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305. *The Influence of Structure on the Ultra-violet Absorption Spectra of Heterocyclic Systems. Part II.* Nitrogen Analogues of the Monobenzofluorenes.*

By G. R. Clemo and D. G. I. Felton.

The ultra-violet absorption spectra of a series of monobenzofluorenes, monobenzocarbazoles, and their aza-analogues are recorded and compared. The observed band shifts are interpreted in terms of the different activating influences present and the effects which these have in producing extended electronic excitations depending on molecular structure.

In Part I,* the absorption spectra of a series of indoloquinolines were studied from the point of view of the fusion of an additional benzene ring to the corresponding pyrroloquinolines. As a result of this, the spectra were divided into two series, according as they were modelled on α- or β-naphthylamine. The groups of maxima were not assigned to

* Part I, *J.*, 1951, 671.

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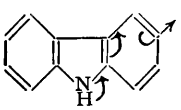
particular modes of excitation and on the evidence available it was not possible to systematise the results further.

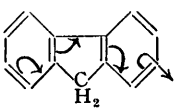
Two simple generalisations were quoted from Braude (*Ann. Reports*, 1945, **42**, 128). These were: (*a*) The spectral characteristics of simple heterocyclic systems in which a nitrogen atom is bound to carbon by single bonds, *e.g.*, pyrrole, indole, carbazole, are not appreciably different from those of their carbocyclic analogues containing a methylene group. (*b*) The series in which a nitrogen atom replaces a methine group, *e.g.*, pyridine, quinoline, acridine, show absorptions very similar to those of their aromatic analogues.

The second generalisation appeared to be supported by the closely similar spectra of indolo(2′ : 3′-5 : 6)quinoline and indolo(3′ : 2′-7 : 8)quinoline (Part I*), in which the position of the nitrogen atom in the quinoline ring seems to be of small consequence. Similar support has been adduced from the benzoquinoline (Johnson and Mathews, *J. Amer. Chem. Soc.*, 1944, **66**, 210) and the naphthoquinoline series (Johnson, Woroch and Mathews, *ibid.*, 1947, **69**, 566) and is provided also by the series anthracene, acridine, and phenazine (amongst other papers, cf. Brown and Lahey, *Austral. J. Sci. Res.*, 1950, *A*, 3, 595) and their benzo-homologues (Badger, Pearce, and Pettit, *J.*, 1951, 3199 *et seq.*).

Further consideration of (*a*) has led us to the conclusion that, theoretically, it is not well based. For, whereas in carbazole the nitrogen atom bears a pair of unshared electrons in a 2*p* orbital, which can coalesce with the π-electrons of the aromatic rings and can thus contribute to the π-electronic state of the molecule as a whole, in fluorene the electrons of the carbon of the methylene group are arranged in tetrahedral sp^3 orbitals and can contribute nothing to the π-electronic distribution, except insofar as they may take part in a hyperconjugative effect. This would be expected to be small in comparison with the polarisation introduced by the hetero-atom in the case of carbazole [Walsh, *Quart. Reviews*, 1948, **2**, 83 (footnote), 84; for the calculated electron distribution in fluorene and carbazole, see Pullman and Berthier, *Bull. Soc. chim.*, 1948, **15**, 551, and Longuet-Higgins and Coulson, *Trans. Faraday Soc.*, 1947, **43**, 87, respectively].

The substitution reactions of carbazole and fluorene are in harmony with this concept. Thus, in carbazole, where the electrons on the nitrogen atom exert the normal directive effect, electrophilic substitution occurs in the order 3, 3 : 6, 1 : 3 : 6, 1 : 3 : 6 : 8 [in agreement with the calculated electron densities (Longuet-Higgins and Coulson, *loc. cit.*)]. In fluorene, on the other hand, the positions of an entering electrophilic group or atom, *e.g.*, NO_2, Br, are 2, 2 : 7; 2 : 4 : 7, etc., where the directive influence on one ring appears to be exercised, not by the methylene group, but by the other aromatic ring (cf. Pullman and Berthier, *loc. cit.*). We may write the polarisation of carbazole as (I) and of fluorene as (II), leading to the quinonoid states (III) and (IV) respectively, among others.


(I)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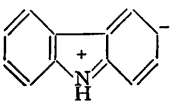
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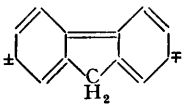
(IV)

In order to test the validity of these rules as applied to fluorene, carbazole, and related compounds leading to the indoloquinolines, we have compared the ultra-violet absorption spectra of compounds of the series (V—XXIII).

