261. *Polycyclic Cinnoline Derivatives. Part VI.*[1] *The Ultraviolet Absorption of Polycyclic Cinnolines and their* N-*Oxides.*

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

The ultraviolet absorption spectra of seven unsubstituted polycyclic derivatives of cinnoline are recorded. The spectra resemble those of the carbocyclic analogues, except that the long-wavelength bands are at longer wavelengths and are more intense in the cinnoline spectra. The intensity increment is in good agreement with that predicted by Platt's "spectroscopic moment." An interesting relation between the wavelengths of the absorption bands and intramolecular overcrowding is observed. In non-polar solvents the cinnoline spectra have an additional absorption band which is ascribed to n–π^* transitions. *N*-Oxidation results in a bathochromic shift of the longer-wavelength absorption and an increase in the intensity of the long-wavelength band.

The polycyclic derivatives of cinnoline are of interest as heterocyclic analogues of the polycyclic aromatic hydrocarbons. Since each nitrogen atom contributes one electron to the π-electron system of the aromatic nucleus, the π-electron systems are similar to those of the carbocyclic analogues, and should therefore give rise to similar absorption spectra. Comparison of the spectra of the polycyclic cinnolines might, therefore, be expected to yield similar relationships to those found by comparison of the spectra of polycyclic aromatic hydrocarbons.

Badger and his collaborators [2,3] have shown that the ultraviolet absorption spectra of a number of polycyclic aza-hydrocarbons closely resemble those of their carbocyclic analogues, the main changes being a shift in the absorption to longer wavelengths, a loss of fine structure, and an increase in the intensity at longer wavelengths. Both the hydrocarbons and the aza-derivatives exhibit three main regions of absorption which have been designated,[2] in order of increasing wavelength, group I (log ε *ca.* 4·6), II (log ε *ca.* 4·0), and III (log ε *ca.* 3·2), these regions corresponding respectively to the β-, *p*-, and α-band of Clar's nomenclature.[4] The spectra of some aza-hydrocarbons in non-polar solvents also exhibit an additional absorption band at longer wavelengths (log ε *ca.* 2·6), which has been ascribed to n-π^* transitions.[5]

Comparison of the Spectra of Cinnolines and their Hydrocarbon Analogues.—Previous work on the spectra of polycyclic cinnolines has been confined to benzo[*c*]cinnoline [2,6,7] (I), substituted benzo[*c*]cinnolines,[7,8] and dibenzo[*c,f*]cinnoline [3,8] (II). We have redetermined the spectra of benzo[*c*]cinnoline and dibenzo[*c,f*]cinnoline, and measured the spectra of benzo[*f*]naphtho[2,1-*c*]cinnoline (III), dibenzo[*c,h*]cinnoline (IV), benzo[*h*]naphtho[1,2-*c*]-cinnoline (V), benzo[*f*]naphtho[1,2-*c*]cinnoline (VI), and tribenzo[*c,f,h*]cinnoline (VII), all in n-hexane solution. Comparison of the spectra with those of the corresponding aromatic hydrocarbons, as determined by Clar and Stewart,[9] shows that the introduction of two nitrogen atoms in place of two adjacent methine groups results in a bathochromic shift of the group II and III bands, a loss of fine structure, particularly in the group II band, and a considerable increase in the intensity of the group III band.

In studies of the spectra of benzene and its substituted derivatives the centres of the absorption bands are usually chosen for comparative purposes. In the higher polycyclic

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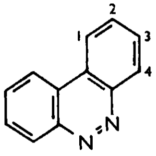
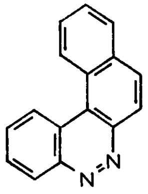
[1] Part V, Corbett and Holt, *J.*, 1960, 3646.
[2] Badger, Pearce, and Pettit, *J.*, 1951, 3199.
[3] Badger and Walker, *J.*, 1956, 122.
[4] Clar, "Aromatische Kohlenwasserstoffe," Springer-Verlag, Berlin, 1952.
[5] Halverson and Hirt, *J. Chem. Phys.*, 1951, **19**, 711; Badger and Walker, *J.*, 1956, 122.
[6] Calderbank and Le Fèvre, *J.*, 1948, 1949.
[7] Ramart-Lucas and Biquard, *Bull. Soc. chim. France*, 1936, 430.
[8] Ross and Kuntz, *J. Amer. Chem. Soc.*, 1952, **74**, 1297.
[9] Clar and Stewart, *J. Amer. Chem. Soc.*, 1952, **74**, 6235.

