn.	Phen.		Cinn.	Phen.	
Position of substn.	obs.	obs.[a]	calc.	obs.	obs.[a]	calc.	obs.	obs.[a]	calc.
1-	−1	0	3	6	4	2	2·5	3	3
2-	2·5	1·5	1	3·5	2·5	3	−1·5	2	1
3-	3·5	2·5	3	1	1	0	6·5	2	2

[a] Estimated from the spectra of polyalkylphenanthrenes.

is probably due to an element of steric bathochromic shift. Peters predicts that substitution in the 2-position (*i.e.*, the 3-position of phenanthrene) should give the smallest shifts in the group III band; in fact, substituents in this position produce a small blue shift while those in other positions produce a red shift.

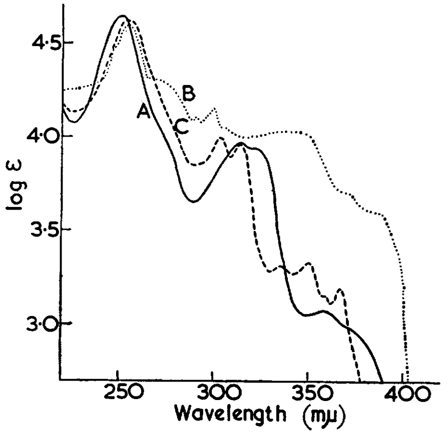

FIG. 2. The spectra of 1,10-dimethylbenzo[c]-cinnoline (A) and its *N*-oxide (B), and of 1,10-methyleneoxymethylenebenzo[*c*]cinnoline (C) in n-hexane.

The spectrum of 1,10-dimethylbenzo[*c*]cinnoline † (Fig. 2), like that of 4,5-dimethylphenanthrene, shows unusual features. The spectrum is almost devoid of fine structure and the bathochromic shifts of the three π–π* bands are considerably more than twice those for 1-methylbenzo[*c*]cinnoline (Table 2). These anomalies can be attributed to ring strain resulting from intramolecular overcrowding of the two methyl groups. That the ring system in 1,10-dimethylbenzo[*c*]cinnoline is twisted, has been demonstrated by the resolution of its 4,7-diamino-derivative.[12] This ring strain will increase the number of vibrational states and thus cause a loss of fine structure. This has been demonstrated by comparing the spectrum of 4,5-dimethylphenanthrene with that of 4,5-methylenephenanthrene; the spectrum of the latter has more fine structure than that of phenanthrene itself.[9]

In Table 4 the spectral shifts of 1-methylbenzo[*c*]cinnoline, some 1,10-disubstituted benzo[*c*]cinnolines and some 4,5-disubstituted phenanthrenes have been compared.

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† The spectrum of " 1,10-dimethylbenzo[*c*]cinnoline in ethanol " ($\lambda_{max.}$ 294 mμ; log ε 5300) reported by Calderbank and Le Fèvre [11] for a material " colourless crystals, m. p. 135—136° " (cf. present work: yellow needles, m. p. 112—113°; $\lambda_{max.}$ 325 mμ; log ε 8900) was evidently that of 2,2′-diamino-5,5′-dimethylbiphenyl (lit., colourless, m. p. 136°). Their material was obtained by the reduction of the cinnoline *N*-oxide with stannous chloride. We found that, while stannous chloride does not reduce benzo[*c*]cinnoline beyond the 1,2-dihydro-compound, it readily reduces the 1,10-dimethylbenzo[*c*]cinnoline to the diamine. This is a further manifestation of the ring strain in this cinnoline.

[11] Calderbank and Le Fèvre, *J.*, 1951, 649.

[12] Theilacker and Baxmann, *Annalen*, 1953, **581**, 117.

TABLE 4.

Spectral shifts (mμ) for some strained and unstrained benzo[*c*]cinnolines and their phenanthrene analogues.

	Group II		Group III	
Benzo[*c*]cinnoline	Cinn.	Phen.	Cinn.	Phen.
1-Methyl	6	4 [a]	2·5	3 [a]
1,10-Dimethyl	20	21	14	6·5
1,10-$CH_2{\cdot}O{\cdot}CH_2$	10	9	6	8
1,10-$(HO{\cdot}CH_2)_2$	21	—	9	—
1,10-$(CH_2Cl)_2$	20	—	14	—

[a] Estimated from the spectra of some 4,*x*-dimethylphenanthrenes ($x \neq 5$).

