The Delocalisation of Electrons in Solid Organic Complexes of Anthracene.

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To elucidate the nature of the bonding, comparative studies have been made on the lithium, sodium, and potassium complexes with anthracene. Methods are described for varying the alkali content x of the solid complexes, $M_x(C_{14}H_{10})$, over a range $x = 1{\cdot}1$ to $2{\cdot}12$ in the case of sodium.

A marked contraction in volume is observed on forming complexes up to the formula $M_2(C_{14}H_{10})$; this contraction depends on the electropositivity of the alkali metal. Measurements on the electron polarisability, electronic conductivity, and other properties of the solids give results suggesting the formation of quasi-metallic bonds between the alkali metal and the aromatic hydrocarbon.

THIS investigation continues previous studies on the delocalisation of electrons in crystals, associated with special types of crystal bonding. At first sight, the range of crystalline solids with metallic properties appears to be limited by the range of atoms in the Periodic System capable of forming the special type of co-operative bonding characteristic of metals. In spite of its powerful mathematical advantages, the Bloch–Brillouin zone model of a crystalline metal does not indicate any very obvious guide for predicting metallic behaviour in a crystal. On the other hand, though it is less suited for the quantitative study of co-operative properties the Pauling model permits a more chemical approach. In this model, a metal crystal is regarded as a giant molecule made up of atoms bonded by covalent linkages, but with a defect of electrons. Transport of electricity without transport of mass is chemically equivalent to electron switching from one site to another in the crystal. For semi-conducting solids Wagner (*Z. phys. Chem.*, 1933, **22**, *B*, 212) has described a model which has analogies with the local or chemical features of Pauling's description of metallic bonding.

Though there may be serious deficiencies in " chemical " models for discussing quantitative co-operative parameters of metallic solids, they do point to an important possible extension of the field of metallic behaviour. Certain types of organic molecules appear to be capable of functioning like the units of structure in crystalline metals. The largest group of such structures is formed by aromatic compounds. Particularly when these contain several fused aromatic nuclei, their electronic characteristics should begin to approximate to those of graphite (cf. Ubbelohde, *Nature*, 1933, **132**, 1002).

Experimental evidence developing these views is beginning to accumulate. The metallic behaviour of solid complexes of graphite with potassium and with bromine has been described by McDonnell, Pink, and Ubbelohde (*J.*, 1951, 191). Both types of complex show a marked increase in general metallic properties, compared with the parent graphite. This behaviour can be interpreted by assuming that layers of fused aromatic nuclei in the crystals act as both electron acceptors and electron donors, and form covalent bonds, as in the Pauling chemical model of a metal. With smaller fused aromatic molecules, the ease of electron switching may be lessened, and the properties of the solid complexes lie nearer to those of a metalloid or semi-conductor solid. For example, with anthracene the alkali metals lithium, sodium, and potassium form solid complexes (Holmes-Walker and Ubbelohde, *J.*, 1954, 720) whose magnetic properties are consistent with quasi-metallic bonding between the alkali atoms and the aromatic molecules, and whose electrical properties are those of semi-conductors. Again, a complex between perylene and bromine (Akamatu, Inokuchi, and Matsunaga, *Nature*, 1954, **174**, 168) exhibits electrical conductivity much greater than that of the parent aromatic hydrocarbon.

The present paper deals with the development of more precise methods than those hitherto available for studing some characteristic properties of these complexes in the solid state. Ways are described for obtaining solids M_xAn in which the proportion x of alkali metal (M) to anthracene (An) can be varied between about $1{\cdot}1$ and $2{\cdot}12$.

The specific volumes of such solids have been determined as a function of x and M, for lithium, sodium, and potassium complexes. By using alternating-current and improved direct-current measurements, electron polarisabilities, electrical conductances, and dielectric-loss factors have also been evaluated for these complexes.

As discussed below, the more extensive information now obtained supports the interpretation previously given, *viz.*, that the bonding between the alkali-metal atoms and the aromatic groups is quasi-metallic. The dark, sodium-rich complexes with $x > 2$ show particularly marked enhancement of the pseudo-metallic properties.

EXPERIMENTAL

Nitrogen was purified in a manner similar to that described by Holmes-Walker and Ubbelohde (*loc. cit.*). The gas (British Oxygen Co.) was freed from oxygen by passage at a low linear velocity through commercial copper turnings electrically kept at 500°. A mild-steel tube, 2″ in diameter and 3′ long, with screwed end-caps, was used to contain 1½ kg. of copper turnings. The issuing gas was dried by a 6 ft. column of potassium hydroxide pellets, followed by a 2 ft. column of magnesium perchlorate, and finally a liquid-air trap packed with chemically clean glass-wool (cf. Ubbelohde, *J.*, 1933, 972). After each cylinder of commercial nitrogen had been used, the copper was regenerated by reduction with a current of hydrogen at 500°.

