402. *Electron-donor and -acceptor Complexes with Aromatic Systems. Part VI.*[*] *Complexes of Nonacyclic Aromatic Molecules.*

By N. D. PARKYNS and A. R. UBBELOHDE.

Solid complexes of the nonacyclic molecules isoviolanthrene and isoviolanthrone have been prepared by vacuum-line techniques. Electron-acceptors used with both aromatic molecules included iodine, iodine monochloride, titanium tetrachloride, and aluminium chloride. Electron-donors used with isoviolanthrene included sodium and potassium.

Both donor and acceptor complexes of isoviolanthrene show very marked lowering of activation energies, accompanying a marked increase of dark-current conductivities. Acceptor complexes of isoviolanthrone show little change in activation energy, but some increase of conductivity over that of the parent aromatic molecule. Density measurements show marked electrostriction of complexes between isoviolanthrene and the electron-donor atoms, sodium or potassium. Little or no electrostriction is observed on complex formation with the acceptors, titanium tetrachloride, aluminium trichloride, or iodine, though there is some contraction with iodine monochloride.

From the observations made, it seems likely that any polarisation bonding between these aromatic molecules and electron-acceptors is weak, and is of the $n \longrightarrow v$ type with isoviolanthrone but of the $\pi \longrightarrow v$ type with isoviolanthrene. Polarisation bonding is stronger between electron-donors and isoviolanthrene, and appears to be predominantly ionic in nature; the quasi-metallic behaviour of these complexes may be interpreted in terms of electron-band theory.

IT is now well established that aromatic molecules can behave as semi-conductors. In some cases, *e.g.*, anthracene,[1] the specific resistance ρ is extremely high, of the order of 10^{16} ohm cm. at room temperature. The thermal activation energy ε controlling the conduction process, as defined by the equation $\rho = \rho_0 \exp \varepsilon/kT$, usually lies between 1 and 2 ev. Formation of polarisation-bond addition complexes between electron-donors and aromatic molecules has been found to reduce both the specific resistance and the activation energy very markedly (cf. Parts I—V of this series). This has been interpreted on the basis of " quasi-metallic " polarisation bonding in the solids. Somewhat analogous complexes are formed between electron-acceptors, such as bromine, and heterocyclic tricyclic aromatic hydrocarbons (Parts III—V). With perylene and other larger aromatic molecules, the lowering of electrical resistance which is observed on formation of complexes with bromine has been reported to be even more striking,[2] but these results are difficult to interpret owing to complications caused by electrophilic substitution by bromine.

Increases of electrical conductance on formation of complexes are of inherent interest for characterising electron states in aromatic molecules, and also because closely related phenomena are found in crystal compounds of graphite.[3,4] Graphite may be regarded in this respect as an aromatic macromolecule in a homologous series of which benzene is the first member.

Isoviolanthrene [†] (I) is probably the largest polynuclear aromatic molecule whose quinone, isoviolanthrone (II), is readily available as a dyestuff, and which can still be

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[*] Parts I—V, *J.*, 1954, 720; 1955, 4089; 1957, 911, 918, 982.

[†] To be termed dehydroviolanthrene by the I.U.P.A.C. 1957 Rules.

[1] Northrop and Simpson, *Proc. Roy. Soc.*, 1956, *A*, **213**, 124; Mette and Pick, *Z. Phys.*, 1953, **134**, 566.

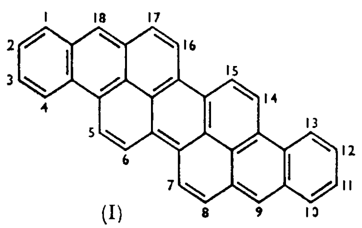
[2] Akamatu, Inokuchi, and Matsunaga, (*a*) *Nature*, 1954, **173**, 168; (*b*) *Bull. Chem. Soc. Japan*, 1956, **29**, 213.

