Electron Transfer in Alkali Metal–Hydrocarbon Complexes.

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Solid complexes formed between lithium, sodium, or potassium and anthracene have been isolated in the solvent-free condition, and some of their physicochemical properties have been investigated.

By various procedures, the ratio of alkali metal (M) to anthracene (An) can be varied roughly within the range M_1An and M_2An. On formation of any of these complexes considerable electrostriction takes place, and the large " aromatic diamagnetism " is replaced by comparatively large paramagnetism, whose dependence on temperature and composition is reported. The complexes show semi-conductor behaviour with activation energy ranging from 1·36 to 0·76 ev.

From these and other properties it is suggested that the complexes are formed by a non-stoicheiometric electron transfer between the alkali-metal atoms and the hydrocarbon molecules.

The addition of potassium or bromine to graphite results in enhanced metallic properties (McDonnell, Pink, and Ubbelohde, *J.*, 1951, 191). From this it was inferred that layers of fused aromatic nuclei in graphite are able both to accept electrons from potassium atoms, and donate them to bromine atoms, yielding in both cases pseudo-metallic structures.

The present research was designed as an investigation of the bonding between alkali-metal atoms and networks of fused aromatic nuclei smaller than in graphite. Methods are described (*a*) of preparing addition compounds of anthracene with lithium, sodium, or potassium in various solvents, and of isolating and handling the solvent-free solids, and (*b*) of varying the composition of the sodium compounds in the range $Na_{1\cdot08}An$ to $Na_{2\cdot12}An$.

From measurements of electrical conductance on these solids, they appear to form a class of semi-conductors with positive temperature coefficient of conductance. This conductance is many times that of the parent hydrocarbon, and varies with the alkali metal and composition of the complex.

Magnetic measurements with sodium anthracene show that the diamagnetism due to the π-electrons of anthracene is destroyed. Instead, the complex is increasingly paramagnetic as the mole-fraction of the metal becomes greater. A tentative interpretation is that electron-transfer bonds (cf. McDonnell, Pink, and Ubbelohde, *loc. cit.*) are formed in the solid between the alkali-metal atoms and the hydrocarbon molecules. The solids described below have electronic analogies with solutions of alkali metals in liquid ammonia.

Experimental

Generally the addition complexes were formed by direct action between the alkali metal and the hydrocarbon, one of the solvents described below being used, in systems protected against access of oxygen or moisture. Access of direct sunlight was also prevented as far as possible by using black cloth wrappings on the vessel (Reid and Ubbelohde, *J.*, 1948, 1597). Special methods of manipulation described below permitted the filtration of excess of solvent from the solids, and the removal of any solvent of crystallisation. The dry solids were then examined for various physicochemical properties, by methods previously described (McDonnell, Pink, and Ubbelohde, *loc. cit.*) except where otherwise stated.

Preliminary experiments have also been carried out on the direct synthesis of the complexes by bombarding the warm crystals of the hydrocarbon with atoms of the alkali metal. These experiments showed promising results, but are not further detailed.

Materials.—Nitrogen. Nitrogen (British Oxygen Co.) was carefully freed from oxygen by passage over copper turnings at 500° and dried by passage through a " Birlec Lab Lectrodryer." All future references to nitrogen imply gas purified as above.

Anthracene. This had setting point 215° as obtained " pure " from the Deutsche Gesellschaft fur Teerverwertung. Though other hydrocarbons form addition compounds more readily, it was important to lessen the burden of exploratory work by selecting an easily available substance.

Alkali metals. Sodium was cleaned by cutting away most of the oxide in air, transferring the metal to a tube continuously swept out by nitrogen, and then again cutting shavings from all faces of the cubes. Metal thus obtained remained brightly reflecting for at least 2 min. after cutting, but then slowly lost its polish, possibly owing to surface recrystallisation. It started to react immediately when added to anthracene suspended in a solvent.

