191. *Electron-donor and -acceptor Complexes with Aromatic Systems. Part V.* Polarisation Bonding in Solid Complexes formed by Some Heterocyclic Aromatic Molecules.*

By W. Slough and A. R. Ubbelohde.

Solid complexes formed by various benzoquinolines with sodium or bromine have been prepared. All the benzoquinolines studied can apparently act either as donors or acceptors of electrons. From the behaviour of the different structures when bonded with a typical electron donor such as sodium or an acceptor such as bromine, the gradation from strongest donor to strongest acceptor properties appears to be in the sequence 2 : 3-benzoquinoline (acridine), 3 : 4-benzoquinoline (phenanthridine), 5 : 6-benzoquinoline, 7 : 8-benzoquinoline.

Methods for preparing the sodium complexes include new findings relating to enrichment by vacuum sublimation. Comparatively easy reversibility of complex formation with bromine permits approach to any desired composition from either side by direct addition or removal of bromine. Density measurements show marked electrostriction on formation of a typical sodium complex. With bromine, the degree of electrostriction with different benzoquinolines depends on the relative acceptor–donor character.

As the proportion Br : aromatic compound rises, there is an anomalous variation of excess of volume suggesting that in a solid complex, dimer formation occurs for low bromine ratios.

Complex formation of the benzoquinolines with either bromine or sodium enhances the electrical conductivity of the solids, which behave as semiconductors. Conductance is non-ohmic at the higher current densities. Systematic information has been obtained on the trend of the parameters σ_0 and E in the conductance–temperature relation $\log \sigma = \log \sigma_0 - E/kT$ as the proportion of heterocyclic molecule in a complex is altered.

The significance of these results is discussed in the light of current theories of the electronic structure of aromatic molecules, and of polarisation bonding in relation to aromatic structure.

The extension of the chemical physics of aromatic systems requires systematic experimental information on the electronic characteristics of groups of closely related structures.

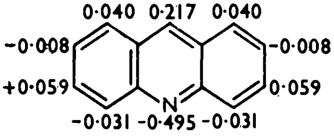
---

* Part IV, *J.*, 1957, 918.

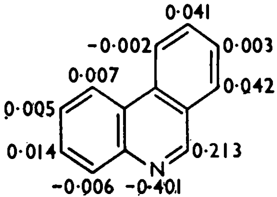
Experimental progress in this direction is often limited by the unavailability of substances whose structure is of key importance in a group, and theoretical knowledge is often scanty about comparative electron affinities and ionisation energies and about energy levels near the ground states in related aromatic systems. Such considerations limit the choice of systems suitable for quantitative studies. Charge-transfer bonding in solution can be conveniently studied, for example, by means of ultraviolet absorption spectra. Differences in the absorption bands for related aromatic molecules can to some extent be related with the parameters already referred to. In the solid state additional information about the nature of the bonding can be obtained from the molar volumes of the complexes and their electronic conductances. Previous papers [1, 2, 3] have discussed the quasi-metallic bonding in solid complexes of aromatic hydrocarbons with electron donors such as the alkali metals, or electron acceptors such as bromine. Solid bromine complexes have also been described.[4, 5]

We now deal with electronic and related properties of solid complexes formed by a group of heterocyclic analogues of anthracene and phenanthrene (I)—(IV). The net charges shown are due to Coulson and Longuet-Higgins.[6]

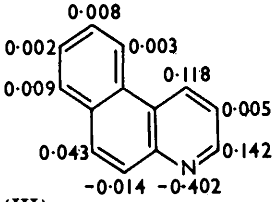
Introduction of one nitrogen atom into an aromatic system is well known to facilitate its acting as an electron acceptor; for example, pyridine forms addition complexes with sodium much more readily than benzene. As is described below, various addition complexes have been prepared between sodium and 2 : 3 (I)-, 3 : 4 (II)-, 5 : 6 (III)-, and 7 : 8 (IV)-benzoquinolines. 6 : 7-Benzoquinoline was not available and has previously only been synthesised with difficulty in very low yield. The benzoquinolines form solid addition complexes with bromine without rapid nuclear substitution of bromine, unlike their hydrocarbon analogues under comparable conditions. Measurements here recorded permit comparisons of the electron donor and acceptor properties of the same molecule, for an interesting diversity of complexes.



