975. *Electron-donor and -acceptor Complexes with Aromatic Systems. Part VII.*[1] *Electron-donor and -acceptor Complexes of Some Tetracyclic Aromatic and Hetero-aromatic Molecules.*

By G. C. MARTIN and A. R. UBBELOHDE.

Naphthacene, 1,2-benzanthracene and their aromatic aza-analogues 2,3-, 3,4-, and 1,2-benzacridine have been investigated with regard to dark-current conductivities of the pure solids at various temperatures. Similar measurements have been made on chloro- and oxo-derivatives of the benzacridines which were obtained in the preparative work. For all the parent molecules, a parallelism is found between the activation energy controlling conduction and the ultraviolet absorption band of lowest energy, $^1E_1$. On this basis, some edge substituents showed lowered activation energies for conduction in the solids.

Complexes of these tetracyclic molecules have been prepared with iodine as a typical electron acceptor, and with sodium as a typical electron donor, and have been studied in various ways. For solutions in carbon tetrachloride, absorption spectra indicate that 1 : 1 complexes with iodine are bonded differently for the homonuclear ($\pi \longrightarrow I_2$) and aza-aromatic ($^n N \longrightarrow I_2$) molecules, except in the case of 3,4-benzacridine where steric effects appear to favour ($\pi \longrightarrow I_2$) polarisation bonds. For the solids, molar volumes determined by pyknometry bear out this difference. $\pi \longrightarrow I_2$ complexes with iodine all showed higher conductivities and the activation energy for conduction was lower than for the parent molecules. $^n N \longrightarrow I_2$ complexes showed higher conductivities, but the energy gap was increased instead of lowered. Where available, measurements of thermoelectric power showed that in these solids majority charge carriers are positive.

Sodium complexes on the other hand showed no clear difference between the aromatic and the aza-aromatic molecules. For all these solids, the conductivity of the complex was condiserably increased, and the energy gap was somewhat lowered, in comparison with that of the parent molecule. Measured molar volumes suggest that polarisation bonds in some of these complexes are predominantly ionic, and measurements of thermoelectric power indicate that the charge carriers are predominantly negative.

Implications of these results are discussed for models of polarisation bonding and of electrical conductance in solid aromatic complexes.

ELECTRONIC properties of aromatic compounds, particularly in the solid state, are attracting increasing attention (cf. review by Garrett[2]). In the present series of researches[1,3]

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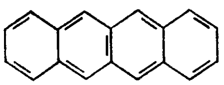
[1] Part VI, Parkyns and Ubbelohde, *J.*, 1961, 2110; cf. *J.*, 1960, 4188.

[2] Garrett in " Semiconductors," ed. N. B. Hannay, Reinhold Publ. Co., New York, 1959.

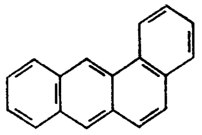
[3] Holmes-Walker and Ubbelohde, *J.*, 1954, 720; Gracey and Ubbelohde, *J.*, 1955, 4089; Slough and Ubbelohde, *J.*, 1957, 911, 918, 982.

special attention has been directed towards the effects of forming polarisation bonds * on the electronic properties.

Because of the nature of π-electron systems, most aromatic molecules show some amphoteric character. They can act as electron donors in complexes with acceptor groups such as bromine or iodine, and as electron acceptors with the alkali metals. Striking increases of electrical conductivity [1,3,6] have been found when polarisation-bond complexes are formed, and it is important to relate these in a systematic way with the structures of the parent aromatic molecules. Such investigations promise to throw light on polarisation bonding generally; they also give access to a group of semi-conductors and conductors with interesting properties. The researches recorded below refer to tetracyclic aromatic molecules. In order to study effects of molecular shape, naphthacene (I) and 1,2-benzanthracene (II) were selected as parent molecules which are fairly readily available. In order to study effects of electronic perturbations on these molecules, the aromatic aza-analogues 2,3- (III), 1,2- (IV), and 3,4-benzacridine (V) have been prepared in the pure state. Properties were also studied of preparative intermediates of benzacridine, namely, the chlorobenzacridines and benzacridones.



(I)



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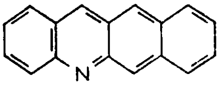

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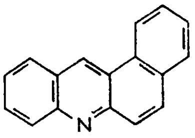

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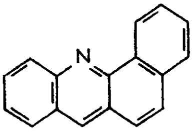

(V)

Polarisation-bond complexes have been prepared with iodine and with sodium. For comparisons between the various solids studied, polycrystalline materials have been used under compression. Their dark-current conductivities have been determined at various temperatures, for carefully purified solids. Preliminary measurements of thermoelectric power have been made in some cases to determine the sign of the predominant charge carriers. Mechanisms suggested for conductance processes in these solids are discussed below.

