666. *Polynuclear Heterocyclic Systems. Part XI.* Absorption Spectra of Compounds containing Five-membered Rings.*

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The absorption spectra of the polycyclic compounds derived from the five-membered heterocyclic systems have been found to resemble those of the related benzenoid hydrocarbons. Three main regions of absorption can generally be resolved, and the chief differences seem to be: (i) that the absorption of the heterocyclic compounds (particularly of the group I bands) is shifted to shorter wavelengths, and (ii) that the group III bands are more intense than those given by the hydrocarbons. The spectra of dicyclic and tricyclic furan systems resemble those of the related hydrocarbons rather less closely.

The absorption spectra of some *S*-oxides and -dioxides have also been compared with those of the parent thiophen derivatives.

THE absorption spectra of the aromatic aza-compounds (pyridine, quinoline, etc.) have been shown to resemble very closely those of the corresponding hydrocarbons,[1] and with certain reservations the spectra of the parent hydrocarbons can be used for structural identification in the aza-series. The polycyclic compounds derived from the five-membered heterocyclic systems furan, pyrrole, and thiophen have, however, received considerably less attention. As part of a comprehensive study of the aromatic character of such heterocyclic compounds, their absorption spectra have been systematically compared with those of the analogous benzenoid systems.

In furan, pyrrole, and thiophen, each hetero-atom has two electrons available for conjugation with the four electrons contributed by the four annular carbon atoms. If the electronegativity of the hetero-atom is very high, its $2p$ orbital is "contracted" relatively to the carbon $2p$ orbitals, so that little conjugation occurs.[2] This is the case with furan. Nitrogen is less electronegative than oxygen, so that pyrrole occupies an intermediate position. With thiophen, however, the electronegativity of the hetero-atom is the same as that of carbon. Moreover, it seems that the two electrons from the sulphur atom may occupy two pd_2 hybrid orbitals, and the resulting conjugation with the carbon π-electrons is thereby greatly facilitated.[3] In all these cases, therefore, the electronic structures are similar to that which occurs in benzene, and it is not surprising that these heterocyclic compounds resemble benzene to some extent.

Benzene shows three main regions of ultraviolet-light absorption: intense absorption, with a maximum at 179 mμ, in the far ultraviolet region (group I band); a region of lower intensity around 200 mμ (group II bands); and of low intensity around 230—260 mμ (group III bands). Thiophen has three similar regions of absorption; but the spectra of furan and pyrrole are much less similar.[2] For example, no group III absorption has been detected with pyrrole. On the other hand, 1-methylpyrrole does show absorption in the 225—260 mμ region, and this is thought to be due to a reduction in the electronegativity of the nitrogen atom by methyl substitution.[2]

A comparable situation has now been found to exist with the bicyclic compounds (Fig. 1). Only thionaphthen (II; X = S) shows three well-defined absorption bands, with maxima at 227 (log ε 4·45), 257 (log ε 3·74), and 288 mμ (log ε 3·31), and the spectrum is similar to that of naphthalene (I). It is of interest that the high extinction coefficient of the group III band of thionaphthen is much greater than in the case of the hydrocarbon. Only two main regions of absorption can be resolved with indole (II; X = NH). The first, with a maximum at 219 mμ, probably corresponds to the group I band of naphthalene. The maximum at 288 mμ probably corresponds to the group III region, so the group

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* Part X, preceding paper.

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

[2] Walsh, *Quart. Rev.*, 1948, **2**, 73.

[3] Longuet-Higgins, *Trans. Faraday Soc.*, 1949, **45**, 173.

II region cannot be clearly distinguished. Only two regions have been resolved for benzofuran (II; X = O). In this case the group I region seems to be beyond the range of the present instrument. The maximum at 244 mμ probably corresponds to the group II region of naphthalene, and that at 281 mμ to the group III region. These heterocyclic compounds all commence absorption at shorter wavelengths than naphthalene.