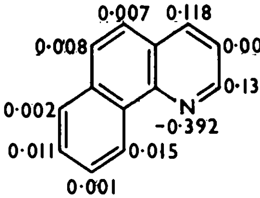
(I)



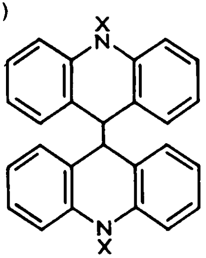
(II)



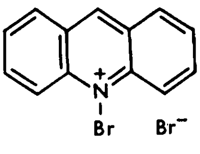
(III)



(IV)



(V)



(VI)

EXPERIMENTAL

Nitrogen (British Oxygen Co. " white-spot "), which originally contained less than 20 p.p.m. of oxygen, was further freed from oxygen by passage through a 100 cm. column tightly packed with copper turnings, the surface of which was constantly renewed by scrubbing it with ammonia solution (*d*, 0·880). The issuing gas was passed through a column packed with glass beads

---

[1] McDonnell, Pink, and Ubbelohde, *J.*, 1951, 191.

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

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

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

[5] Akamatu, Inokuchi, and Matsunaga, *Nature*, 1954, **173**, 168.

[6] Coulson and Longuet-Higgins, *J.*, 1949, 971.

moistened with concentrated sulphuric acid to remove ammonia and finally through another 100 cm. column packed with potassium hydroxide pellets to remove any sulphuric acid and to dry the nitrogen, which was then passed through a glass trap packed with chemically clean glass wool, maintained in liquid nitrogen; this trap was near its point of use to minimise reintroduction of moisture. All preparations and manipulations were protected from air and moisture by means of this gas. Where possible direct incidence of strong light was also avoided.

Diethyl ether and dioxan were purified as described by Mackle and Ubbelohde [7] and Holmes-Walker and Ubbelohde.[2] Dimethoxyethane was stored over potassium hydroxide pellets for seven days, refluxed over sodium for 12 hr., and distilled at 81—82°.

Preparation of Sodium Addition Complexes.—A slurry of sodium–acridine complex in dioxan has been described.[8] Complexes between other benzoquinolines and sodium have not hitherto been reported.

Preparations in ethereal solution were preferred where possible, as the solvent is easily removed. Sodium–3 : 4-benzoquinoline and –7 : 8-benzoquinoline, were prepared by refluxing the heterocyclic compound in diethyl ether with sodium wire for 2—3 days.

5 : 6-Benzoquinoline reacted too slowly in diethyl ether, so dimethoxyethane was used. 2 : 3-Benzoquinoline in both dimethoxyethane and dioxan gave a characteristic green complex, but dioxan was used in definitive preparations because it gave bigger yields. The slurries were converted into solvent-free powders by methods similar to those previously described.[2, 3]

Their conductance parameters and colours are recorded in Table 1.

So far as we know, limiting compositions of the complexes $(Na)_xArN$ were attained in preparations where sufficient reaction time was allowed, as recorded in Table 1.

A much more rapid method of preparation (cf. Part IV), by use of ultrasonic activation of the sodium, gave approximately the same limiting composition for the monosodium complex which appears to refer to an equilibrium between the benzoquinoline in ether and solid sodium on one side and the monosodium complex as a solid in contact with ether on the other at the boiling point of diethyl ether.

Further enrichment of the solvent-free solids was achieved as previously described [2, 3] by warming them to about 100° in high vacuum. This led to sublimation of some unchanged 3 : 4-benzoquinoline (identified by mixed m. p.) and darkening. Thus $Na_{1\cdot1}$(3 : 4-benzoquinoline) is orange whereas $Na_{1\cdot49}$(3 : 4-benzoquinoline) is black. Vacuum sublimation gave no further enrichment of the sodium–acridine complex prepared in dioxan, [$Na_{1\cdot07}$(2 : 3-benzoquinoline)]. Enriched complexes are asterisked in Table 1.