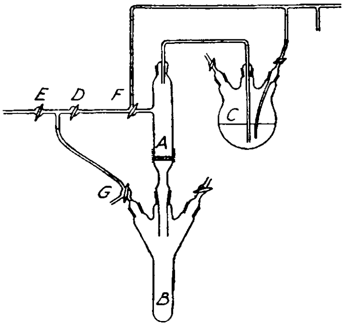


FIG. 1. *Apparatus for preparing potassium anthracene.*

Lithium (B.D.H. 98% pure) was freed from mineral oil with filter-paper, and then treated in the same way as sodium.

Potassium (B.D.H. " pure ") was scraped as free as possible from oxide, filtered through a glass capillary *in vacuo*, and then distilled with the precautions previously described (*idem, loc. cit.*).

Solvents. All solvents were rigorously dried and purified unless otherwise specified. Diethyl ether was purified as described by Mackle and Ubbelohde (*J.*, 1948, 1161). Dimethoxyethane, recommended as a solvent because of its low C : O ratio (Scott, Walker, and Hansley, *J. Amer. Chem. Soc.*, 1936, **58**, 2442; Jeanes and Adams, *ibid.*, 1937, **59**, 2608), was not conveniently available.

Particularly where a higher temperature was advantageous, some preparations were achieved with " AnalaR " dioxan refluxed over sodium and distilled off the metal in the range 100—101·5°. Generally, however, preparations with diethyl ether were more straightforward.

Preparation of Complexes.—Previous methods were not concerned with preparation of the complexes completely free from solvent (Schlenk, *Ber.*, 1914, **47**, 473; Scott *et al.*, *loc. cit.*). After some investigation two useful methods were developed for preparing the solids in a solvent-free condition.

The apparatus (Fig. 1) was suitable for comparatively involatile solvents such as dioxan. It was first swept out with nitrogen as far as tap *E*. Gas flow was adjusted by the rate of bubbling through the solvent in the three-necked flask *C*. A weighed amount of anthracene (about 2 g.) and about 100 ml. of dioxan were then placed in the sintered-filter vessel *A*. An upward stream of nitrogen served to prevent any filtration at this stage, and also prevented entry of air at the top of *A*. Excess of alkali metal M, about 20% over the amount required for the complex M_2An, was added to the mixture in *A*, counter-currents of nitrogen being used to protect the metal. A heater was used to raise the temperature and increase the solubility of the anthracene in dioxan. However carefully the dioxan had been purified, at first a transparent skin formed on the metal. Possibly this was due to the transformation to acetal (Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier Publishing Co., Inc., 1950, p. 502) with concurrent formation of metal oxide. This skin slowed down the reaction, but above the m. p. globules of metal burst through. As the reaction proceeded slowly, a strong blue colour developed round the metal. When the b. p. of the solvent was reached, the whole solution became an intense royal-blue, which gradually changed to the deep green described by Scott *et al.* (*loc. cit.*). After about 1 hr., during which the nitrogen pressure was controlled by a mercury U-tube gauge, the hot solution was filtered into *B* by suitable operation of the taps *D, E, F,* and *G*. All insoluble matter remained on the filter. The hot, deep green filtrate on cooling deposited dark green crystals. However, these tended to become yellow if kept in dioxan for long periods. To obviate this, the dioxan was sucked off. Any dioxan adhering to the crystals was replaced by successive decantations with diethyl ether. The potassium anthracene complex was dark green, and became bluer as the dioxan was replaced by ether. The solvent-free complex was grey. The above method was used for the potassium compound, where the higher temperature was an advantage. However, in view of the slow interaction of the complex with dioxan, the following method was developed for lithium and sodium compounds.

Anthracene (2—3 g.) was added to diethyl ether (200 ml.) under nitrogen in a three-necked flask. On introduction of an excess of lithium or sodium protected by nitrogen, and mechanical stirring, the reaction started immediately. Within 10 min. the whole solution was deeply coloured—purple in the case of lithium, and indigo with sodium. After some 48 hr. or so the stirring was stopped, and the ethereal layer siphoned off. The coloured solid was washed by decantation with several portions of ether. When the remaining ether was removed by increasing the flow of nitrogen, the deep colour—purple with lithium, and blue-green with sodium—remained until all traces of ether were removed. The resulting homogeneous powder was yellow for lithium, and a red-pink for sodium. Any pieces of metal which had not reacted could then be picked out, as they remained bright.