Because of the chemical interrelation between these aromatic systems, changes observed in the conductance parameters can to a considerable extent be correlated with structure. Further information about these correlations has been obtained from studies of the ultra-violet absorption spectra in solution, and from studies of the molecular volumes of the solid complexes.

EXPERIMENTAL

Source of Materials.—Naphthacene (I) (L. Light & Co.) and 1,2-benzanthracene (II) (Rutgerswerke A.G.) were purified as described below. 2,3-Benzacridine (III) was synthesised as described by Albert, Brown, and Duewell.[7] 9-Chloro-2,3-benzacridine and 2,3-benzacridone

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* The general term " polarisation bond " (cf. McKeown, Ubbelohde, and Woodward [4]) may conveniently be used to describe a specific interaction between molecules forming this bond. in cases when this can be distinguished from the non-specific van der Waals attraction between molecules, and from primary covalent or ionic bonding. The term " charge transfer " bond refers to a particular theoretical interpretation of certain polarisation bonds, due to Mulliken.[5]

[4] McKeown, Ubbelohde, and Woodward, *Acta Cryst.*, 1951, **4**, 391.

[5] Mulliken, *J. Amer. Chem. Soc.*, 1950, **72**, 600.

[6] Akamatu, Inokuchi, and Matsunaga, *Bull. Chem. Soc. Japan*, 1956, **29**, 213; Kommandeur and Hall, *J. Chem. Phys.*, 1961, **34**, 129; Singer and Kommandeur, *ibid.*, p. 133.

[7] Albert, Brown, and Duewell, *J.*, 1948, 1284.

which occur as intermediates in this synthesis were also isolated and purified for physical measurements.

1,2-Benzacridine (IV) was synthesised from 9-chloro-1,2-benzacridine (cf. Bryant, Bachman, and Picha [8]) by reduction with lithium aluminium hydride.[9] 1,2-Benzacridone was also isolated and purified for physical measurements.

3,4-Benzacridine (V), 9-chloro-3,4-benzacridine, and 3,4-benzacridone were prepared by methods analogous to those used for the 1,2-isomer.

Purification of Materials.—Because of the small concentration of charge carriers present in many organic solids, their electrical properties can be particularly sensitive to the presence of comparatively minute concentrations of inorganic or organic impurities (cf. Parkyns and Ubbelohde [1]). Suitable methods of purification of these comparatively large molecules depend on their physicochemical properties. The procedure adopted for all the present compounds except the benzacridones was as follows:

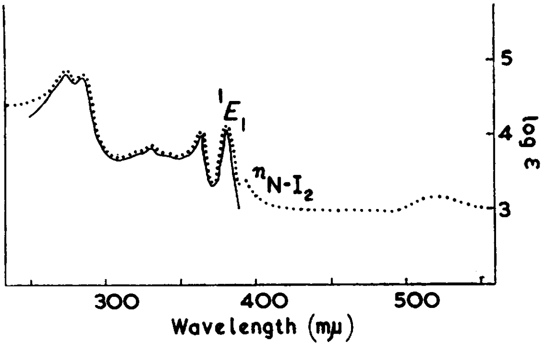

FIG. 1A: ——— 10^{-5}M-1,2-Benzacridine. ····· 10^{-5}M-1,2-Benzacridine plus 2 × 10^{-5}M-iodine.

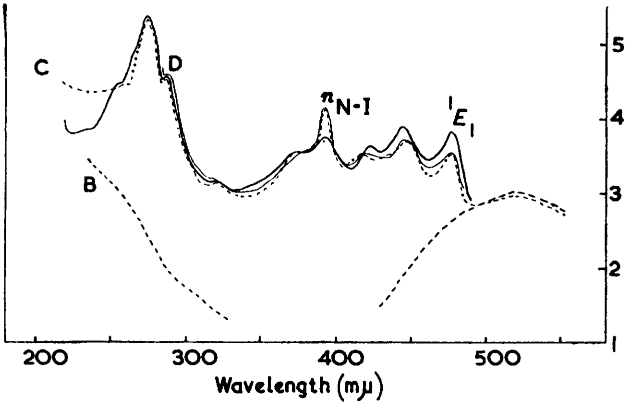

Fig. 1B: A, 10^{-5}M-2,3-Benzacridine. B, 10^{-3}M-Iodine. C, Complex from 10^{-5}M-2,3-benzacridine plus 10^{-3}M-iodine. D, Complex from 10^{-4}M-2,3-benzacridine and 10^{-4}M-iodine.

FIG. 1. Ultraviolet absorption spectra of carbon tetrachloride solutions.