Clearly, the red shift increases with the extent of overcrowding; thus, for the methyleneoxymethylene compounds, which molecular models show are capable of assuming an unstrained configuration, the shift is approximately double that for a monosubstituted compound: the shifts for the dimethyl and the bishydroxymethyl compound are considerably greater. The close parallel between the shifts for the benzo[*c*]cinnoline derivatives and their phenanthrene analogues is again evident.

The spectrum of only one alkylphenanthridine, 8,10-dimethylphenanthridine, is recorded in the literature.[13] The observed shifts of 2, 5·5, and 6 mμ compare well with the values of 2·5, 5·0, and 6·5 mμ (group I, II, and III bands) expected on the assumption that the shifts would be intermediate between those of the phenanthrene and benzo[*c*]-cinnoline analogues.

The effect of protonation of the methylbenzo[*c*]cinnolines on their spectra (Table 5) is similar to that for benzo[*c*]cinnoline itself. The steric bathochromic shift of the 1,10-dimethylbenzo[*c*]cinnolinium ion is even more pronounced than that of the neutral molecule. Thus the shifts produced by protonation of the unstrained benzo[*c*]cinnolines are about the same as those for benzo[*c*]cinnoline, but those for the 1,10-dimethyl compound are considerably greater. Again, 1,10-methyleneoxymethylenebenzo[*c*]cinnoline exhibits the shifts expected for an unstrained system.

TABLE 5.

$\lambda_{max.}$ (mμ) for some benzo[*c*]cinnoline derivatives in 2N-hydrochloric acid (in parentheses the shifts relative to their spectra in ethanol).

Subst.	Group I	Group II	Group III
None	250 —	356 (48)	*420* (60)
1-Methyl	250 (1)	364 (50)	*420* (58)
1,10-Dimethyl	262 (10)	395 (70)	*450* (75)
1,10-$CH_2{\cdot}O{\cdot}CH_2$	254 (−1)	368 (52)	*425* (55)
2,9-Dimethyl	250 (0)	360 (48)	*420* (60)
3,8-Dimethyl	260 (3)	358 (50)	*430* (60)

Bromo-derivatives.—In an earlier paper[1] we reported the spectra of eight bromo-derivatives of benzo[*c*]cinnoline in carbon tetrachloride (group II and III bands) and in ethanol (group I band). The spectral shifts produced by the substituents were additive and dependent on the position of substitution. The shifts for monosubstitution are given in Table 6, and those for the group II band are compared with the values calculated by Peters for similar substitution in phenanthrene.[8] The observed shifts of the group II band agree qualitatively with the calculated values; the large bathochromic shift for substitution in the 1-position parallels that observed for 1-methylbenzo[*c*]cinnoline and again is probably a steric effect. The molecular-orbital method is particularly successful in predicting a negligible shift of the group II band for substitution in the 3-position and a small shift of the group III band for substitution in the 2-position (Table 3). In fact, small blue shifts are observed for the latter with methyl, bromo-, and chloro-substituents.

The shifts of the three bands resulting from bromo-substituents are greater than those

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[13] Smolinski, *J. Amer. Chem. Soc.*, 1960, **82**, 4717.

TABLE 6.

Spectral shifts (mμ) for bromo-substitution of benzo[*c*]cinnoline.

Position	Group I	Group II obs.	Group II calc.[a]	Group III
1-	0	11	3	7
2-	3	6	5	−1
3-[b]	8	0	0	9
4-	4	11	6	6·5

[a] For the phenanthrene analogue.[8] [b] The observed shifts for the phenanthrene analogue are 3, 2, and 3·5 mμ, respectively.

produced by methyl substituents; however, the order 3- > 2- > 1-, 1- > 2- > 3-, and 3- > 1- > 2- for the group I, II, and III bands, respectively, is the same in both series. The larger shift for bromine is to be expected, at least for the group II band, from the values of the (β_{rs}/β) and α terms in the molecular-orbital equations; further, the same relative order is to be expected since, in each series, the shift is proportional to $c_{ar}{}^2$.

To test the additivity of spectral shifts and the suggestion [8] that chloro-substituents should produce the same shifts as bromo-substituents, the spectra of some chloro-, chloromethyl-, and bromo-methyl-benzo[*c*]cinnolines have been determined (Table 7). The observed shifts agree well with the estimated values, and the shifts produced by chloro- are almost identical with those produced by bromo-substituents.

TABLE 7.

$\lambda_{max.}$ (mμ) and the observed and estimated[a] shifts for some derivatives of benzo[*c*]cinnoline in carbon tetrachloride.

