171. *Electron Donor and Acceptor Complexes with Aromatic Systems. Part III.* Absorption Spectra of Some Benzoquinolines and of their Complexes with Bromine in Solution.*

By W. SLOUGH and A. R. UBBELOHDE.

Absorption spectra of 2 : 3-, 3 : 4-, 5 : 6-, and 7 : 8-benzoquinoline have been determined in *cyclo*hexane solution over the range 2000—4000 Å. For each substance complex formation with bromine in solution has been established and new charge-transfer bands are reported. Special techniques allow for the broad absorption regions of bromine in *cyclo*hexane (2000—3000 Å) or 1 : 2-dimethoxyethane (2600 Å into the visible region), due to polarisation or charge-transfer interaction with these solvent molecules. This effect is practically absent in solutions of bromine in perfluoromethyl*cyclo*hexane (C_7F_{14}) in which bromine exhibits absorption much as in the vapour state (in the region 4100 Å).

Perfluoromethyl*cyclo*hexane does not dissolve either the heterocyclic molecules or their bromine complexes appreciably, and so cannot be used to investigate charge-transfer bands in solution. However, when any of the heterocyclic molecules is added to solutions of bromine in 1 : 2-dimethoxyethane, the broad absorption shrinks into a distinct much narrower band specific to each heterocyclic molecule. This behaviour is interpreted on the assumption that in these solutions the bromine forms complexes preferentially with the heterocyclic molecules. When the proportion of bromine in the complex $(Br_2)_y,C_{13}H_9N$ is increased progressively, only the narrow band characteristic of this complex is observed till y reaches about 2 or more. Beyond this the excess of bromine forms complexes with solvent and the much broader absorption region reappears. Comparisons between the behaviour of the heterocyclic molecules and of benzene in forming charge-transfer complexes with bromine are also recorded.

DURING purification of four isomeric benzoquinolines by chromatography and by other methods, before preparation of solid complexes with bromine or with sodium,[1,2] a sensitive test was required for the purity of the organic substances. For this purpose, studies of the ultraviolet absorption spectra were combined with melting-point measurements, Results for the pure benzoquinolines are recorded in this paper.

Absorption spectra of solutions of complexes of these heterocyclic molecules with

---

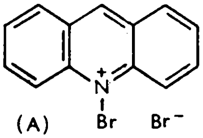
* *J.*, 1954, 720; 1955, 4089, are considered to be Parts I and II.

[1] Holmes-Walker and Ubbelohde, *J.*, 1954, 720.

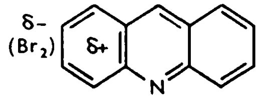
[2] Gracey and Ubbelohde, *J.*, 1955, 4089.

bromine prove of exceptional interest. Bromine was readily removed from these solid complexes under a high vacuum and the compounds behaved as addition products (cf. Part V of this series, unpublished). In principle, bromine might add at the heterocyclic atom to form derivatives[3] of type (A).

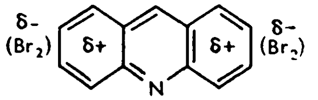
Charge-transfer complexes involving one or more of the aromatic nuclei, might also be formed by the additional successive bromine molecules, symbolised by the stages (B) and (C). And finally, the solvent molecules might in certain cases compete for the bromine with the heterocyclic molecules, to form association complexes, possibly involving charge transfer of the type $(\overset{\delta+}{\text{Solvent}})(\overset{\delta-}{\text{Br}_2})$.



(A)



(B)



(C)

Three types of solvent have been tried.

(i) Perfluoromethyl*cyclo*hexane C_7F_{14} gives solutions of pure bromine whose absorption spectra are similar to those of gaseous bromine. This solvent thus appears not to form association complexes with bromine, but it had no appreciable solvent power for the heterocyclic substances or for their complexes with bromine, so that it could not be applied for the present purpose.

(ii) *cyclo*Hexane gives solutions of pure bromine with marked absorption regions over 2000—3000 Å. It dissolves the heterocyclic molecules to a sufficient extent to permit determination of their absorption spectra in the pure state. On the other hand, the solubility of heterocycle-bromine *complexes* is very low. Solutions approx. 10^{-4}M show no evidence of charge transfer, for reasons discussed below. Stronger solutions could not be obtained at room temperature.

