24. *Polynuclear Heterocyclic Systems. Part IX.*† n-π*-*Transitions in the Spectra of Aromatic Aza-hydrocarbons.*

By G. M. Badger and I. S. Walker.

The ultraviolet spectra of a number of polycyclic aromatic aza-hydrocarbons have been examined in both ethanol (polar solvent) and *cyclo*hexane or carbon tetrachloride (non-polar solvents). Three main regions of absorption, similar to those given by the corresponding aromatic hydrocarbons, are generally obtained. In the long-wavelength region many of the aza-compounds show an additional absorption region (particularly in non-polar solvents) which has been assigned to a transition involving the promotion of a non-bonding electron from the nitrogen atom to an unfilled π orbital (n–π^* transition).

When ethanol is used as a solvent, the ultraviolet and visible absorption spectra of the aromatic aza-hydrocarbons (pyridine, quinoline, phenanthridine, etc.) resemble those of the corresponding aromatic hydrocarbons very closely (Badger, Pearce, and Pettit, *J.*, 1951, 3199). Three main regions of absorption (designated the group I, II, and III bands) can usually be distinguished in both carbocyclic and heterocyclic series. These absorption bands correspond to π–π^* electronic transitions and move progressively to longer wavelengths as the number of rings increases. In addition, and especially in *cyclo*hexane and other non-polar solvents, a number of monocyclic aromatic aza-hydrocarbons have been shown to give a further absorption band at longer wavelengths than the group-III absorption. These long-wavelength bands have been assigned to transitions involving the excitation of an electron from a non-bonding orbital on the nitrogen atom (n-electron) to an unoccupied π orbital (n–π^* transition) (Halverson and Hirt, *J. Chem. Phys.*, 1951, **19**, 711; Hirt and Schmidt, *ibid.*, 1955, **23**, 600; Platt, *J. Opt. Soc. Amer.*, 1953, **43**, 252; Kasha, *Discuss. Faraday Soc.*, 1950, **9**, 14; McConnell, *J. Chem. Phys.*, 1952, **20**, 700).

In polar solvents (ethanol, water, etc.) the solvent–solute interactions, probably involving hydrogen bonding in most cases, change the character of the non-bonding orbital, and the absorption resulting from n–π^* transitions is shifted to shorter wavelengths, where it is often more or less hidden under the group-III (π–π^*) absorption bands. Polar solvents also appear to smooth out much of the fine structure. It seemed likely that the relatively intense long-wavelength absorption obtained with the polycyclic aromatic aza-hydrocarbons in ethanol (Badger, Pearce, and Pettit, *loc. cit.*) might be due to a superposition of the group-III and n–π^* absorptions. A number of such compounds have accordingly been examined not only in ethanol (as a polar solvent), but also in *cyclo*hexane or in carbon tetrachloride (as non-polar solvents) in an attempt to resolve the two band systems.

In *cyclo*hexane solution the n–π^* transition of pyridine appears as a series of shoulders on the long-wavelength side of the group-III bands; but with monocyclic diazines, it becomes a well-defined band at long wavelengths. Pyridazine, for example, gives a distinct n–π^* absorption band (in *cyclo*hexane) with a maximum around 3450 Å, the group-III absorption (π–π^*) having a maximum around 2500 Å, similar to that of benzene. In water as a polar solvent the n–π^* band was found to be shifted to shorter wavelengths, the maximum being about 3000 Å (Halverson and Hirt, *loc. cit.*; Evans and Wiselogle, *J. Amer. Chem. Soc.*, 1945, **67**, 60).

The spectra of the dicyclic diazines also show well-defined n–π^* absorption bands. With cinnoline (I) in *cyclo*hexane (Hearne, Morton, and Simpson, *J.*, 1951, 3318) the absorption below 2300 Å clearly corresponds to the group-I bands in naphthalene, the two maxima at 2755 and 2860 Å correspond to the group-II bands, the three maxima at 3085, 3170, and 3225 Å to the group-III region; and the low-intensity absorption with a maximum at 3900 Å may be identified as an n–π^* transition. With quinoxaline (II) in ethanol the group-III bands are far more intense than the corresponding bands in naphthalene and

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there is a pronounced shoulder at long wavelengths due to the superposition of the n–π^* absorption. In *cyclo*hexane this n–π^* absorption moves to longer wavelengths and has some fine structure (Fig. 1).