compounds the group II and III bands are partly masked by the previous, higher-intensity band, thus making the placing of the centre of these bands impossible. To obviate this difficulty, Platt,[10] in his theoretical treatment of the intensities of group III bands, chose the intensity of the smoothed curve at the wavelength of the longest-wavelength maximum in the band. We have chosen the wavelength of the longest wavelength maximum in each absorption band (called here λ_{I}, λ_{II}, and λ_{III}) for the purpose of evaluating shifts due to (*a*) the replacement of methine groups by nitrogen atoms and (*b*) nuclear annelation.


(I)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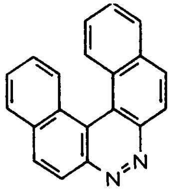
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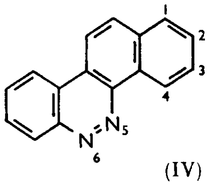
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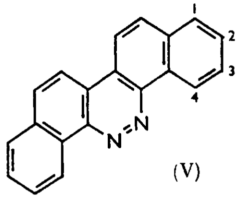
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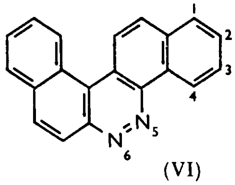
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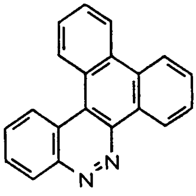
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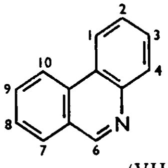
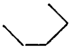
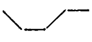
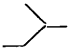

(VIII)

The bathochromic shifts of the group II band, resulting from the replacement of two methine groups by nitrogen atoms vary between 11 and 26 mμ, with the majority being about 11 mμ (Table 1). The shifts of the group III bands are between 10 and 17 mμ, except in the case of benzo[*h*]naphtho[1,2-*c*]cinnoline (V), for which the shift is only 2 mμ.

TABLE 1. *Values of* λ_{I}, λ_{II}, *and* λ_{III} *for polycyclic cinnolines (columns* " a "*) and their carbocyclic analogues (columns* " b "*). The shapes are obtained by joining the centres of the rings.*

		λ_{I} (mμ)			λ_{II} (mμ)			λ_{III} (mμ)		
Cpd.	Shape	a	b	(a − b)	a	b	(a − b)	a	b	(a − b)
I		250	*252*	−2	304	*293*	11	361	*346*	15
II		280	*281*	−1	327 ^{s}	*315*	12	387	*372*	15
III		304	*310*	−6	340 ^{s}	*329*	11	412	*395*	17
IV		272	*267*	5	330	*319*	11	371	*360*	11
V		284	*287*	−3	344 ^{s}	*329*	15	378	*376*	2
VI		297	*293*	4	347 ^{s}	*321*	26	396	*386*	10
VII		281	*286*	−5	345	*334*	11	383	*371*	12

^{s} = shoulder.

Shifts of the group I band are small, less than 6 mμ, and are sometimes bathochromic and sometimes hypsochromic. It is interesting to compare these shifts with those of the corresponding phenanthridines, in which only one methine group is replaced by a

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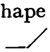
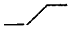
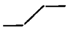
[10] Platt, *J. Chem. Phys.*, 1951, **19**, 263.

nitrogen atom. The spectra of phenanthridine [2] (VIII), benzo[*a*]phenanthridine,[11] benzo[*k*]phenanthridine,[11] benzo[*c*]phenanthridine,[12] and benzo[*i*]phenanthridine (all determined in ethanol) show very little shift of any of the three bands (Table 2).

