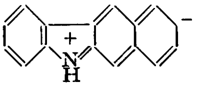
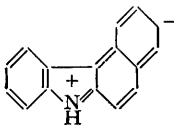
306. *The Influence of Structure on the Ultra-violet Absorption Spectra of Heterocyclic Systems. Part III.* Some Dibenzocarbazoles.*

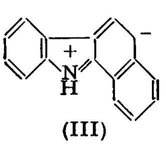
By D. G. I. FELTON.

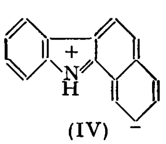
The explanation advanced in Part II for the absorption spectra of the monobenzocarbazoles is shown to apply to three of the dibenzocarbazole series.

PART II * records a study of the spectra of the three monobenzocarbazoles (amongst other compounds). It was found that the differences observed in both envelope shape and position of maxima could be explained by the interaction of the lone-pair π-electrons on the nitrogen atom with those of the aromatic residues, with some indefinite, but not decisive, contribution from the interaction of the aromatic residues among themselves, as in the benzofluorene series. By using the assumptions that *p*-quinone-type excitations were more probable than *o*-quinonoid excitations and that an extended flux of electrons will be excited more easily by light of lower energy than will a less extended system, it was possible to account for the facts that absorption of light of longer wave-lengths occurred with 2 : 3- and 3 : 4-benzocarbazoles, with the probable transitions (I) and (II), than with 1 : 2-benzocarbazole, where the transition (III), which is more probable than the *o*-quinonoid (IV), is less extended.


(I)

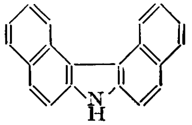

(II)

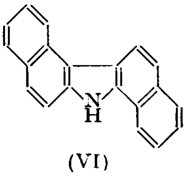

(III)

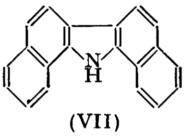

(IV)

The same considerations explained the parallels in the spectra of the benzofluorenones and benzocarbazoles and the reversal exhibited in the spectra of both these series of compounds when compared with those of the analogous benzofluorenes (see Part II and Orchin and Friedel, *J. Amer. Chem. Soc.*, 1949, **71**, 3002).

It was desirable, therefore, to test these conclusions further. A closely related series of compounds are the dibenzocarbazoles, three of which (V, VI, and VII) contain the chromophoric systems under investigation arranged in pairs. If the above-mentioned explanation is correct, then (V), which contains two of the extended chromophores of (II), should possess extremely easily excited π-electrons and hence should absorb at longer wave-lengths than (VII), the two chromophores of which are both of the less easily excited type (*i.e.*, III or IV). The analogue (VI), on the other hand, contains a blend of both of the chromophoric types in question and hence may be expected to exhibit facets of both types of spectra, though of less intensity since the probability of a particular transition is less.


(V)


(VI)


(VII)

The spectra are recorded in Fig. 1 and the values of the absorption maxima (with values of log $\varepsilon_{\max.}$ in parentheses) are given in the Table, together with those of the only comparable dibenzofluorene, *i.e.*, 1 : 2-5 : 6-dibenzofluorene, which are available from the literature (Mayneord and Roe, *Proc. Roy. Soc.*, 1937, *A*, **158**, 634). As in Part II, we have classified the bands into three groups, which may be traced from the fluorene spectrum. Those maxima, which are characteristic of the less easily excited transitions and are common to the spectra of (VI) and (VII), are printed in italics. It will be seen that for

---

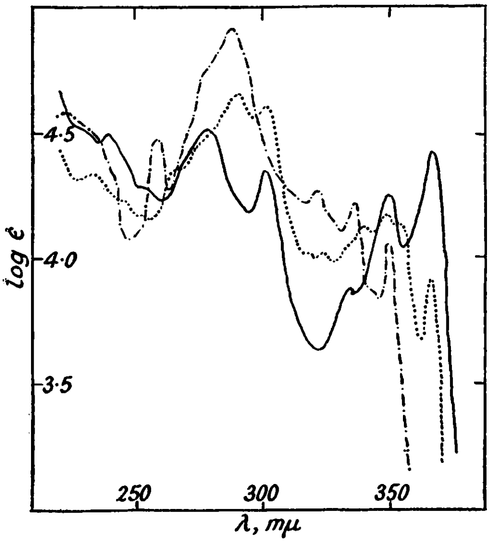
* Part II, preceding paper.

the majority of maxima tabulated, our contention is fully upheld, though there are some bands, *viz.*, those at 240, 252, 280, 335, and 349 mμ, which are common to all three spectra. In the absence of further information, however, we cannot infer that in all three cases it is the same transitions which are concerned.

It is evident from Fig. 2 in which the spectrum of (VI) is compared with the curve obtained by plotting log $\frac{1}{2}[\varepsilon_{V} + \varepsilon_{VII}]$ against wave-length, so blending the spectra of (V) and (VII) in the simplest possible fashion, that there is a considerable contribution from excitations extending over the molecule as a whole. This molecular contribution is indeterminate in all three cases.