All the complexes were spontaneously inflammable in air, and Na_x(7 : 8-benzoquinoline) occasionally decomposed explosively. Safety screens were used where appropriate.

Analysis. After trials of alternative methods the sodium complexes were analysed gravimetrically as follows: 0·1—0·5 g. of the addition compound was weighed under nitrogen and dissolved in 50 ml. of N-hydrogen chloride in approximately 95% ethyl alcohol. This solution was then evaporated to dryness and baked under two 250 w infrared lamps. A few ml. of distilled water were added to the solids, and the insoluble organic product was filtered off from the aqueous sodium chloride solution, which was then dried and baked to constant weight with the infrared lamps. The sodium content was calculated from the weight of pure sodium chloride so obtained. As a check, the water-insoluble organic portion was dried and weighed; it's total mass corresponded in all cases examined with the sodium analysis. The success of this method of analysis depended in part upon the fact that the organic products of decomposition of 3 : 4-, 5 : 6-, and 7 : 8-benzoquinoline complexes were practically insoluble in water. Under comparable conditions the 2 : 3-isomer gave an organic product readily soluble in water; in this case, after the solution obtained on decomposition had been evaporated to dryness, the white organic product was cautiously burned away with a Bunsen flame, which left the sodium chloride unchanged.

From sodium–acridine the organic decomposition product was apparently dihydroacridine, and was slightly soluble in dilute hydrochloric acid. The brown or black decomposition products from the other sodium complexes were insoluble in water, diethyl ether, or benzene, and melted between 200° and 300°. Possibly dimers (V) are obtained, though these could be formed at the moment of exchange of a proton for the sodium.

---

[7] Mackle and Ubbelohde, *J.*, 1948, 1161.

[8] Schlenk and Bergmann, *Annalen*, 1928, **463**, 281.

Addition Complexes with Bromine.—Originally, complexes were precipitated from carbon tetrachloride solution by addition of bromine.[4] A more convenient and flexible route was direct addition of bromine from the vapour. For this purpose the appropriate heterocyclic substance was contained as a thin layer at the bottom of a weighed glass vessel provided with a standard ground stopper. A set of such containers were left open inside a desiccator together with a dish of bromine, and were closed and removed after various periods. Excess of bromine vapour was then removed from above the solid in any container, by blowing nitrogen for 5 min. over it, and the open container was finally kept for several hours over potassium hydroxide pellets in a vacuum desiccator to permit equilibration in the solid by diffusion. It was then weighed. At room temperature any loss of bromine from the solids proceeded only very slowly. For example, $(Br_2)_{1\cdot41}$(3 : 4-benzoquinoline) changed to $(Br_2)_{1\cdot40}$(3 : 4-benzoquinoline) during 18 hours' storage over potassium hydroxide in a partially evacuated desiccator.

On being warmed in a vacuum of about 10^{-3} mm. Hg to just below the m. p. (*ca.* 100°), any complex lost bromine more rapidly. Over 95% of the bromine could be recovered quantitatively in a liquid-nitrogen trap in a few hours, thus verifying that no permanent substitution had occurred in the heterocyclic nucleus. Complete removal of bromine from $(Br_2)_{1\cdot40}$(3 : 4-benzoquinoline) in this way yielded 3 : 4-benzoquinoline. Heating of the solids for shorter periods in this way led to intermediate compositions, which gave a convenient alternative approach from the bromine-rich end for some of the compositions required.

Analysis. When the bromine addition complexes were formed from the solid heterocyclic compounds, compositions were determined by direct weighing. The complex precipitated on adding bromine in carbon tetrachloride to acridine in carbon tetrachloride[4] was isolated, washed, and analysed by dissolving it in warm ethyl alcohol and estimating the bromine with potassium iodide and sodium thiosulphate. Considerable oxidation of the alcohol to acetaldehyde was observed. Similar oxidative properties were shown by the 1 : 1 bromine adducts [Br_2(benzoquinoline)] of the other benzoquinolines or when the bromine content exceeded this composition; it was verified that up to 90% of the bromine present oxidised ethyl alcohol to acetaldehyde, at least for $y \geqslant 2$ in $(Br_2)_y$(benzoquinoline).