The spectra of the following compounds have been taken from the literature: (V) (Mayneord and Roe, *Proc. Roy. Soc.*, 1937, **158**, *A*, 634), (VI) (Menczel, *Z. physikal. Chem.*, 1926, **125**, 195; Pruckner and Witkop, *Annalen*, 1943, **554**, 130), (VIII) (Horner, *ibid.*, 1939, **540**, 73), (IX) (Mayneord and Roe, *loc. cit.*; Orchin and Friedel, *J. Amer. Chem. Soc.*, 1949, **71**, 3002), (XIII) (Orchin and Reggel, *ibid.*, 1948, **70**, 1247; Orchin and Friedel, *loc. cit.*). Spectra of (XII) and (XXIII) have already appeared in Part I (*loc. cit.*).

The spectra of the other members of the series have been determined in ethanolic solution (see Experimental section). Our results for indolo(3′ : 2′-2 : 3)quinoline ("quindoline") (XVIII) agree well with those of Géllert, Raymond-Hamet, and Schlittler (*Helv. Chim. Acta*, 1951, **34**, 642) recorded in connection with the alkaloid cryptolepine.

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TABLE 1. *Position of maxima* (mμ); log $\varepsilon_{max.}$ *in parentheses.*

Substance	Group A		Group B		Group C	
V	206	(4·61)	260	(4·28)	290	(3·87)
			264·5	(4·27)	294	(3·81)
					301	(3·98)
VI	243	(4·38)	280	(4·10)	318	(3·47)
	255	(4·08)	286	(4·15)	331	(3·47)
			292	(4·28)		
VII	—	—	267	(4·22)	286	(4·04)
					297	(3·99)
VIII	239	(4·66)	284	(4·40)	340	(3·83)
IX	254	(4·67)	285	(4·10)	316	(4·14)
	263	(4·86)	296	(4·20)	327	(3·36)
			306	(4·18)	345	(3·09)
X	240	(4·44)	280	(4·63)	323	(3·76)
	246	(4·47)	302	(4·29)	338·5	(3·75)
	252	(4·56)	306	(4·30)	355	(3·79)
	258	(4·52)				
XI	259	(4·61)	286	(3·92)	328	(4·0)
	265·5	(4·69)	300	(3·94)	344	(4·15)
			312	(4·01)		
XII	245	(4·48)	292	(4·58)	*ca.* 333 *	(3·55)
XIII	255	(4·71)	286	(4·08)	326	(3·85)
	263	(4·84)	303·5	(4·20)	331	(3·44)
			317	(4·30)	340	(3·85)
XIV	268	(4·81)	317	(4·03)	374	(3·70)
	282	(4·69)	332	(4·13)	394	(3·72)
	292	(4·56)				
XV	259	(4·54)	287	(4·01)	329	(4·19)
	264	(4·60)	301	(3·96)	336·5	(4·08)
	266·5	(4·59)	312	(4·06)	345	(4·30)
			320	(3·99)		
XVI	272	(4·73)	319	(4·13)	372	(3·57)
			334	(4·28)		
XVII	263	(4·64)	313	(3·96)	327·5	(4·26)
					335	(4·16)
					344	(4·44)
XVIII	272	(4·67)	343	(4·25)	385	(3·58)
XIX	269	(4·45)	346	(4·29)	362·5	(4·32)
XX	270	(4·75)	345	(4·25)	396	(3·65)
			355	(4·31)		
XXI	231	(4·68)	302·5	(4·05)	324	(4·10)
	243·5	(4·42)	313	(4·19)	330	(4·06)
	252	(4·20)	—	—	335	(4·19)
XXII	264	(4·67)	316	(4·03)	*ca.* 345 *	(3·70)
	285	(4·00)	326	(4·11)	365	(3·60)
XXIII	245·5	(4·48)	343	(3·98)	—	—
	280	(4·50)				

* Signifies a point of inflexion.

TABLE 2. *Band shifts* (*in* mμ) *on replacement of* $>CH_2$ *by* $>NH$.
(+, *bathochromic*; —, *hypsochromic*).

Pair of compounds studied	Group A	Group B	Group C
V—VI	+37	+26; +27·5	+28; +30
VII—VIII	?	+17	+43
IX—X	−2, −5	−5; +6; 0	+7; +11·5; +10
XI—XII	−20·5	−20	−11(?)
XIII—XIV	+5	+13·5; +15	+48; +54
XV—XVI	+5·5	+18; +14	+43
XVII—XVIII	+9	+30	+41
XIX—XX	+1	+9	+33·5
XXI—XXII	+33; +33	+13·5; +13	+21; +30