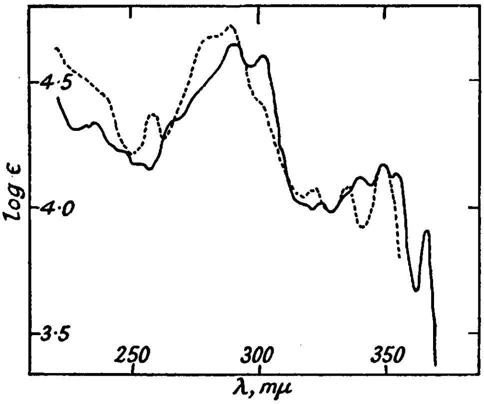
A comparison of the spectra of 1 : 2-5 : 6-dibenzo-fluorene and -carbazole (VI) gives us a further example of the bathochromic shift observed on substituting >NH· for $>CH_2$ (cf. fluorene and carbazole, Part II). Since both compounds possess one each of the two types of chromophore residues under consideration, this comparison will be largely unaffected by the dependence of spectral reversal on structure noted for the monobenzofluorenes and -carbazoles. It may be seen that the group A bands (which here are taken as including *all* the short wave-length bands including those which in the fluorene and benzofluorene series occur at too short a wave-length for observation) undergo a bathochromic shift of 40—50 mμ. Group B bands move to longer wave-lengths by about the same amount, while group C bands move by only about 15 mμ. The envelope shape is largely preserved in this comparison.

FIG. 1.



———— 3 : 4-5 : 6-*Dibenzocarbazole* (V).
- - - - - - - 1 : 2-5 : 6-*Dibenzocarbazole* (VI).
— · — · — 1 : 2-7 : 8-*Dibenzocarbazole* (VII).

FIG. 2.



———— *Plot of* log ε_{VI} *against* λ.
- - - - - - - *Plot of* log $[\frac{1}{2}\varepsilon_{V} + \frac{1}{2}\varepsilon_{VII}]$ *against* λ.

The family resemblances of the spectral curves of (V), (VI), and (VII), compared to those of the related monobenzocarbazoles, are retained, *e.g.*, the spectrum of (V) shows the virtual disappearance of the group B bands and the characteristic deep minimum (cf. the spectrum of 3 : 4-benzocarbazole, Part II, Fig. 4).

EXPERIMENTAL

The spectra were determined in purified ethanol solutions, with a Unicam photoelectric spectrophotometer (Model SP 500).

3 : 4-5 : 6-Dibenzocarbazole (V) was received from Dr. C. T. Beer as a white solid, m. p. 156° unchanged on resublimation (lit., m. p. 154°, 155°, 157°).

3 : 4-Dihydro-1 : 2-5 : 6-dibenzocarbazole was prepared from 2-naphthylhydrazine hydrochloride (3 g.), sodium acetate (2·1 g.), and 1-tetralone (2·2 ml.), the crude intermediate hydr-

azone being cyclised by heating it with dilute sulphuric acid (14% v/v). On crystallisation from glacial acetic acid, the product formed almost colourless prisms, m. p. 197°. Buu-Hoï, Hoán, and Khôi, of whose paper (*J. Org. Chem.*, 1949, **14**, 492) we were unaware until after the completion of this work, cyclised the hydrazone by means of hydrogen chloride–acetic acid and report m. p. 197°.

1 : 2-5 : 6-*Dibenzocarbazole* (VI).—The above dihydro-compound was heated with palladised charcoal at 250—260° under nitrogen for 2 hours. The mass was extracted with hot benzene, and the solution, after filtration, was evaporated to dryness. The residue, purified by sublimation from a trace of palladised charcoal at 200°/0·1 mm., yielded a very pale yellow solid, m. p. 237° (Buu-Hoï *et al.* give m. p. 237—238°).

Values of $\lambda_{\text{max.}}$ *(in* mμ*), with the corresponding values of log* $\varepsilon_{\text{max.}}$ *in parentheses.*

Substance	Group A		Group B		Group C	
1 : 2-5 : 6-Dibenzofluorene	248	(4·71)	276	(4·09)	333	(4·30)
	255	(4·77)	285	(4·10)	349	(4·32)
			294	(4·09)		
3 : 4-5 : 6-Dibenzocarbazole (V)	240	(4·50)	334	(3·88)	349	(4·25)
	252 *	(4·28)			366	(4·43)
	279	(4·52)				
	301	(4·35)				
1 : 2-5 : 6-Dibenzocarbazole (VI)	235	(4·33)	318 *	(4·01)	*349*	*(4·17)*
	246 *	(4·23)	*324*	*(4·01)*	354·5	(4·13)
	252 *	*(4·17)*	*335* *	(4·05)	366	(3·91)
	268 *	(4·35)	340	(4·12)		
	280 *	*(4·50)*				
	290	*(4·65)*				
	302	(4·60)				
1 : 2-7 : 8-Dibenzocarbazole (VII)	222	(4·58)	*321*	*(4·27)*	*349*	*(4·06)*
	240 *	(4·35)	*335*	*(4·22)*		
	252 *	*(4·12)*				
	259	(4·48)				
	280 *	*(4·78)*				
	289	*(4·92)*				

* Signifies a point of inflexion.

1 : 2-7 : 8-*Dibenzocarbazole*.—When prepared similarly from 1-naphthylhydrazine hydrochloride (3 g.) and 1-tetralone (2·2 ml.), 3 : 4-dihydro-1 : 2-7 : 8-dibenzocarbazole formed colourless prisms (from dilute acetic acid), m. p. 184° (Buu-Hoï *et al.*, *loc. cit.*, give m. p. 178°). Dehydrogenation was effected as for (VI). After several sublimations, 1 : 2-7 : 8-dibenzocarbazole formed a nearly colourless solid, m. p. 221—222° (lit., m. p. 216°; Buu-Hoï *et al.*, *loc. cit.*, give m. p. 212°, though this may be a misprint).

The author thanks Dr. C. T. Beer for the gift of a sample of 3 : 4-5 : 6-dibenzocarbazole and gratefully acknowledges the award of an I.C.I. Fellowship by the University of Durham. He is warmly indebted to Professor G. R. Clemo, F.R.S., for his interest in this work.

KING'S COLLEGE, UNIVERSITY OF DURHAM,
NEWCASTLE-ON-TYNE, 1.

[*Received, December* 21*st*, 1951.]