Specific Volumes of the Complexes.—The object was to evaluate the excess volume $V_1 - V_2 = V_{ex.}$ where V_1 is the volume occupied by one formula weight of the complex X_n(benzoquinoline), and V_2 is the sum of the volumes occupied by one formula weight of the aromatic molecule and n formula weights of the electron donor or acceptor X.

Excess volume is plotted as a function of y for bromine complexes in Fig. 1. For $Na_{1\cdot07}$(2 : 3-benzoquinoline) the excess volume was found to be $-30{\cdot}4$ c.c. per g.-atom of sodium.

All densities were measured at 20°. The low m. p.s of the complexes of bromine with 7 : 8-benzoquinoline (they are viscous liquids at room temperature) made it necessary to melt these into the pycnometer. Results are recorded in Fig. 1.

Electrical Conductances of the Solids.—Electrical conductivities of the complexes were measured in a valve-voltmeter circuit. *H* was the live terminal, and *I* the neutral.

The clean, dry cell (Fig. 2) was flamed with a soft Bunsen flame and evacuated. After about 15 min. pure nitrogen was allowed to fill the cell through *F*. Thereafter a constant stream of nitrogen was maintained throughout the measurements. Sufficient powder was introduced from a sample tube, fitted with an adaptor through *A*, to pack a column a few mm. long between copper electrodes *B* and *C* fitted with platinum caps. The upper electrode joined to the end of a brass stem was then carefully lowered on the powder and a rubber sleeve *D* was slipped on the main arm of the cell. A small glass tube *G* passing through this sleeve helped to keep the stem vertical; it formed the outlet for the nitrogen stream, and reduced it to the minimum necessary for protection of the sample. Finally, cylindrical lead weights were placed on the platform *E* fused to the stem, and the length of the sample column was measured with the aid of a lens and small steel scale. Pressures applied in this cell were 8—12 kg./cm.^{2}. Within this range the conductances were not appreciably affected by pressure and the results were reproducible in a temperature cycle.

The filled cell was placed in a liquid-paraffin bath maintained to $\pm 0{\cdot}5°$ over a range of about 30°. Resistances of the sample were measured so as to calculate the specific conductivity. The use of a valve voltmeter[3] calibrated with standard resistances up to 10^{10} ohms permitted measurements of column resistance with current densities as low as 5×10^{-10} A/cm.^{2} and with voltage gradients as low as 2 v/cm.

As previously described,[2] specific conductances, σ, were obtained by calculation from smoothed linear plots of resistance against column length for sodium–acridine (with $n = 1{\cdot}07$); these plots passed through zero, showing that electrode effects could be neglected. For the other complexes a single column length was used, and electrode effects were neglected in calculating σ. In the case of $Na_{2\cdot01}$(7 : 8-benzoquinoline), resistances were also measured at higher dielectric strains, up to 7500 v/cm. at up to 1×10^{-8} A/cm.^{2}. For this purpose a conventional sensitive D.C. galvanometer was used with a high-tension supply. Fig. 3 is a plot of dielectric strain against current. Conductance at these higher current densities is non-ohmic. Plots of log σ against $1/T$ (not shown) were in all cases linear within experimental error. Conductance results can thus be compactly recorded as in Table 1 on the basis of the equation

$$\log \sigma = \log \sigma_0 - E/kT$$

FIG. 1. *Excess molar volume as a function of molar proportion of bromine in the benzoquinoline complex.* (*For* I, II, III, IV, *see formulae, p.* 983.)