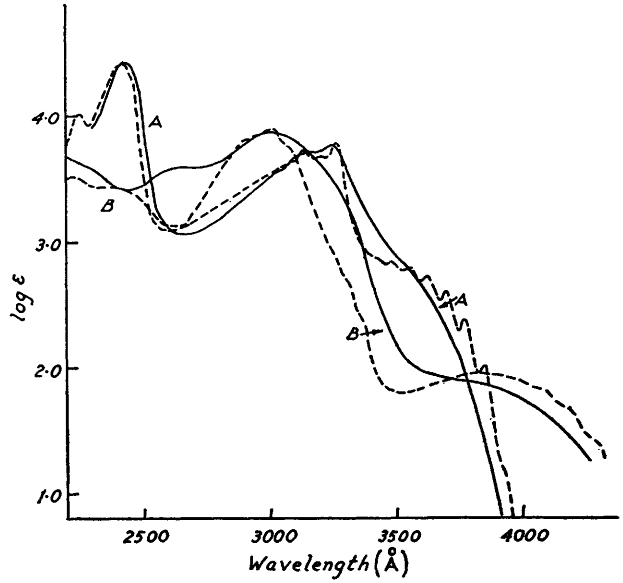


FIG. 1. *Absorption curves of* (*A*) *quinoxaline and* (*B*) *pteridine in ethanol* (——) *and* cyclo*hexane* (– – – – –).

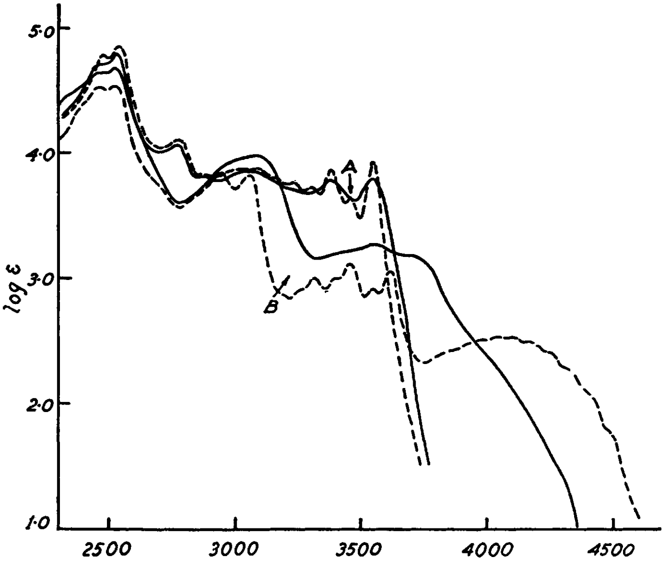
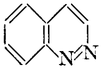


FIG. 2. *Absorption curves of* (*A*) 1 : 4-*diazatriphenylene and* (*B*) 3 : 4-*benzocinnoline in ethanol* (——) *and* cyclo*hexane* (– – – – –).

The absorption spectrum of phthalazine (III) is somewhat similar (Hirt, personal communication), the n–π^* absorption appearing as a shoulder in ethanol solution, and as a more pronounced shoulder at longer wavelengths in *cyclo*hexane. The spectrum of 1 : 4-diphenylphthalazine (IV) has now been examined in ethanol, in *cyclo*hexane, and in carbon tetrachloride. Here again the n–π^* absorption appears as a shoulder in ethanol and moves to longer wavelengths in the non-polar solvents. In this and in some other cases, carbon tetrachloride and *cyclo*hexane were found to be interchangeable, the same absorption curve being obtained in both solvents.

The spectra of pteridine (V) in polar and non-polar solvents may be compared with those of quinoxaline. The absorption around 3000 Å corresponds to the group-III absorption and the *n*–π* absorption appears as a shoulder in ethanol and as a distinct band (at somewhat longer wavelength) in *cyclo*hexane (Fig. 1).