Subst.	Group II $\lambda_{max.}$	Group II obs.	Group II est.	Group III $\lambda_{max.}$	Group III obs.	Group III est.
None	296, 308	0	—	331, 347, 362	0	—
2,9-Cl_2	307, 319	11	12	— 344, 360	−2	−2
3,8-Cl_2	*296*, 308	0	0	349, 363, 381	18·5	18
1-Br-3-Me	307, 318	11	11	343, 358, 374	12	13
3,8-Br_2-2,9-Me_2	303, 315	7	7	348, 362, 379	16	15
4,7-Br_2-2,9-Me_2	323, 336	28	29	— *358*, 373	11	10
3,8-Cl_2-2,9-Me_2	303, 314	7	7	345, 360, 376	14	15

[a] Estimated on the assumption of addivity, from the shifts in Tables 2 and 6.

Nitrobenzo[c]*cinnolines*.—Nitro-groups have a considerable effect on the spectra of polycyclic aromatic hydrocarbons except when there is steric hindrance to the coplanarity of the nitro-group and the ring system.[14] Nitro-groups in the 1-, 2-, 3-, and 9-positions of phenanthrene produce large spectral changes, but a 4-nitro-group has only a minor effect.[15]

TABLE 8.

Values of $\lambda_{max.}$ (log ε) for benzo[*c*]cinnoline and some nitro-derivatives in carbon tetrachloride.

Subst.	Group II	Group III
None	296 (3·9), 308 (3·85)	331 (3·05), 347 (3·1), 362 (3·05)
1-NO_2	300 (3·9), 312 (3·85)	332 (3·15), 346 (3·15), 364 (3·05)
2-NO_2	318 (3·95), 326[s] (3·9)	358 (3·4), 364 (3·4), 377 (3·2)
4-NO_2	300 (3·85), 308 (3·8)	348 (3·15), 362 (3·05)
1,10-Me-4-NO_2	324 (4·0), 330 (4·0)	*a*
1,10-Me_2-4,7-$(NO_2)_2$	— — 328 (3·95)	*a*

[a] Gradual tailing off to 420 mμ. [s] Shoulder.

The effect of nitro-groups on the spectrum of benzo[*c*]cinnoline is surprisingly small. The spectra of the 1- and the 4-nitro-compound (Table 8) are almost identical with that

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[14] Jones, *Chem. Rev.*, 1947, **41**, 353.

[15] Bavin, Ph.D. Thesis, London, 1955; Bavin and Dewar, *J.*, 1955, 4485.

of benzo[*c*]cinnoline. For 1-nitrobenzo[*c*]cinnoline, the analogue of 4-nitrophenanthrene, this is explained by steric hindrance to coplanarity but this does not apply to 4-nitrobenzo[*c*]cinnoline. In this case repulsion between the negative oxygen of the nitro-group and the electrons in the lone-pair orbital of the neighbouring atom may prevent coplanarity of the two chromophores. The spectrum of 8-nitroquinoline, in which the nitro-group is similarly situated with respect to the heteroatom, is similar to that of quinoline.[16]

The spectrum of 2-nitrobenzo[*c*]cinnoline shows that a nitro-group in this position produces a red shift and a loss of fine structure in both the group II and the group III band. The change is, however, much less marked than that produced by similar substitution in phenanthrene.

The spectra of 1,10-dimethyl-4-nitro- and of 1,10-dimethyl-4,7-dinitro-benzo[*c*]-cinnoline (Table 8), compared with that of 4-nitrobenzo[*c*]cinnoline, show the large red shift (22 mμ) of the group II band and the loss of fine structure which is characteristic of 1,10-disubstituted benzo[*c*]cinnolines.

n–π Transitions.*—In the spectra of substituted benzo[*c*]cinnolines, the features attributable to *n–π** transitions appear as shoulders ($\lambda_{\text{max.}}$ 400—430 mμ, log ε 2·5—2·7) which show no fine structure. Methyl substituents have little or no effect on the position of this band, but halogen in the 1- and the 4-position produces a large, and in the 3-position a small, red shift. In the 2-position, halogen produces a small blue shift. These shifts resemble those observed for the *n–π** transitions in the spectra of the chlorocinnolines,[17] but they contrast with the usual blue shift caused by halogen substituents in the monocyclic azines [18] and in the hetero-ring of cinnoline.[17]

Substituted Benzo[c]*cinnoline* N-*Oxides.*—The spectra of derivatives of benzo[*c*]-cinnoline *N*-oxide, given in Table 9, closely resemble that of the parent *N*-oxide except that substitution in the 1-position (hindered) produces changes consistent with ring strain. The spectrum of 1,10-dimethylbenzo[*c*]cinnoline *N*-oxide (Fig. 2) has little fine structure, the group III band appearing merely as two shoulders. Similarly, the group III bands given by the 1-bromo-compounds have lower intensities and less fine structure than those of the other substituted *N*-oxides, although no loss of fine structure was observed in the group III bands of the 1-bromobenzo[*c*]cinnolines.