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

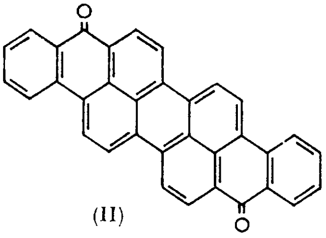
[4] Ubbelohde, Blackman, and Mathews, *Nature*, 1959, **184**, 454.

prepared in the highly pure condition [5] necessary for a study of the electronic properties. The present paper describes studies of solid donor and acceptor complexes formed by these two nonacyclic aromatic molecules.

Choice of suitable electron-accepting molecules was made from species unlikely to cause nuclear substitution, and at first fell on aluminium chloride, iodine monochloride, and titanium tetrachloride. The first two of these were known to produce marked lowering of specific resistance on formation of crystal compounds with graphite.[6] However, on trial, it was found that iodine monochloride causes substitution by chlorine in isoviolanthrene, so that iodine was used in its place to obtain a closely analogous complex. Titanium tetrachloride has been used in solution to prepare positive ions of diphenylpolyenes,[7] and complexes with *cis*- and *trans*-stilbene have also been reported.[8] Brass *et al.*[9] have isolated solid complexes between metal halides and a variety of hydrocarbons and quinones; these products are probably related to those dealt with in this paper, but no studies of the relevant properties appear to have been carried out.



(I)



(II)

Choice of electron-donors fell in the first place on alkali-metal atoms; potassium and sodium proved suitable, but experimental difficulties precluded the use of lithium in the procedures described below.

Few theoretical calculations have yet been published about the electronic properties of either isoviolanthrene or its quinone. Preliminary calculations [10] indicate that the positions of highest free-valency number are 9 and 18 (I.U.P.A.C. numbering given above); these positions are analogous to the *meso*-positions in anthracene, and it is interesting that the free-valency number calculated for them is 0·540 as compared with 0·520 for the *meso*-positions in anthracene. On the basis of a general parallelism between high free-valency and chemical reactivity, isoviolanthrene would be expected to be even more reactive chemically than anthracene. Some of its protonation and oxidation reactions in acid solution have been discussed on this basis in a previous paper.[5]

The preparation of solid adducts of graphite with electron donors and acceptors by vacuum-line techniques is well known. Analogous procedures starting with the smaller aromatic molecules have not been previously reported, though once solid complexes have been formed with alkali-metal atoms their composition can be modified by vacuum-sublimation (Part II). Compounds (I) and (II) have vapour pressures sufficiently low to permit the use of vacuum-line techniques *ab initio*, as recorded below. Measurements were carried out on the dark-current electrical conductance of the polycrystalline powders.[5] Densities were also measured, as described below. Although determinations of thermo-electric power were hampered by experimental difficulties, its sign and approximate magnitude were established in as many cases as possible, because of the information this gives about the predominant charge-carrier species.

[5] Parkyns and Ubbelohde, *J.*, 1960, 4188.

[6] Blackman, Mathews, and Ubbelohde, *Proc. Roy. Soc.*, 1960, *A*, **256**, 15.

[7] Van der Meij, Thesis, Amsterdam, 1958.

[8] Brackmann and Plesch, *J.*, 1953, 1289.

[9] Brass and Tengler, *Ber.*, 1931, **64**, 1650; Brass and Fanta, *Ber.*, 1936, **69**, 1.

[10] Pullman, Proc. Third Conference on Carbon, Pergamon, Buffalo, 1959, p. 3.

The behaviour of electron-donors and -acceptors could be compared for the hydrocarbon (I); but, for the quinone (II), only electron-acceptor complexes could be prepared if decomposition was to be avoided. In a number of cases of complex formation striking changes in electrical properties are observed. These are discussed below.