(iii) 1 : 2-Dimethoxyethane gives solutions of pure bromine with an extensive absorption regions from about 2000 Å into the visible region. Solutions of the pure heterocyclic molecules give absorption spectra similar to those in *cyclo*hexane. Solutions of the heterocycle-bromine complexes can be conveniently obtained in this solvent, with concentrations 10^{-2}M or more at room temperature. Examination of their absorption spectra shows a fairly narrow charge-transfer band, characteristic of each heterocyclic molecule. However, when the bromine : heterocycle ratio exceeds about the composition $(Br_2)_2$,ArN the excess of bromine seems to be attached preferentially to the solvent since the strong broad absorption reappears exactly as for the solutions of pure bromine.

The experiments described serve to illustrate the competition in formation of complexes with bromine exerted by different kinds of attractive centres in the heterocyclic molecules, and by the solvent molecules.

EXPERIMENTAL

Properties of the Pure Benzoquinoline.—Absorption spectra in the various solvents were all measured on a Hilger Uvispek photoelectric spectrophotometer H700/302.

Commercially pure organic heterocyclic compounds were further purified by chromatography through alumina (Peter Spence, Type H) with benzene as solvent, and elution with ether. Concentration of these ethereal solutions gave the crystalline heterocyclic compounds. They were then freed from residual solvent under a vacuum and finally just melted and then allowed to resolidify under a stream of pure nitrogen. M. p.s of the original and purified compounds were determined in sealed capillaries, filled at atmospheric pressure, as follows :

Benzoquinoline	2 : 3-	3 : 4-	5 : 6-	7 : 8-
M. p.	108·5—109°	102·5—103·5°	85·5—86°	52·0—52·5°

---

[3] Acheson, Hoult, and Barnard, *J.*, 1954, 4142.

With these large aromatic molecules, m. p.s do not provide a very sensitive test for the absence of closely similar molecular structures, since these tend to remain in solid solution. Ultraviolet absorptions of the chromatographed and untreated compounds were compared in *cyclo*hexane solution over the range 2000—4000 Å, and showed that chromatography removed impurities to some extent. If, for acridine, the increase in peak absorptions is attributed to the presence of non-absorbing impurity in the original sample, the proportion of such impurity originally present and removed by chromatography would be about 6%. This altered the m. p by about 3°. On chromatography yet once more there was no appreciable further change in the absorption curve. General practice was therefore to chromatograph the compounds only once.

The ultraviolet absorption spectra of the purified molecules are recorded in Fig. 1.

Formation and Absorption Spectra of Bromine Complexes.—Marked forces of interaction are exerted between molecules such as bromine and the heterocyclic molecules now studied. For example, a solid complex is precipitated from carbon tetrachloride solutions of acridine when bromine is added.[3]

FIG. 1. *Absorption spectra of* (A) 2 : 3-*benzoquinoline,* (B) *its adduct with* 0·23 Br, (C) 7 : 8-, (D) 5 : 6-, *and* (E) 3 : 4-*benzoquinoline, and* (F) *the adduct of the last with* 2·80 Br.

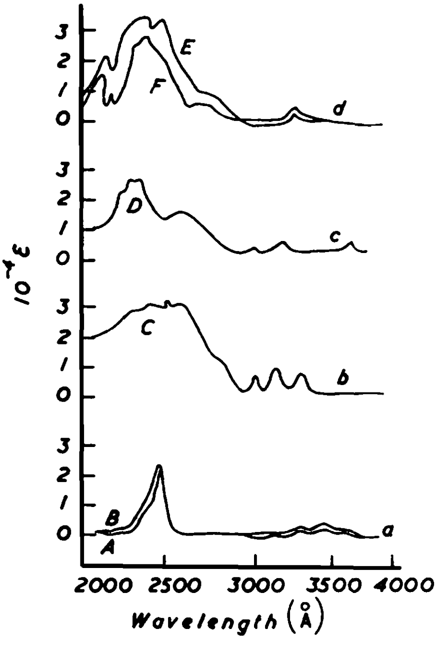
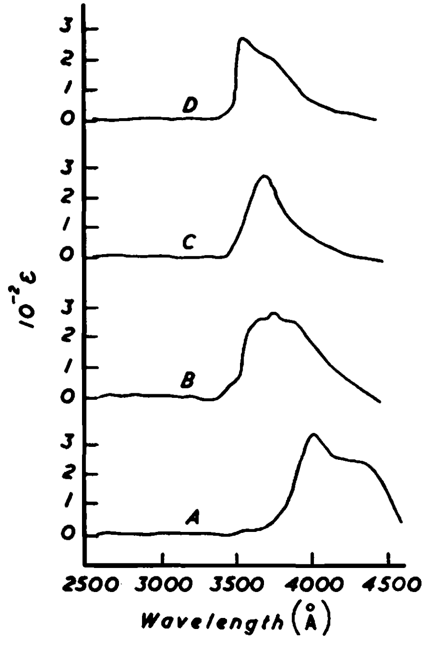