Potassium was difficult to be made to react under ether. Ampoules of the redistilled metal had to be broken in the flask, and any exposed metal rapidly became covered with blue product. The reaction then stopped.

Densities.—In connection with the measurements of magnetic properties, rough determinations were made of the bulk densities in the Gouy tubes. Results are recorded in Table 1. Measurement of the true density was made on a sample of sodium anthracene under nitrogen, a conventional pycnometer being used. Purified Nujol, used as the fluid, was dried by keeping it at 120° for 12 hr. while nitrogen was bubbled through it. The measured density of sodium anthracene $Na_{1\cdot70}An$ at 20° was 1·33 g./c.c. Similarly the density at 20° of $Na_{1\cdot60}An(Et_2O)_{0\cdot30}$ was 1·26 g./c.c.

Analysis of Products.—Direct action of water or dilute acids on the solids produced tars. This suggests the intermediate liberation of free radicals which polymerise. After some investigation two methods were found to be satisfactory.

(1) A sealed ampoule containing the solid was weighed and broken into about 100 ml. of 50% aqueous methyl alcohol. A known volume of standard hydrochloric acid was added. After the liberated hydrocarbon had been filtered off and washed, the solution was made up to a known volume and titrated against standard sodium hydroxide solution, with bromocresol-green as indicator. The amount of acid neutralised was proportional to the sodium present in the compound. The hydrocarbon recovered melted at 110° and appeared to be dihydroanthracene. This analysis was quite straightforward provided small amounts of complex were used. With amounts greater than 0·5 g., intermediate products were obtained which prevented a true end-point in the titration.

(2) A weighed ampoule containing the solid complex was broken into benzene. The sodium was then removed by washing with water, and weighed as sulphate. Finally, the hydrocarbon produced in the benzene layer was isolated; from the solid with approximate composition Na_2An it was identified as dihydroanthracene.

Determination of retained ether. Following an unpublished method developed by Nichol and Ubbelohde, ether is oxidised in the cold on being kept with an excess of strongly acidified dichromate solution. Unchanged dichromate is determined by back-titration against standard ferrous ammonium sulphate solution.

Ether was removed from a weighed amount of the highly coloured complex, which retains it only moderately, by passing a stream of nitrogen, and was collected by passing the gas through a liquid-air trap. The contents of the trap were treated with 20 ml. of 0·5N-potassium dichromate solution previously acidified with 20 ml. of concentrated sulphuric acid. Separate tests showed that after 20 min. the ether was quantitatively oxidised to acetic acid. The unchanged dichromate was estimated by back-titration against 0·5N-ferrous ammonium sulphate solution, *N*-phenylanthranilic acid being used as indicator. The composition established by analysis (see Table 1) suggests that part of the ether was lost during handling. The dark, highly coloured powders studied may have consisted of a mixture of solvated complex and solvent-free crystals. Co-ordination of the solvent appears to play a part in the structure of the highly coloured compounds formed in electron-donor solvents, in view of the change in colour observed when the last traces of solvent are removed. This possibility was left for future study, since, as explained above, the present paper deals primarily with the solvent-free solids.

Magnetic Measurements.—Susceptibility measurements were made at 90° K and 288° K by the Gouy method already described (McDonnell, Pink, and Ubbelohde, *loc. cit.*). The field strength used was approx. 3600 gauss. Results are recorded in Table 1.

TABLE 1. *Magnetic susceptibilities* (*c.g.s. units* × 10^6) (χ_m is based on 1 mole of anthracene throughout).