The average spectral shifts caused by substituents are given in Table 10. Additivity of shifts, again evident, is less consistent than for substituted benzo[*c*]cinnolines, particularly for the group II band which is ill-defined in the spectra of some of the substituted *N*-oxides. Further, there is no relation between the shifts for benzo[*c*]-cinnoline and those for its *N*-oxide, and the shifts of the group III band due to chloro-substituents are somewhat lower than those due to bromine.

Aminobenzo[c]*cinnolines.*—An amino-group considerably affects the absorption spectrum of an aromatic hydrocarbon. Interaction between the lone-pair electrons of the nitrogen atom and the π-electrons of the aromatic nucleus produces a complete loss of fine structure, a red shift of some or all of the absorption bands, and a new broad band at longer wavelengths.[19] In acid solution, there are no lone-pair electrons and the spectrum reverts to that of the parent hydrocarbon.[20]

The absorption spectra of amino-derivatives of acridine,[21] quinoline,[22] isoquinoline,[4] and cinnoline [4] in neutral solution show features similar to those in the spectra of the

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[16] Dewar and Maitlis, *J.*, 1957; 2521.

[17] Osborn and Schofield, *J.*, 1956, 4207.

[18] Halverson and Hirt, *J. Chem. Phys.*, 1951, **19**, 711.

[19] Friedel and Orchin, ref. 5; Jones, *J. Amer. Chem. Soc.*, 1945, **67**, 2127.

[20] Harberts, Heertjes, van der Hulst, and Waterman, *Bull. Soc. chim. France*, 1936, **3**, 643; de Borst, Heertjes, van der Hulst, and Waterman, *ibid.*, 1938, **5**, 3397.

[21] Craig and Short, *J.*, 1945, 419.

[22] Steck and Ewing, *J. Amer. Chem. Soc.*, 1948, **70**, 3397; Hearn, Morton, and Simpson, *J.*, 1951, 3329.

TABLE 9.

Values of $\lambda_{max.}$ and log ε and of substituent shifts (δλ) for some derivatives of benzo[*c*]cinnoline *N*-oxide.

Substituents	*x*-Band		Group II		Group III	
	$\lambda_{max.}$	δλ	$\lambda_{max.}$	δλ	$\lambda_{max.}$	δλ
(i) *In n-hexane.*						
None	286, 297 4·1 4·1	0	329, 337 4·0 3·95	0	344, *354*, 361, 370, 380 4·0 3·9 3·8 3·7 3·95	0
1,10-Me_2	*290*, 302 4·1 4·15	4·5	348 4·0	?	— — *372*, — *388* 3·7 3·6	10
2,9-Me_2	289, 300 4·2 4·2	3	338, 345 4·0 4·0	8·5	345, *354*, 363, 372, 382 4·05 3·85 3·9 3·7 3·95	2
3,8-Me_2	289, 300 4·25 4·2	3	*330*, 338 3·95 4·0	1	352, 362, 369, *380*, 389 4·0 3·9 3·95 3·8 3·95	9
(ii) *In carbon tetrachloride.*						
None	287, 299 4·1 4·1	0	331, 339 4·0 3·95	0	345, *355*, 363, *372*, 382 4·0 3·95 3·9 3·65 3·9	0
1-Br	288, 301 4·05 4·15	1·5	*331*, 340 4·1 4·1	0·5	— — 364, — 383 3·85 3·8	1
2-Br	289, 301 4·1 4·15	2	333, *341* 4·05 *4·05*	2	348, 357, 365, *374*, 385 4·05 3·9 4·05 *3·65* 3·95	2·5
2,9-Br_2	293, 305 4·2 4·3	6	336, 344 4·05 4·05	5	350, *358*, 367, 376, 387 4·1 3·95 4·05 3·75 4·0	4·5
2,9-Cl_2	292, 303 4·2 4·35	4·5	337, *344* 4·05 *4·0*	5	350, *358*, 367, 377, 387 4·1 3·9 4·05 3·75 4·0	4·5
2,4-Br_2	297, 310 4·2 4·25	10·5	*337, 343* *4·06 4·1*	5	353, 358, 369, *378*, 389 4·1 *3·85* 3·9 *3·7* 3·9	6·5
3-Br	290, 303 4·15 4·15	3·5	*331*, 339 *3·95 3·9*	0	*351, 361*, 370, *375*, 389 *3·85 3·8* 3·85 *3·55* 3·85	6·5
3,8-Br_2	294, 306 4·25 4·25	7	*333, 339* *4·0 3·95*	1	358, 368, 376, — 396 3·9 3·8 3·75 3·8	13
3,8-Cl_2	294, 306 4·25 4·25	7	— *339* *3·9*	0	355, — 373, — 392 3·9 3·8 3·85	10
1,7-Br_2	296, 307 4·2 4·25	8·5	341 4·1	?	— — *365, 374*, 386 *4·0 3·8* 3·75	4
1-Br-3-Me	*290*, 303 *4·2* 4·15	3·5	340 4·1	?	— — 369, — 388 *3·85* 3·6	6
3,8-Br_2-2,9-Me_2	296, 308 4·35 4·35	9	338, 345 4·1 4·1	7	359, 370, 377, — 398 4·1 3·9 4·05 4·0	15
3,8-Cl_2-2,9-Me_2	296, 308 4·3 4·3	9	339 — 4·05	8	355, — 374, — 394 4·1 4·0 4·15	11