Very great care is necessary in preparing the solid complexes in solvent-free form, and sufficiently pure to permit reliable measurements of important physical properties. Improvements in previously published details for handling these compounds (Holmes-Walker and Ubbelohde, *loc. cit.*; Reid and Ubbelohde, *J.*, 1948, 1597) were as follows:

All solvents were rigorously dried and handled throughout under pure nitrogen. Diethyl ether was purified as described by Mackle and Ubbelohde (*J.*, 1948, 1161). 1 : 2-Dimethoxyethane was not commercially available when most of this work was carried out. It was prepared by methylating 2-methoxyethanol with methyl sulphate by a method provided by Professor Wright (Toronto University, personal communication). It was purified by storage over sodium under nitrogen. Removal of final traces of water was achieved by adding just sufficient dried benzophenone to produce the blue ketyl, and then distilling off the solvent under nitrogen. Benzene ("AnalaR") was first dried by refluxing over sodium wire under nitrogen. The benzene was then distilled off and stored over sodium wire. Before use it was distilled directly into the required container. Anthracene (British Drug Houses) was purified by molecular distillation (f. p. 214°). Rather better results were found with material obtained from the Deutsche Gesellschaft für Teerverwertung (f. p. 215·0° after sublimation). Purification and handling of the alkali metals was as previously described (McDonnell, Pink, and Ubbelohde; Holmes-Walker and Ubbelohde, *locc. cit.*).

Preparation of Complexes.—Earlier workers (Schlenck, *Ber.*, 1914, **47**, 473; Scott *et al.*, *J. Amer. Chem. Soc.*, **1936**, **58**, 2442) were not concerned with the isolation of the solid complexes. Accordingly, the particulars below detail especially the steps in isolating these solids. The addition complexes were generally formed by direct interaction of alkali metal and hydrocarbon in dimethoxyethane–diethyl ether (1 : 10) (cf. Scott *et al.*, *loc. cit.*). Successful preparations were also carried out in cyclic ethers and in pyridine, though these were not used for the physical measurements. Access of direct sunlight was prevented by using black cloth wrappings on the containing vessel (Reid and Ubbelohde, *J.*, 1948, 1897).

In a typical preparation pure anthracene (10 g.) was placed in a 1-l. three-necked flask with constant turning over of the powder and gentle warming under a flow of nitrogen for about 6 hr. to ensure complete expulsion of all moisture and oxygen. Approx. 600 c.c. of solvent were then added either by distilling or syphoning in, again under nitrogen.

On introduction of excess of alkali metal either as cubes or as sodium sand, protected by nitrogen, the reaction generally started immediately. Occasionally an induction period was noted. This could be eliminated by the addition of a small drop of slightly damp solvent. Presumably, this catalysed the reaction by breaking up a surface film of oxide on the alkali metal or by providing a medium for ionic reactions. Potassium was introduced by breaking sealed ampoules of metal under the solvent in the reaction flask.

Within approx. 10 min. of the onset of the reaction the whole solution was deeply coloured, purple in the case of lithium and indigo for both sodium and potassium. Stirring was continued as long as possible (7 days), normally terminated by the evaporation of all free solvent. The highly coloured solid was then broken up and warmed to remove all co-ordinated solvent. Recovery tests on solids prepared in dimethoxyethane–diethyl ether showed that the solvent at first retained in the complex was dimethoxyethane, and special preparations in unmixed solvents were used in the attempt to determine its proportion. Direct weighing of the reaction flask before and after warming showed that, before warming, up to 1 mole of dimethoxyethane was retained for every 2 g.-atoms of alkali metal. Values obtained with diethyl ether were similar, but not very reproducible owing to the greater volatilisation of this ether even before warming. The resulting solvent-free homogeneous powder was yellow for lithium, red-brown for sodium, and grey for potassium. Any pieces of metal which had escaped reaction could then be picked out with tweezers, as they remained bright.

The empirical formula of the complex solid M_xAn could next be varied in the range $x = 0$ to $x = 2$ by elutriating out excess of anthracene with hot benzene (cf. Holmes-Walker and Ubbelohde, *loc. cit.*).

Complexes with $x > 2$ were only investigated in the case of sodium and were prepared by two methods. On heating the M_2An complex (prepared as above) in a high vacuum to above 200°, small amounts of anthracene crystals appeared on the surface of the powder. This "sublimed" anthracene was removed by washing out with hot benzene, and the process repeated. Approximately ten such sublimations were required to reach the $M_{2\cdot12}An$ formula. The second method of preparation of metal-rich complexes consisted in heating the M_2An complex in a high vacuum to 120° in an atmosphere of alkali-metal vapour. Complexes were obtained up to the $M_{2\cdot12}An$ formula by both methods.