Substance	90° K χ_s	90° K χ_m	288° K χ_s	288° K χ_m	Bulk density (g./c.c.)
Anthracene (An)	—	—	−0·718	−127·9	0·389
$Na_{1\cdot42}An$	+0·502	+105·6	+0·183	+ 38·4	0·360
$Na_{1\cdot70}An$	+0·510	+110·7	+0·082	+ 17·8	0·403
$Na_{1\cdot96}An$	—	—	+0·338	+ 75·4	0·408
$Na_{2\cdot02}An$	+3·86	+864·6	+3·25	+728·1	0·300
$Na_{2\cdot12}An$	—	—	(+1·22)	(+262·0)	0·302
$Na_{1\cdot60}An(Et_2O)_{0\cdot30}$	(+0)	(±0)	+0·255	+ 60·3	0·398

Notes. (1) The results for $Na_{2\cdot12}An$ are less reliable, owing to the smaller quantities available. (2) The values for $Na_{1\cdot60}An(Et_2O)_{0\cdot30}$ are within experimental error approximately zero at 90° K. Fluctuations were obtained in successive readings.

Electrical Conductance (σ) *of Solids.*—The apparatus used (Fig. 2) was a modification of that used by McDonnell, Pink, and Ubbelohde (*loc. cit.*). Electrodes were of copper. All measurements were made under nitrogen, and the solid complex was introduced into the cell chamber by rotation at the greased joints *C* and *E*. Temperature variation was effected by means of a small air-furnace wound on a Pyrex tube lagged with asbestos, and fitted with baffle-screens to eliminate temperature fluctuations; 220 volts D.C. was applied across the electrodes, and the resulting currents were measured with a sensitive galvanometer and optical system, giving resistance measurements up to 2 × 10^{13} ohm. A typical plot of resistance–column height is given in Fig. 3. The curve is not a straight line, possibly owing to very slight irregularities in column packing. Fig. 4 illustrates plots of log $_{10}\sigma$ against $1/T$. In two cases at least this representation of the plot by a single straight line is inadequate; these are shown in Fig. 5. The electrical parameters are summarised in Table 2.

TABLE 2. *Electrical conductance of anthracene and its complexes.*

Substance	Conductance (ohm^{-1} cm.$^{-1}$), $10^{12}\sigma$	Concn. of metal, x in M_xAn	$10^5\sigma_0$ (ohm^{-1} cm.$^{-1}$)	E (ev)
Li anthracene	7·73	1·16	335	1·32
	4·54	1·16	907	1·36
K anthracene	6·38	1·18	445	1·10
	5·29	1·18	1,773	1·13
	14·2	1·18	473	1·07
Na anthracene	45·3	1·08	288,400	1·20
	341	1·42	513,300	1·16
	714	1·70	10·3	0·88
	1885	2·02	0·191	0·76
	320	2·12	3·2 × 10^{-5}	0·58
	5040		66·0	0·99
$Na_{1\cdot60}An(Et_2O)_{0\cdot30}$	16·1	1·60	2·56 × 10^{-9}	0·13
	41·7		4,055	1·23

Notes. (1) Values of *E* and σ_0 are calculated from the expression $\sigma = \sigma_0 e^{-E/kT}$, where σ is the specific conductance at temperature *T*. (2) The values of σ quoted are at 293° K for all substances except Li anthracene which is calculated for 353° K. (3) The values for *E* are the mean values of the results obtained by calculation of lines of closest fit (cf. Figs. 4 and 5).

Where the log σ–$1/T$ plots break up roughly into two straight lines, two values are given.

Electrical Conductance of Solutions.—Scott *et al.* (*loc. cit.*) reported that the coloured solutions of sodium naphthalene in dimethoxyethane were "highly conducting," but it appears possible that this conductance was due, at least in part, to sodium hydroxide formed by traces of water in the systems described. When the solvent-free solids were added to solvents such as dioxan, diethyl ether, anisole, or benzene, the dark solutions were not re-formed, but instead a brown suspension was obtained. Thus the change from highly coloured solids to the solvent-free solids on removing all the retained solvent is not readily reversible. Mercury had no visible effect on the coloured solutions or the solvent-free complexes, unlike its effect with more reactive complexes (Schlenk, *loc. cit.*).