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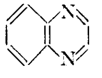

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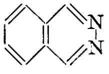
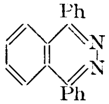
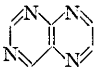


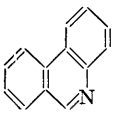
(III)



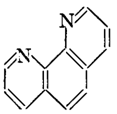
(IV)



(V)



(VI)



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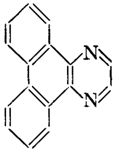

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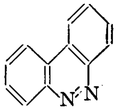

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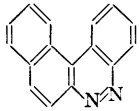


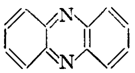
(X)

No *n*–π* absorption could be identified in the spectra of phenanthridine (VI) and of *o*-phenanthroline (VII), there being no significant change in moving from a polar to a non-polar solvent. The spectrum of 1 : 4-diazatriphenylene (VIII) likewise showed no *n*–π* band although the spectrum in *cyclo*hexane shows more fine structure (Fig. 2). In these cases it seems likely that the absorption due to the *n*–π* transition is of very low intensity and that it remains hidden under the group-III (π–π*) bands.

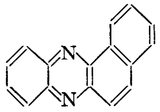
The spectrum of 3 : 4-benzocinnoline (IX) in ethanol (Fig. 2) shows the three main regions of absorption (around 2500, 3000, and 3500 Å) analogous to those given by phenanthrene (Badger, Pearce, and Pettit, *loc. cit.*). The chief difference is that absorption in the group-III region is more intense and extends to longer wavelengths with the heterocyclic compound. In *cyclo*hexane, however, this long-wavelength absorption can be resolved as a separate band system with a maximum at 4100 Å, and this can be assigned to the *n*–π* transition.

With 3 : 4-5 : 6-dibenzocinnoline (X) the absorption spectrum in ethanol (Fig. 3) is again similar to that of the corresponding hydrocarbon, 3 : 4-benzophenanthrene, except that the group-III bands around 3700 Å are more intense. In *cyclo*hexane the *n*–π* transition shifts the absorption still further to longer wavelengths.

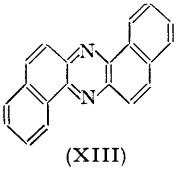
In a series of linear benzologues of benzene (naphthalene, anthracene, naphthacene, etc.) the group-II bands move more rapidly to longer wavelengths with each additional ring than do the group-III bands (see Badger, " The Aromatic Compounds," Cambridge Univ. Press, 1954, p. 393). In anthracene and the higher members of the series, for example, the group-III bands are " swamped " under the more intense group-II bands. A similar situation seems to hold in the corresponding heterocyclic series [pyrazine, quinoxaline, phenazine (XI), etc.]. Here the group-II bands move more rapidly to longer wavelengths than both the group-III and the *n*–π* absorption bands. The change from polar to non-polar solvent does cause a small shift of the long-wavelength absorption to still longer wavelengths for phenazine; but no *n*–π* absorption can be identified in the spectra of 1 : 2-benzophenazine (XII) or 1 : 2-5 : 6-dibenzophenazine (XIII).



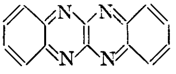
(XI)



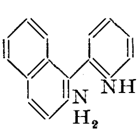
(XII)



(XIII)



(XIV)



(XV)

On the other hand, although the spectrum of 5 : 6 : 11 : 12-tetra-azanaphthacene (XIV) in a polar solvent (chloroform) is similar to that of the corresponding hydrocarbon in the 2000—5000 Å region, the heterocyclic compound shows increased absorption at long wavelengths, with a " tail " extending to 6000 Å (Fig. 4). In a non-polar solvent (carbon tetrachloride) this long-wavelength absorption is resolved as an additional absorption region between 5000 and 6400 Å. Here again, therefore, a n–π^* transition seems to be involved.

Most of the compounds required for this investigation were prepared by known methods. 3 : 4-5 : 6-Dibenzocinnoline (X), however, was prepared by the oxidation of 1-*o*-aminophenyl-2-naphthylamine (XV) with Caro's acid.