The substance was first recrystallised from ethanol or benzene until its m. p. was unchanged (within ±0·5°) by further crystallisation. The recrystallised material was passed in "AnalaR" benzene (dried over sodium) through a column (1¼″ × 18″) of alumina (Peter Spence Type H). The solid was separated from the solvent by vacuum-distillation and to ensure that limiting purification had been attained the chromatography was repeated with fresh benzene. Finally, vacuum-sublimation was used to remove the last trace of solvent. Owing to the low solubility of the benzacridones in convenient solvents, purification by chromatography was omitted for these substances. Vacuum-sublimation of the recrystallised material was repeated until the sublimate had the same m. p. within 0·5° as the material being sublimed.

Ultraviolet Absorption Spectra.—These were determined by means of a Hilger Uvispek model

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[8] Bryant, Bachman, and Picha, *J. Amer. Chem. Soc.*, 1946, **68**, 1599.

[9] Cf. Badger, Pearce, and Pettit, *J.*, 1951, 3199, 3204.

H 700/302 with stoppered quartz cells, previously calibrated. For the parent molecules, these spectra provided a check on the purity and indicated the wavelength of the peak absorption for the transition of lowest energy. Absorption spectra were also investigated for solutions of the aromatic hydrocarbons and bases in carbon tetrachloride (B.D.H. " special for spectroscopy "), to which iodine had been added in 1 : 1 molar ratio. These solutions were prepared by dissolving weighed amounts of the organic material and of resublimed iodine, whilst oxygen was excluded by bubbling dry nitrogen through the solvent. The vessel was shielded from direct light. The solutions were diluted to 10^{-5}M and matched against three check cells containing, respectively, the pure solvent, an equimolar solution of the aromatic substance, and an equimolar solution of iodine. Some characteristic absorption spectra are plotted in Figs. 1A and B.

Preparation of Solid Complexes with Iodine.—An equimolar solution of the hydrocarbon (0·228 g.) and of iodine (0·257 g.) in carbon tetrachloride (100—150 ml.) was prepared by bubbling dry oxygen-free nitrogen (cf. Part VIII) through the mixture. The solvent was then evaporated completely at room temperature under a moderate vacuum in a slow stream of nitrogen. Analytical checks of the compositions of the resulting solids (Table 1) point to some loss of iodine from those complexes in which it is only weakly held. This probably occurred during evaporation or during handling. Complexes with 2,3- and 1,2-benzacridine and with their chloro-derivatives retained iodine more strongly and gave analyses close to the theoretical 1 : 1 formula.

TABLE 1.

Analyses of complexes with iodine, ArI_m.

Ar	Found (%)				1 : 1 Molecular complex requires for Calc. (%) for $m = 1$				m
	C	H	N	I	C	H	N	I	
Naphthacene *	47·3	2·6		51·4	44·0	2·5		52·6	1·78
3,4-Benzanthracene *	47·7	2·7		49·8	44·0	2·5		52·6	1·74
2,3-Benzacridine	42·35	2·4	2·95	52·4	42·3	2·3	2·9	52·5	2·0
2,3-Benzacridone	55·0	2·9		33·3	40·8	2·2	2·8	51·0	1·30
9-Cl-2,3-Benzacridine	45·3	2·2		42·3	39·4	1·9	2·7	49·1	1·74
1,2-Benzacridine	42·45	2·6	3·0	52·4	42·3	2·3	2·9	52·5	2·0
1,2-Benzacridone	56·75		3·4	31·6	40·8	2·2	2·8	51·0	1·26
9-Cl-1,2-Benzacridine	44·9	2·2		42·05	39·4	1·9	2·7	49·1	1·72
3,4-Benzacridine	43·3	2·6	2·7	51·3	42·3	2·3	2·9	52·5	1·76

* Direct addition of iodine and weighing.

Preparation of Solid Complexes with Sodium.—This was carried out as described in the following paper, which also gives details for handling of these reactive materials.

Compositions of the alkali-metal complexes (Table 2) were determined by weighing, decomposition in aqueous ethanol, and titration against hydrochloric acid.

TABLE 2.

Analyses of sodium adducts, $ArNa_m$.

Ar	Found (%)			Calc. (%) for $m = 1$ or 2			m
	C + H	N	Na	C + H	N	Na	
Naphthacene	84·8		15·2	83·2		16·8	1·80
3,4-Benzanthracene	91·55		8·45	91·6		8·4	1·02
2,3-Benzacridine		91	9·0		91·6	8·4	0·93
1,2-Benzacridine		83·3	16·7		83·2	16·8	1·99
3,4-Benzacridine		83·5	16·5		83·2	16·8	1·97

Conductivity.—This was measured for compressed polycrystalline material. The parent substance or a complex freshly prepared and stored under nitrogen was made into a pellet at room temperature in a screw press exerting about 200 kg./cm.^{2}. The pellet was transferred by extrusion to a conductivity cell either in a protective nitrogen box (cf. following paper) or under protection of a flow of nitrogen. With the parent substance and its complexes with iodine, a number of measurements were made by carrying out all these operations in air instead of under nitrogen: no significant change was observed in the conductance parameters, indicating that oxygen had a negligible effect. With sodium complexes, access of air led to rapid and sometimes violent reaction and all operations were fully protected by nitrogen.