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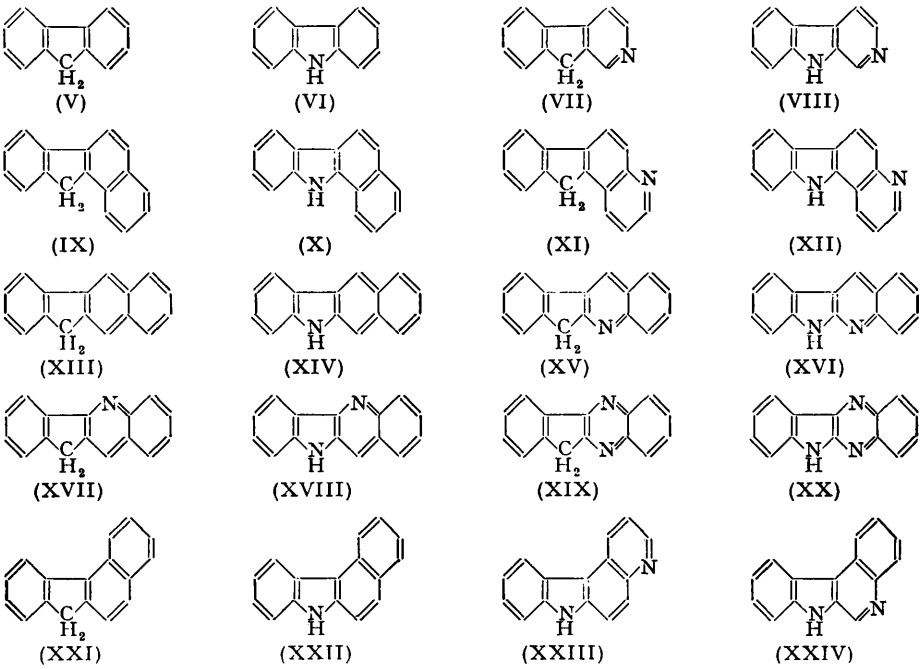
It will be seen from the series that we have systematically studied the effect on the spectra of the replacement of the methylene group in fluorene and the monobenzofluorenes by >NH, at the same time substituting —N= for a methine group in both the fluorene and carbazole series. There is one omission from the series, that of indeno(3′ : 2′-5 : 6)quinoline,



related to (XXIII). The spectral curves are shown in pairs, demonstrating in each case the effect of replacement of methylene by >NH. Where possible, the effect of replacing a methine group by —N= is shown by the pair of curves immediately above, in order to facilitate comparison.

The maxima are tabulated in Table 1, with values of log $\varepsilon_{max.}$ in parentheses, and are arranged in three groups A, B, and C. These groups are determined by inspection and comparison of curves in each case and are not dependent upon values of log $\varepsilon_{max.}$ (cf. Braude, *loc. cit.*, pp. 123, 128) since these can vary widely as substitution of heterocyclic atoms alters the transition probabilities for each group of bands. (The division of bands into groups may be traced from fluorene throughout the whole series of compounds under examination.)

The influence of structural changes on the position of the groups of bands is shown in Table 2, which lists the band shifts observed on replacement of the methylene group by >NH, and in Table 3, where the effect of replacement of a methine group by a nitrogen

TABLE 3. *Band shifts (in* mμ*) on replacement of* —CH= *by* —N=.

Pair of compounds studied	Group A	Group B	Group C
V—VII	?	+2·5	−4; −4
VI—VIII	−4	−8	+9
IX—XI	+5; +2·5	+1; +4; +6	+12; −1
X—XII	−8	−10(?)	−5(?)
XIII—XV	+4; +3·5	+1; +8·5; +3	+3; +5·5; +5
XIII—XVII	0	+9·5	+1·5; +4; +4
XIII—XIX	+6	+29	+22·5
XIV—XVI	+4	+2; +2	−2
XIV—XVIII	+4	+11	+11
XIV—XX	+2	+28; +23	+22
XXII—XXIII	+24(?)	+17	—

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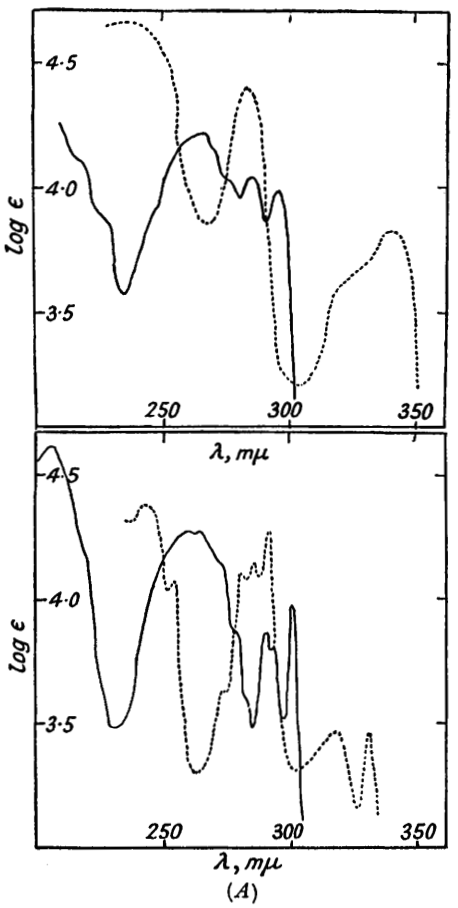
atom in comparable pairs of compounds is tabulated. Where loss of fine structure in a band or group of bands occurs, there has been some dubiety in the comparison of maxima and this is indicated in the tables by a question mark.