EXPERIMENTAL

Preparation of Titanium Tetrachloride Complexes.—Attempts to prepare these along the same lines as the aluminium chloride adducts (see below) proved inconvenient; the apparatus finally developed is shown in Fig. 1. The small container, fitted with a B24 cone, was chilled in liquid nitrogen, and liquid titanium tetrachloride (5 ml.) was added. This immediately froze and was then easily transferred to the apparatus without hydrolysis. The apparatus was evacuated and the first bulb C was chilled to trap titanium tetrachloride, which distils off at room temperature. When bulb C was almost full the first constriction was sealed off without admission of air. The distillation was repeated into bulb B by a similar method, and the apparatus was sealed at the constrictions between the tubes carrying bulbs C and B and between the reaction tube A and the evacuating pumps. The titanium tetrachloride obtained in bulb B in this way was clear and colourless and evaporated without yielding bubbles of hydrogen chloride. Reaction was carried out by putting the reaction tube A containing the quinone or hydrocarbon into a furnace at 200° and gently warming bulb B. After a few hours the final constriction (between A and B) was sealed and the solid was allowed to reach equilibrium at 250° during 12 hr. Both quinone and hydrocarbon complexes were black and showed no other appearance of reaction [Found, for quinone (II): C, 49·85; H, 2·9; TiO_2, 18·3. Calc. for $C_{34}H_{16}O_2(TiCl_4)_{1\cdot87}$: C, 50·4; H, 2·0; TiO_2, 18·5. Found, for hydrocarbon (I): C, 60·4; H, 2·8; TiO_2, 15·25. Calc. for $C_{34}H_{18}(TiCl_4)_{1\cdot29}$: C, 60·0; H, 2·7; TiO_2, 15·4%). The analyses were subject to experimental difficulties but the ratio TiO_2 : hydrocarbon appears to be reliable.

FIG. 1.

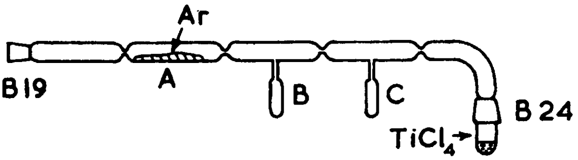
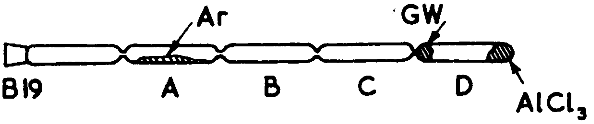


FIG.2.



Preparative apparatus.
Ar = *Aromatic compound.* GW = *Glass wool.*

Preparation of Quinone–Iodine Monochloride Complexes.—These were prepared analogously to the bromine–benzoquinoline complexes, as described in Part V. The composition of the complexes was established by direct weighing. No feature of the preparation calls for special comment; the reaction was speeded by warming to about 30° because of the low vapour pressure of iodine monochloride. The colour of the complexes was very similar to that of complexes with aluminium chloride.

Preparation of Hydrocarbon–Iodine Complexes.—Complexes of the hydrocarbon were not prepared with iodine monochloride because electrophilic substitution took place. For comparison a complex was made with iodine, by the method adapted for violanthrene by Akamatu, Inokuchi, and Matsunaga [2b] from that of Brass and Clar.[11] Compositions were calculated from the gain in weight.

Preparation of Aluminium Chloride Complexes.—Because of the possibility of formation of a Friedel–Crafts type of adduct, the preparation of these complexes was carried out both *in vacuo* and in a stream of hydrogen chloride. However, no obvious difference in properties could be

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[11] Brass and Clar, *Ber.*, 1939, **72**, 1882.

established in the two sets of products. The formation of two different adducts, as described by Baddeley,[12] may perhaps require the presence of a solvent. Water and oxygen were scrupulously kept from contact with the final product, which appeared to be somewhat susceptible to hydrolysis so that analysis proved difficult.