Values of the specific conductivity σ are given in Tables 3 and 4 which record the parameters defining straight-line logarithmic plots of the results, according to the equation $\sigma = \sigma_0 \exp -\varepsilon/\boldsymbol{k}T$. For intrinsic semiconductors the energy gap $\Delta\varepsilon = 2\varepsilon$. Illustrative logarithmic plots are shown in Figs. 2, 3, 4, and 5. Thermoelectric power (T.E.P.) was measured as described in the following paper.

Densities were measured by conventional pyknometry, with precautions against access of air or moisture (cf. following paper). Values are recorded in Tables 5a and b. These Tables

TABLE 3.

Conductance parameters of aromatic complexes with iodine (ArI$_m$) at 30°.

Ar	m	σ (10^{-12} ohm^{-1} cm.$^{-1}$)	log σ_0	ε (ev)	T.E.P. of complex (μv/°c)
Naphthacene	—	0·7	1·0	0·8	
,, $+ I_2$ ...	1·76	100	−0·85	0·55	Small +ve
1,2-Benzanthracene ...	—	0·0001	1·3	1·04	
,, $+ I_2$	1·74	1·0	2·98	0·90	Small +ve
2,3-Benzacridine	—	0·0008	−1·3	0·83	
,, $+ I_2$	2·0	950·0	10·0	1·2	+350
2,3-Benzacridone	—	0·003	−6·2	0·5	
,, $+ I_2$	1·3	790·0	7·5	1·0	+250
9-Cl-2,3-Benzacridine	—	0·002	−1·4	0·7	
,, $+ I_2$	1·72	0·19	8·10	1·25	+330
1,2-Benzacridine	—	0·0007	2·3	1·05	
,, $+ I_2$	2·0	0·018	9·65	1·4	+370
1,2-Benzacridone	—	0·0007	−6·4	0·53	
,, $+ I_2$	1·26	200	1·9	0·70	+190
9-Cl-1,2-Benzacridine	—	0·003	−1·2	0·80	
,, $+I_2$	1·72	0·15	6·2	1·15	+300
3,4-Benzacridine	—	0·001	4·5	1·18	
,, $+ I_2$	1·76	1·2	3·88	0·95	Small +ve

TABLE 4.

Conductance parameters of aromatic complexes with sodium, ArNa$_m$, at 30° (for the parent compounds see Table 3).

Ar	m	σ (10^{-12} ohm^{-1} cm.$^{-1}$)	log σ_0	ε (ev)	T.E.P. of complex (μv/°c)
Naphthacene	1·8	42,000	−2·06	0·32	Negative, ~10
1,2-Benzanthracene	1·02	110	1·03	0·66	Negative, small
2,3-Benzacridine	0·93	1900	5·76	0·87	Negative, small
1,2-Benzacridine	1·99	90	—1·73	0·50	Negative, small
3,4-Benzacridine	1·97	1800	−3·26	0·33	Negative, small

TABLE 5.

(a) Molar volumes (c.c) of iodine complexes ArI$_m$.

	Parent		Complex			
Ar	Density (g./c.c.)	M.V. (c.c.)	Density (g./c.c.)	M.V. (c.c.)	Δ (c.c.)	m
Naphthacene	1·40	163	2·21	204	5·0	1·78
1,2-Benzanthracene	1·28	178	2·08	216	7·0	1·74
2,3-Benzacridine	1·42	161	1·98	243	−31·0	2·0
2,3-Benzacridone	1·41	173	2·08	197	9·0	1·30
9-Cl-2,3-Benzacridine	1·30	202	1·85	260	−14	1·72
1,2-Benzacridine	1·29	177·5	2·38	202	27·0	2·0
1,2-Benzacridone	1·39	175	2·05	198	9·0	1·26
9-Cl-1,2-Benzacridine	1·34	196	2·27	212	29·0	1·74
3,4-Benzacridine	1·24	184	2·06	219	10·0	1·76
Iodine (per atom)	4·94	25·7	—	—		

Δ = Theor. molar volume (no interaction between donor and acceptor) — obs. molar volume. Δ is positive if a contraction has occurred.

(b) Molar volumes (c.c.) of sodium complexes ArNa$_m$.