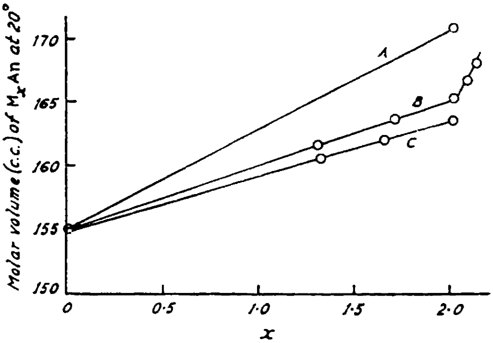


FIG. 1.
A, K–anthracene.
B, Na–anthracene.
C, Li–anthracene.

Analysis.—About 1 g. of the complex was transferred into a 3-necked weighing bottle previously swept out by nitrogen. This known quantity was then decomposed by a 1 : 1 mixture of dilute sulphuric acid and absolute alcohol and evaporated to dryness under infrared lamps. From the solid residue all the hydrocarbon could be extracted quantitatively by repeated washings with benzene. The inorganic residue was then removed and weighed as sulphate, the precautions described by Vogel ("Quantitative Inorganic Analysis," Longmans, London, 1947) being used. The hydrocarbon recovered from complexes with formula M_2An was identified (mixed m. p.) as 9 : 10-dihydroanthracene. For complexes with $x > 2$ only dihydroanthracene was recovered, whereas with $x < 2$ a mixture of anthracene and dihydroanthracene was found.

Density Measurements.—A conventional pyknometer was fitted with two ground-glass joints (A.7) to facilitate weighing under nitrogen. Purified Nujol was used as the pyknometer fluid. This was first thoroughly dried by bubbling nitrogen through it at 120° for 48 hr. Density measurements were found to be reproducible to within $\pm 0{\cdot}001$ g./c.c. Molar volumes obtained from density measurements by multiplying the specific volume by the mass of complex containing one mole of anthracene are recorded in Fig. 1.

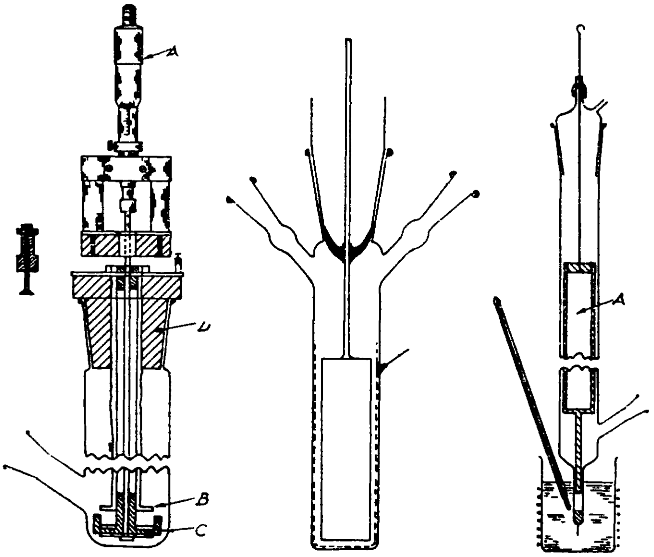
Molar Polarisations.—Direct measurements of the optical refractivities were prohibited by the highly reactive nature and low solubility of the solid complexes. Molar polarisations were evaluated from measurements of the dielectric constants of the powdered solids.

Polarisation of powdered solids and the evaluation of the true dielectric constant have been extensively discussed by Böttcher ("Theory of Electric Polarisation," Elsevier, 1952). Three types of cell (Fig. 2) were used for the dielectric and conductivity experiments. All three were designed to permit filling and use under nitrogen. To achieve filling, a transference tube was used fitted with two joints, one connected to the cell, and the other to the flask containing the powdered complex. Rotation at the greased ground-glass joints enabled filling to be accomplished with full nitrogen protection.

Cell No. 1. This cell was designed to permit measurements of dielectric constant and dielectric loss to be made on the samples of the powdered complexes under moderate compression. A micrometer screw *A* served both to measure the thickness of the sample and to apply known values of compression by means of the friction drive. From the accompanying diagram it will be seen that the circular cell electrodes *B* + *C* (outside diam. 35 mm.) are mounted so that the cell spacing is directly measurable on the micrometer. All the metal parts were made from brass. Insulation between the two electrodes was by polystyrene throughout (heavily shaded) chosen for rigidity and low loss factor. The tapered joint (B.50) was machined from Tufnol as were the two mounting platforms for the micrometer head. The complete electrode assembly and micrometer head were movable in the vertical plane by means of the threaded brass tube *D*. A small hole (not shown) drilled in *D* enabled the nitrogen flow to escape up the inside of the threaded tube *D*.