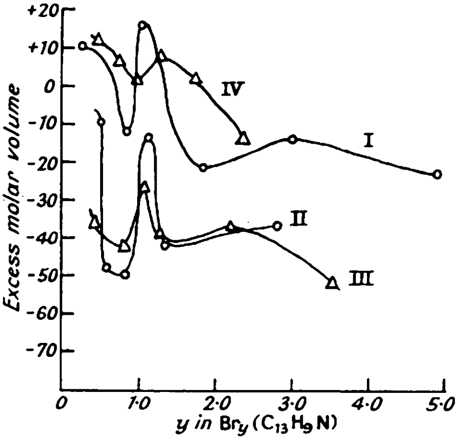
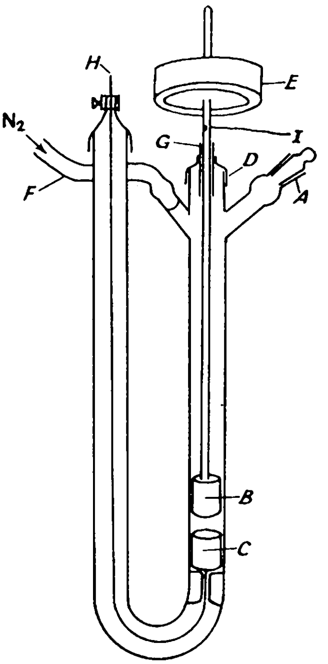


FIG. 2. *Conductivity cell.*



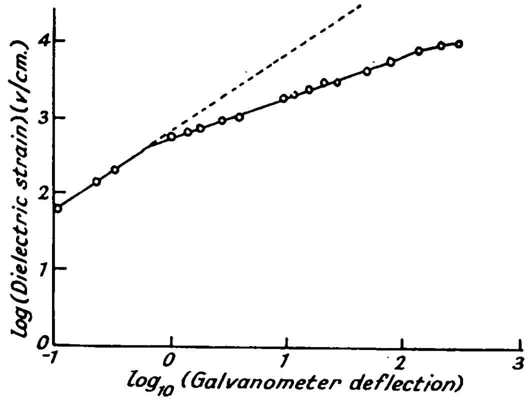


FIG. 3. *Non-ohmic characteristic of* $Na_{2\cdot01}$*(7 : 8-benzoquinoline).*

Broken curve corresponds to linear ohmic behaviour.

To test how far chance access of oxygen might alter the results, some samples of the complexes were deliberately exposed to air before making resistance measurements. The general effect was that complexes such as $Na_{2\cdot 01}$(benzoquinoline) showed marked increase of electrical conductance. Complexes such as Br_2(benzoquinoline) remained practically unaltered.

TABLE 1. *Conductivity parameters of benzoquinoline complexes.*

	Sodium complexes						Bromine complexes				
Isomer	Prepn. or solvent *	x *	Colour †	$\log_{10}\sigma_{293}$ (ohm^{-1} cm.$^{-1}$)	E (ev)	$\log_{10}\sigma_0$ (ohm^{-1} cm.$^{-1}$)	Prepn. or solvent	y	$\log_{10}\sigma_{293}$ (ohm^{-1} cm.$^{-1}$)	E (ev)	$\log_{10}\sigma_0$ (ohm^{-1} cm.$^{-1}$)
2 : 3	C	0	y	−18·25	2·52	24·955	+B	0·23	−15·020	2·39	25·880
,,	D	1·07	g	−15·74	1·99	18·375	+B	4·90	−15·420	2·09	20·380
3 : 4	E	1·11	o-br	−21·61	2·34	18·515	+B	0·49	−10·250	0·75	2·600
3 : 4	E	1·26	d-br	−12·65	1·49	12·90	−B	1·19	−6·893	0·45	0·822
3 : 4	E	1·49	b	−9·88	0·35	−3·88	−B	1·89	−6·750	1·57	22·830
3 : 4	—	—	—	—	—	—	−B	2·43	−6·323	0·50	2·260
3 : 4	—	—	—	—	—	—	+B	2·81	−5·607	0·37	0·710
5 : 6	M	1·60	d-v	−12·86	1·18	7·38	+B	3·39	−7·500	0·85	7·009
7 : 8	E	1·10	o-br	−18·38	2·15	16·49	+B	1·92	−6·125	1·49	19·430
7 : 8	E	2·01	b	−13·50	1·11	5·53	—	—	—	—	—
7 : 8	E	2·09	b	−10·07	1·00	7·07	—	—	—	—	—

* C, Chromatography; D, dioxan; E, diethyl ether; M, dimethoxyethane; +B, addition of bromine vapour; −B, removal of bromine vapour.