Ar	Mol. vol. (c.c.)	Δ	m	Ar	Mol. vol. (c.c.)	Δ	m
Naphthacene	195	15·4	2	1,2-Benzacridine	201	24	2
1,2-Benzanthracene ...	203	−1	1	3,4-Benzacridine	211	20	2
2,3-Benzacridine	184	1	1	Sodium (metal)	23·7		

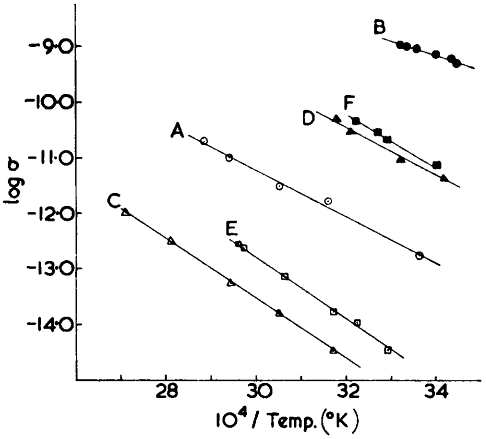


FIG. 2: A, Naphthacene. B, Naphthacene + I_2. C, 1,2-Benzanthracene. D, 1,2-Benzanthracene + I_2. E, 3,4-Benzacridine. F, 3,4-Benzacridine + I_2.

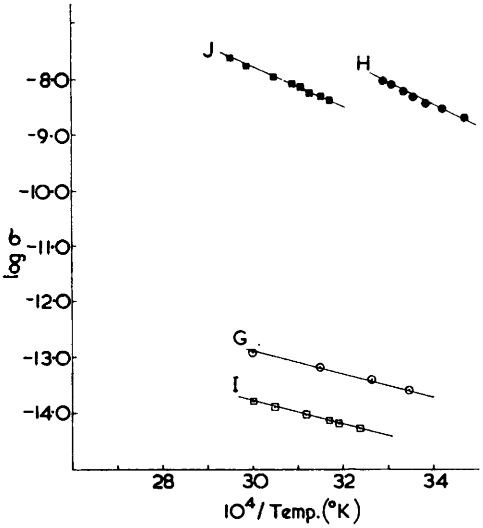


FIG. 3: G, 2,3-Benzacridone. H, 2,3-Benzacridone + I_2. I, 1,2-Benzacridone. J, 1,2-Benzacridone + I_2.

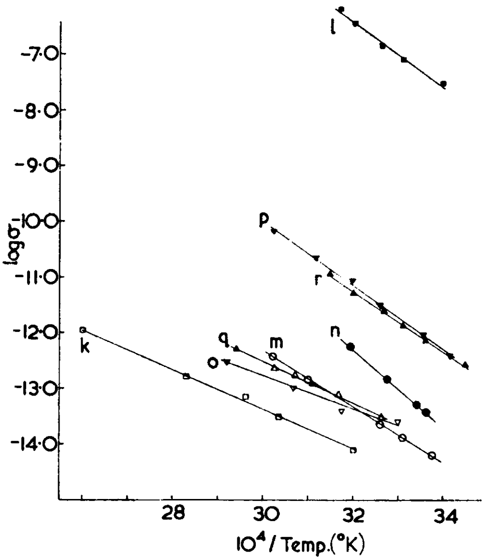


FIG. 4: K, 2,3-Benzacridine. L, 2,3-Benzacridine + I_2. M, 1,2-Benzacridine. N, 1,2-Benzacridine + I_2. O, 9-Chloro-2,3-benzacridine. P, 9-Cloro-2,3,-benzacridine + I_2. Q, 9-Chloro-1,2-benzacridine. R, 9-Chloro-1,2-benzacridine + I_2.