An attempt was made to measure the conductance of solutions of sodium anthracene. A pair of platinum electrodes, each 0·6 cm. × 1·3 cm. and 0·2 cm. apart, were used at temperatures from 0° up to 100°, at which the concentration of dissolved material was about 3 g. per 100 ml. of solvent. The specific resistance was greater than 10^{12} ohm cm. in both ether and dioxan solutions of the dark solvated or lighter coloured unsolvated complexes. However, in pure dry anisole, prepared by the general methods described for ether, a new phenomenon was observed. The specific resistance of the solvent was greater than 10^{12} ohm cm. When excess of the solvent-free sodium anthracene $Na_{1\cdot70}An$ was added, the resistance remained high, but the suspended particles showed a tendency to migrate towards the anode. On gradual rise of the temperature to the b. p. of anisole, the resistance gradually decreased to about 4×10^{10} ohm cm. The colour of the suspended solid deepened from brown to almost black, and now it tended to cluster round the cathode. By degrees, " bridges " were formed across to the anode. When the current was switched off, the solid fell away, to repeat the phenomenon as soon as the current was switched on again. On cooling, the resistance slowly rose. After a day or so the brown colour was restored to the solid, which was once more attracted to the anode. Samples taken from the supernatant anisole solution showed differential extraction of

FIG. 2. *Electrical conductance apparatus.*

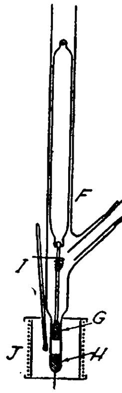


FIG. 3. *Electrical resistance of sodium anthracene.*

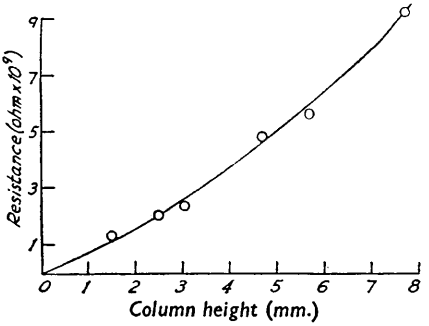
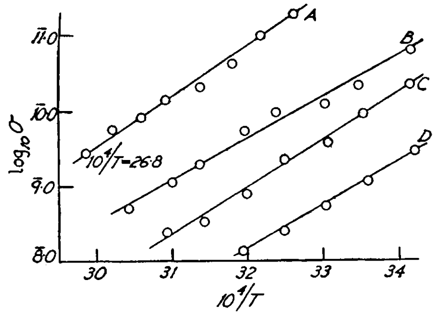


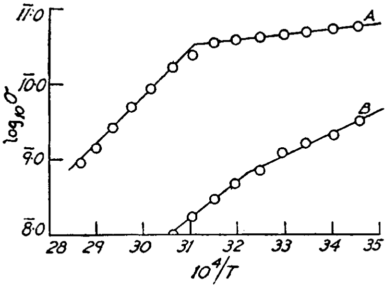
FIG. 4. *Logarithmic plot of specific conductance.*



*Curve A * represents values for* $Li_{1\cdot16}An$.
,, *B* ,, ,, $K_{1\cdot18}An$.
,, *C* ,, ,, $Na_{1\cdot08}An$.
,, *D* ,, ,, $Na_{1\cdot42}An$.

* Note shift of zero on the *x*-axis for this curve.

FIG. 5. *Logarithmic plot of specific conductance.*



Curve A represents values for $Na_{1\cdot60}An(Et_2O)_{0\cdot30}$.
,, *B* ,, ,, $Na_{2\cdot12}An$.

anthracene from the complex, as described below. Extraction of anthracene by the anisole was also shown by the marked fluorescence of the clear solution at the higher temperature.

Physicochemical Stability of the Complexes.—Stability towards air or water varied considerably with the amount of solvent present. The ethereal sludge containing the deeply coloured solid decomposed rapidly. Even when all the easily removed ether was driven off, the highly coloured complexes reacted violently with air or water. When all traces of retained solvent had been removed, decomposition of the much less highly coloured unsolvated solids was rapid but less violent.