The group III band in the spectra of the polycyclic aromatic hydrocarbons is attributed to a forbidden transition, and owes its intensity to vibrational interaction with stronger allowed transitions. The introduction of an aza-nitrogen atom in place of a methine group results in a perturbation leading to changes in the dipole moment during the transition, with a consequent increase in the intensity of absorption. According to the theory of Sklar,[13] Forster,[14] and Platt [10] the intensity increment, produced in the group III band of the spectrum of an aromatic hydrocarbon as a result of substitution, is proportional to a spectroscopic moment. Platt [10] gives a value of 38 for the spectroscopic moment of an aza-nitrogen atom, calculated as the square root of the observed intensity increment for pyridine and some of its substituted derivatives. Vector addition for 1,2-diaza-hydrocarbons predicts an intensity increment of 1444. The group III bands for phenanthrene and the higher polycyclic hydrocarbon analogues of the cinnolines under discussion have intensities between 125 and 400; it would thus be expected that the corresponding maxima in the cinnoline spectra would have intensities between 1550 and 1850 (*i.e.*, log ε *ca.* 3·2), which is found to be the case. The theory further predicts that the intensity increment for a mono-azahydrocarbon should be the same as for a 1,2-diaza-compound. The group III maxima of phenanthridine and the four benzophenanthridines referred to above have the predicted intensity (log ε *ca.* 3·2).

TABLE 2. *Values of* λ_{I}, λ_{II}, *and* λ_{III} *for some monoaza-hydrocarbons.*

Monoaza-hydrocarbon	Shape	λ_{I}	λ_{II}	λ_{III}
Phenanthridine [a]		250	296	343
Benzo[*k*]phenanthridine [b]		283	315[*]	376
Benzo[*a*]phenanthridine [b]		278	314	375
Benzo[*c*]phenanthridine [c]		266	325	359
Benzo[*i*]phenanthridine [c]		262	320	359

[a] Badger, Pearce, and Pettit, *J.*, 1951, 3199; [b] Mills and Schofield, *J.*, 1956, 4213; [c] Badger and Seidler, *J.*, 1954, 2329; [*] shoulder.

Effect of Nuclear Annelation of Benzo[c]*cinnoline.*—Nuclear annelation at the 1,2-bonds of benzo[*c*]cinnoline (I) produces analogues of the strained ring systems of benzo[*c*]phenanthrene and dibenzo[*c,g*]phenanthrene,[15] while annelation at the 3,4-bonds produces analogues of the unstrained chrysene and picene. The spectra of these two groups of cinnolines (Fig. 1) show differences in general shape, particularly in the group II band, which is well defined in the spectra of the unstrained cinnolines (I), (IV), and (V) but is a series of shoulders in the spectra of the strained systems (II) and (III). The spectra of benzo[*f*]naphtho[1,2-*c*]cinnoline (VI) and tribenzo[*c,f,h*]cinnoline (VII), in which only one of the additional rings produces ring strain, show well-defined group II bands.

Clar and Stewart [9] found that the ratio $\lambda_{I}/\lambda_{III}$ in the spectra of the polycyclic aromatic hydrocarbons is related to the extent of strain in the ring system. The ratio $\lambda_{I}/\lambda_{III}$ for the cinnolines shows no such relation, but a relation is evident for the ratios λ_{I}/λ_{II} and $\lambda_{II}/\lambda_{III}$ (Table 3). The former is 0·82 for the cinnolines free from ring strain, but increases as the extent of ring strain increases. The value for tribenzo[*c,f,h*]cinnoline (VII) is anomalous.

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[11] Mills and Schofield, *J.*, 1956, 4213.

[12] Badger and Seidler, *J.*, 1954, 2329.