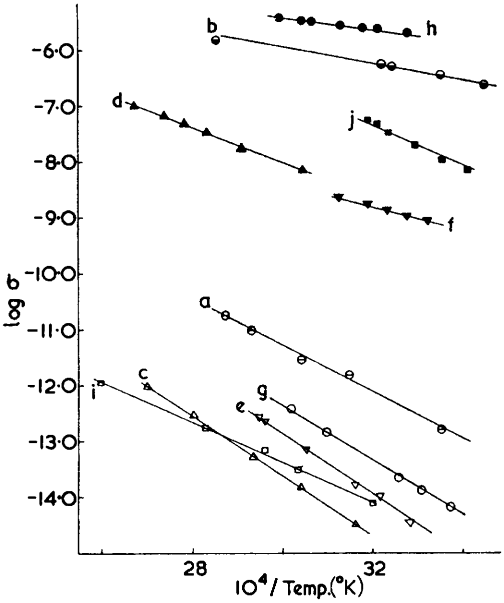


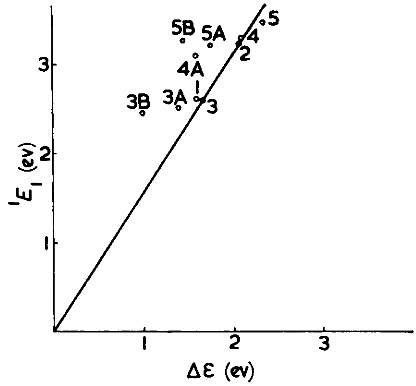
FIG. 5. Conductivities of sodium complexes and parent molecules. a, Naphthacenes b, Naphthacene + 2Na. c, 1,2-Benzanthracene. d, 1,2-Benzanthracene + Na. e, 3,4-Benzacridine. f, 3,4-Benzacridine + 2Na. g, 1,2-Benzacridine. h, 1,2-Benzacridine + 2Na. i, 2,3-Benzacridine. 2,3-Benzacridine + Na.

FIGS. 2—4. Conductivities of iodine complexes and parent molecules.

include the difference Δ between the sum of the molar volumes of the reactants, and the molar volume of the complexes formed from them; positive values of Δ imply a shrinkage on complex formation.

Discussion

Table 3 yields directly some systematic conclusions about the electronic parameters of the parent molecules in relation to their molecular structure. Substitution of one nitrogen atom for a CH group has little effect on ε. Values of ε for angular are consistently higher than for linear isomers. These conclusions parallel the consequences of structural changes on the absorption band of lowest energy $^1E_1$ of the parent molecules, as is shown by the linear plot in Fig. 6. Owing to the weak intermolecular forces in the crystals absorption bands for the solids are not very different from those for the free molecules (cf. Kasha and McGlynn [10]). Since both the electron affinities and the ionisation potentials are also linearly related [11] to values of $^1E_1$, either of these parameters might equally have been plotted in Fig, 6; they are, however, not directly known for many of the present molecules.



1, Naphthacene. 2, 1,2-Benzanthracene. 3, 2,3-Benzacridine. 3A, 9-Chloro-2,3-benzacridine. 3B, 2,3-Benzacridine. 4, 1,2-Benzacridine. 4A, 9-Chloro-1,2-benzacridine. 5, 3,4-Benzacridine. 5A, 9-Chloro-3,4-benzacridine. 5B, 3,4-Benzacridone.

FIG. 6. Correlation of lowest singlet absorption level $^1E_1$ with intrinsic energy gap $\Delta\varepsilon$ for conduction of the solids.

Formation of Complexes with Electron Acceptors.—Measurements of ultraviolet absorption can reveal charge-transfer complexes in solution, since these should have " peaks " distinct from those of the parent aromatic molecule. In the present researches this could not be verified for either naphthacene or 1,2-benzanthracene. Owing to their high extinction coefficients and low solubilities in carbon tetrachloride, solutions containing these molecules could not be conveniently measured over the whole spectral range, at concentrations greater than 10^{-5}M. At these concentrations, the absorption of free iodine in carbon tetrachloride extends to about 2600 Å and swamps any evidence of charge-transfer bands due to complexes with the aromatic molecules.

Figs. 1A and B show that with 2,3- and 1,2-benzacridine, weak charge-transfer bands due to complexes with iodine were observed even at 10^{-5}M-concentration, with peaks at 3970 and 3940 Å respectively. At higher concentrations these bands become more prominent. They may be attributed to ^{n}N–I_2 interaction between the iodine molecule and the aromatic base, since they occur in the spectral region expected for this. The absorption spectrum of acridine hydrochloride is analogous with that of the complex between acridine and bromine.[12] Charge-transfer absorption peaks for complexes between halogens and other monoaza-aromatic molecules also lie in this region of wavelengths.[12,13]

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[10] Kasha and McGlynn, *Amer. Rev. Phys. Chem.*, 1956, **17**, 407.

[11] Matsen, *J. Chem. Phys.*, 1956, **24**, 602.

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

[13] Chaundhuri and Basu, *Trans. Faraday Soc.*, 1959, **55**, 898.

Further support for the $^{n}N-I_2$ attribution is provided by the present finding that whereas both 2,3- and 1,2-benzacridine complexes with iodine give these absorption peaks, that with 3,4-benzacridine fails to do so. Scaled repulsion envelopes around molecular models show that the nitrogen atom in 3,4-benzacridine is sterically blocked by the hydrogen atom of the angular benzene ring adjacent to it. In this instance the I_2 molecule cannot approach sufficiently close to nitrogen to give effective $^{n}N-I_2$ interaction in the plane of the aromatic system. Properties of the crystalline complexes with iodine bear out this conclusion. The analyses show that iodine is only weakly held by the homonuclear hydrocarbons and by 3,4-benzacridine, whereas 2,3- and 1,2-benzacridine and their chloro-derivatives retain iodine strongly, giving complexes with definite m. p.s (2,3- 158°; 3,4- 165°). Molar volumes (Table 5a) again indicate very weak interaction for complexes between iodine and the first three aromatic molecules, but marked electrostriction for 1,2-benzacridine. For the 2,3-benzo-compounds the expansion may be attributed to salt formation giving 2,3-benzacridine N-iodonium iodide.