Discussion

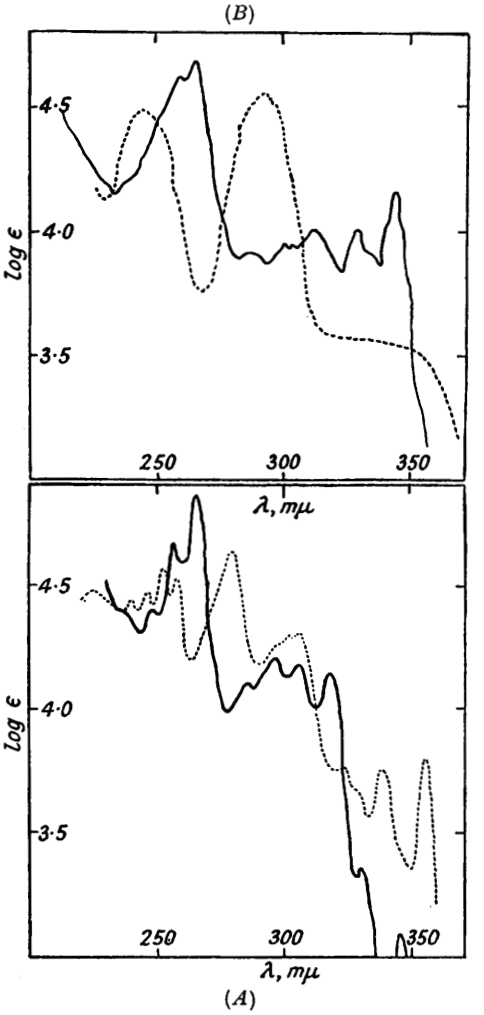
In the case of the fluorene group (V)—(VIII) (Figs. 1*A* and 1*B*), replacement of the methylene group by >NH has led in both cases to pronounced bathochromic shifts, owing to the π-electrons on the nitrogen atom entering into conjugation with those of the aromatic

Fig. 1.



(*A*) ———— *Fluorene* (V).
– – – – – – *Carbazole* (VI).
(*B*) ———— 2-*Azafluorene* (VII.
– – – – – – β-*Carboline* (VIII).

Fig. 2.



(*A*) ———— 1 : 2-*Benzofluorene* (IX).
– – – – – – 1 : 2-*Benzocarbazole* (X).
(*B*) ———— *Indeno*(2′ : 3′-5 : 6)*quinoline* (XI).
– – – – – – *Indolo*(2′ : 3′-5 : 6)*quinoline* (XII).

rings, so producing a more mobile electronic system. On the other hand, the replacement of a methine group by a nitrogen atom does not add to the number of available mobile electrons and consequently produces very little change in the position of the maxima. Fine structure in individual bands is largely lost, while the intensities in the aza-series tend to be somewhat higher.