About 0·5 g. of purified quinone or hydrocarbon was placed in tube A of a vacuum reaction system (Fig. 2). Crude aluminium chloride (B.D.H.) was placed in the far end (then open) of tube D which was next sealed. The whole apparatus was evacuated to 10^{-3} mm. Hg and the aluminium chloride was heated at about 120° so that it distilled into tube C. The lumps tended to decrepitate; to prevent resulting contamination glass wool was placed between tubes D and C. After this distillation, tube D was sealed off from tube C at the constriction and the aluminium chloride was redistilled into tube B. Careful control of the distillation made it possible to obtain aluminium chloride in tube B coloured only faintly yellow. The apparatus was then sealed at the constrictions between tubes C and B, and between tube A and the vacuum pump, and reaction was brought about by heating both tubes A and B at 200° for about 12 hr. This left an excess of aluminium chloride in the reaction tube, which was distilled off by raising the temperature of tube A to 220° and lowering that of tube B to 180°. The reaction tube A was then sealed off and heated to 250° for 12 hr. to ensure uniform equilibration throughout the solid product. The quinone adduct was reddish-violet; the hydrocarbon had a dark violet sheen. Although analysis of these complexes was not completely consistent the complexes fit best to compositions indicated in Tables 1 and 2.

The preparations were repeated under a stream of dry hydrogen chloride, obtained by dropping concentrated sulphuric acid on to solid ammonium chloride and bubbling the gas through concentrated sulphuric acid. The reaction tube was very similar to that of Fig. 2 but the tube was not evacuated and the gas was admitted through tube D. The quinone or hydrocarbon was heated at 180° and the aluminium chloride containing hydrogen chloride was passed over it to ensure that the reactants were present in excess. After complete reaction, the tube was sealed off and the contents were homogenised as before.

Preparation of Alkali-metal–Hydrocarbon Complexes.—In previous work, preparation of alkali-metal adducts of hydrocarbons was carried out in ethereal solution. This process is greatly accelerated by using the cavitating effect of ultrasonic activation (cf. Part V). In the present case, however, because of the low solubility of isoviolanthrene even in relatively high-boiling ethers such as 2.2′-dibutoxydiethyl ether (b. p. 255°), the method previously described was impracticable. On the other hand, the low vapour pressure of the hydrocarbon makes feasible preparation by direct addition of alkali-metal vapour to the solid hydrocarbon. Details of the experimental procedure, which are analogous to those used for potassium–graphite,[13] will be described in Part VII of this series.

Complexes of relatively high metal content, for example, $K_{4\cdot05}Ar$, and $K_{4\cdot55}Ar$, were normally obtained, but lower metal contents could be attained by using lower temperatures and shorter exposures to alkali-metal vapour. As in the case of powdered potassium–graphite,[3] all the complexes were immediately decomposed by water and many were pyrophoric in air. All appeared black.

Analysis was effected by weighing 0·1—0·2 g. of powder into a stoppered bottle under nitrogen and decomposing it cautiously with slightly damp ether to which ethanol was added if necessary. The decomposed complex was boiled with 1 : 1 aqueous ethanol to complete the reaction. The solid was filtered off in a sintered-glass crucible, dried at 110°, and weighed. It was assumed to be predominantly the dihydro-derivative of compound (I), on the basis of the known reactions of other hydrocarbon–alkali-metal adducts with water.[14] The product obtained from metal-rich complexes was insoluble in sulphuric acid, presumably because the 9,18-positions were blocked by hydrogen. Reaction may have produced some tetrahydro-product, but its presence or that of other hydrogenation products would hardly affect calculations of the composition. The filtrate was acidified with sulphuric acid and evaporated to dryness under a 250 w infrared lamp. Any remaining organic matter was oxidised with nitric and sulphuric acid, and the alkali metal was weighed as the metal hydrogen sulphate. In all cases agreement within 1% was obtained between the two methods of calculation; the latter was probably the more accurate.

[12] Baddeley, *Quart. Rev.*, 1954, **8**, 355.

[13] Fredenhagen, Cadenbach, and Suck, *Z. anorg. Chem.*, 1929, **178**, 333.

[14] Hoijtink, *Rec. Trav. chim.*, 1957, **76**, 885.