FIG. 2. *Charge-transfer absorption for* (A) $Br_{0\cdot30}$–2 : 3-*benzoquinoline,* (B) $Br_{3\cdot78}$–7 : 8-*benzoquinoline,* (C) $Br_{0\cdot72}$–5 : 6-*benzoquinoline, and* (D) $Br_{0\cdot49}$–3 : 4-*benzoquinoline.*



Other more direct methods of studying the interaction of bromine with the heterocyclic molecules in the solid state will be described in Part V (in the press). It is likewise important to know how these complexes behave in solution since this could throw light on the bonding in the solids.

Solid complexes between bromine and the various heterocyclic molecules were prepared by direct addition (cf. Part V). Compositions were established by direct weighing. Spectra for two bromine adducts in *cyclo*hexane are recorded in Fig. 1.

The absence of any charge-transfer absorption band in Figs. 1*a* and *d* has been interpreted on the hypothesis that the bromine first forms complexes such as (A). If this is correct, increasing the proportion of bromine beyond the composition $Br_2,C_{13}H_9N$ might permit subsequent bromine molecules to be attached to the aromatic nuclei by charge transfer. This possibility could not be tested in *cyclo*hexane since the solubility of the complexes at room temperature decreases steeply as the proportion of bromine increases.

1 : 2-Dimethoxyethane was found to be a better solvent. It was purified by distillation and drying, and by chromatography on alumina and was practically transparent at wavelengths 2000—4500 Å when freshly prepared.

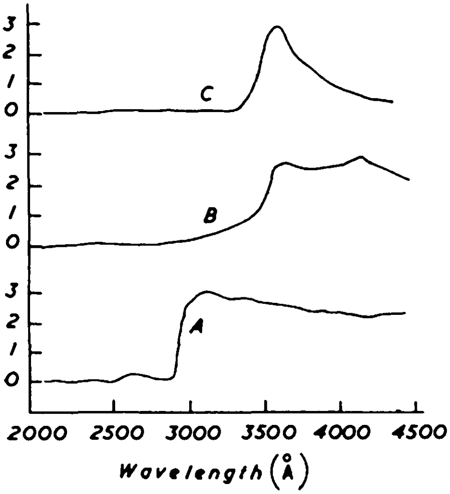


FIG. 3. *Absorption in* 1 : 2-*dimethoxyethane of* (A) $Br_{4\cdot00}$–5 : 6-*benzoquinoline* (*plus excess of bromine*), (B) $Br_{3\cdot93}$–5 : 6-*benzoquinoline, and* (C) $Br_{0\cdot72}$–5 : 6-*benzoquinoline.*

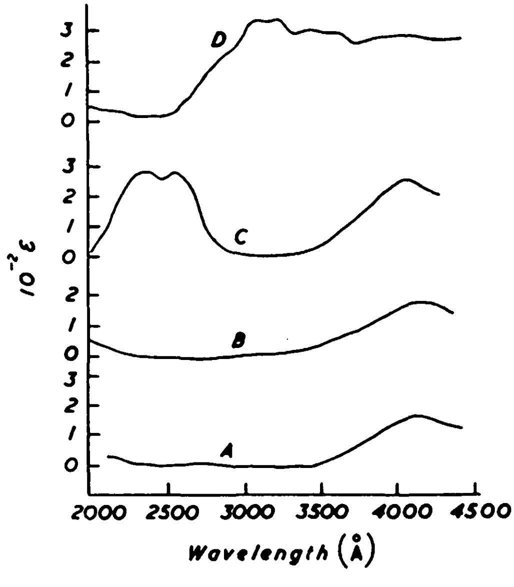


FIG. 4. *Absorption of bromine in* (A) *the vapour state* (*Evans,* J. Chem. Phys., 1955, **23**, 1426), (B) *in perfluoromethyl*cyclo*hexane,* (C) cyclo*hexane, and* (D) 1 : 2-*dimethoxyethane.*

Absorption spectra of solutions of the complexes in this solvent were established by the "difference" method; two cells containing the same solution of heterocyclic substance in the ether were used, one of which also contained a known quantity of bromine (determined by titration).