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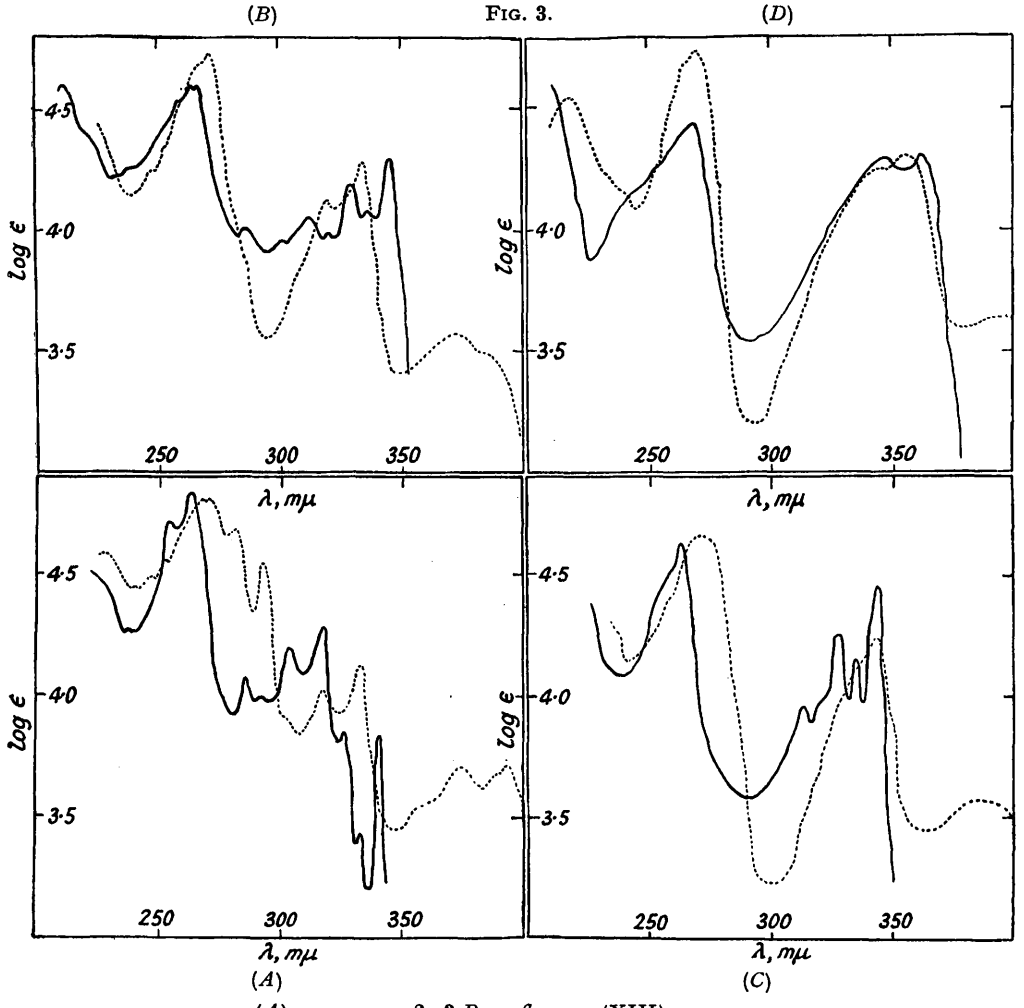
In the 1 : 2-benzofluorene group (IX)—(XII) (Figs. 2*A* and 2*B*), replacement of methylene by >NH causes hypsochromic shifts, in some cases very marked, except for the group C maxima of (X). A more profound variation in the envelope shape is noted also in both pairs of spectra. Substitution of —N= for —CH= has produced little effect on the position of the bands in the pair of compounds (IX) and (XI), while increasing the intensities of group C maxima. In the pair of compounds (X) and (XII), hypsochromic shifts occur though there is some doubt about the comparison of the maxima.

FIG. 3.



(*A*) ———— 2 : 3-*Benzofluorene* (XIII).
------ 2 : 3-*Benzocarbazole* (XIV).
(*B*) ———— *Indeno*(2′ : 3′-2 : 3)*quinoline* (XV).
------ *Indolo*(2′ : 3′-2 : 3)*quinoline* (XVI).
(*C*) ———— *Indeno*(3′ : 2′-2 : 3)*quinoline* (XVII).
------ *Indolo*(3′ : 2′-2 : 3)*quinoline* (XVIII).
(*D*) ———— *Indeno*(2′ : 3′-2 : 3)*quinoxaline* (XIX).
------ *Indolo*(2′ : 3′-2 : 3)*quinoxaline* (XX).

With the linear 2 : 3-benzofluorene group (XIII)—(XX) we are dealing with more than two pairs of analogous compounds, since here we have also studied the effect on the spectra of the position of the aza-atom. In each pair of absorption curves (Figs. 3*A*, 3*B*, and 3*C*) replacement of methylene by >NH had produced a large bathochromic shift, especially in the group C bands, which are shifted by at least 40 mμ in every

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case, though the envelope shape is largely retained with loss of fine structure, *i.e.*, the spectra of the carbazole members appear to have been stretched in the direction of longer wave-lengths. In the same three pairs of compounds (XIII)—(XVIII), substitution of —CH= by —N= produces some slight bathochromic shifts and in (XVII) (Fig. 3*C*) a modification of the envelope shape by the virtual extinction of group B maxima. In the two indenoquinolines (XV) and (XVII), this substitution has led to a large increase in the group C intensities, while in the corresponding two indoloquinolines (XVI) and (XVIII) the group B maxima are of higher intensity than the group C bands. The last pair [(XIX) and (XX)] contain the quinoxaline ring, *i.e.*, both methine groups are replaced simultaneously by nitrogen atoms. This causes the loss of all fine structure and a considerable variation in the envelope shape (Fig. 3*D*). Again, replacement of the methylene group by >NH produces a bathochromic shift of the group C bands. Compared to the parent benzofluorene and benzocarbazole, the introduction of the two aza-atoms causes very large shifts (*ca.* 20 mμ) of both group B and group C bands.