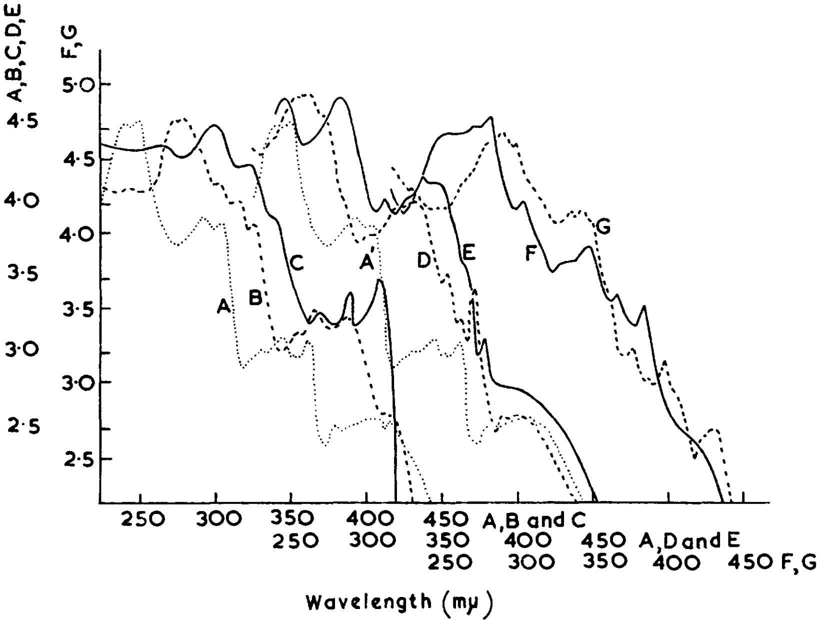
[13] Sklar, *J. Chem. Phys.*, 1942, **10**, 135.

[14] Forster, *Z. Naturforsch.*, 1947, **2a**, 149.

[15] Schmidt and Herbstein, *J.*, 1954, 3302; Johnson, *J. Org. Chem.*, 1959, **24**, 833; McIntosh, Robertson, and Vand, *J.*, 1954, 1661.

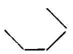
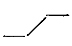
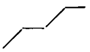
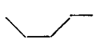
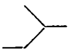
The ratio $\lambda_{II}/\lambda_{III}$ increases with increasing number of rings in the series of unstrained ring systems (I), (IV), and (V), but does not increase when the additional ring results in slight ring strain [see values for (I) and (II) and for (IV), (VI) and (VII)]. The value of this ratio for the highly strained system (III) is lower than that for any of the other cinnolines.

FIG. 1. *The absorption spectra of* (*A and A'*) *benzo*[c]*cinnoline*; (B) *dibenzo*[c,f]*cinnoline*; (C) *benzo*[f]*naphtho*[2,1-c]*cinnoline*; (D) *dibenzo*[c,h]*cinnoline*; (E) *benzo*[h]*naphtho*[1,2-c]*cinnoline*; (F) *tribenzo*[c,f,h]*cinnoline*; *and* (G) *benzo*[f]*naphtho*[1,2-c]*cinnoline, all in n-hexane solution.*



The expected bathochromic shift of the group I and group III bands, with increase in the number of rings, which we shall call the "annelation shift," is greater for annelation at the 1,2-bond than for annelation at the 3,4-bond. The annelation shift of the group II band is independent of the position of annelation, and is about 26 mμ for one, and about 40 mμ for two added rings. Masking by the high-intensity group I bands thus accounts for the lack of definition of the group II bands in the spectra of (II) and (III).

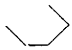
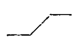
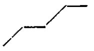
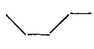
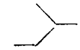
TABLE 3. *Ratios* λ_I/λ_{II}, $\lambda_{II}/\lambda_{III}$, *and* λ_I/λ_{III} *for some polycyclic cinnolines.*

Cinnoline	I	II	III	IV	V	VI	VII
Shape							
λ_I/λ_{II}..................	0·82	0·86	0·89	0·82	0·82	0·86	0·81
$\lambda_{II}/\lambda_{III}$	0·84	0·84	0·82	0·89	0·91	0·88	0·90
λ_I/λ_{III}	0·69	0·73	0·74	0·72	0·75	0·75	0·73

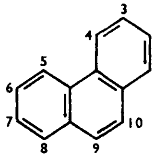
The annelation shift of the group III band (Table 4) is about 9 mμ per additional ring for fusion at the 3,4-bond,and about 26 mμ at a 1,2-bond. The spectrum of benzo[*f*]-naphtho[1,2-*c*]cinnoline (VI) shows a shift of 35 mμ for λ_{III} compared with that of benzo[*c*]-cinnoline (I); this agrees with the expected value (9 + 26 mμ) for annelation at a 1,2- and a 3,4-bond. The low value of the shift for tribenzo[*c,f,h*]cinnoline (VII) may be due to the fact that both the additional rings are fused to the same ring. Comparison of λ_{III} for the benzophenanthridines with λ_{III} for phenanthridine (VIII) shows that the shifts are greater for fusion at the 1,2- or the 9,10-bond than for fusion at the 3,4- or 7,8-bond (Table 4).