TABLE 10.

The average spectral shift[a] (mμ) caused by a single substituent in benzo[*c*]cinnoline *N*-oxide.

Position	*x*-Band			Group II			Group III		
	Me	Br	Cl	Me	Br	Cl	Me	Br	Cl
1-	—	1·5	—	—	0·5	—	—	1·0	—
2-	1·5	2·5	2·0	4·0	2·5	2·5	1·0	2·5	2·0
3-	1·5	3·5	3·5	0·5	0	0	4·5	6·5	5·0
4-	—	8·0	—	—	2·5	—	—	4·0	—

[a] Estimated from the data in Table 9.

aromatic hydrocarbon amines. However, on protonation there is still a general red shift of the spectrum, which includes the broad long-wavelength band, indicating that the heteroatom rather than the amino-group is the basic centre.

It is difficult to relate the various features in the spectra of the amino-derivatives (Figs. 3 and 4) to those of benzo[*c*]cinnoline itself. It seems likely that the maxima with log ε 4·4 are related to the group I band and those with log ε 4·0 to the group II band of benzo[*c*]cinnoline: ·the values in Table 11 have been grouped in this way. The spectra of the aminobenzo[*c*]cinnolines are unusual in that, while they show the normal broad absorption band at long wavelengths, the group II bands, and the group I bands relevant to the 1-, 2-, and 4-amines, are at slightly shorter wavelengths than in the spectrum of benzo[*c*]cinnoline. An amino-group in the 3-position produces a large red shift of the group I band, and the group II band is partially masked (Fig. 3).

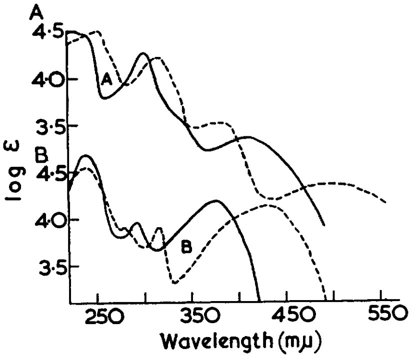

FIG. 3. The spectra of 1-amino- (A) and 2-amino-benzo[*c*]cinnoline (B) in ethanol (full line) and in 0·1N-hydrochloric acid (broken line).

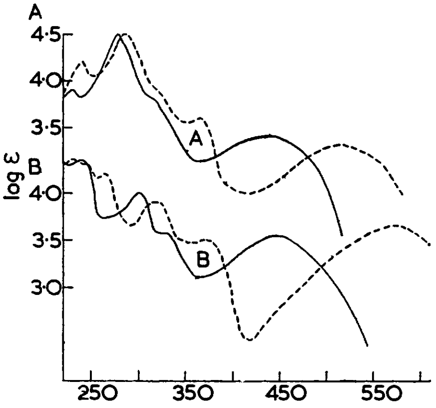

FIG. 4. The spectra of 3-amino- (A) and 4-amino-benzo[*c*]cinnoline (B) in ethanol (full line) and in 0·1N-hydrochloric acid (broken line).