Most complexes were attacked by water or oxygen, so that, after preparation *in vacuo*, handling was done in a completely inert atmosphere. Details will be described in Part VII, along with the methods by which these labile compounds were transferred to cells for electrical measurements and to weighing bottles for analysis and density determinations.

RESULTS

Densities.—Densities of the complexes are shown in Table 1, together with relevant molar volumes. In the calculations, molar volumes of the parent aromatic compounds were obtained from direct pyknometry. For the inorganic adducts the following molar volumes (c.c.) were assumed: $TiCl_4$ 110, $AlCl_3$ 109, ICl 51·1, K(metal) 45·4, Na(metal) 23·7.

TABLE 1. *Densities and molar volumes of complexes.*

Arom. mol. (Ar)	Complex composition ArX_m	Density (g./c.c.)	Theoretical molar volumes			Exp. molar vol. (V_2; c.c.)	$V_2 - V_1$ (ΔV; c.c.)
			Arom. mol. Ar	Inorg. adduct	Total V_1		
Quinone	(Pure)	1·47	—	—	—	310	—
	$(AlCl_3)_{3\cdot7}$	1·87	310	203	513	508	−5
	$(TiCl_4)_{1\cdot87}$	1·56	310	216	516	520	+4
	$(ICl)_{1\cdot69}$	1·93	310	86	396	378	−18
Hydro-carbon	(Pure)	1·47	—	—	—	290	—
	$(TiCl_4)_{1\cdot29}$	1·55	290	142	432	433	+1
	$I_{1\cdot52}$	1·89	290	39	329	327	−2
	$K_{4\cdot55}$	1·76	290	206	496	343	−153
	$K_{4\cdot05}$	1·75	290	184	474	333	−141
	$K_{1\cdot42}$	1·59	290	64	354	303	−51
	$Na_{3\cdot37}$	1·51	290	56	346	318	−28
	$Na_{0\cdot31}$	1·49	290	7	297	291	−6

TABLE 2. *Specific resistance parameters for addition complexes of compounds* (I) *and* (II).

Arom. mol. (Ar)	Complex ArX_m	ρ_{20° (ohm cm.)	ρ_0 (ohm cm.)	ε (ev)	Thermoelectric power (μv/°c)
Quinone	(Pure)	$3\cdot2 \times 10^{14}$ (av.)	520 (av.)	0·68	—
	$(AlCl_3)_{3\cdot7}$	$2\cdot6 \times 10^{12}$	13	0·65	—
	$(AlCl_3)_{3\cdot7}$ *	$2\cdot5 \times 10^{12}$	5·9	0·67	—
	$(TiCl_4)_{1\cdot87}$	$3\cdot0 \times 10^{10}$	0·69	0·64	—
	$(ICl)_{3\cdot73}$	$1\cdot1 \times 10^{9}$	1·9	0·49	—
	$(ICl)_{1\cdot90}$	$2\cdot2 \times 10^{8}$	15	0·47	—
	$(ICl)_{1\cdot45}$	$4\cdot5 \times 10^{11}$	7·1	0·62	—
Hydrocarbon	(Pure)	$3\cdot6 \times 10^{14}$	20	0·81	—
	$(AlCl_3)_{3\cdot2}$	36	0·7	0·11	—
	$(AlCl_3)_{3\cdot3}$ *	800	3·2	0·14	—
	$(TiCl_4)_{1\cdot29}$	354	2·6	0·13	—
	$I_{1\cdot52}$	580	7·6	0·11	−300
	$K_{4\cdot35}$	27	8·9	0·030	−20
	$K_{4\cdot05}$	100	3·7	0·083	−10
	$K_{1\cdot42}$	2600	5·2	0·014	—
	$Na_{2\cdot37}$	61	10	0·048	−10
	$Na_{0\cdot31}$	$3\cdot1 \times 10^{5}$	2·6	0·21	—

* Prepared under HCl.