Typical difference spectra obtained in this way are recorded in Fig 2.

In one case (5 : 6-benzoquinoline) the effect of "loading" the heterocyclic molecule progressively with more bromine was determined, as recorded in Fig. 3. Fig. 4 records the absorption spectra of solutions of pure bromine in the three solvents.

DISCUSSION

Spectra of Pure Benzoquinolines.—From the absorption spectra of 2 : 3-, 3 : 4-, 5 : 6-, and 7 : 8-benzoquinoline in *cyclo*hexane (Fig. 1*a*—*d*) the following points emerge :

(1) The absorption of acridine is greater than that of the other three isomers. For the absorption band in the 2500 Å region the total oscillator strengths[4] are given by $f = 4{\cdot}31 \times 10^{-9}\int \varepsilon \, . \, d\nu$. These values have been obtained by graphical integration and the ratios are as follows :

			f
2 : 3-Benzoquinoline (acridine)	2·18	5 : 6-Benzoquinoline	1·00
3 : 4-Benzoquinoline (phenanthridine)	1·43	7 : 8- ,,	1·68

(2) Peaks at 3150 and 3300 Å are present in the absorption curves for 5 : 6- and 7 : 8-benzoquinoline but are absent from the 3 : 4-benzoquinoline curve. The absorption peak at 3450 Å, present in the phenanthridine curve, is considerably higher in the 5 : 6- and 7 : 8-benzoquinoline curves, as is the intensity of the whole absorption from about 3000 to 3800 Å.

The increased oscillator strength and narrower absorption peak of acridine, compared with the other isomeric benzoquinolines, indicate that in this molecule excited levels are relatively more closely spaced. These findings have a bearing on studies of solid complexes of acridine with sodium or with bromine, described in Part V.

As also reported by Badger and Walker[5] there appears to be no absorption band in the longer-wave region for phenanthridine which could be attributable to a transition of non-bonding nitrogen electrons to excited levels (n–π^*) ; any such transition may be hidden under the group III absorption bands (*ca.* 2500 Å). However, for 5 : 6- and 7 : 8-benzoquinoline there exist two distinct absorptions (at 3150 and 3300 Å) not shown by phenanthridine; these together with a general increase in absorption in this region may be due to n–π^* transitions.

Absorption Spectra of Complexes with Bromine.—As stated above, both *cyclo*hexane and 1 : 2-dimethoxyethane show regions of marked absorption when they contain dissolved bromine. Curves are illustrated in Fig. 4. Similar effects have been previously reported for solvents such as heptane.[6] They have been attributed to the formation of charge-transfer complexes which may be symbolised as dissociation equilibria (1) and (2) on the

$$\mathrm{C_6H_{12}} + \mathrm{Br_2} \rightleftharpoons (\overset{\delta+}{\mathrm{C_6H_{12}}})(\overset{\delta-}{\mathrm{Br_2}}) \qquad . \; . \; . \; . \; . \; . \; (1)$$

$$K_1 = \left[(\overset{\delta+}{\mathrm{C_6H_{12}}})(\overset{\delta-}{\mathrm{Br_2}})\right]/\left[\mathrm{Br_2}\right]\left[\mathrm{C_6H_{12}}\right]$$

$$(\mathrm{MeO})_2\mathrm{C_2H_4} + \mathrm{Br_2} \rightleftharpoons \left\{(\overset{\delta+}{\mathrm{MeO}})_2\mathrm{C_2H_4}\right\}\overset{\delta-}{\mathrm{Br_2}} \qquad . \; . \; . \; . \; (2)$$

$$K_2 = \left[\left\{(\overset{\delta+}{\mathrm{MeO}})_2\mathrm{C_2H_4}\right\}\overset{\delta-}{\mathrm{Br_2}}\right]/\left[(\mathrm{MeO})_2\mathrm{C_2H_4}\right]\left[\mathrm{Br_2}\right]$$

usual assumption that the bromine[7] acts as acceptor. Perfluoromethyl*cyclo*hexane apparently does not form such complexes to any appreciable extent (Fig. 4) but unfortunately its solvent power is too low to permit its use as a solvent in a study of the complexes. Any complex formation between the heterocyclic molecules and bromine must therefore be studied in competition with the equilibria (1) or (2).