The physicochemical stability of the solvent-free sodium complexes was tested more extensively in two further ways. When heated in a high vacuum the compounds remained unchanged up to 60°. At about 80° the solid began to darken, and a white sublimate appeared. Mixed m. p. tests confirmed that this sublimate was anthracene. Slight further darkening occurred up to 500°. At 550° the residue rapidly shrivelled and blackened.

Other samples of the solvent-free sodium complexes were washed on a sintered-glass filter under nitrogen with successive aliquot portions of a solvent. Both benzene and ether were used, as shown in Table 3. When the solutions were analysed, as above, the results showed that the solid initially lost more anthracene than sodium until it reached a limiting composition approximately corresponding to Na_2An. The amount of sodium recovered from each washing remained constant for a particular solvent, and was greatly increased if the solvent was not perfectly dry.

TABLE 3. *Analysis of fractions after sodium anthracene had been washed with successive aliquot portions of solvent.*

Solvent	Component	Millimoles of substance per 10 ml. of solvent in washing no.: 1	2	3	4	5	6
Benzene	Anthracene	0·124	0·018	0·017	0·018	0·018	0·017
	Sodium	0·028	0·035	0·035	0·035	0·032	0·035
Ether	Anthracene	0·140	0·020	0·017	0·018	0·016	0·017
	Sodium	0·035	0·034	0·035	0·032	0·032	0·032

X-*Ray Examination of Sodium Anthracene.*—Very thin Pyrex specimen tubes filled and sealed off under nitrogen being used, *X*-ray photographs were taken by means of an Ubbelohde multiple-exposure camera with Cu radiation and Ni filter. Pure anthracene and several specimens of sodium anthracene, with compositions ranging from $Na_{1\cdot40}An$ to $Na_{1\cdot96}An$, were examined. With increasing mole-fractions of sodium, there was a gradual replacement of some of the lines due to anthracene, and a strengthening of others, as if solid solution was taking place. Further analysis awaits detailed comparisons with the corresponding potassium complexes and, if possible, study on single crystals.

DISCUSSION

Electro-striction on Complex Formation.—From the density measurements, the volume of $Na_{1\cdot70}An$ containing 1 mole of anthracene is 163·4 c.c. This compares with 155·0 c.c. per mole of pure anthracene, and 40·3 c.c. corresponding with the amount of pure metallic sodium present. As in the case of potassium graphite, the volume shrinkage, $155\cdot0 + 40\cdot3 - 163\cdot4 = 31\cdot9$ c.c., is much too large to be accounted for in terms of isolated atoms of sodium dispersed in some way in the anthracene without any strong electron interaction. Some kind of electrostriction is indicated. Suppose the change in volume of anthracene after electron transfer to form An^- is Δ c.c. per mole. If a close-packed ionic compound $(Na^+)_2\ An^-$ is formed, the molar volume of Na^+ can be calculated to be 3·67 c.c. from the equation $V = 1\cdot70N(4/3\pi r^3)$, where N is Avogadro's number, and $r = 0\cdot95$ Å is the radius of the Na^+ ion. The volume of such a complex would be $155\cdot0 + \Delta + 3\cdot67$ c.c. Though the increment Δ cannot yet be assessed acurately, it is likely to be a small positive value. The near correspondence between $158\cdot67 + \Delta$ c.c. and the observed 163·4 c.c. suggests that the structure may be nearly but not wholly ionic.

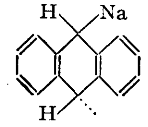
A similar calculation can also be made for the results on the complex $Na_{1\cdot60}An(Et_2O)_{0\cdot30}$. This gives a volume of 188·1 c.c. containing 1 mole of anthracene. Allowing 30 c.c. for the 0·30 mole of ether, the net contraction in this case is thus $155\cdot0 + 37\cdot9 + 30 - 188\cdot1 = 34\cdot8$ c.c. This contraction is even larger than for the solvent-free complex, suggesting that electrostriction may be greater in the solvated complex.

