

704. Polynuclear Heterocyclic Systems. Part I. Introduction.

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The absorption spectra of several polynuclear heterocyclic aromatic compounds have been compared and contrasted with those of their carbocyclic analogues. Marked resemblances are noted, and the chief differences seem to be: (i) that the group-III absorption bands of the azahydrocarbons are much more intense than those of the hydrocarbons; (ii) that in the heterocyclic anthracene analogues (which do not exhibit group-III absorption) the group-II bands are sometimes slightly more intense than those of anthracene; (iii) that there is loss of fine structure in replacing a CH group by N; and (iv) that the absorption of the azahydrocarbons often begins at slightly longer wave-lengths than that of their hydrocarbon analogues.

IN many ways the aromatic heterocyclic systems closely resemble their carbocyclic analogues. Each annular nitrogen atom and each annular carbon atom contribute one π electron to the "aromatic sextet," so that pyridine, pyrimidine, and other nitrogen-containing aromatic compounds (termed aromatic azahydrocarbons) are all closely related to benzene and to substituted benzenes. Although the polynuclear heterocyclic systems have not yet been extensively investigated, it is known that many of the similarities are also to be found among the larger molecules. On the other hand, there are many important differences. For example, many of the aromatic azahydrocarbons undergo nucleophilic (anionoid) substitution very much more readily than the related hydrocarbons; many amino- and hydroxy-derivatives of aza-compounds are tautomeric and exist largely in quinonoid forms; some of the azahydrocarbons form highly coloured molecular compounds with their dihydro-derivatives; and so on. It seemed, therefore, that a systematic investigation of the relation between the aromatic hydrocarbons and their heterocyclic analogues, with particular reference to the polynuclear systems, would be of interest. In the present paper the ultra-violet absorption spectra of the aromatic nitrogen-containing compounds are compared and contrasted with those of the related aromatic hydrocarbons. This seemed necessary to enable the absorption spectra of the azahydrocarbons to be used for structural identification.

The aromatic hydrocarbons generally exhibit three main regions of absorption in the ultra-violet or the visible region. Benzene has an intense region of absorption (maximum at 1790 Å) in the far ultra-violet (Price and Walsh, *Proc. Roy. Soc.*, 1947, *A*, 191, 22), a second region of relatively high intensity around 2000 Å, and a third region, of low intensity, around 2300—2600 Å (Henri, *J. Phys. Radium*, 1922, **3**, 180). Most of the dicyclic and polycyclic aromatic hydrocarbons also exhibit three main regions of absorption, the bands in each group being referred to as the group-I, -II, and -III bands, respectively, III being the region of low intensity (Braude, *Ann. Reports*, 1945, **42**, 123; Clar, "Aromatische Kohlenwasserstoffe," Berlin, 1941; Badger and Pearce, *J.*, 1950, 3072). The only exceptions are the linear condensed ring compounds anthracene, naphthacene, pentacene, etc., which show only two regions of absorption.

An examination of the published absorption curves of aromatic azahydrocarbons and of those now reported for the first time shows that these compounds also give rise to three main regions of absorption and that the two sets of curves have many features in common. Pyridine

has an intense region of absorption (maximum at 1700 Å) in the far ultra-violet (Price and Walsh, *loc. cit.*), a second region at about 2000 Å, and a third around 2500 Å (Menczel, *Z. physikal. Chem.*, 1927, 125, 161; Swain, Eisner, Woodward, and Brice, *J. Amer. Chem. Soc.*, 1949, 71, 1341). It is noteworthy, however, that although some of the maxima seem to be shifted towards shorter wave-lengths compared with benzene, the absorption of pyridine begins at somewhat longer wave-lengths, at about 2900 Å as against 2750 Å. Moreover, the intensity of absorption in the group-III region is about ten times as great for pyridine as for benzene. Similar comparisons can be made for other compounds. Maccoll (*J.*, 1946, 670) compared the group-III absorption bands of benzene, pyridine, pyrimidine, pyridazine, and *s*-tetrazine, and concluded that the absorption is shifted progressively to the red with each additional nitrogen atom, the effect being most marked when the nitrogen atoms are adjacent.