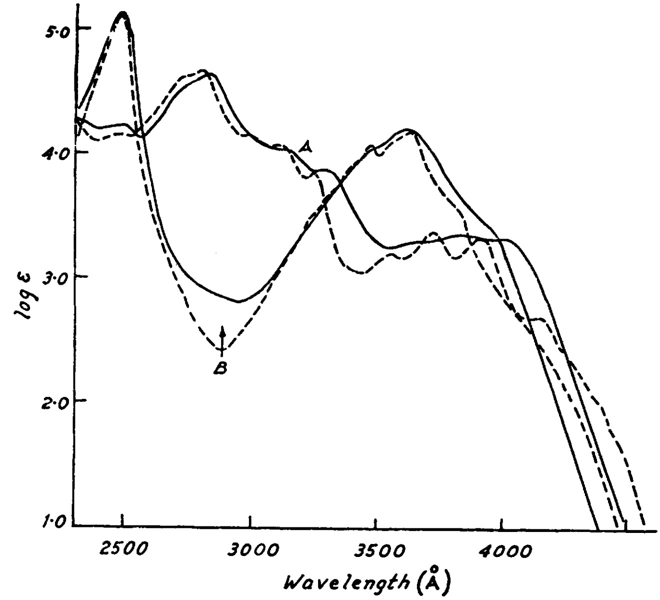


Fig. 3. *Absorption curves of* (*A*) 3 : 4-5 : 6-*dibenzocinnoline and* (*B*) *phenazine in ethanol* (——) *and* cyclo*hexane* (– – – – –).

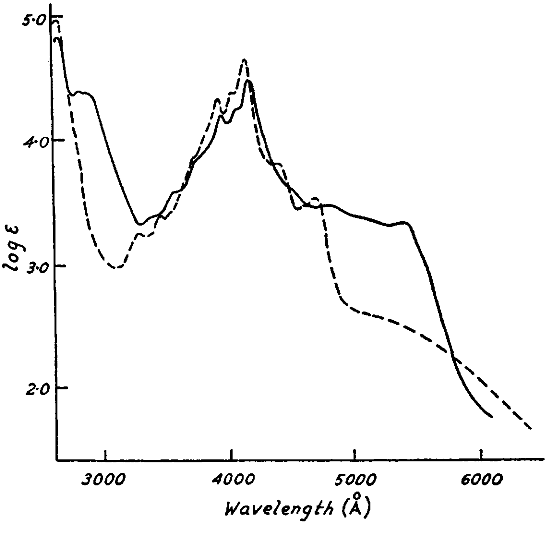


Fig. 4. *Absorption curves of* 5 : 6 : 11 : 12-*tetra-azanaphthacene in chloroform* (——) *and carbon tetrachloride* (– – – – –).

Experimental.—Materials. We are indebted to Professor A. Albert for a generous gift of pteridine, and to Mr. R. G. Buttery for the 1 : 2-5 : 6-dibenzophenazine. Other compounds were prepared as follows: quinoxaline, Cavagnol and Wiselogle, *J. Amer. Chem. Soc.*, 1947, **69**, 795; 1 : 4-diphenylphthalazine, Guyot and Catel, *Compt. rend.*, 1905, **140**, 1348; 1 : 2-benzophenazine, Ullmann, and Heisler, *Ber.*, 1909, **42**, 4263; 3 : 4-benzocinnoline, Badger, Seidler, and Thomson, *J.*, 1951, 3207; 1 : 4-diazatriphenylene, Mason, *Ber.*, 1886, **19**, 112; 5 : 6 : 11 : 12-tetra-aza-naphthacene, Hinsberg and Pollak, *Ber.*, 1896, **29**, 784.

3 : 4-5 : 6-*Dibenzocinnoline.* 1-*o*-Aminophenyl-2-naphthylamine (XV) was prepared in 25% yield according to the method of Fucks and Nizel (*Ber.*, 1927, **60**, 209) and had m. p. 154·5°.

Ammonium persulphate (12·4 g.) was added to 92% sulphuric acid (13·2 g.), and the mixture was shaken until all dissolved (1 hr.). The solution was then diluted with ice (55 g.), and finally the diamine (3·0 g.) was added all at once. After 3 min. the solution was poured on ice (200 g.) and basified with sodium carbonate. The precipitate was dried, and purified by chromatography in benzene on alumina. Recrystallisation from benzene–hexane gave 3 : 4-5 : 6-*dibenzocinnoline* (0·5 g.) as yellow leaflets, m. p. 156·5—157·5° (Found : C, 83·4; H, 4·3; N, 12·5. $C_{16}H_{10}N_2$ requires C, 83·5; H, 4·4; N, 12·2%).

Absorption spectra. Spectra were determined with a Hilger Uvispek spectrophotometer.

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