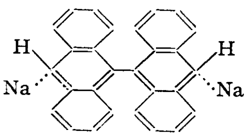
Marked electrostriction would be expected if every atom of sodium in the crystal Na_2An transferred one electron to the neighbouring anthracene molecule, thus forming a truly ionic compound $(Na^+)_2\ An^=$, similar, for example, to Na_2S. Reasons for supposing that the structure is not simply salt-like are discussed below. The model at present envisaged consists of a crystal in which different fractions of the lattice sites are occupied by An molecules carrying charges -2, -1, and 0. The neighbouring sodium atoms carry charges $+1$ or 0, so as to preserve substantial electrostatic neutrality over any plurality of sites. This model is equivalent to saying that there is transfer of electrons in the crystal on a statistical basis, but not 100% stoicheiometric transfer. The electrical conductivity results from movements of electrons in the crystal, as in Pauling's theory of metals. However, the fact that the conductivity shows marked activation energy indicates that, unlike the position in true metals, there must be appreciable potential barriers opposing conduction in our solids.

Magnetic Properties.—Results show that the large " aromatic " diamagnetism of the anthracene is replaced by paramagnetism. This behaviour is again parallel with that of potassium graphite, except that with anthracene complexes the paramagnetic susceptibility generally increases with falling temperature. Temperature dependence is particularly marked for solids whose overall analysis shows a ratio of sodium to anthracene well below 2 : 1.

One explanation could be that the solid complexes include some " free-radical " monosodium anthracene (I). The formation of such a radical in solution is suggested by Schlenk (*loc. cit.*) and is also indicated by the production of the bright blue colour in the early stages of the dioxan preparations which later gave place to the dark green colour. With methods of preparation at present available it cannot be decided whether such a free radical is in solid solution, or whether it is present as a pure crystalline component in a mixture of crystals. The hydrocarbon recovered from chemical analysis, and from elutriating the solids with excess of solvent, indicates that no appreciable amounts of dianthracene derivatives (II) such as are formed in the solid (cf. Schlenk and Bergmann, *Annalen*, 1928, **463**, 1). Alternatively, if they are formed, coupling between mono-radicals in the solid must be fairly labile and easily dissociated by excess of sodium atoms such as would be left on extraction of some of the anthracene.

(I)





(II)

Because of this uncertainty in the distribution of sodium atoms and free valencies in the solid, the magnetic and electrical properties quoted for the solids should for the present be regarded as illustrative of the order of magnitude encountered in the different preparations. Thus it may be found that, when prepared in slightly different ways, the properties of the solids show fairly large differences in magnetic behaviour. The high susceptibility indicated for Na_2An is of the same order as for some of the metallic rare earths. Further studies are being made as stated below. Electrical properties of different samples were quite reproducible, but insufficient magnetic measurements could be achieved to test whether this was also true for the magnetic properties. The free radical would appear to have one uncoupled spin, and would thus exhibit increasing paramagnetism with falling temperature (Selwood, " Magnetochemistry," Interscience Publ., New York, 1943).

When the ratio of sodium to anthracene rises, the paramagnetism is greatly increased, but the temperature coefficient sinks to a much lower value. Eventually the paramagnetism becomes comparable with the values observed per g.-atom of sodium in sodium–ammonia solutions (see below).

Electrical Conductance.—The solids show marked positive temperature coefficients. For complexes with approximately the same composition activation energies are in the same sequence as the ionisation energies of the metals (Table 4).

Apart from variation in the alkali metal, the effect of varying the composition with a given alkali metal has noteworthy effects on the conductance parameters, as might be expected if the solid behaves as a semi-conductor with an adjustable number of electron-donor atoms and electron-acceptor molecules in the crystal.

TABLE 4.

Compound	E (ev)	Ionisation potential, I	E/I
$Li_{1\cdot16}An$	1·34	5·39	0·25
$Na_{1\cdot08}An$	1·20	5·14	0·23
$K_{1\cdot18}An$	1·10	4·34	0·25

As the anthracene is progressively extracted by elutriation from the solid, the electrical conductance rises steeply, and the activation energy E sinks (Table 2). This might perhaps be attributed to the removal by the solvent of diluent crystals of anthracene, or of monosodium anthracene, from a more highly conducting disodium anthracene. However, the accompanying changes in magnetic properties (Table 1) indicate that solvent-extraction of some of the hydrocarbon involves a much more fundamental change for the mobile π-electrons than would be realised merely on removing one component from a mechanical mixture of different crystals. Further discussion is deferred pending the investigation of more highly compressed powders and of complexes with other aromatic molecules.