For 1 : 2-dimethoxyethane, certain conclusions from Fig. 2 are clear. Each of the

---

[4] Chako, *J. Chem. Phys.*, 1934, **2**, 644.

[5] Badger and Walker, *J.*, 1956, 122.

[6] Evans, *J. Chem. Phys.*, 1955, **23**, 1424, 1426, 1429.

[7] Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811.

heterocyclic molecules (ArN) is associated much more strongly with bromine than is the solvent. Equilibria such as:

$$\mathrm{ArN} + \mathrm{Br_2} \rightleftharpoons \overset{\delta+}{\mathrm{ArN}},\overset{\delta-}{\mathrm{Br_2}}$$

$$K_3 = \left[\overset{\delta+}{\mathrm{ArN}},\overset{\delta-}{\mathrm{Br_2}}\right]/\left[\mathrm{Br_2}\right]\left[\mathrm{ArN}\right]$$

and

$$\mathrm{ArN} + 2\mathrm{Br_2} \rightleftharpoons \overset{2\delta+}{\mathrm{ArN}},\overset{2\delta-}{2\mathrm{Br_2}}$$

$$K_4 = \left[\overset{2\delta+}{\mathrm{ArN}},\overset{2\delta-}{2\mathrm{Br_2}}\right]/\left[\mathrm{Br_2}\right]^2\left[\mathrm{ArN}\right]$$

apparently have K_4 and K_3 much lower than K_2. As a result, the broad absorption region due to $[\overset{+\delta}{(\mathrm{MeO})_2\mathrm{C_2H_4}},\overset{\delta-}{\mathrm{Br_2}}]$ vanishes, and the charge-transfer band characteristic of the complex can be studied. Similar experiments in which benzene is added to dimethoxyethane–bromine systems did not show any reduction of absorption, so that the affinity of benzene for bromine is relatively small compared with that of the other molecules now studied.

The position of the charge-transfer band maxima is of interest in relation to the electronic properties of the heterocyclic molecule. The respective maxima are: 2 : 3-, 4000 Å; 3 : 4-, 3550 Å; 5 : 6-, 3700 Å; and 7 : 8-benzoquinoline, 3750 Å.

On this interpretation of the charge-transfer bands observed in dimethoxyethane, it is of interest to study what happens as the heterocyclic molecule is loaded progressively with more bromine. Fig. 3 shows the results for 5 : 6-benzoquinoline. The other heterocyclic molecules have not yet been studied in this way, but similar behaviour is expected. It will be seen that a sharp absorption band is formed even for proportions of bromine as low as $(\mathrm{Br_2})_{0\cdot 36}$,ArN in this solvent and at this concentration. The first step in complex formation thus appears to be the formation of a polarisation bond with the aromatic nucleus, by charge transfer. Any formation of a compound such as (A) remains subsidiary, if the absorption spectra attributed to such ions have been correctly described.[3] Even with the complex $(\mathrm{Br_2})_{1\cdot 97}$,ArN the band has not shifted appreciably at its short-wavelength edge, though is has extended more towards the visible. Tentatively this could be taken to imply that the system $\overset{\delta-}{(\mathrm{Br_2})},\overset{2\delta+}{\mathrm{ArN}},\overset{\delta-}{(\mathrm{Br_2})}$ exhibits a second absorption band at somewhat longer wavelengths compared with the less loaded molecule $\overset{\delta-}{\mathrm{Br_2}},\overset{\delta+}{\mathrm{ArN}}$.

The possibility that one of the bromine molecules is held at the nitrogen atom rather than by charge transfer with the aromatic nucleus cannot at present by excluded. But it is an unnecessary hypothesis since at least one of the bromine molecules must be held at the aromatic part of the molecule.

When the loading exceeds the composition $(\mathrm{Br_2})_2$,ArN, sufficient free bromine is present to form association complexes with the solvent, in regions of much shorter wavelength.

Substitution of electron-donating methyl groups in place of hydrogen in the aromatic molecule has been shown to move the charge-transfer band maxima to longer wavelengths.[8] The present findings thus suggest that the sequence of decreasing power of electron-donation is 2 : 3- > 7 : 8- > 5 : 6- > 3 : 4-benzoquinoline.