TABLE 11.

Spectra ($\lambda_{max.}$ in mμ) of some aminobenzo[*c*]cinnolines in various solvents.

Amino-groups	Solvent	Group I	[a]	Group II	[a]	Group III	Long-wave-length band
None	Ethanol	251	—	308	—	354	
	2N-HCl	250	—	356	—	*420*	—
1-	Ethanol	228, 239	—	303	*338*	—	412
	0·1N-HCl	*234*, 247	—	318	386	—	508
	5N-HCl	250	—	358	—	*420*	—
2-	Ethanol	250	—	300	—	—	386
	0·1N-HCl	249	288	324	—	—	442
	5N-HCl	250		350	—	*420*	—
3-	Ethanol	230, 276	—	*306*	—	—	440
	0·1N-HCl	236, 285	—	318	368	—	505
	5N-HCl	250	—	353	—	*415*	—
4-	Ethanol	240, *245*	—	305	*332*	—	448
	0·1N-HCl	230, 241, *251*	267	324	371	—	575
	5N-HCl	250	—	367	—	*420*	—
1,10-	Ethanol	*260*	*280*	323	—	—	402
	0·1N-HCl	245	—	290	340	—	[b]
	80% H_2SO_4	254	—	395	—	—	—
2,9-	Ethanol	260	—	303	346	—	402
	0·1N-HCl	250	—	316	—	—	462
	80% H_2SO_4	250	—	348	—	*422*	—
3·8-	Ethanol	280	—	*318*	—	—	478
	0·1N-HCl	295	—	—	362	—	550
	80% H_2SO_4	250	—	353	—	*425*	—
1,10-Me_2-4-NH_2	Ethanol	237, *250*	—	320	*370*	—	465
	0·1N-HCl	248	282	344	408	—	594
	6N-HCl	264	—	405	—	—	—

[a] The origin of these features is not known. [b] There is no maximum or shoulder; the absorption gradually tails off to zero at *ca.* 400 mμ.

No successful correlation has been made of the long-wavelength bands in the spectra of aromatic amines with those of the corresponding aromatic hydrocarbon spectra, and no such correlation is to be expected, since the lower energy transitions should originate from the amino-group lone-pair electrons, conjugated to a smaller or greater degree with the nucleus. In *N*-aromatic amines the conjugation should be substantial, owing to the inductomeric effect of the nuclear nitrogen atom(s).

The spectra of the monocations (in 0·1N-hydrochloric acid) show that protonation occurs at one of the heteroatoms since it causes the expected shift (which we shall call the "protonation shift") towards the red of all the bands and of the long-wavelength band in particular. Even so, the group II bands in the spectra of the monocations are at shorter wavelengths than that in the spectrum of the benzo[*c*]cinnolinium ion. This is again unusual among amino-derivatives of nitrogen heterocycles. The heteroatom which becomes protonated in the monocations is, presumably, that which can take part in "additional ionic resonance." The spectra of aminobenzo[*c*]cinnolines in 5N-hydrochloric acid (Table 11) are those expected for the dications in which the amino-group and one of the heteroatoms are protonated; the long-wavelength band is absent and the spectrum resembles that of the benzo[*c*]cinnolinium ion.

The $\lambda_{\text{max.}}$ of the long-wavelength band in the spectra of the aminobenzo[*c*]cinnolines depends on the position of the amino-group, being in the order 4- > 3- > 1- > 2- in ethanol and 4- > 1- > 3- > 2- in acid. A similar order holds for the aminocinnoline analogues (Table 12).[4] Moreover, the protonation shifts are in the order 4- > 1- > 3- > 2- (benzo[*c*]cinnoline) or 8- > 5- > 7- > 6- (cinnoline) and the magnitude of the shift for an aminocinnoline is similar to that for the corresponding benzo[*c*]cinnoline derivative.

TABLE 12.

Comparison of data for the long-wavelength bands in the spectra of aminobenzo[*c*]cinnolines and of aminocinnolines.

	Aminobenzo[*c*]cinnoline				Aminocinnoline [a]		
Position	$\lambda_{\text{max.}}$ (EtOH)	$\lambda_{\text{max.}}$ (acid)	$\delta\lambda$	Position	$\lambda_{\text{max.}}$ (EtOH)	$\lambda_{\text{max.}}$ (acid)	$\delta\lambda$
1-	412	508	96	5-	382	490	108
2-	386	442	56	6-	362	416	54
3-	440	505	65	7-	385	446	61
4-	448	575	127	8-	395	520	125

[a] Osborn, Schofield, and Short, *J.*, 1956, 4191.