TABLE 3. *Relative changes in conduction parameters on complex formation.*

Quinone complexes	$\varepsilon/\varepsilon_{(parent)}$	$\rho_0/\rho_{0(parent)}$	Hydrocarbon complexes	$\varepsilon/\varepsilon_{(parent)}$	$\rho_0/\rho_{0(parent)}$
$(AlCl_3)_{3\cdot7}$	0·96	0·025	$AlCl_3)_{3\cdot2}$ *	0·14	0·03
$(AlCl_3)_{3\cdot7}$ *	0·98	0·011	$(AlCl_3)_{3\cdot3}$	0·17	0·16
$(TiCl_4)_{1\cdot87}$	0·94	0·001	$(TiCl_4)_{1\cdot29}$	0·16	0·13
$(ICl)_{0\cdot45}$	0·91	0·014	$I_{1\cdot52}$	0·14	0·38
$(ICl)_{1\cdot90}$	0·69	0·029	$K_{1\cdot42}$	0·17	0·26
$(ICl)_{3\cdot73}$	0·72	0·003	$K_{4\cdot05}$	0·10	0·19
			$K_{4\cdot55}$	0·04	0·45
			$Na_{0\cdot31}$	0·26	0·13
			$Na_{2\cdot37}$	0·06	0·50

* Prepared under HCl.

Resistance Parameters.—All complexes were found to obey the general equation:

$$\log_{10} \rho = \log_{10} \rho_0 + \varepsilon/2{\cdot}303kT$$

Values of ε and ρ_0 were obtained in the usual way from graphical plots. In Table 2 values of ρ_{20°, ρ_0, and ε are shown for all the complexes.

Table 3 illustrates these changes on a relative basis so that relations can be more easily seen.

DISCUSSION

One of the most striking results of this investigation is that extremely low activation energies are found with some of the hydrocarbon complexes with alkali metals. These solids are almost metalloid in character. In order to visualise these and other results in perspective, it is useful to discuss probable bond structures of the complexes and then to examine their bearing on the electronic properties.

Donor-acceptor Complexes of Aromatic Molecules.—Much attention has been paid to the " polarisation bonds " (Parts I—V) between aromatic molecules and electron-donors or -acceptors. For interpretation of the results so far available, probably the most satisfactory theoretical treatment is due to Mulliken.[15] An alternative suggestion by Dewar,[16] to explain the formation of complexes between electrophilic reagents and the π-electrons of double bonds, will not be discussed here. Mulliken's description has as basic feature contributions to the polarisation bond in a complex, both from the " no-bonding " ground state and from excited states in which charge-transfer has occurred. A solid adduct molecule may form polarisation bonds with more than one neighbouring aromatic molecule, provided these are suitably located in space. This faculty leads to the possibility of the adduct forming a " polarisation bridge " between neighbouring aromatic molecules. An immediate distinction is apparent between complexes formed by the two molecules, isoviolanthrone and isoviolanthrene, with electron-acceptors. In isoviolanthrone the more or less localised " lone pair " electrons of the oxygen form localised polarisation bonds with electron-acceptors such as aluminium chloride, and these are quite stable. Unless the crystal structure happens to be favourable, only one such bond can be formed by any one adduct molecule, and there are no polarisation-bond bridges. Table 1 shows that electrostriction is weak with this type of complex. Some effect of this polarisation bonding on the electronic properties may be inferred from Tables 2 and 3.

Isoviolanthrene forms a quite different class of complex with electron-acceptors. Since no lone-pair electrons are available, charge transfer must occur from the π-electron system; the polarisation bonds are described by Mulliken as $\pi \longrightarrow v$. The possibilities of forming polarisation bonds with more than one neighbouring aromatic molecule appear to be much greater. From the free-valency numbers positions of likely attachment of electrophilic groups would be 9 and 18, with 1, 8, 10, and 18 somewhat less reactive. The maximum uptake m of electron-accepting adduct groups in this type of complex, ArX_m, is probably determined, not only by free-valency number, but also by steric factors. With most electron-acceptors the first pronounced threshold at $m = 2$ does not appear to have been reached. In the absence of *X*-ray data it is not yet clear whether this represents an approach to an uptake of two molecules. Electrostriction in this group of complexes appears to be weak (Table 1).