† b, Black; g, green; br, brown; o, orange; v, violet; y, pale yellow; d, dark.

DISCUSSION

In Part III,[9] the charge-transfer bonds between the benzoquinolines and the bromine were examined in solution. From the positions of the absorption bands, there was evidence that the sequence of increasing electron-donor properties follows the order 3 : 4-benzoquinoline < 5 : 6-benzoquinoline < 7 : 8-benzoquinoline < 2 : 3-benzoquinoline.

When solids of composition corresponding to the complexes previously examined in solution are studied, there are obvious possibilities of further polarisation interactions with nearest neighbours. Any electron-transfer processes that apply for a complex such $Na_x(C_{13}H_9N)$ or $(Br_2)_y(C_{13}H_9N)$ in isolation will obviously be profoundly modified when the nearest neighbours in the solid all have the same electronic affinity. Possibilities for switching electrons from one site to another in a solid solution of sodium or bromine with an aromatic molecule almost certainly account for the marked increase in electrical conductivity over that of the parent aromatic substance. The model previously suggested for such solid solutions [2,3] is that " quasi-metallic " bonds form between an acceptor or donor and the aromatic molecules packed in contract with it in the crystal. When these heterocyclic molecules function as acceptors with sodium the behaviour is similar to that of the homocyclic molecules previously studied.[2,3] There is a systematic trend of electronic properties as the proportion of sodium rises. Even quite small proportions of sodium markedly increase the conductance of the solid. As this proportion rises, the conductance rises, the activation energy for conductance falls (Fig. 4), and various other properties such as the deepening colour suggest increasing delocalisation of electrons in these solid complexes. In one case, sodium–acridine, marked electrostriction occurs on forming the complex, just as in the homocyclic complexes with anthracene. Thus the measured molecular volume of $Na_{1\cdot 07}(C_{13}H_9N)$ is 154·7 c.c. and the calculated molecular volume of $C_{13}H_9N$ and 1·07Na is 187·2 c.c. Hence the excess volume = −32·5 c.c. or −30·4 per g.-atom of sodium. This corresponds to an almost completely ionic bond, the theoretical, calculated molecular volume for $Na^{+}{}_{1\cdot 07}(C_{13}H_9N^{-})$ being 164·1 + Δ c.c., where Δ is a small term to allow for the increase in volume for the formation of a negative ion: $C_{13}H_9N \longrightarrow C_{13}H_9N^{-}$.

When the heterocyclic molecules act as donors, polarisation bonding is more complex, possibly because of the dual rôle of the nitrogen atom and of the aromatic fused rings. Effects of progressive addition of bromine can be studied from the excess volume changes (Fig. 1) and from the conductance parameters. A tentative interpretation is that a dimeric

---

[9] Slough and Ubbelohde, *J.*, 1957, 911.

bromide (V) is first formed, as previously claimed to occur in concentrated slurries of sodium–acridine.[4] This leads to a break at the composition $Br(C_{13}H_9N)$; further addition of bromine leads to progressive loading of the system with more charge-transfer bonds and quite high total proportions of bromine can be held in this way.

An alternative view is that the first step on adding bromine is to form an *N*-bromoquinolinium bromide[4] of the composition (VI); subsequent bromine molecules then add at the various aromatic rings in the benzoquinoline molecule. Though this possibility cannot be excluded, at present there seems less evidence for it (cf. Part III[9]). There is also some evidence to suggest that the *N*-bromoquinolinium bromide does not form until a composition of $Br_2(C_{13}H_9N)$ is approached (cf. Fig. 4).