The spectra of 2,9- and 3,8-diaminobenzo[*c*]cinnoline are similar to those of the 2- and 3-monoamines, respectively. Both the 2-amino- and the 2,9-diamino-derivative have high-intensity long-wavelength bands and solutions show a greenish fluorescence; solutions of the other amines are not fluorescent. A second amino-group has little effect on the spectrum. There are small red shifts of the group I and II bands. The red shifts of the long-wavelength bands, resulting from protonation, are of about the same magnitude as for the corresponding monoamine. The spectra of the amines in 80% sulphuric acid are similar to that of the benzo[*c*]cinnolinium ion, indicating that both amino-groups are protonated.

When compared with that of 1-aminobenzo[*c*]cinnoline, the spectrum of 1,10-diaminobenzo[*c*]cinnoline shows a number of anomalies. In ethanol, the spectrum of the diamine exhibits a steric bathochromic shift of the group II band, the magnitude of which (20 mμ) is similar to that of the shift given by 1,10-dimethylbenzo[*c*]cinnoline. The long-wavelength band of the diamine is at shorter wavelengths than that of the 1-amino-compound. This can be attributed to the mutual interference of the two amino-groups, one of which, in the excited state, must be planar and coplanar with the ring system. The spectral changes resulting from the protonation of the diamine do not resemble those observed for the other amino-compounds, the whole spectrum undergoing a blue shift instead of the usual red shift.

The spectrum of the diamine in 80% sulphuric acid resembles that of the 1,10-dimethylbenzo[*c*]cinnolinium ion (Table 5) rather than that of the benzo[*c*]cinnolinium ion. The steric red shift caused by 1,10-disubstitution of benzo[*c*]cinnoline is exemplified by the similarity of the spectra of the 1,10-dimethylbenzo[*c*]cinnolinium ion, the dication of 1,10-dimethyl-4-aminobenzo[*c*]cinnoline and the trication of 1,10-diaminobenzo[*c*]cinnoline. Further, the shifts of the group II band in these spectra relative to those in the spectra of the benzo[*c*]cinnolinium ion, the dication of 4-aminobenzo[*c*]cinnoline, and the benzo[*c*]-cinnolinium ion, respectively, are 39, 38, and 39 mμ.

Conclusion.—The shifts introduced by substituents such as methyl and halogen in the spectra of substituted benzo[*c*]cinnolines are additive and dependent on the position of substitution. They are related to those caused by similar substitution in phenanthrene. The L.C.A.O. methods used for even alternant hydrocarbons[8] can be extended to their heterocyclic analogues and spectral data, both experimental and theoretical, can assist in determining the orientation of new compounds.

A large bathochromic shift of the group II band and a loss of fine structure are characteristic of ring twisting due to substituents in the 1- and the 10-position.

The spectra of the four monoaminobenzo[*c*]cinnolines are individually distinctive and should prove valuable in studying the nitration of substituted benzo[*c*]cinnolines, the nitro-derivatives of which could be reduced to amines.

EXPERIMENTAL

The preparation of the bromo-, 1,10-bishydroxymethyl-, 1,10-bischloromethyl-, 1,10-methylenoxymethylene-, 1,10-diamino-, 2,9-diamino-, 3,8-dibromo-2,9-dimethyl-, and 3,8-dichloro-2,9-dimethyl derivatives of benzo[*c*]cinnoline and *N*-oxides have been described previously.[1, 23–25] The preparation of the nitro-, 1-, 2-, and 4-amino-, and methyl derivatives of benzo[*c*]-cinnoline will be described later.

3-Aminobenzo[*c*]cinnoline was prepared by the method of Arcos *et al.*[26] as yellow-brown needles, m. p. 165° (lit., m. p. 163—165°).

2,9-*Dimethylbenzo*[c]*cinnoline* N-*Oxide.*—5,5′-Dimethyl-2,2′-dinitrobiphenyl[27] (0·7 g.) in boiling ethanol (50 ml.) was treated with sodium sulphate nonahydrate (1·2 g.) and sodium hydroxide (0·1 g.) in water (5 ml.). The mixture was refluxed for 5 hr., filtered, and concentrated. The crude product was precipitated by addition of water, separated, and recrystallised from ethanol. 2,9-*Dimethylbenzo*[c]*cinnoline* N-*oxide* formed almost colourless needles, m. p. 202° (Found: C, 74·2; H, 6·2; N, 12·5. $C_{14}H_{14}N_2O$ requires C, 74·3; H, 6·2; N, 12·4%).