Comparison of λ_{III} for the higher polycyclic aromatic hydrocarbons with λ_{III} for phenanthrene (IX) shows a bathochromic shift of about 25 mμ per additional ring for annelation at the 1,2-bond, and of about 15 mμ per additional ring for annelation at a 3,4-bond (Table 4). Benzo[*c*]chrysene (X) shows a shift for λ_{III} of 40 mμ, which agrees with the expected value (25 + 15 mμ) for annelation at both a 1,2- and a 3,4-bond. Benzo[*g*]chrysene (XI), the carbocyclic analogue of tribenzo[*c,f,h*]cinnoline (VII), exhibits a bathochromic shift of only 25 mμ, instead of the expected 40 mμ. The value of 332 mμ for λ_{III} of triphenylene (XII), which is derived by annelation of phenanthrene at the 9,10-bond, indicates that such annelation results in a *hypsochromic* shift of 14 mμ. Thus the low value for benzo[g]chrysene (XI) might be due to the presence of a triphenylene moiety in the molecule. A similar effect might account for the low value of λ_{III} for tribenzo[*c,f,h*]cinnoline (VII).

TABLE 4. *Annelation shifts* (*in* mμ) *of* λ_{III} *of the polycyclic cinnolines, hydrocarbons, and monoaza-hydrocarbons relative to* λ_{III} *for benzo*[c]*cinnoline, phenanthrene, and phenanthridine respectively.*

Shape						
Cinnoline	26	51	10	17	35	22
Hydrocarbon	26	49	14	30	40	25
Monoaza-hydrocarbon	28 27	— —	11 11	— —	— —	— —

n-π* *Transitions.*—Badger and Walker[3] attributed the extra band in the spectrum of benzo[*c*]cinnoline (I) (at 410 mμ; log ε 2·6) in non-polar solvents, to an *n*-π* transition.



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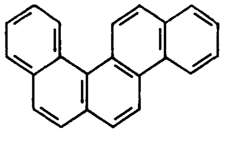
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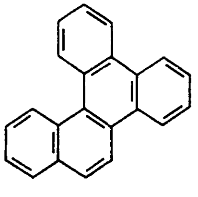
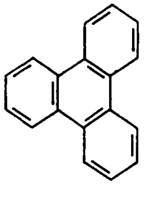

(XI)


(XII)

The higher polycyclic cinnolines show similar absorption at longer wavelengths. Well-defined bands or shoulders of similar intensity (log ε *ca.* 2·6) occur at wavelengths between 400 and 430 mμ in the spectra of compounds (II), (IV), (V), (VI), and (VII), and are attributable to *n*-π* transitions. This feature is probably masked by the group III band in the spectrum of benzo[*f*]naphtho[2,1-*c*]cinnoline (III).

The spectra of benzo[*c*]cinnoline (I) and dibenzo[*c,f*]cinnoline (II) in ethanol show no fine structure and no *n*-π* transition.[3] This is true also for the spectra of dibenzo[*c,h*]cinnoline (IV) and of benzo[*f*]naphtho[1,2-*c*]cinnoline (VI) in ethanol. Solvent-solute interaction, involving hydrogen bonding to the aza-nitrogen atoms, would increase the energy of the *n*-π* transition and result in an hypsochromic shift of the band which would then be masked by the group III band.