Differences in the conductance parameters run parallel with these differences in physicochemical properties. Table 3 shows that complex-formation with iodine increases the conductivity in all cases, but the influence on ε differs according to the nature of the bonding. Where the (weak) interaction may probably be described as $\pi-I_2$, ε is lowered on passing from the parent molecule (naphthacene, 1,2-benzanthracene, or 3,4-benzacridine) to the complex with iodine. On the other hand, for strong interactions (2,3- and 1,2-benzacridine, etc.) ε is increased on passing to the complex.

Values of thermoelectric power (T.E.P.) were readily measurable in many cases; they were positive with respect to the cold junction, indicating that the majority of carriers of electricity are positive. Observed values around 300—400 μv/°c are comparable with those of inorganic semiconductors. For $\pi-I_2$ complexes, T.E.P.'s are much smaller but also positive. Accurate values could not be obtained except by using large temperature differences, at which decomposition of the complex took place.

Complexes with Electron Donors.—Results listed in Tables 4 and 5b show that the behaviour of complexes between tetracyclic aromatic molecules and alkali metals closely resembles that reported for similar complexes with smaller aromatic systems.[3] It was interesting that only monosodium derivatives of 1,2-benzanthracene and 2,3-benzacridine were formed even after prolonged ultrasonic activation. For these, the electrostriction is also much smaller (Table 5b). Naphthacene, 1,2- and 3,4-benzacridine readily gave disodium derivatives. Although present lack of knowledge about the electron affinity of aromatic mononegative ions obstructs definitive interpretation of this difference, it is interesting that the lower homologues acridine [3] and phenanthrene [14] likewise form only monosodium derivatives in solution.

Conductance parameters (Tables 3 and 4) show that complex formation with sodium lowers the specific resistance by a factor of 10^6—10^8 in all cases. In all instances the thermoelectric power was small and was negative with respect to the cold junction, indicating that most of the carriers in these complexes are negatively charged.

In solution, ultraviolet-absorption spectra and reduction potentials, as measured, point to the presence of negative ions of the hydrocarbons (cf. Hoijtink [14,15]) which are also indicated from measurements on electron-spin resonance of monosodium complexes in ethereal solvents.[16] Molar volumes (cf. Table 5b) indicate a predominantly ionic character of the solids. Conductance parameters of these complexes appear to be less sensitive to individual molecular structure in this group of aromatic molecules than for corresponding complexes with electron acceptors.

Conduction Mechanisms in the Parent Aromatic Hydrocarbons.—On the basis of LCAO MO calculations for fused aromatic hydrocarbons the ultraviolet absorption band $^1E_1$ of

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[14] Hoijtink, *Rec. Trav. chim.*, 1957, **76**, 813.
[15] Hoijtink, *Rec. Trav. chim.*, 1954, **73**, 355; 1955, **74**, 277; 1956, **75**, 487.
[16] Lipkin, Paul, Townsend, and Weissman, *Science*, 1953, 117, 534.

longest wavelength is attributed to excitation of an electron from the highest filled π-bonding orbital to the lowest empty π*-antibonding orbital within the same molecule (cf. Coulson [17]). For the heterocyclic molecules, the absorption band of longest wavelength is attributed to a $^{n}N \longrightarrow \pi$ transition, in which the ground state is associated with a nitrogen atom. Normally, substitution of nitrogen for CH in the ring shifts the absorption edge to longer wavelengths, by about 15 mμ. If the correlation between $\Delta\varepsilon$ and $^{1}E_1$ indicated by the linear plot of Fig. 6 for the parent molecules is significant, this mode of excitation could provide a clue to the mechanism controlling conduction. Alternatively, a correlation has also been proposed [18] between $\Delta\varepsilon$ and the excitation energy to the first triplet level $^{3}E_1$. This transition is, however, strongly forbidden in the free molecule, and in the absence of strong perturbations in the crystal its contribution to the conduction mechanism seems rather less likely.