The last series of compounds, based on 3 : 4-benzofluorene, is incomplete. From the spectra (Fig. 4) it can be seen that replacement of the methylene group by >NH has

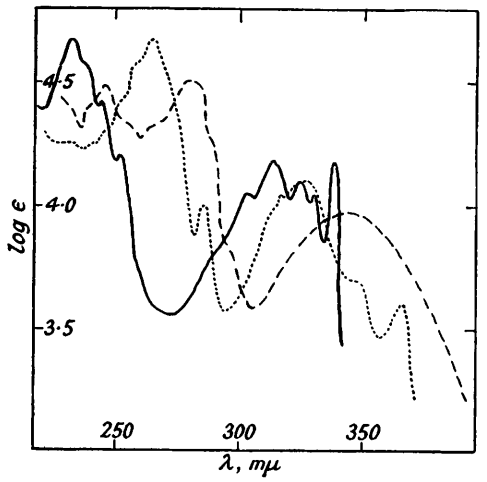

FIG. 4.

——— 3 : 4-*Benzofluorene* (XXI).
- - - - - - 3 : 4-*Benzocarbazole* (XXII).
——·—·—· *Indolo*(3′ : 2′-5 : 6)*quinoline* (XXIII).

caused large bathochromic shifts of all three groups of bands with considerable loss of fine structure. Introduction of a second nitrogen atom to give the indoloquinoline (XXIII) leads to a further shift to longer wave-lengths and a merging of the group B and C maxima into a wide, ill-defined band.

There is thus an apparent exception to our hypothesis that the greater π-electronic flux caused by the replacement of a fluorene methylene group by >NH leads to bathochromic shifts, *viz.*, the 1 : 2-benzofluorene group, wherein such replacement causes a hypsochromic shift of some of the bands, especially in the aza-series. This apparent exception, however, is a strong point in favour of such a hypothesis. Orchin and Friedel (*loc. cit.*) have pointed out that the spectra of 1 : 2-benzofluorene (IX) and 2 : 3-benzofluorene (XIII) closely resemble each other, while that of 3 : 4-benzofluorene is strikingly distinct, and have attributed this to the close formal resemblance between the latter compound and α-phenylnaphthalene, and the two former structures and β-phenylnaphthalene, respectively. There is a similar pairing in the benzocarbazole series, though in this case it is between the 2 : 3- and the 3 : 4-benzo-isomer, with 1 : 2-benzocarbazole as the exception; the resemblance between the latter pair is not as close as in the benzofluorene series. It may be attributed to a formal relation with β-phenylnaphthylamine, while the 1 : 2-isomer is related to α-phenylnaphthylamine. (In Part I, we attributed the difference in the spectra of individual indoloquinolines and the related pyrroloquinolines to structural analogies with α- and β-naphthylamines.) In the benzofluorene series it is the other aromatic ring which determines the electronic polarisation, apart from some hypercon-

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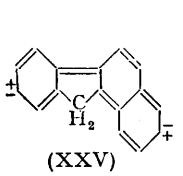
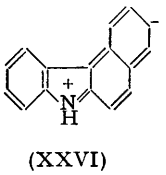
jugative effect of the methylene group. In the benzocarbazole series, however, the main electronic polarisation appears to arise, as predicted, from the lone pair of π electrons on the >NH group; some contribution may be expected from the other aromatic ring as in the benzofluorenes and this may perhaps account for the less close resemblances between the two similar spectra. It is to be expected that electronic polarisations will lead most easily to *p*-quinone like structures in the naphthalenic portion of the molecule. Such *p*-quinonoid structures in the case of carbazole (III) and fluorene (IV) may be invoked to explain the primary electrophilic substitution products of these molecules. Albert, Goldacre, and Phillips (*J.*, 1948, 2240) have suggested a similar increased availability of π electrons for *p*-quinonoid electronic polarisations over the corresponding *o*-quinonoid structures to account for the greatly increased basic strengths of 2- and 5-aminoacridines over the 3- and 4-amino-isomers. Granted such an assumption, we can see that π-electrons will be more available for excitations such as (XXV) and (XXVI), than for (XXVII) and (XXVIII) respectively.


(XXV)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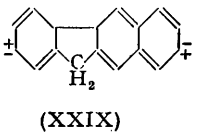
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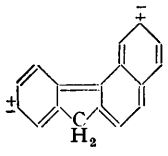
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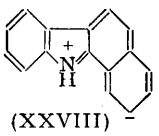
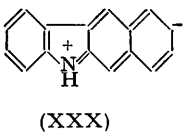

(XXVIII)


(XXX)