A cylindrical, earthed, copper screen surrounded the cell when in use. For measurements of dielectric loss, the cell was found to be satisfactory, but owing to the relatively large amount of dead capacity a different design of cell was preferred for evaluations of the dielectric constant.

FIG. 2.



Cell Nº 1 Cell Nº 2 Cell Nº 3

Cell No. 2. A concentric cylindrical electrode arrangement was used in this design. This had the advantage of very low dead capacity, high dielectric capacity, and easy filling for powdered solids and liquids.

A 2-mm. tungsten rod was plug-sealed into a B.24 ground-glass cone to support the centre electrode assembly. One end of this rod was brazed into the centre electrode, which was hollowed to lessen its weight and so reduce strain on the glass–metal seal. The tungsten rod served as the lead to the live electrode.

The outer electrode was built into a B.24 socket. Two A.7 sockets were sealed into the neck of this B.24 socket for filling and nitrogen protection. The electrode was silver-plated directly on to the glass. A platinum-wire seal brought the lead from this electrode through the glass. Spacing between the electrodes was 2 mm. The air capacity was found to be 28·6 pF and the loss factor negligibly small except at frequencies below 300 c/s.

Filling of the cell was accomplished with the precautions already described, aided by gentle tapping. This ensured complete filling around the bottom of the electrodes. For measurements at 20° or above, the cell was immersed in a liquid-paraffin bath thermostatically controlled. For lower temperatures a Dewar flask with ice–salt or alcohol–solid carbon dioxide mixtures was used. An alcohol thermometer was found to give sufficient accuracy in temperature measurement down to −40°.

Cell No. 3. A modification of the cell used by Holmes-Walker and Ubbelohde was employed for the measurements of conductivities and breakdown voltages. In order to reduce the effects of intercrystalline resistances it is desirable to compress the powdered solid. Compressions of up to 20 kg./cm.^{2} were obtainable by loading the hollow chamber *A* with lead weights. A 7/16-in. stainless-steel rod attached to *A* formed the live electrode. The live lead was carried by the stainless-steel chamber *A* and associated support.

The lower electrode consisted of a short length of 7/16-in. stainless-steel rod with a platinum lead sealed through the glass. The thickness of sample contained within these electrodes was measured by means of a Pye travelling microscope. Filling was carried out by using the B.19 side arm.

Measurements from room temperature to 80° were made by immersing the electrode assembly in a small paraffin-bath fitted with an external heater fed from a Variac transformer. Temperature was recorded by using an ordinary thermometer.

In principle, polarisations *P* can be calculated from the dielectric constants of the solids. There are, however, difficulties in calculating molar polarisations from measurements on powders, owing to local variations of internal field arising from gaseous crevices and holes in the powder. In addition to corrections proposed for this effect by Böttcher (*loc. cit.*), non-spherical crystals of a substance with marked anisotropy of polarisability along the principal axes can give a packing of the powder which does not average the different orientations completely.

As a test, measurements of dielectric constants were made with powdered anthracene. When Böttcher's corrections are applied to these measurements, $P_{\mathrm{An}} = 56{\cdot}2$ c.c. This compares with a mean molar refractivity for anthracene which is stated to be 62 c.c. Various attempts to increase randomisation of crystallisation in the powder, or filling the gas spaces by a fluid hydrocarbon (Nujol) gave no better agreement. It was therefore decided to treat the calculated polarisabilities by using Böttcher's corrections as relative values only; since the different complexes are likely to behave in a similar way, significant information can be derived from comparative results.

Dielectric constants of the powdered solids were measured by using the heterodyne-beat method. The true value of the dielectric constant ε_0 was obtained from the formula

$$(\varepsilon - 1)/(3\varepsilon) = V(\varepsilon_0 - 1)/(\varepsilon_0 + 2\varepsilon) \quad . \; . \; . \; . \; . \; . \; . \; . \quad (1)$$

where *V* is the volume occupied by the crystals and ε is the dielectric constant of the particles (Böttcher, *loc. cit.*). Results are collected in Tables 1 and 2. Polarisations were calculated from

$$P = M(\varepsilon_0 - 1)/d(\varepsilon_0 + 2) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (2)$$

To test for the presence of temperature effects, measurements on selected solids were made at various temperatures from −40° to +40° maintained by manual control of a simple thermostat.