When a solvent-free solid is compared with a solid retaining some ether (Figs. 4 and 5), notwithstanding striking differences in colour, the properties are similar. Too much weight cannot be put on this conclusion, since analysis suggests that part of the ether was lost during handling. Fig. 5*A* may indeed refer to mechanical mixtures of ether-retaining and solvent-free complexes.

Analogy between the Alkali Metal–Hydrocarbon Solids and Alkali Metal–Liquid Ammonia Solutions.—As has been described above, the changes in properties observed on removal of anthracene, by extraction with solvents or by vaporisation, suggest that the complexes behave as solid solutions with semiconducting properties.

Considerable attention has been devoted to the remarkable physical and chemical properties of solutions of alkali metals in liquid ammonia (Hüster, *Ann. Physik*, 1938, **33**, 498; Farkas, *Z. physikal. Chem.*, 1932, **161**, 355; Krauss and Lucasse, *J. Amer. Chem. Soc.*, 1922, **44**, 1941, 1949). It is suggested that the alkali metal–hydrocarbon solids now isolated have analogous properties in certain respects. Compared with this particular hydrocarbon, at corresponding bulk concentrations the specific conductance is much higher with ammonia as solvent for the sodium. But although the conductances differ widely for the two systems, in the solid complexes now studied allowance must be made for considerable intergranular resistance (cf. McDonnell, Pink, and Ubbelohde, *loc. cit.*). The conductance of sodium anthracene shows a steep rise with increase in mole-fraction of sodium, not unlike the rise for $Na–NH_3$. This suggests that the electrons from the sodium atoms acquire a limited freedom of mobility in the solid owing to the (moderate) electron affinity of the anthracene. The solid solution may be thought to consist of a giant assemblage of neutral and ionised sodium atoms, and neutral and negative anthracene molecules. Some bond formation may also occur between neighbouring anthracene molecules in 10 : 10′-positions. Finite, but not very large activation energy appears to be required for the electrons to migrate from one anthracene molecule to the next. Bowen (*J. Chem. Phys.*, 1945, **13**, 306; *Quart. Reviews*, 1947, **1**, 1) has shown that migration of "excitons" is quite extensive in the anthracene lattice.

In making magnetic comparisons with $Na–NH_3$, intercrystalline barriers in the powders should have much less influence. On the convention that the susceptibility of the electron-accepting molecule (ammonia or anthracene) remains constant, this is subtracted from the combined value for the complex to obtain the apparent susceptibility of the dissolved sodium atoms, in Table 5.

TABLE 5. *Apparent atomic susceptibility of sodium in sodium anthracene.*

Compound	$Na_{1\cdot42}An$	$Na_{1\cdot70}An$	$Na_{1\cdot96}An$	$Na_{2\cdot02}An$
$10^6\,\chi_{Na}$	+117·0	+85·7	+103·7	+424·0

Though the numerical results must be regarded with caution, it seems noteworthy that in the Na–NH_3 systems the susceptibility of sodium reaches quite similar values of paramagnetism, but at higher dilutions.

So far as it goes, the present evidence is against the possibility that electron transfer in the complexes proceeds as far as complete ionisation. The shift of the ultra-violet absorption bands of the anthracene into the visible region, owing to partial transfer of the electrons to anthracene in the solvated and solvent-free complexes, may be compared with effects in the spectra of other substituted aromatic hydrocarbons. The inclusion in the nucleus of electron-donating groups such as NH_2 or CH_3 is well known to cause a shift toward longer wave-lengths. Sodium anthracene is probably more like sodium antimonide than sodium nitride in the electronic character of the solid. Analogies can also be suggested with some of the metallic sulphides, selenides, and tellurides.

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