The spectra of the tricyclic compounds (IV) resemble that of the related hydrocarbon (III) rather more closely (Fig. 2). Phenanthrene[4] has three main regions of absorption at 250, 270—290, and 310—345 mμ, and both dibenzothiophen and carbazole have very similar absorption curves, except that the group I bands are shifted to somewhat shorter wavelengths. Thus dibenzothiophen has three main absorption regions at 235, 275—285, and 305—330 mμ, and carbazole absorbs around 240, 280—295, and 320—340 mμ. In both cases the intensity of the long-wavelength absorption (group III) is considerably greater for the heterocylic compounds than for phenanthrene. As with the bicyclic compounds the oxygen-compound, dibenzofuran, shows less resemblance to the aromatic hydrocarbon, and only two regions of absorption are clearly resolved (220—250 and 270—300 mμ).

FIG. 1.

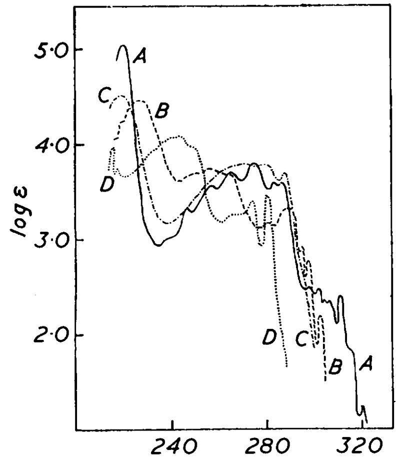

FIG. 2.

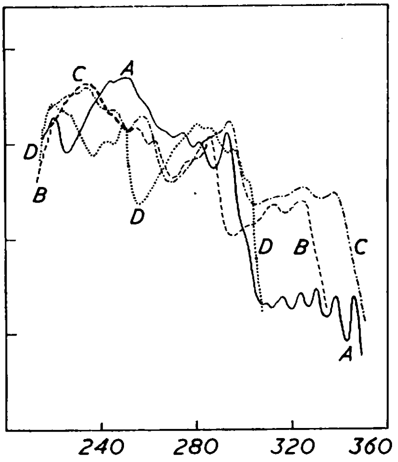

FIG. 1. *Absorption curves of (A) naphthalene* (Mayneord and Roe [4]), *(B) thionaphthen, (C) indole, and (D) benzofuran.*

FIG. 2. *Absorption curves of (A) phenanthrene, (B) dibenzothiophen, (C) carbazole, and (D) dibenzofuran.*

The same pattern is repeated with 1 : 2-benzanthracene (V) and the related heterocyclic compounds (VI) : the group I absorption occurs at shorter wavelengths with the heterocyclic compounds, and their group III absorption is much more intense than that of the hydrocarbon (Fig. 3). Thus 1 : 2-benzanthracene (V) shows three main regions of absorption, at 275—290, 320—360, and 370—390 mμ; 9-thia-2 : 3-benzofluorene (VI; X = S) shows three main regions at 260—275, 310—330, and 350—370 mμ; and 2 : 3-benzocarbazole (VI; X = N) absorbs at 260—280, 310—330, and 370—400 mμ. The oxygen derivative in this series, β-brazan (VI; X = O), has an absorption curve which does show the three main regions of absorption characteristic of its analogues, but the group III bands are shifted to much shorter wavelengths and are more intense than those of the hydrocarbon.

These conclusions apply with equal force to the two remaining series (VII, VIII; IX, X) of tetracyclic compounds (Figs. 4 and 5). Chrysene[4] has three main regions of absorption at 250—270, 280—320, and 340—360 mμ. 9-Thia-1 : 2-benzofluorene (VIII; X = S) has three main bands at 240—280, 290—310, and 325—355; 1 : 2-benzocarbazole (VIII;

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[4] Mayneord and Roe, *Proc. Roy. Soc.*, 1935, *A*, **152**, 299.

X = N) has three main bands at 240—260, 270—310, and 330—360 mμ; and 4′ : 5′-benzofurano(1′ : 2′-1 : 2)naphthalene (VIII; X = O) has three main regions of absorption at 250—260, 270—310, and at 320—340 mμ. Similarly 3 : 4-benzophenanthrene (IX) has three regions of absorption at 260—280, 290—330, and 350—370 mμ; 9-thia-3 : 4-benzofluorene (X; X = S) has three regions at 250—270, 280—320, and 330—350 mμ; and 3 : 4-benzocarbazole (X; X = N) at 250—270, 290—330, and 340—370 mμ.