1,10- *and* 3,8-*Dimethylbenzo*[c]*cinnoline* N-*Oxide.*—These compounds were prepared by methods described in the literature. The 1,10-isomer formed pale yellow needles, m. p. 153° (lit.,[28] m. p. 153°), and the 3,8-isomer formed yellow crystals, m. p. 205° (lit.,[29] m. p. 209°).

4,4′-*Dichloro*-2,2′-*dinitrobiphenyl.*—1-Bromo-4-chloro-2-nitrobenzene (10 g.) in dimethylformamide (100 ml.) was heated under reflux with copper bronze (10 g.) for 5 hr. The mixture was filtered while hot and the filtrate was concentrated and poured into water. The precipitate was filtered off and extracted with hot benzene. The extract was concentrated and allowed to cool. The biaryl (4·9 g., 74%) separated as golden prisms, m. p. 136—137° (lit., m. p. 136°).

3,8-*Dichlorobenzo*[c]*cinnoline.*—4,4′-Dichloro-2,2′-dinitrobiphenyl (5 g.) was reduced with lithium aluminium hydride in benzene–ether as described previously.[1] The cinnoline formed silky yellow needles, m. p. 255° (lit., m. p. 248°,[30] 259—260°[11]).

Oxidation of the cinnoline with hydrogen peroxide in acetic acid gave the N-*oxide*, m. p. 258—259° (lit.,[11] m. p. 244—245°) (Found: C, 53·8; H, 2·2. $C_{12}H_6Cl_2N_2O$ requires C, 54·3; H, 2·3%).

2,9-*Dichlorobenzo*[c]*cinnoline.*—A solution of 2,2′-bisacetamidobiphenyl (5·2 g.) and 1,3-dichloro-5,5-dimethylhydantoin (4 g.) in carbon tetrachloride (100 ml.) was refluxed for 24 hr. The dimethylhydantoin was filtered off and the solution was washed with aqueous sodium

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[23] Corbett and Holt, *J.*, 1961, 3695.
[24] Holt and Hughes, *J.*, 1960, 3216.
[25] Braithwaite, Holt, and Hughes, *J.*, 1958, 4073.
[26] Arcos, Arcos, and Miller, *J. Org. Chem.*, 1956, **21**, 651.
[27] Case and Koft, *J. Amer. Chem. Soc.*, 1941, **63**, 510.
[28] Sako, *Bull. Chem. Soc. Japan*, 1934, **9**, 393.
[29] Ullmann and Dieterle, *Ber.*, 1904, **37**, 23.
[30] Jerchel and Fischer, *Annalen*, 1954, **590**, 216.

hydroxide and water. The organic layer was dried and evaporated. The residue recrystallised from ethanol, to give *2,2′-bisacetamido-5,5′-dichlorobiphenyl* as colourless clusters, m. p. 248° (Found: C, 56·9; H, 4·3. $C_{16}H_{14}Cl_2N_2O_2$ requires C, 57·0; H, 4·15%).

The amide was refluxed in ethanol and hydrochloric acid (4 : 1 v/v). The crude amine was dissolved in acetic acid and treated with an excess of hydrogen peroxide (80% w/v). After 24 hr. at 50°, the solution was poured into water and the precipitate was recrystallised from ethanol, to give *2,9-dichlorobenzo*[c]*cinnoline* N-*oxide* as pale yellow needles, m. p. 285° (Found: C, 54·5; H, 2·2; Cl, 26·8; N, 10·5. $C_{12}H_6Cl_2N_2O$ requires C, 54·3; H, 2·26; Cl, 26·8; N, 10·5%).

The *N*-oxide was reduced with lithium aluminium hydride to give *2,9-dichlorobenzo*[c]*cinnoline*, m. p. 269° (Found: C, 57·7; H, 2·5. $C_{12}H_6Cl_2N_2$ requires C, 57·8; H, 2·6%).

Solvents.—n-Hexane, ethanol, and carbon tetrachloride were of B.D.H. spectrometric grade, and the acids were of " AnalaR " grade.

Spectra.—The spectra were determined with a Unicam SP 500 and an Optika spectrophotometer.

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