Effect of N-*Oxidation on Spectra.*—Calderbank and Le Fèvre,[6] comparing the spectra of benzo[*c*]cinnoline (I) and its *N*-oxide in ethanol, found that *N*-oxidation resulted in a bathochromic shift of the group II and III bands of about 30 mμ. We compared the spectrum of benzo[*c*]cinnoline (I) and its *N*-oxide in n-hexane (Fig. 2), and found that the shift of the group II band is 38 mμ, and that of the group III band is 21 mμ. In addition, the intensity of the group III band is considerably increased and the group I band is broadened to longer wavelengths. This broadening is also evident in the spectrum of the ethanolic solution, but it is resolved into two additional peaks, at 286 and 296 mμ, in n-hexane. Comparison of the spectrum of benzo[*c*]cinnoline *N*-oxide in n-hexane and in ethanol (Fig. 2) shows that while solvent–solute interaction has resulted in some loss of fine structure, the change is much less than that for benzo[*c*]cinnoline (I).[3]

FIG. 2.

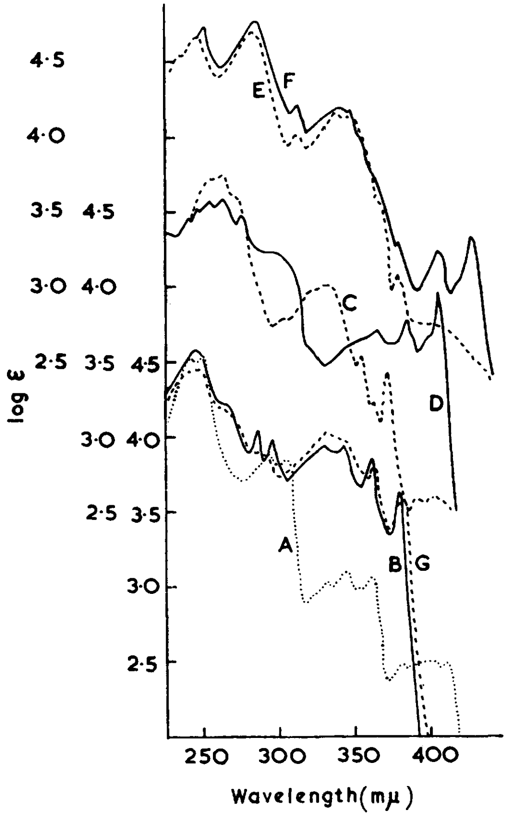


FIG. 3.

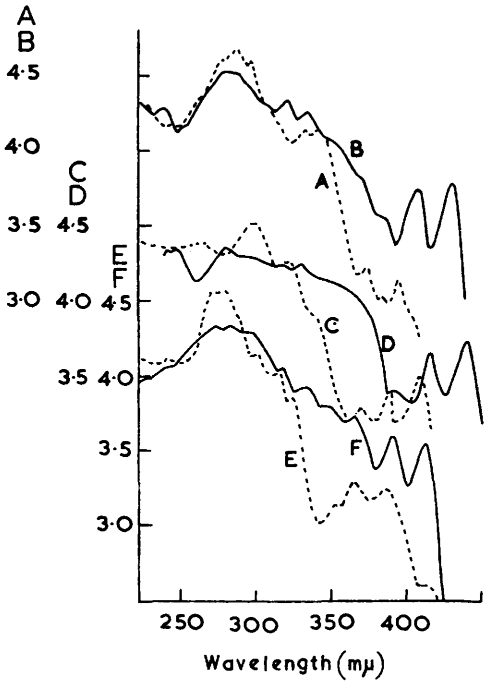


FIG. 2. *Absorption spectra of* (A) *benzo*[c]*cinnoline;* (B) *benzo*[c]*cinnoline* N-*oxide;* (C) *dibenzo*[c,h]*cinnoline;* (D) *dibenzo*[c,h]*cinnoline* 6-*oxide;* (E) *benzo*[h]*naphtho*[1,2-c]*cinnoline; and* (F) *benzo*[h]*naphtho*[1,2-c]*cinnoline* N-*oxide, in n-hexane solution, and of benzo*[c]*cinnoline* N-*oxide* (G) *in ethanol.*