Fig. 3.

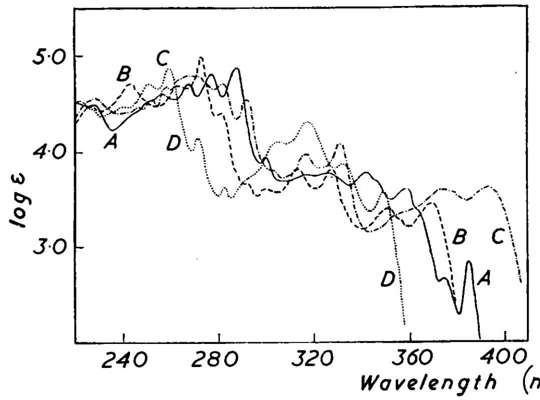


Fig. 4.

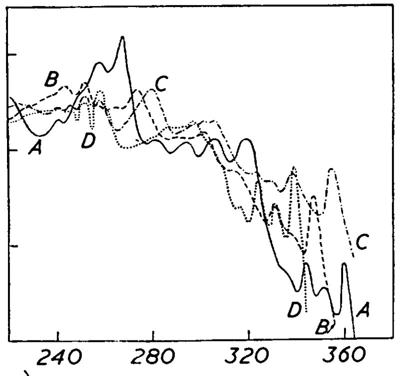
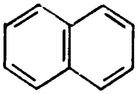
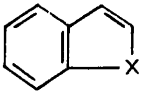


Fig. 3. *Absorption curves of* (*A*) 1 : *2-benzanthracene,* (*B*) *9-thia-2* : *3-benzofluorene,* (*C*) 2 : *3-benzocarbazole, and* (*D*) *β-brazan.*

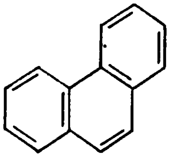
Fig. 4. *Absorption curves of* (*A*) *chrysene* (Mayneord and Roe [4]), (*B*) *9-thia-1* : *2-benzofluorene,* (*C*) 1 : *2-benzocarbazole* (Clemo and Felton [5]), *and* (*D*) 4 : *5′-benzofurano*(1′ : 2′-1 : 2)*naphthalene.*



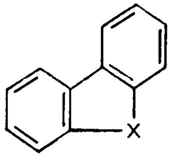
(I)



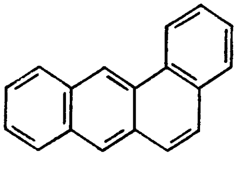
(II)



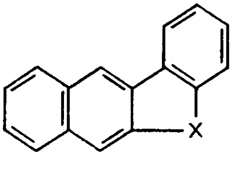
(III)



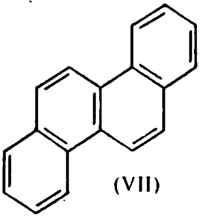
(IV)



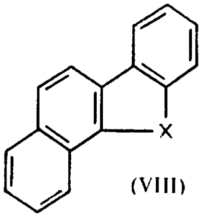
(V)



(VI)

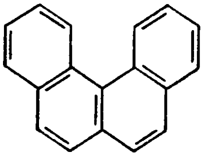


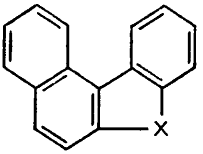
(VII)



(VIII)

(IX)





(X)

It seems reasonable to conclude, therefore, that the absorption spectra of the polycyclic compounds derived from the five-membered heterocyclic systems are fundamentally similar to those of the related benzenoid hydrocarbons. Three main regions of absorption

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[5] Clemo and Felton, *J.*, 1952, 1658.

FIG. 5.

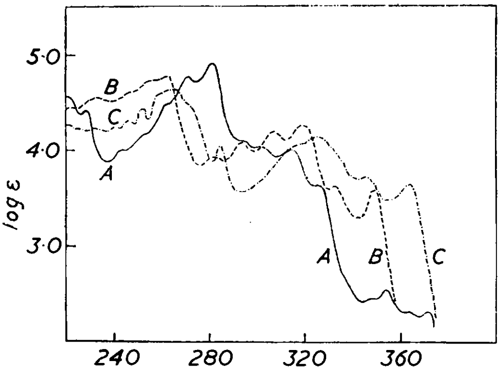

FIG. 6.