Electron-donor Complexes.—In Mulliken's notation adducts of alkali-metal atoms with the hydrocarbon (I) appear to present extreme forms of the $\sigma \longrightarrow \pi$-type of complex. For the highly coloured solutions obtained by reaction of aromatic hydrocarbons dissolved in ethereal solvents with alkali metals, various lines of evidence suggest that aromatic mono- and di-negative ions are present.[17] In fairly dilute solutions ($<10^{-3}$M), no ion-pair

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[15] Mulliken, *J. Amer. Chem. Soc.*, 1952, **74**, 811; *J. Phys. Chem.*, 1952, **56**, 801.
[16] Dewar, *Bull. Soc. chim. France*, 1951, **18**, 71.

association has been detected[17] and electron transfer may be assumed to be complete. In the solid state, neighbouring molecules are much more important. Evidence previously reviewed (Parts I, II, V) suggests that the crystal lattice is predominantly ionic, but that the degree of electron transfer from the *s*-electron shell of the alkali metal to the π-aromatic system is not quite complete. A partly covalent character of the polarisation bond for such complexes gave an explanation of both the strong electrostriction and the marked electrical conductivity of these solids. The present results support and extend these conclusions.

If the adduct with an alkali metal is fully salt-like, the observed molar volume would be expected to be less on conversion of metallic atoms into ions. The specific volume is assumed to be $\frac{4}{3}\pi r^3$ Å^3. For potassium ions the ion contact radius[18] assumed is $r = 1{\cdot}33$ Å, and for sodium ions 0·95 Å. A small expansion δ would be expected for the conversion of one molecule of aromatic hydrocarbon into the negative ion Ar^{m-}. If the free space in the hypothetical close-packed salt $\mathrm{Ar}^{m-}\mathrm{X}^{+}{}_{m}$ is assumed to be comparable with that in the parent hydrocarbon, as seems reasonable in view of the structure, the observed shrinkage $\Delta V = V_2 - V_1$ may be compared with the theoretical shrinkage

$$\Delta V_0 = -Nm\delta + m(V_{\text{metal}} - V_{\text{ion}})$$

If bonding were completely ionic, ΔV_0 would be slightly smaller than ΔV, owing to the term in δ. For more nearly metallic bonding, ΔV would be much smaller than the theoretical shrinkage ΔV_0. It can be seen from Table 4 that the experimental findings agree as well as can be expected with the assumption of a model that is approximately salt-like when the concentration of alkali metal is low, and becomes more metallic as this concentration increases.

TABLE 4. *Apparent expansion on forming salt-like adducts,* $\mathrm{Ar}^{m-}\mathrm{X}^{+}{}_{m}$.

m of adduct	$(\Delta V_0 - \Delta V)$ (Å^3)	$(\Delta V_0 - \Delta V)/m$	m of adduct	$(\Delta V_0 - \Delta V)$ (Å^3)	$(\Delta V_0 - \Delta V)/m$
	Potassium			Sodium	
1·42	8	5·6	0·31	2	6·4
4·05	31	7·7	2·37	39	16·4
4·55	43	9·4			

Electronic Properties.—(i) From Tables 2 and 3 the conclusion is that, with the quinone, electron-acceptors show definite but comparatively small changes in the conductance parameters. This can be understood if conductivity in these aromatic solids is associated with systems of π-electrons, since the formation of local $n \longrightarrow v$ adducts at the quinone-oxygen atoms would not be expected to introduce more than second-order effects within the π-systems. Further, with iodine chloride no significant change in ε is observed beyond $m \sim 1{\cdot}9$, indicating that even after $n \longrightarrow v$ complex formation has proceeded to completion, the excess of adduct does not perturb the π-electron systems to any marked extent.