Thus it will be seen that depending on the source of the π-electrons conjugated with the naphthalenic portion of the structure (*i.e.*, the other benzenoid ring in the case of the benzofluorenes and the >NH group in the benzocarbazole series), the most extended conjugated system will be determined by the angular nature of the compound involved. In the benzofluorene series this is the 1 : 2-benzo-isomer, while in the benzocarbazoles it is the 3 : 4-benzo-compound. Both linear 2 : 3-benzo-isomers are capable of yielding the most extended polarisation, (XXIX) and (XXX). Such extended polarisations lead to "looser" π-electrons, *i.e.*, low-energy excitations, and imply bathochromic shifts. We then see that, the extra electrons introduced by the >NH group being neglected, 1 : 2-benzofluorene should absorb at higher wave-lengths than 1 : 2-benzocarbazole, while the reverse should be true for the 3 : 4-isomers, or, in other words, 1 : 2-benzofluorene should resemble 2 : 3-benzofluorene, while in the benzocarbazole series it should be the 2 : 3- and the 3 : 4-benzo-isomer which should be alike, as in fact is the case. This simple picture is complicated by the bathochromic shift caused by the change from $>CH_2$ to >NH, as exemplified by fluorene and carbazole, but this in addition to the above effect produces the large bathochromic shift, in the case of the 2 : 3- and 3 : 4-benzo-fluorenes and -carbazoles while accounting for the small hypso- and batho-chromic shifts in the 1 : 2-benzo-series.

The band shifts on passing from fluorene to a benzofluorene, and from carbazole to a benzocarbazole are shown in Table 4. The change on annellation is given for each of the possible positions of the additional aromatic residue. It will be seen that, in the fluorene series, bands in groups A and C are moved most for the 1 : 2- and the 2 : 3-isomers (there are unexplained discrepancies in group B bands), while in the carbazole series the larger shifts are seen for the 2 : 3- and the 3 : 4-isomer, for all three groups of bands. In the benzofluorene series the order is brought out well by the shifts of the longest wave-length maximum [see figure in Orchin and Friedel (*loc. cit.*) where this is shown very clearly].

Orchin and Friedel have reported that the spectra of the benzofluorenones show a reversal

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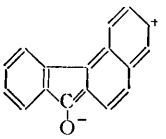
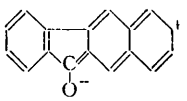
in this order, *i.e.*, the 2 : 3- and the 3 : 4-benzo-isomers are similar, while 1 : 2-benzofluorenone is easily distinguishable, and they attribute this to hydrogen bonding in the last case. It seems very probable that our explanation of the difference in the benzocarbazole series is applicable here. Instead of the >NH group with its extra π-electrons

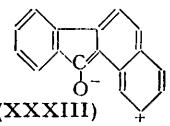
TABLE 4. *Positional effect of annellation on fluorene and carbazole.* (*Band shifts in* mμ.)

Position of additional fused ring	Group A	Group B	Group C
		Fluorene	
1 : 2	+57	+25; +31·5	+26; +33; +44
2 : 3	+57	+26; +39	+36; +37; +39
3 : 4	+25	+42·5; +48·5	+34; +36; +34
		Carbazole	
1 : 2	+ 9; +3	0; +16; +14	+20·5; +24
2 : 3	+25; +27	+31; +40	+56; +63
3 : 4	+21; +30	+30; +34	+27; +34

leading to polarisations in a direction different from that in the benzofluorene series, we have the cationoid effect of the carbonyl group causing polarisations in the same direction as in the benzocarbazoles, but in the opposite sense. Thus one would expect electrons to be more readily available for excitations such as (XXXI) and (XXXII) than for (XXXIII).


(XXXI)


(XXXII)


(XXXIII)

Our explanation is supported, not only by the results from the simple benzo-fluorenes and -carbazoles, but also by their aza-analogues. Thus the spectra of (XI) and (XV) resemble each other very closely, with (XVII) as a somewhat modified member of the trio (B bands eclipsed). Likewise, (XVI) and (XXIV) (for spectrum see Part I) are very similar, while (XVIII) and (XXIII), again both very similar, differ somewhat from the former pair by virtue of a bathochromic shift of group B bands. It may be seen from the data for compounds (XVI), (XVIII), (XXIII), and (XXIV) that the position of the aza-atom exerts some effect on the position of band maxima, albeit a small one. This may be attributable to the larger electronegativity of the aza-atom compared with the methine group which it replaces, leading to a clustering of the π-electrons around it, but the effect which this will have on the electronic polarisation is difficult to predict.

In view of the very close similarity between the spectra of (XI) and (XV) (see Table 1), it is worth noting that the structure of (XI) has not been settled unambiguously. Bremer and Hamilton (*J. Amer. Chem. Soc.*, 1951, **73**, 1844) have shown that the Conrad–Limpach synthesis, applied to 2-aminofluorene, yields 4-hydroxyindeno(2′ : 3′-5 : 6)-quinoline and have implied that the Skraup reaction follows the same route. We have attempted to prove this by replacing the hydroxyl group by chlorine and removing this by catalytic hydrogenolysis to yield (XI). However, all attempts to obtain 4-chloroindeno-(2′ : 3′-5 : 6)quinoline have been unsuccessful. Phosphorus oxychloride, alone or with phosphorus pentachloride, has invariably yielded a product containing covalently bound phosphorus, while thionyl chloride, on prolonged refluxing, has given a sulphur-containing product. In view of the well-known tendency for the Skraup reaction to give an angular product, where possible, we consider that (XI) is a reasonable assumption in the absence of contra-indicating fact.