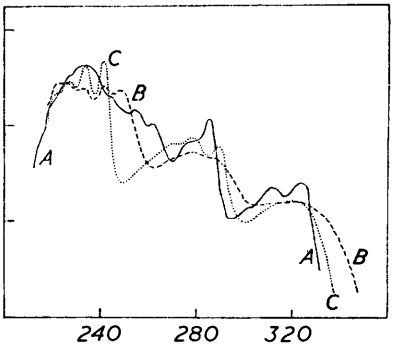

FIG. 5. *Absorption curves of* (*A*) 3 : 4-*benzophenanthrene,* (*B*) 9-*thia*-3 : 4-*benzofluorene, and* (*C*) 3 : 4-*benzocarbazole.*

FIG. 6. *Absorption curves of* (*A*) *dibenzothiophen,* (*B*) *dibenzothiophen* 9-*oxide, and* (*C*) *dibenzothiophen* 9 : 9-*dioxide.*

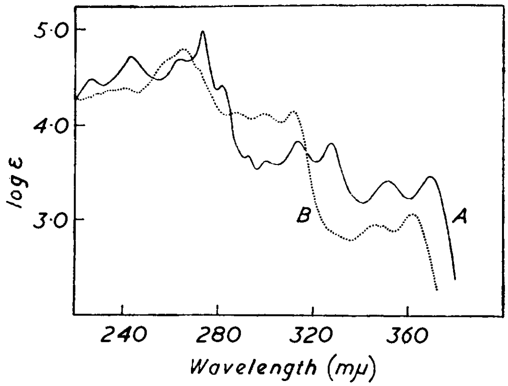

FIG. 7. *Absorption curves of* (*A*) 9-*thia*-2 : 3-*benzofluorene, and* (*B*) 9-*thia*-2 : 3-*benzofluorene* 9 : 9-*dioxide.*

FIG. 8.

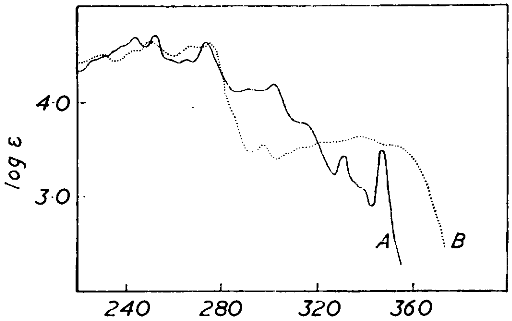

FIG. 9.

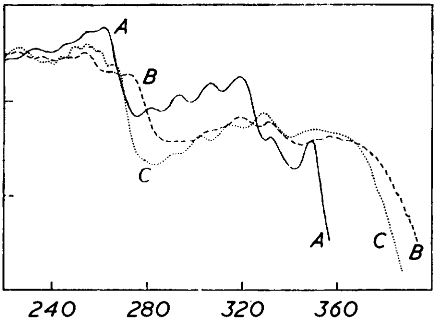

FIG. 8. *Absorption curves of* (*A*) 9-*thia*-1 : 2-*benzofluorene and* (*B*) 9-*thia*-1 : 2-*benzofluorene* 9 : 9-*dioxide.*

FIG. 9. *Absorption curves of* (*A*) 9-*thia*-3 : 4-*benzofluorene,* (*B*) 9-*thia*-3 : 4-*benzofluorene* 9-*oxide, and* (*C*) 9-*thia*-3 : 4-*benzofluorene* 9 : 9-*dioxide.*

comparable to the group I, II, and III bands of the aromatic hydrocarbons and aza-compounds can generally be resolved. The chief differences seem to be : (i) that the absorption (particularly the group I bands) is shifted to shorter wavelengths; and (ii) that the group III bands have much higher extinction coefficients than those given by the hydrocarbons. Moreover, in agreement with the view that the strong electronegativity of the oxygen atom prevents complete conjugation in the furan system, the absorption spectra of the furan derivatives (particularly the dicyclic and the tricyclic systems) resemble those of the hydrocarbons rather less closely.