It is of obvious interest to determine how far the properties measured for these solids can be quantitatively related with the aromaticity of the molecules as measured in other ways. One significant property refers to the maximum number of donor or acceptor groups that can be held per heterocyclic molecule when the complex is allowed to reach equilibrium with free sodium or bromine, since this maximum gives some guide to a steep change in the strength of polarisation bonds as more donor or acceptor molecules are taken up. Though values are only approximate these maxima are at the following values of x: 7 : 8-, 2·09; 5 : 6-, 1·60; 3 : 4-, 1·49; 2 : 3-benzoquinoline, 1·07; and of y: 2 : 3-, 4·90; 3 : 4-, 3·80; and 5 : 6-benzoquinoline, 3·50. Br_n(7 : 8-benzoquinoline) forms liquids at the maximum uptake of bromine. Full interpretation of the interesting trends observed in the conductance parameters and in the molar volumes of the complexes must await a determination of structures, *e.g.*, by *X*-ray methods. Attention may be drawn to the steep changes of these parameters for certain complexes as the proportion of donor or acceptor increases. For example in the sodium complexes with 3 : 4- and 7 : 8-benzoquinoline the addition of alkali metal up to the composition $Na(C_{13}H_7N)$ appears to yield complexes with considerably lower electron energy levels than beyond this composition since the activation energy, *E*, for shifting an electron from the ground state of the complex to the conduction band shows a steep decrease near this composition. This parallels findings previously reported[3] for the compositions $Na_{2\cdot08}$(anthracene) and $Na_{2\cdot12}$(anthracene).

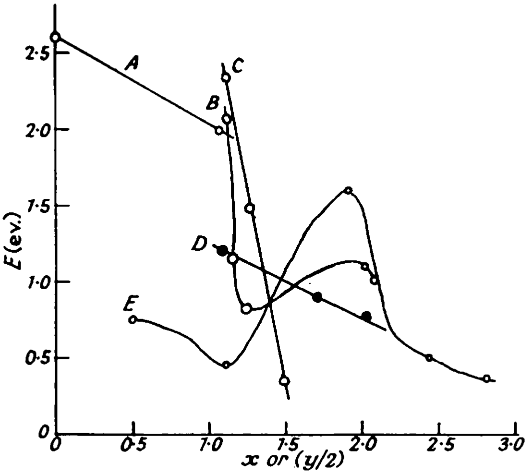


FIG. 4. *Activation energy E as a function of molar proportion of sodium or bromine in benzoquinoline complexes.*

A, Na(2 : 3-benzoquinoline); *B*, Na(7 : 8-benzoquinoline); *C*, Na(3 : 4-benzoquinoline); *D*, Na(anthracenes); *E*, $(Br_2)_y$(benzoquinolines).

Owing to difficulties in varying the proportion of sodium in a solid complex, it is inconvenient to follow relationships between *E* and *x* in more detail for sodium complexes.

For the bromine complexes, marked variations in the excess molar volume with composition point to more than one type of bond formation, as previously stated.

Other Characteristics of the Electronic Conductance of the Solid Complexes.—For both acceptor and donor complexes the usual correlation is found between small values of E and small values of log σ_0. This probably arises from a decrease in mobility as the number of conductance electrons rises. Numerical calculations on the basis of a model suggested by Mauy, Harnik, and Gerlich[10] use the equation $\sigma = en\mu$, where μ is the electron mobility (cm.^{2} volt^{-1} sec.$^{-1}$) and $n = N_0 \exp(-E/kT)$ where N_0, the effective density of states in the conducting levels of the crystal, is assumed to be 10^{21}.

Such calculations, not reproduced, again show that high mobilities are associated with high activation energies. This can be understood if the mean free path of the conduction electrons in these solids is determined by the average distance between activated sites, which also act as electron traps and become more numerous as E falls.

The non-ohmic conductance (Fig. 3), examined in detail for $Na_{2\cdot01}$(7 : 8-benzoquinoline), is found to be reversible in the sense that if the same sample is tested again at a lower voltage gradient, the original lower conductance reappears. It is presumed that if the voltage gradient is at all large, the dielectric strain on the polarisation bond increases the proportion of conduction electrons. The activation energy of such electrically strained samples is found to decrease, in accordance with this view.

A somewhat analogous model has been suggested for pure aromatic hydrocarbons.[11] The trend of the curve in Fig. 3 suggests that progressive electrical breakdown of the solid occurs as the strain increases.

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

[*Received, September 4th*, 1956.]

---

[10] Mauy, Harnik, and Gerlich, *J. Chem. Phys.*, 1955, **23**, 1733.
[11] Northrop and Simpson, *Proc. Roy. Soc.*, 1956, *A*, **234**, 124.