TABLE 1. *Dielectric constants ε_0 and polarisation P at 20°.*

Substance	Density (g./c.c.)	ε_0 (powdered solids)	*P* (c.c.)	ε_0 (suspension) in Nujol	Substance	Density (g./c.c.)	ε_0 (powdered solids)	*P* (c.c.)	ε_0 (suspension) in Nujol
Anthracene	1·150	2·71	56·2	2·59	$Na_{2\cdot12}An$ ...	1·347	5·38	99·6	—
$Na_{1\cdot30}An$ ...	1·290	3·00	64·5	2·79	$Li_{1\cdot31}An$ ...	1·165	2·77	59·6	—
$Na_{1\cdot70}An$ ...	1·329	3·10	67·5	2·90	$Li_{1\cdot65}An$ ...	1·619	2·78	60·5	—
$Na_{2\cdot00}An$ ...	1·355	3·18	69·5	2·95	$Li_{2\cdot00}An$ ...	1·173	2·80	61·4	—
$Na_{2\cdot08}An$ ...	1·349	3·70	79·4	—	$K_{2\cdot00}An$ ...	1·496	3·79	77·5	—

TABLE 2. *Variation of dielectric constant ε_0 with temperature.*

Substance	−40°	−20°	0°	+20°	+40°
$Na_{1\cdot30}An$	2·91	2·94	2·97	3·00	3·02
$Na_{2\cdot00}An$	3·10	3·11	3·15	3·18	3·21
$Na_{2\cdot08}An$	3·57	3·60	3·66	3·71	3·95

Dielectric Loss.—For the radio frequencies from 5 × 10^4 to 5 × 10^7 c/s the method of reactance variation in a tuned circuit (Hartshorn and Ward, *J. Inst. Elect. Eng.*, 1936, **79**, 597) was used in a modified form. For frequencies in the range from 10^2 c/s to greater than 10^6 c/s a General Radio type 716—1 capacitance bridge was used, which gave direct reading in both capacitance and tan δ. A substitution method of evaluating the dielectric loss was used. Dielectric constants obtained were corrected by using equation (1). The variation of tan δ with frequency is shown in Fig. 2.

Conductivity Measurements.—Holmes-Walker and Ubbelohde measured the conductivities of complexes by direct galvanometer reading of the small current passed when a large potential is applied to thin layers of the lightly compressed sample. This method has disadvantages in that voltage gradients of the order of 10^3 v/cm. must be used for the complexes under investigation to obtain a measurable current. In view of the comparatively low breakdown voltages now observed for the complexes, it was thought desirable to measure conductivities at lower voltage gradients. Use was made of a sensitive valve voltmeter incorporating six switched ranges between 0 and 100 v with constant input impedance of 11 megohms on all ranges. The resistance of the sample (in megohms) is given by

$$R = 11(V_A - V_B)/V_B \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where V_A is the applied voltage and V_B is the measured voltage after passing through the sample. Conductances of the alkali-metal–anthracenes are given in Table 3.

TABLE 3. *Conductance parameters of alkali-metal–anthracenes at 20°.*

(equation: $\log \sigma = \log \sigma_0 + E/kT$)

Substance	V_A (v)	σ (ohm^{-1} cm.$^{-1}$)	σ_0 (ohm^{-1} cm.$^{-1}$)	E (ev per molecule)
$Na_{1.42}An$	220 *	3.51×10^{-10}	$5.14 \times 10^{+10}$	1·16
$Na_{2.08}An$	30	1.6×10^{-9}	$3.61 \times 10^{+4}$	0·70
$Na_{2.08}An$	60	1.65×10^{-9}	$3.5 \times 10^{+4}$	0·68
$Na_{2.12}An$	30	5×10^{-9}	$8.9 \times 10^{+3}$	0·65
$Na_{2.12}An$	60	5.7×10^{-9}	$8.3 \times 10^{+3}$	0·63
$Na_{2.12}An$	220	6.3×10^{-9}	$7.4 \times 10^{+3}$	0·60

V_A is the voltage applied across the sample. In view of the low breakdown voltages it is interesting to note the slight change in σ with change in V_A. * Holmes-Walker and Ubbelohde, *loc. cit.*

Breakdown Voltages.—For reasons discussed by Daniel and Stark (*Trans. Faraday Soc.*, 1951, **47**, 149) the behaviour of the dielectric constant at low frequencies under D.C. polarising fields was though to be of interest. During these experiments indications were obtained of comparatively low breakdown voltages.

In order to obtain more accurate breakdown voltages, the E.H.T. voltage was applied directly to the cell with a sensitive milliamp-meter connected in series. The onset of breakdown or conduction could be detected by the sudden onset of current flowing through this meter. Difficulty was experienced in obtaining reproducible results owing to poor regulation of the radiofrequency E.H.T. voltage on load. Results recorded in Table 4 are accurate only to within several hundred volts/cm.