If the usual assumption is made that one of the two canonical structures involves electron transfer from the aromatic molecule to the bromine:

$$\overset{+}{(\mathrm{C_{13}H_9N})},\overset{-}{\mathrm{Br_2}} \qquad \mathrm{C_{13}H_9NBr_2}$$

then the simplest interpretation of the relative positions of the maxima of the charge-transfer bands is that the electron-donating energy levels in the heterocyclic molecules lie at increasing intervals above the ground states, in sequence 2 : 3-, 7 : 8-, 5 : 6-, 3 : 4-benzoquinoline. This interpretation may not be valid if the polarisabilities of the hetero-

---

[8] Keefer and Andrews, *J. Amer. Chem. Soc.*, 1950, **72**, 4677.

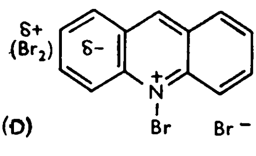
cyclic molecules are very different, as is perhaps indicated by the oscillator strengths of absorption bands for the pure substances (see above).

Formation of "Bromodinium Bromides."—The absence of charge-transfer bands in dilute *cyclo*hexane solutions, even when the proportion Br : ArN is as high as 3·8 : 1 may be due to the large value of the dissociation constants of the complexes in *cyclo*hexane at room temperature. An alternative explanation is that in *cyclo*hexane the first molecule of bromine adds to these heterocyclic aromatic molecules to form " bromodinium bromides," a typical structure being (A). In the light of the present findings, previous spectroscopic evidence[3] in support of this suggestion loses much of its force, since the solid complexes might simply dissociate into their components in solution, as stated above. On the other hand, formation of " bromodinium bromides " as the first step when bromine is added in *cyclo*hexane solutions, would help to account for the minor changes observed in the absorption spectra where charge-transfer bands are not found (Figs. 1*a* and *d*). The low solubility in *cyclo*hexane of bromine addition products with these heterocyclic molecules is likewise possibly due to the salt-like structure of " bromodinium " derivatives. A more problematical point about the positions of maximum absorption may be briefly mentioned. Cationic ionisation of acridine in hydrochloric acid shifts the ultraviolet absorption. Acridine and its derivatives are still far too complex to allow treatment by the spectral theories of Sklar, Forster, or Mulliken; but Lewis and Calvin's approximation appears to be of relevance in discussion of shifts of absorption peaks to longer wavelengths, observed with the higher bromo-complexes. Briefly, the theory correlates the process of light absorption of a molecule with excitation of electric charge in that molecule. The electric vector of the exciting light is then assigned either to the x direction (greatest length of molecule) or to the y direction at right angles to it. Any change in a molecule, either substitution or ionisation, which increases the contribution of charged structures in the ground state will increase the wavelength of the corresponding maximum absorption. $\lambda_{\text{max.}}$ is governed by the separation of ground states and the first excited levels; any increased importance of charged structures due to substitution or ionisation reduces E and so gives bathochromic shifts.

A bathochromic shift of 50 Å (about 1 kcal.) is observed for the band of $Br_{3\cdot80}$–acridine complex in 1 : 2-dimethoxyethane.

In the ultraviolet absorption of sodioanthracene in diethyl ether, production of the complex shifts the absorption bands to longer wavelengths; electron-transfer in the bromine complex here described appears to parallel that for sodioanthracene. In view of these considerations, in the present complexes bromine may also be acting as donor, not as acceptor as is usually supposed.

In solutions the loading of polynuclear aromatic molecules with donor or acceptor groups at successive fused-ring positions seems a novel suggestion. It is theoretically conceivable, since in crystal compounds such progressive loading apparently leads to quite strong retention, *e.g.*, of bromine (cf. Part V). With the benzoquinolines the progressive increase in the charge of the aromatic molecule if this acts as donor (i) in " bromodinium " formation and (ii) in charge-transfer processes must ultimately set an electrostatic limit to the loading process. If the bromine molecules act as acceptors at one part of the molecule and as donors at another part in a quasimetallic arrangement (D), the high retentivity of the benzoquinolines for bromine would be easier to understand.



(D)

Comparable studies on aromatic homocyclic molecules are in train but are often hampered by actual chemical interaction of the bromine with the aromatic molecule. This will be further discussed in Part V.

Department of Chemical Engineering,
Imperial College of Science and Technology,
S. Kensington, London, S.W.7.

[*Received, July* 30*th*, 1956.]