The published curves for quinoline, *isoquinoline*, and *quinazoline* (Ewing and Steck, *J. Amer. Chem. Soc.*, 1946, 68, 2181; Elderfield, Williamson, Gensler, and Kremer, *J. Org. Chem.*, 1947, 12, 405) show the same three main regions of absorption as naphthalene. In each case the most marked difference between the homocyclic and the heterocyclic compounds is that the group-III region is considerably more intense for the aromatic azahydrocarbons than for naphthalene.

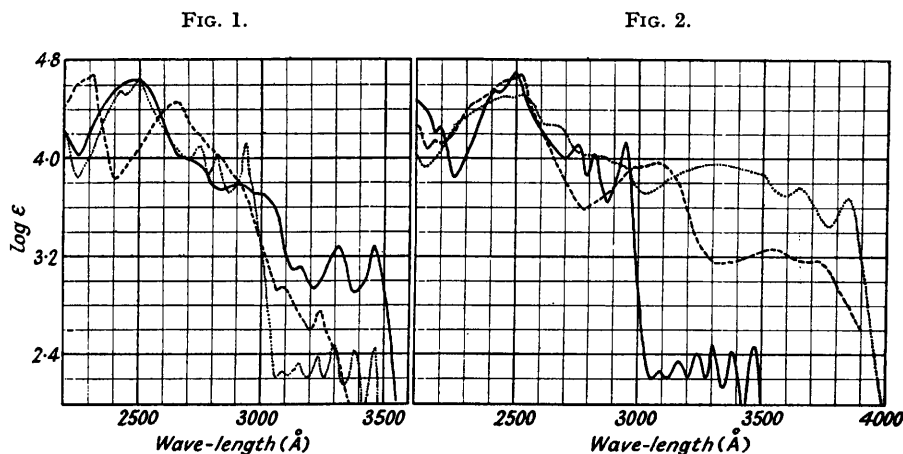
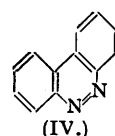
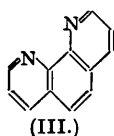
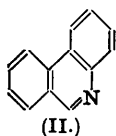
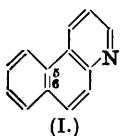


FIG. 1. Absorption curves of phenanthrene (.....) (Mayneord and Roe, 1935, *loc. cit.*), *o*-phenanthroline (III) (-----), and phenanthridine (II) (———).

FIG. 2. Absorption curves of phenanthrene (———) (*idem, ibid.*), 3:4-benzocinnoline (IV) (-----), and 3:4-benzocinnoline *N*-oxide (.....).

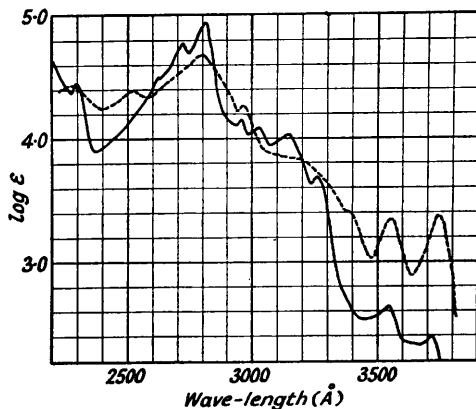
Phenanthrene also shows three main regions of absorption, at about 2500, at 2930—2750, and at 3140—3450 Å (Mayneord and Roe, *Proc. Roy. Soc.*, 1935, *A*, 152, 299). Only one aromatic azahydrocarbon having the same ring system, namely, 5:6-benzoquinoline (I), seems to have been examined previously (Johnson, Woroch, and Mathews, *J. Amer. Chem. Soc.*, 1947, 69, 566), but the spectra of several other representatives of this class, phenanthridine (II), *o*-phenanthroline (III), 3:4-benzocinnoline (IV), and 3:4-benzocinnoline *N*-oxide, have now been examined. The curves for (I), (II), and (III) (Fig. 1) are all very similar to that of phenanthrene, and show the same three regions of absorption. However, the maxima of the absorption bands in each region are shifted to shorter wave-lengths with each replacement of a methine group by a nitrogen atom. The group-I maximum for phenanthrene is at 2507 Å, but that for 5:6-benzoquinoline is at 2350 Å, and that for *o*-phenanthroline at 2310 Å.