(ii) Electron-acceptors cause much more profound changes in adducts with the hydrocarbon. The remarkably low activation energies recorded in Table 3 all lie around 0·15 ev and suggest a common feature in the conductance process of the various solids. From the ready formation of R^{+} or R^{2+} ions by the hydrocarbon (I) in strongly acid solutions[5] a corresponding process seems likely in solid adducts with electron-acceptors, though the absence of marked electrostriction (Table 1) is evidence against any substantial salt formation in these solids. In these complexes easier formation of ions may be apparent in the excited state, without much increasing the strength of the charge-transfer bonding in the ground state. The hypothesis seems worth considering that the

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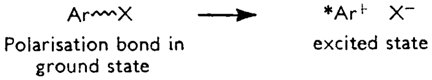
[17] Balk, Hoijtink, and Schrews, *Rec. Trav. chim.*, 1957, **76**, 813; Balk, de Bruijn, and Hoijtink, *ibid.*, p. 860.

[18] Wells, " Structural Inorganic Chemistry," Oxford Univ. Press, 1950, p. 70.

activation energies recorded refer to the energy required to convert a charge-transfer bond into an ion pair. This may be symbolised:



From such an activated ion pair electron-switching could easily occur to other molecules. The effect of benzanthrone as impurity on the conductance of the quinone [5] has not yet been studied with these complexes, which were all made from highly purified material. As already pointed out, for the solids, charge-transfer bonds may be formed between any one adduct molecule and more than one aromatic system in its immediate proximity. Although a formal 3-dimensional version of Mulliken's theory of charge-transfer bonds is not yet available, it can be seen in general terms how this kind of adduct formation in the solid can greatly increase the conductance. In particular, if thermal excitation at a charge-transfer bond leads to an actual separation of charges, the positive hole Ar^+ or the extra electron of the anion X^- could then migrate separately in an applied electric field, leading to the observed electrical conductance.[19] From the sign of thermoelectric power of the isoviolanthrene–iodine complex (Table 2) electrons appear to be more mobile than holes, at any rate in this electron-acceptor adduct.

(iii) Electron-donor complexes between alkali-metal atoms and isoviolanthrene clearly exhibit much stronger interactions than are present in the electron-acceptor complexes, as is shown, for example, by the marked electrostriction in the solid adducts. Because of the near-stoicheiometric transfer of electrons on complex formation, π-electron systems of individual molecules are likely to undergo profound disturbances in these crystals. Electron-switching across adduct bridges from one aromatic molecule to another no longer seems a useful model to describe conduction in this instance, and a band system applying to the solid as a whole seems necessary to give even an approximate description of the conduction process. If the model of a salt-like lattice applies even approximately to this group of complexes, their high conductance compared with the insulator properties of a salt such as sodium chloride presumably arises from the overlap of electronic energies of the aromatic ions. Tables 2 and 3 show that the conductance increases as the proportion of alkali metal incorporated increases. This can almost certainly be attributed to increased band overlap.

Until detailed *X*-ray studies of the structures of the adducts can be made, it does not seem profitable to discuss their conductance mechanisms in much greater detail. Knowledge about structures of simpler polarisation-bond adducts, such as silver perchlorate–benzene [20] and benzene–bromine,[21] suggests a " sandwich " type of arrangement in which the foreign molecules lie underneath and probably slightly skew to the benzenoid planes. The direction of principal conductivity would be expeced to be largest normal to these planes, in the direction of the polarisation bonds. For this type of electrical conductance, when potassium is intercalated, or when crystalline compounds are formed with various electron-acceptors,[6] a limiting case appears to be presented by the electronic properties in the direction of the *c*-axis of the polynuclear layers in graphite. Further development of this electronic analogy between graphite and large aromatic molecules [22] presents some interesting possibilities.

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