TABLE 4. *Breakdown voltages of alkali-metal–anthracenes at 20°.*

Substance	$Na_{1.7}An$	$Na_{2.0}An$	$Na_{2.08}An$	$Na_{2.12}An$
Breakdown voltage (kv/cm.)	11·4	9·1	6·1	5·3

DISCUSSION

Apart from information from magnetic measurements, which will not be further discussed here, three main lines of evidence about the nature of the bonding in these solid complexes can be discussed in the light of the experimental findings reported above.

Molar Volumes.—As pointed out previously (Holmes-Walker and Ubbelohde, *loc. cit.*), if the solid complexes approximate to close-packed ionic structures, the volume should be approximately the sum of the volume of the alkali-metal cation, and the anthracene anions. Though the volume of ions such as An^{2-} is not known, by analogy with other anions it is likely to be larger, but not much larger, than the volume of uncharged anthracene, as a result of electrostatic repulsive forces. The molar volume of the anthracene anions being written as (155·0 + Δ) c.c., where Δ is the enlargement due to the negative charges, the volume of a complex such as $(M^+)_2An^{2-}$ should be $V_{\text{complex}} = 2V_{M^+} + 155.0 + \Delta$.

Here V_{M^+} is the volume of the positive cation $= \frac{4}{3}\pi r_+^3 N$, where r_+ is the radius of the cation in ionic structures and N is Avogadro's number. The new results permit a much more complete check of this hypothesis, since comparisons can be made between the cations Li^+, Na^+, K^+, which have very different sizes and also exert different electrostatic fields at their surfaces of contact with the anions. Relevant data for the complexes Li_2An, Na_2An, and K_2An are given in Table 5.

Several interesting conclusions emerge from these results. The fact that $V_{An^{2-}}$ (col. 5) is approximately the same in spite of the very different molar volumes of the complexes is in accordance with the hypothesis of structures approximating to close-packed ionic. At

TABLE 5. *Molar volumes of complexes* M_2An.

M	Ionic * radii (r_+, in Å)	$2V_{M^+}$ (c.c.)	$V_{complex}$ (obs.)	$V_{An^{2-}}$ if wholly ionic	Δ (c.c. per mole)	Shrinkage on formation from metal and hydrocarbon (c.c.)
Li	0·60	1·1	163·6	162·5	7·5	17·4
Na	0·95	4·35	165·6	161·25	6·25	37·1
K	1·35	11·95	171·3	159·35	4·35	74·4

* From Wells, " Structural Inorganic Chemistry," Oxford, 1950.

the same time, the differences in Δ are probably real. These differences are found both in the values for M_2An, and for M_xAn with $x < 2$ which give smooth plots as functions of x (Fig. 1). Evidence referred to in the next sections suggests that these complexes of intermediate composition are solid solutions. Reasons for supposing that electron transfer is not 100% complete even up to the composition M_2An are discussed further below.

In alkali-rich complexes, so far studied only for sodium, additional metal atoms beyond the composition M_2An cause far less shrinkage. Volume increments rapidly approach the closeness of packing in metallic sodium itself (Table 6).

Thermodynamic Evidence.—No complete exploration of the phase equilibria has yet proved possible. Evidence so far obtained suggests that homogeneous solid solutions are formed over the whole range of values of x in M_xAn. The partial molal free energy of removal of one or other of the components from the complex has still to be studied quantitatively but the following indications are significant.

TABLE 6. *Molar volumes* (*c.c.*) *of* Na_xAn *with* $x > 2$ (*at* 20°).

		Increment (c.c.) over Na_2An :		
x	$M.V._{obs.}$	Obs.	calc. if Na is metal	calc. if Na is ion
2·08	166·7	1·1	1·9	0·35
2·12	168·3	2·7	2·85	0·53

(i) Anthracene can only be removed with difficulty from the solids, by sublimation, contrary to what would be expected if they consisted of hetero-crystalline mixtures of M_2An with anthracene. On elutriation with hot benzene, anthracene dissolves out progressively up to the composition M_2An, beyond which further removal in solution becomes very difficult. At ordinary temperatures around 20° the concentration of anthracene in equilibrium with M_xAn is about 0·5% (w/v), which is only one-sixth of the value for crystalline anthracene, again indicating solid solutions rather than a hetero-crystalline mixture.

(ii) On exposure of the complexes to the vapour pressure of sodium at 120°, a steady state is reached when $x \approx 2{\cdot}12$. This corresponds with very nearly one sodium atom in eight groups of Na_2An and may involve a new crystallographic packing.