Primary thermal excitation of the pure hydrocarbon either to the $^{1}E_1$ or to the $^{3}E_1$ state in the crystal could not produce charge carriers directly. Such excitation could become the controlling mechanism, if there were a directly linked consecutive process in the solids leading to conduction. Since the centres of the molecules are fixed in the crystals one possibility is that " tunnelling " of electrons occurs much more readily between neighbouring molecules in the excited and the ground state than between two molecules in the ground state because of the increase in effective molecular size on excitation. Another possibility is that the excited states wander through the crystal as " excitons " with little or no thermal degradation, until they encounter special defect sites in the crystal where an electron can be trapped, leaving a positive charge carrier which migrates when a field is applied. The positive sign of the charge carriers for both dark-current and photocurrent measurements (Chynoweth and Schneider [19]) lends some support to the second possibility, which may also help to explain the behaviour of charge-transfer complexes discussed below.

A third possibility is that direct thermal excitation to ionised states of the aromatic molecule in the crystal provides the mechanism controlling conduction. Thus in anthracene [20] the energy required to transfer an electron from any molecule to a region remote from it in the crystal is about 3·0 ev, compared with the ionisation energy of the free molecule [11] of about 7·23 ev. But if the electron is merely transferred to a neighbouring molecule, creating an ion pair, $(Ar^{-})(Ar^{+})$, this requires only about 2·2 ev (ref. 9) which is close to observed values for $\Delta\varepsilon$ of 1·97 ev. Even ion pairs would not provide charge carriers directly, but their interaction with neighbouring aromatic molecules in the crystal could lead to a narrow conduction band (cf. Fox [21]). If an electric field is applied to crystals containing ion pairs, then, when the strain becomes sufficiently large, additional charge carriers could result by disruption and could lead to non-ohmic conductance. However, a lower limit to the field strength required appears to lie around 10^3 v/cm. In the present experiments we used fields not exceeding 200 v/cm., and conductance was ohmic throughout (cf. following paper).

The Effect of Substitution on the Conductance Parameters.—As seen from Fig. 6, chlorobenzacridines have a markedly lower thermal-energy gap than their parents. By analogy with the ultraviolet spectra of the molecule in solution, a small lowering in $\Delta\varepsilon$ might be expected, owing to the bathochromic effect of chloro-substitution, but in the solid state the effect on the energy gap is much more striking.

Craig and Hobbins [22] showed that the electronic transitions in the solid state depend largely on intermolecular vibrational interactions and multipole electrostatic interactions.

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[17] Coulson, " Valence," Clarendon Press, Oxford, 1952.

[18] Northrop and Simpson, *Proc. Roy. Soc.*, 1956, *A*, **234**, 124.

[19] Chynoweth and Schneider, *J. Chem. Phys.*, 1954, **22**, 1021.

[20] Lyons, *J.*, 1957, 5001.

[23] Fox, *J. Phys. Chem. Solids*, 1959, **8**, 439.

[22] Craig and Hobbins, *J.*, 1955, 539, 2309.

Many strong transitions in the free molecule are weakened in the solid in favour of the low-probability transitions; there are other changes of low-energy transitions in the solid state even at liquid-helium temperatures. Since the vibrational characteristics of the chloro-substituent are markedly different from those of the hydrogen it replaces, and since larger dipole and multipole moments probably occur for a chloro-substituent, it is to be expected that chloro-substitution affects electronic transitions in the solid much more markedly than in the free molecule. Formation of ion-pair crystal states is likely to depend on near-neighbour molecular interactions similar to those of the parent molecules, so that chloro-substitution can produce marked lowering in the thermal excitation required for conduction. This probably also explains why the bulk photocurrent for chloroanthracene is larger than for anthracene.[23]

For the benzacridones, where the lowering of thermal excitation energy (Fig. 6) is even greater than for the the chloro-isomers, similar considerations may apply. There is also the possibility of proton migration in the crystals by way of nitrogen, hydrogen, and oxygen bridges, but no other evidence has yet been obtained to suggest that at low field strengths (~200 v/cm.) the currect might in part be carried by such means.

Conduction Mechanisms in Solid Polarisation-bond Complexes.—The ion-pair model of thermal activation for conduction in pure hydrocarbons described above is supported by the consideration that addition complexes between aromatic molecules and either electron acceptors or electron donors are likely to yield ion pairs in much greater concentration than could be produced by mere thermal excitation of the parent molecules.

For complexes with electron acceptors, the electrostriction of molar volumes is generally small (Table 5a), and a similar description of conductance starting from ion pairs is probably still useful. With electron donors such as sodium, the strong co-operative interaction in the crystals indicated by the electrostriction (Table 5b) suggests that electron levels of the aromatic molecules must be profoundly perturbed; probably they are broadened and fused, to give new energy bands for the crystals, resembling those for metals or intermetallic semi-conductors.

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[23] Lyons, Bree, and Morris, Proc. 3rd Carbon Conf., Pergamon Press, London, 1959, 87.