FIG. 3. *Absorption spectra of* (A) *benzo*[f]*naphtho*[1,2-c]*cinnoline,* (B) *benzo*[f]*naphtho*[1,2-c]*cinnoline* 6-*oxide,* (C) *benzo*[f]*naphtho*[2,1-c]*cinnoline,* (D) *benzo*[f]*naphtho*[2,1-c]*cinnoline* N-*oxide,* (E) *dibenzo*-[c,f]*cinnoline,* (F) *dibenzo*[c,f]*cinnoline* N-*oxide, all in n-hexane.*

Figs. 2 and 3 compare the spectra of five higher polycyclic cinnolines with those of their *N*-oxides. The change in the spectrum of dibenzo[*c*,*h*]cinnoline (IV) on *N*-oxidation (Fig. 2) is similar to that for benzo[*c*]cinnoline, except that the bathochromic shifts of the group II and III bands are 32 and 34 mμ respectively, and that the broadening of the group I band is in the form of a shoulder. In the spectra of the *N*-oxides of dibenzo[*c*,*f*]-cinnoline (II), benzo[*f*] naphtho[2,1-*c*]cinnoline (III) and benzo[*f*]naphtho[1,2-*c*]cinnoline (VI), the broadening of the group I band has caused the group I and II bands to merge, with the production of a broad absorption region between 250 and 370 mμ (Fig. 3). As before, the bathochromic shift of the group III band [28 mμ for (III), 27 mμ for (II), and 36 mμ for (VI)] is accompanied by a large increase in the intensity.

The effect of *N*-oxidation on the spectrum of benzo[*h*]naphtho[1,2-*c*]cinnoline (V) (Fig. 2) differs, in some respects, from its effect on the spectra of other cinnolines. While there is a large bathochromic shift (48 mμ) of the group III band, the increase in its intensity is less marked, and the group I and group II bands are not altered appreciably. This abnormality may be ascribed to intramolecular overcrowding between the oxygen atom and the 4-hydrogen atom, resulting in the bending of the N–O bond out of the plane of the ring system, thus reducing the interaction of the unshared electrons of the oxygen atom with the π-electron system of the nucleus. This contrast supports our earlier suggestion,[16] that the *N*-oxides of dibenzo[*c,h*]cinnoline (IV) and of benzo[*f*]naphtho[1,2-*c*]cinnoline (VI) are the 6-oxides.

Conclusion.—The generalisations which appear from this series of spectra may be summarised as follows. The spectra of polycyclic cinnolines resemble, in form, those of their carbocyclic analogues, but the group II and III bands are shifted to longer wavelengths, the shifts being considerably greater than those of the corresponding monoaza-hydrocarbons.

There appears to be a relation between the features of the spectra and the position of annelation of benzo[*c*]cinnoline (I) and the extent of ring strain resulting from intramolecular overcrowding. Thus annelation at the 1,2-bond produces a much larger bathochromic shift of the group I and II bands than does annelation at the 3,4-bond. The ratio $\lambda_{II}/\lambda_{III}$ increases with increasing number of rings only if the additional rings do not result in ring strain. The ratio λ_{I}/λ_{II} is constant for molecules in which there is no strain but increases with the extent of ring strain.

N-Oxidation results in an increase in intensity and a bathochromic shift of the group III band.

Experimental.—Cinnolines and cinnoline N-*oxides*. Benzo[*c*]cinnoline was prepared by the method of Badger *et al.*[17] and benzo[*c*]cinnoline *N*-oxide by that of King and King.[18] The preparation of dibenzo[*c,f*]cinnoline, dibenzo[*c,h*]cinnoline, and benzo[*f*]naphtho[1,2-*c*]cinnoline,[16] and of benzo[*f*]naphtho[2,1-*c*]cinnoline and benzo[*h*]naphtho[1,2-*c*]cinnoline [19] and their *N*-oxides has been described previously, as has the preparation of tribenzo[*c,f,h*]cinnoline.[20] All materials were purified by chromatography on alumina in benzene-light petroleum.

Solvents.—Ethanol and n-hexane were B.D.H. special spectrophotometric grade.

Spectra.—The spectra were determined by using a Unicam 500 spectrophotometer.

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[18] King and King, *J.*, 1945, 824.
[19] Braithwaite and Holt, *J.*, 1959, 3025.
[20] Corbett, Holt, and Hughes, *J.*, 1960, 3643.