The spectra of the cinnolines seem to be different in this respect (Fig. 2) for there is very little if any shift in the positions of the group-I maxima to shorter wave-lengths. As a matter

of fact, the chief point of interest in the curve for (IV) is that the absorption begins (about 4100 Å) at longer wave-lengths than for phenanthrene (3500 Å). This effect always seems to be most marked with compounds having two adjacent nitrogen atoms. The absorption spectrum of 3 : 4-benzocinnoline *N*-oxide (Fig. 2) is also of interest. The formation of the *N*-oxide involves the nitrogen "lone pair," and not the π electrons, so its absorption spectrum would be expected to resemble that of the parent compound about as closely as any substituted compound resembles a parent ring system, and this is found to be the case. The most note-

FIG. 3.



Absorption curves of 3 : 4-benzophenanthrene (—) (Mayneord and Roe, Proc. Roy. Soc., 1937, A, 158, 634) and of 1'-aza-3 : 4-benzophenanthrene (V) (-----).

FIG. 4.

FIG. 5.

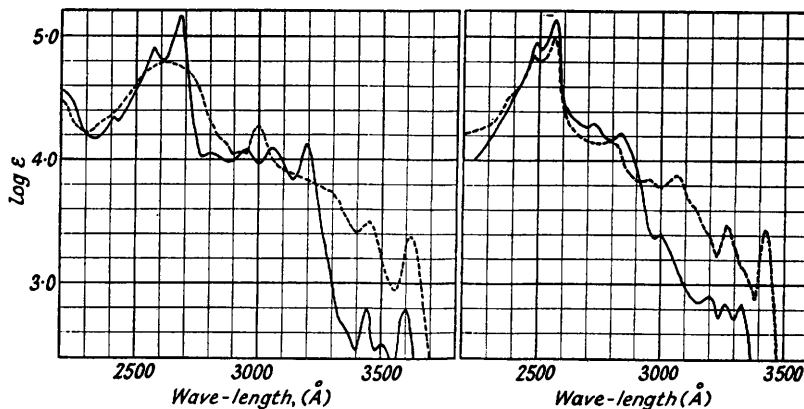


FIG. 4. Absorption curves of chrysene (—) (Mayneord and Roe, 1935, loc. cit.) and of 1-azachrysene (-----).

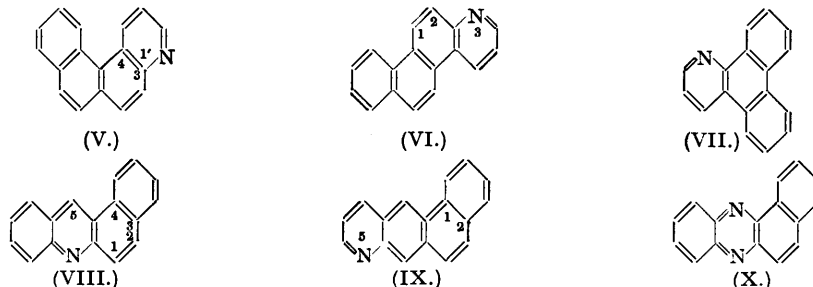
FIG. 5. Absorption curves of triphenylene (—) (Clar and Lombardi, Ber., 1932, 65, 1411) and of 1-azatriphenylene (VII) (-----).

worthy difference is that the group-III bands are even more intense in the oxide than in the parent substance. The group-III absorption of 3 : 4-benzocinnoline itself, as well as that of all the other aromatic tricyclic azahydrocarbons examined, is about ten times more intense than that of phenanthrene.

There are several benzophenanthrenes, namely, 3 : 4-benzophenanthrene, 1 : 2-benzanthracene, chrysene, and triphenylene, and all have absorption spectra somewhat similar to that of phenanthrene except that the bands are shifted to longer wave-lengths. The same is true of the aza-derivatives. The spectrum of 1'-aza-3 : 4-benzophenanthrene (V) resembles that of 3 : 4-benzophenanthrene very closely (Fig. 3). The maxima in the group-I and group-III regions are almost identical, but the intensity of the group-III bands for the azahydrocarbon

is again about ten times that for 3:4-benzophenanthrene (see also Johnson, Woroch, and Mathews, *loc. cit.*). Similarly, the spectrum of 3-azachrysene (VI) resembles that of chrysene (Fig. 4). There is considerable loss of fine structure, it is true, and again the intensity of the group-III region is about ten times that for the hydrocarbon (see also *idem, ibid.*). The spectrum of 1-azatriphenylene (VII) is likewise closely related to that of the hydrocarbon (Fig. 5), the group-III region again being more intense in the case of the azahydrocarbon.