EXPERIMENTAL

The ultra-violet absorption spectra of the compounds studied were determined in ethanolic solution on a Unicam photoelectric spectrophotometer (Model SP 500), in ethanol which was

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shown to be optically void in the region under examination. Values of log ε below 3·0 are not plotted since absorption fell off rapidly with increasing wave-length.

2-*Azafluorene* (VII).—This, m. p. 84—85° (after repeated sublimation at 70°/0·01 mm.), was prepared according to Mills, Palmer, and Tomkinson (*J.*, 1924, **125**, 2365), who give m. p. 78°.

1 : 2-*Benzocarbazole* (X).—Tetrahydro-1 : 2-benzocarbazole (m. p. 139°; Oakeshott and Plant, *J.*, 1928, 1840) (0·75 g.) was heated under reflux with chloranil (1·67 g.) in xylene (50 ml.) for 24 hours and the mixture was worked up in the usual manner (Barclay and Campbell, *J.*, 1945, 530). The product, after crystallisation from aqueous ethanol, was purified by sublimation from a trace of palladised charcoal at 150°/0·01 mm. It formed a white solid, m. p. 227—228°.

Indeno(2′ : 3′-5 : 6)*quinoline* (XI).—This was prepared by a modified Skraup reaction on 2-aminofluorene, with sodium *m*-nitrobenzenesulphonate instead of arsenic acid (Diels and Staehlin, *Ber.*, 1902, **35**, 3275). The product, after crystallisation from light petroleum, was sublimed twice at 120°/0·01 mm., forming a white solid, m. p. 127°, depressed to 103—108° on admixture with 2-aminofluorene, m. p. 127°. Diels and Staehlin gave m. p. 133°.

2 : 3-*Benzocarbazole* (XIV).—Authentic 2 : 3-benzocarbazole, for which we are greatly indebted to Professor J. W. Cook (Glasgow), was resublimed at 280°/0·01 mm., and had m. p. 342°.

Indeno(2′ : 3′-2 : 3)*quinoline* (XV).—*o*-Aminobenzaldehyde (5 g.) and indan-2-one (5·5 g.) were heated under reflux in 2N-hydrochloric acid (65 ml.) for 15 minutes. The brownish-purple hydrochloride was collected and basified with hot dilute sodium hydroxide solution, and the free base collected, dried, and recrystallised successively from ethyl acetate and methanol. After two sublimations (at 130—140°/0·01 mm.) it formed a very pale yellow solid, m. p. 144° (Borsche, *Annalen*, 1937, **532**, 127, gives m. p. 140°) (Found: C, 88·5; H, 5·05. Calc. for $C_{16}H_{11}N$: C, 88·6; H, 5·1%).

Indolo(2′ : 3′-2 : 3)*quinoline* (XVI).—This was prepared following Holt and Petrow (*J.*, 1948, 922) and had m. p. 347° after resublimation.

Indolo(3′ : 2′-2 : 3)*quinoline* (XVIII).—Flavindine [4-carboxyindolo(3′ : 2′-2 : 3)quinoline] was decarboxylated by heating it under reflux with zinc dust in alkaline suspension, and the resulting dihydro-compound, after filtration, was oxidised by a current of air. The product, crystallised from toluene and then sublimed, had m. p. 251—252° (cf. Fichter and Rohner, *Ber.*, 1910, **43**, 3491).

Indeno(2′ : 3′-2 : 3)*quinoxaline* (XIX).—Prepared according to Perkin, Roberts, and Robinson (*J.*, 1912, **101**, 234) and sublimed at 130°/0·01 mm., this formed a pale yellow solid, m. p. 166—167° (lit., 164—165°).

Indolo(2′ : 3′-2 : 3)*quinoxaline* (XX).—This was obtained from isatin and *o*-phenylenediamine, following Schunck and Marchlewski (*Ber.*, 1895, **28**, 2528). After sublimation at atmospheric pressure, it formed long golden-yellow needles, m. p. 286°.

3 : 4-*Benzocarbazole*.—The corresponding tetrahydro-compound (Oakeshott and Plant, *loc. cit.*) was dehydrogenated by chloranil in boiling xylene, and the product, after crystallisation, was sublimed from a little palladised charcoal at 120°/0·01 mm., forming a colourless solid, m. p. 135°.

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