Electrical Properties.—The solid complexes exhibit a range of rather special electrical properties, as may be expected on the basis of the interpretation that they consist of alkali-metal atoms dispersed in solid solution in the crystals of the aromatic hydrocarbon, with substantial but not complete transfer of electrons between alkali atoms and anthracene. Though no complete exploration of all these peculiarities has yet proved possible, the new findings permit certain leading conclusions to be made.

Electrical Polarisation of the Crystals.—From Table 2 it can be seen that the dielectric constant of the solid is practically independent of temperature over the range —40° to +40°. If the temperature coefficient had been similar to that found, *e.g.*, in solid hydrogen chloride above the " rotational " transition point (Böttcher, *loc. cit.*, p. 404), the value of ε at —40° would have decreased by about 10% at +40°. The inference is that in these complexes there is little or no freedom of orientation of any dipoles through the above range of temperatures. Actually there is a small increase in ε which may be due to increased polarisability at the larger molar volumes.

It is further noteworthy that the dielectric constant of the solids was found to be practically independent of the frequency from 50 Mc/s to 1 kc/s. Below about 1 kc/s there was a small increase (5%) in dielectric constant, possibly owing to a very small concentration of free ions in solid solution. By contrast, truly ionic crystals such as alkali halides show a large increase on passing from the refractive index of about $n^2 = 2\cdot2$ to the static dielectric constant $\varepsilon \approx 7$.

As a further test for the absence of free ions, the dielectric constant at low frequencies (1 kc/s) was measured whilst applying a high polarising field, of about 10^4 v/cm. With an equimolecular hetero-crystalline mixture of sodium chloride and anthracene, application of the D.C. field led to a small but definite drop in ε as a result of this freezing of the free ions present (Daniel and Stark, *Trans. Faraday Soc.*, 1951, **47**, 149). With the complexes M_xAn on the other hand no change in ε could be observed when the D.C. field was applied.

From the measured dielectric constants, it was desirable to determine whether there was much change in polarisabilities resulting from the change,

$$2\text{Na (gas)} + \text{anthracene} \longrightarrow \text{solid complex}$$

since such changes would throw light on the nature of the bonding.

There are two main conclusions. First, on formation of the complexes in the process $2M_{\text{gas}} + \text{An} \longrightarrow M_2\text{An}$ there is a big decrease in polarisability corresponding with the big shrinkage in volume : $(P_{\text{obs.}} - 56\cdot2 - 2P_{\text{M}^+})$ is a large negative quantity.

On the other hand, it will be seen that if cation polarisabilities are used, the calculated $P_{\text{An}^{2-}}$ though not wholly constant is reasonably consistent (Table 7). Much larger discrepancies would be obtained if atomic polarisabilities of the metal atoms were used as in the last column. Just as for the calculations of molar volumes, the polarisabilities give definite support to the hypothesis of electron transfer from the alkali metal to the anthracene. The difference $\Delta_2 = P_{\text{obs.}} - (P_{\text{An}} + 2P_{\text{M}^+})$ is of the same order as the change on forming I^- from I atoms $(P_{\text{I}^-} - P_{\text{I}} = 5$ c.c.). As in the case of the molar volumes, the variation in Δ_2 with the different alkali-metal atoms is probably real, and arises from the fact that transfer is not 100% complete at the composition M_2An. With lithium the bonding is more covalent than with, *e.g.*, potassium, owing to the more electropositive nature of the latter. In this connection it is noteworthy that ionic anthracene An^{2-} is likely to have higher polarisability than a covalent-bonded dimetal addition product, because of the greater delocalisation of electrons in the ion An^{2-} or ion MAn^-.

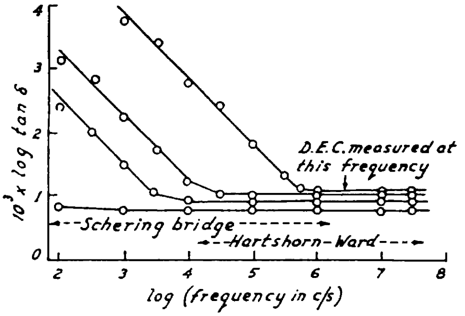


FIG. 3. *Dielectric loss for sodium complexes,* M_xAn.
Curves, from top to bottom: $\text{Na}_{2\cdot12}$An, $\text{Na}_{2\cdot0}$An, $\text{Na}_{1\cdot3}$An, anthracene.

TABLE 7. *Molar polarisations of complexes* M_2An (*c.c./mole*).