The spectrum of 1:2-benzanthracene exhibits three groups of absorption bands, with twelve peaks in all, and has already been fairly extensively investigated (Jones, *J. Amer. Chem. Soc.*, 1940, **62**, 148; Badger and Pearce, *loc. cit.*). 3:4-Benzacridine (VIII), 5-aza-1:2-benzanthracene (IX), and 1:2-benzophenazine (X) have now been examined (Figs. 6 and 7), and the same general principles seem to hold; *i.e.*, the curves show a general resemblance



to one another, there is a loss of fine structure with the azahydrocarbons, and the group-III region of absorption is much more intense with the azahydrocarbons than for 1:2-benzanthracene itself. Moreover, the absorption of the diaza-compound, 1:2-benzophenazine,

FIG. 6.

FIG. 7.

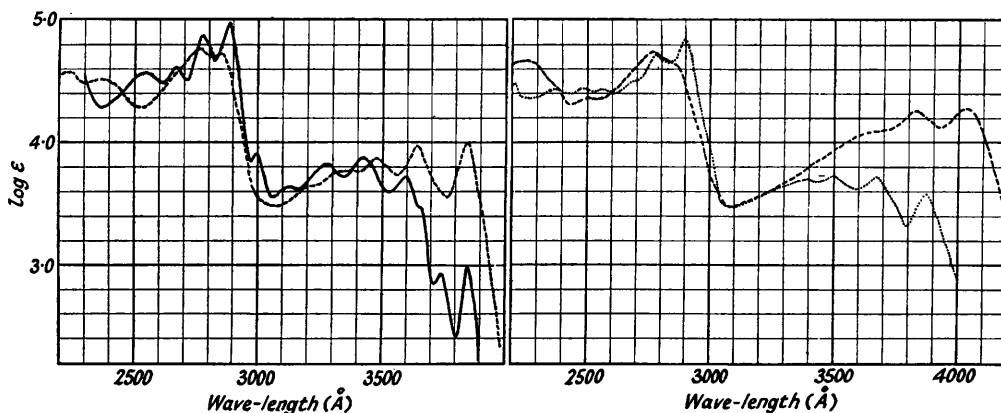


FIG. 6. Absorption curves of 1:2-benzanthracene (—) (Badger and Pearce, *loc. cit.*) and of 3:4-benzacridine (-----).

FIG. 7. Absorption curves of 1:2-benzophenazine (X) (-----) and of 5-aza-1:2-benzanthracene (IX) (.....).

begins at a longer wave-length than that of the hydrocarbon, and this substance is pale yellow whereas the hydrocarbon is colourless.

Unlike the compounds already mentioned, anthracene has only two regions of absorption. The first (group-I bands) at about 2515 Å corresponds to the benzene absorption at about 1790 Å. The second (group-II) extends from about 3000 to about 3750 Å, and corresponds to the benzene absorption in the 2000 Å region. The group-III bands of anthracene, corresponding to the 2500 Å region of benzene, are hidden under the group-II bands, for, as Clar (*loc. cit.*) has shown, the group-II bands move more to the red for every additional linear benzene ring than do the group-III bands. Four heterocyclic analogues of anthracene have now been examined: acridine, 1-aza-anthracene, 2-aza-anthracene, and phenazine (see Figs. 8 and 9).

There are very close resemblances between the curves but the intensities of the group-II regions in acridine and phenazine are about twice that in the hydrocarbon. It is also noteworthy that the absorption of the azahydrocarbons, especially of phenazine, begins at longer wave-lengths than for anthracene. For this reason phenazine is pale yellow but anthracene and acridine are colourless.

It seems reasonable to conclude from the above survey that, in general, the absorption spectra of the azahydrocarbons closely resemble those of their carbocyclic analogues. The chief differences seem to be: (i) that the group-III absorption bands are much more intense than those of the hydrocarbons; (ii) that in anthracene analogues (which do not exhibit group-III absorption), the group-II bands of the azahydrocarbons are sometimes slightly more intense than those of the hydrocarbon; (iii) that there is a considerable loss of fine structure in replacing

FIG. 8.