In this connection it was thought of interest to examine the spectra of a series of *S*-oxides and -dioxides of polycyclic thiophen derivatives (Figs. 6—9). In the dioxides the sulphur atom can no longer contribute two electrons to the aromatic sextet; but the ring system in the monoxides remains essentially aromatic. Consequently the monoxides would be expected to have the same relation to the heterocyclic compounds as substituted hydrocarbons have to the parent hydrocarbon. This is generally found to be the case, for the spectra of the monoxides resemble those of the parent thiophen derivatives, except that there is a loss of fine structure and a bathochromic shift, particularly of the group III bands.

The spectra of the dioxides, in which the hetero-ring is no longer aromatic, nevertheless show a pronounced similarity to those of the parent ring system and of the corresponding monoxides. For example, dibenzothiophen 9 : 9-dioxide shows a much greater similarity to dibenzothiophen than to 9 : 10-dihydrophenanthrene, which it might be expected to parallel. It is evident that the SO_2 group also contributes strongly to the conjugation.

EXPERIMENTAL

Materials.—We are indebted to Professor W. Davies for gifts of 9-thia-3 : 4-benzofluorene, and of its oxide and dioxide, and to Dr. I. S. Walker for a gift of 3 : 4-benzocarbazole. Benzofuran was prepared in 84% yield by decarboxylation [6] of coumarilic acid, and was obtained as a colourless oil, b. p. 174° (lit., 174°). 2 : 3-Benzocarbazole was prepared according to Bucherer and Sonnenburg,[7] and purified by recrystallisation from toluene followed by sublimation in a high vacuum; it was obtained as pale yellow needles, m. p. 337° (lit.,[7,5] 330—332°; 340°). 9-Thia-2 : 3-benzofluorene was prepared by Mayer's method [8] by reduction of the corresponding quinone; it crystallised from hexane in colourless needles, m. p. 160° (lit.,[8,9] 154—155°; 160°). 9-Thia-1 : 2-benzofluorene was prepared by the Elbs cyclodehydration of 3-*o*-toluoylthionaphthen [10] and formed colourless plates, m. p. 185°, from hexane. Other compounds were purified commercial specimens.

Absorption Spectra.—These were determined for solutions in 95% ethanol with a Hilger Uvispek spectrophotometer.

9-*Thia*-2 : 3-*benzofluorene* 9 : 9-*Dioxide.*—Hydrogen peroxide (1 c.c.; 30%) was added to a suspension of 9-thia-2 : 3-benzofluorene (0·2 g.) in glacial acetic acid (3 c.c.), and the mixture raised to the b. p. After 3 min. the mixture became clear and shortly afterwards a white precipitate appeared. Refluxing was continued for 30 min.; the product was collected and recrystallised from light petroleum–benzene. The dioxide formed colourless needles, m. p. 267° (lit.,[9] 261°) (Found : C, 72·4; H, 4·1; S, 12·1. Calc. for $C_{16}H_{10}O_2S$: C, 72·2; H, 3·8; S, 12·0%).

9-*Thia*-1 : 2-*benzofluorene* 9 : 9-*Dioxide.*—Hydrogen peroxide (1 c.c.; 30%) was added to 9-thia-1 : 2-benzofluorene (0·25 g.) in glacial acetic acid (4 c.c.), and the mixture refluxed for 2 hr. The *product* crystallised from the mixture overnight. After recrystallisation from benzene it formed pale yellow prisms, m. p. 236° (Found : C, 72·5; H, 3·75; S, 12·2%).

Microanalyses were carried out by the C.S.I.R.O. Microanalytical Laboratory, Melbourne.

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[6] Cf. Shepard, Winslow, and Johnson, *J. Amer. Chem. Soc.*, 1930, **52**, 2083.
[7] Bucherer and Sonnenburg, *J. prakt. Chem.*, 1910, **81**, 29.
[8] Mayer, *Annalen*, 1931, **488**, 259.
[9] Werner, *Rec. Trav. chim.*, 1949, **68**, 520.
[10] Badger and Christie, preceding paper.