M	$P_{\text{obs.}}$	$2P_{\text{M}^+}$ *	$P_{\text{An}^{2-}}$ (if wholly ionic)	$\Delta_2 = P_{\text{obs.}} - (P_{\text{An}} + 2P_{\text{M}^+})$	$2P_{\text{M}}$ (gas)+ *
Li	61·4	0·30	61·1	4·9	60·6
Na	69·5	0·97	68·5	12·3	121·6
K	77·5	4·54	73·0	16·8	171·0

* From Syrkin and Dyatkina, " Structure of Molecules," London, 1952.

TABLE 8. *Polarisation in* Na_xAn *with* $x > 2$ (*c.c. mole*).

x	$P_{\text{obs.}}$	ΔP	Calc. contribution if excess Na present as free atoms
2·00	69·5	0	—
2·08	79·4	9·9	4·9
2·12	99·6	30·1	7·3

A second striking conclusion is that there is a relatively enormous increase in polarisability in complexes with $x > 2$(Table 8). The increment ΔP is markedly greater than that calculated for a dispersion of sodium atoms in Na_2An without any electron interaction. This agrees with the dark colour and general metalloid behaviour of these sodium-rich complexes, which begin to resemble alloys of electropositive metals with metalloid atoms.

Dielectric Loss.—Two loss mechanisms are indicated from a plot of log tan δ against log frequency (Fig. 3). A constant A.C. loss is evident for all the complexes with values of the order tan $\delta = 0{\cdot}010$. This compares closely with that for anthracene with measured tan $\delta = 0{\cdot}006$. The low value of loss is indicative of the absence of free or impurity ions, thus confirming the behaviour of the dielectric constant under polarising fields.

At low frequencies an abrupt change of slope to approximately 45° occurs. This is characteristic of D.C. conductivity. No corresponding increase in dielectric constant occurs, which shows that the conductivity is not of an ionic nature but must be electronic. This concurs with the observed increase in electron polarisation. The D.C. conductivity for complexes with $x < 2$ has already been examined by Holmes-Walker and Ubbelohde. Comparison of the observed losses and calculated losses by using $\delta = 2\pi$ f.c.r. with losses calculated from conductance values obtained by these workers shows fair agreement.

For the lowest frequencies (10^2 c/s), a slight tendency for the slope of the loss plot to decrease may be due to the limited ionic polarisation as suggested previously.

The absence of other loss phenomena is of interest. If complexes with $x < 2$ are regarded as dispersions of diluent hetero-crystalline anthracene in conducting crystals of M_2An, then a Maxwell–Wagner type absorption would be expected. The absence of such an absorption suggests that the excess of anthracene in such complexes is bound in some manner. Confirmation for this view is provided by electrostriction data. The evidence thus obtained agrees with the view that the excess of anthracene is distributed in the crystal to form a solid solution.

Dielectric Breakdown.—Comparatively low values of breakdown voltages of the order of 10^4 v/cm. were obtained for the alkali-metal complexes. This compares with values of 10^6 v/cm. for the alkali halides and with 6×10^3 v/cm. for powdered magnesium (Swann, Symp. on Static Electrification, *J. Appl. Phys.*, 1953).

Von Hippel (*Z. Physik*, 1936, **98**, 580) and Coulson ("Valence," Oxford Univ. Press, 1951) have suggested that in an insulator in a high electric field a small number of electrons will leave one of the fully occupied bands and move into the conduction band. The resulting conduction will occur probably by an electron-avalanche mechanism. If the electrons from the alkali-metal atoms acquire a limited degree of mobility, as suggested earlier, then the low values of breakdown voltage may be explained. The solid solution is thought to consist of a giant assemblage of neutral and ionised alkali-metal atoms, and neutral and negative anthracene molecules. Finite, but not very large, activation energy appears to be required for the electrons to migrate from one anthracene molecule to the next. Holmes-Walker and Ubbelohde have found values of the order of 1 ev for complexes with $x < 2$. Bowen (*J. Chem. Phys.*, 1945, **1**, 1) has shown that "exciton" migration is quite extensive in the anthracene lattice. Clearly, the low breakdown voltages must be caused by the increased electron mobility in the complexes and by the low activation energies required for electron migration. More evidence for bonding of anthracene in complexes with $x < 2$ is provided by the small differences in breakdown voltage with variation in alkali-metal content x. If the excess of anthracene is present as diluent hetero-crystals in M_2An, a considerable increase in breakdown voltage might be expected.

D.C. Electrical Conductivities.—New results with a method less liable to give difficulties due to breakdown effects and on the sodium-rich complexes are summarised in Table 3. The sodium-rich complexes still exhibit a positive temperature coefficient of conductance, showing that the electrons have to be activated to pass into a conducting energy band. The activation energies are notably smaller than those previously measured, indicating that as the proportion of alkali-metal atoms to anthracene molecules in the crystal increases, it becomes easier to delocalise the electrons giving rise to conduction.

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