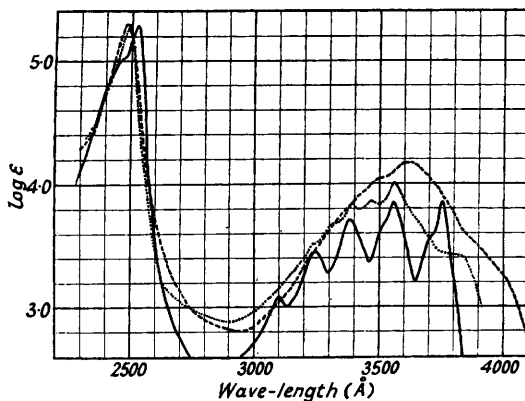


FIG. 8. Absorption curves of anthracene (—) (Mayneord and Roe, 1935, loc. cit.), of phenazine (-----), and of acridine (.....).

FIG. 9.

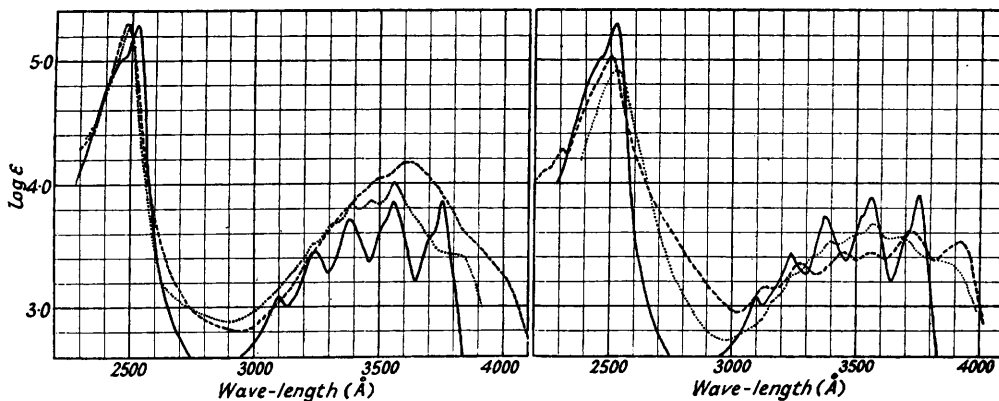


FIG. 9. Absorption curves of anthracene (—) (Mayneord and Roe, 1935, loc. cit.), of 1-aza-anthracene (.....), and of 2-aza-anthracene (-----).

CH groups by N, but that as far as can be ascertained the various maxima are not shifted to any marked extent; and (iv) that the absorption of the azahydrocarbons often begins at slightly longer wave-lengths than that of the hydrocarbons. This effect is not very apparent, if at all, in compounds containing only one nitrogen atom, but is marked with all the diaza-compounds examined, and especially with those compounds in which the two nitrogen atoms are adjacent. These differences being borne in mind, it seems that the absorption spectra of the hydrocarbons can be used for structure identification purposes with azahydrocarbons, with little possibility of error.

EXPERIMENTAL.

Materials.—We are indebted to Dr. A. Etienne for gifts of 1- and 2-aza-anthracene (cf. Etienne, *Ann. Chim.*, 1946, 1, 5), and to Dr. E. Mosettig for gifts of 5-aza-1:2-benzanthracene, 1-azatriphenylene, 3-azachrysene, and 1'-aza-3:4-benzophenanthrene (cf. Mosettig and Krueger, *J. Org. Chem.*, 1938, 3, 317; Krueger and Mosettig, *ibid.*, 1940, 5, 313). 1:2-Benzophenazine was prepared by Ullmann and Heisler's method (*Ber.*, 1909, 42, 4263), and purified by sublimation in a high vacuum and recrystallisation from acetic acid. The preparations of the 3:4-benzocinnoline, 3:4-benzocinnoline *N*-oxide, 3:4-benzacridine, and of the phenanthridine used are described in Part III (*J.*, 1951, 3207); the other materials were obtained commercially.

Absorption Spectra.—Spectra were determined with a Beckman DU spectrophotometer, absolute alcohol being used as solvent. The absorption curves of the parent hydrocarbons given in the figures are those recorded in the literature, and have usually been determined with other instruments. In many cases, however, we have re-examined the spectra, using the Beckman instrument, and have obtained curves in good agreement with the original workers.

We are grateful to Dr. A. Etienne and to Dr. E. Mosettig for gifts of materials, and to the Director of Chemistry (Mr. R. J. Cowan), South Australian Government Department of Chemistry, for permission to use the Beckman spectrophotometer. We are also indebted to the Commonwealth Government Research Fund for maintenance grants (to R. S. P. and R. P.).