furnishes a convenient and accurate determination of particle diameter.

None of the methods of study employed here has been applied to all of the available samples. The limitations are imposed by the availability of sources and, in some cases, by the geometries of the measuring apparatus. With light sources in the near-ultraviolet, the powder pattern technique could be extended to smaller samples. A blue laser would facilitate single-crystal studies, while sources and detectors in the near-infrared would permit the latex reflectance studies to be applied to the larger particle diameters.

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The Electrical Conductivity of Some Acridizinium Compounds

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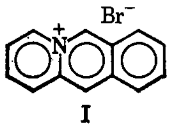
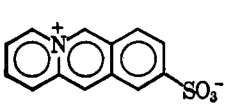
Contribution from the Department of Chemistry, Duke University, Durham, North Carolina. *Received December 1, 1967*

Abstract: Measurements of the electrical conductivity (dark) of the following solid acridizinium-type compounds have been made over a range of temperatures and the activation energies for conduction determined. These included acridizinium bromide, perchlorate, and anthraquinone-2-sulfonate and the betaine of 9-sulfoacridizinium hydroxide (a zwitterion), as well as the conductivity of a higher member of the series, 12a,14a-bis(azonia)pentaphene.

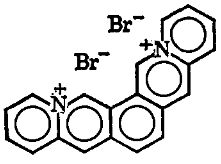
In recent years fairly extensive measurements have been made of the electrical conductivity of solid organic compounds of certain classes such as polynuclear hydrocarbons, long-chain polymers, and dyes.[3] Since no electrical measurements have been reported on compounds of the general type of acridizinium bromide (I), the dark conductivity of I was determined as well as that of a series of related compounds. These included two other salts, acridizinium perchlorate (II) and anthraquinone-2-sulfonate (III), the betaine of 9-sulfoacridizinium hydroxide (IV), which is a zwitterion, and the hydrate (V) and dimer (VI) of acridizinium bromide. Measurements were also made on a higher member of the series, 12a,14a-bis(azania)pentaphene dibromide (VII).



I



IV



VII

The acridizinium cation in some of these compounds has a fairly close structural similarity to the anthracene molecule, and the conjugated ring system involved is essentially the same as that found in a number of other organic semiconductors. In view of this, a number of measurements on anthracene were carried out to provide a reliable comparison base for the data, using the same apparatus and procedural techniques as those employed for the acridizinium compounds.

The series of salts (I–III) was of interest in connection with possible ionic contributions to the conductivity because of the wide variance in the size of the anions involved, and the conductivity data for the zwitterion IV provided a comparison case in which such ionic contributions were not possible. The fact that the bromide (I) is actually prepared first as a monohydrate (V) made it possible to determine and compare the conductivity of the hydrated and anhydrous forms, a matte orf considerable interest as there are very little data in the literature regarding the conductivity of hydrates.

Experimental Section

A. Materials. **Acridizinium bromide** (I) was prepared by the method of Parham.[4] The cyclic acetal of picolinaldehyde [2-(1,3-dioxolan-2-yl)pyridine] was mixed with 10% excess of benzyl bromide and dissolved in the minimum possible amount of tetramethylene sulfone; the mixture kept 2 days at room temperature. The viscous product was washed (ethyl acetate), dissolved (methanol), and crystallized (methanol–ethyl acetate), and the resulting white quaternary salt was cyclized by refluxing for 18 hr in 50% HBr. The HBr was removed *in vacuo* giving crude yellow acridizinium bromide (85% yield) which was crystallized alternately from ethyl acetate–methanol, and from H_2O until a constant melting point was obtained. The final product melted with decomposition at 245–246° and was a monohydrate which on prolonged drying at 110° lost 6.5% of its weight (calculated loss, 6.48%) to give the anhydrous acridizinium bromide.

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[1] Based in part on the dissertation submitted by J. D. Bashaw for the degree of Doctor of Philosophy at Duke University.

[2] Author to whom inquiries should be addressed.

[3] F. Guttman and L. E. Lyons, "Organic Semiconductors," John Wiley and Sons, Inc., New York, N. Y., 1967, *cf.* pp 706–767.

[4] J. C. Parham, Ph.D. Thesis, Duke University, Durham, N. C., 1963.

Acridizinium Perchlorate (II). Excess $HClO_4$ was added to a hot aqueous solution of I cooled to room temperature, and the precipitated yellow acridizinium perchlorate was recrystallized (H_2O) to mp 204–205°. This salt decomposed less on melting than the bromide.

Acridizinium Anthraquinone-2-sulfonate (III). An excess of aqueous sodium anthraquinone-2-sulfonate solution was added to a hot aqueous solution of acridizinium bromide and cooled to room temperature, and the crystals of the sulfonate salt were recrystallized (H_2O) to a constant melting point of 272–273°. On melting there was complete decomposition. Since this compound had not been previously characterized, it was analyzed.

Anal. Calcd for $C_{27}H_{17}O_5NS$: C, 69.36; H, 3.67; N, 3.00; S, 6.86. Found: C, 69.09; H, 3.83, N, 2.96; S, 6.79.

Betaine of 9-Sulfoacridizinium Hydroxide (IV). This was prepared by the method of Bradsher and Parham,[5] which differs from that described for I above in the substitution of methyl *p*-(bromomethyl)benzenesulfonate for benzyl bromide in the quaternization step. Furthermore, there is loss of the methyl group in this step, leaving a negative charge on the SO_3^- group so that the final compound (IV) is a zwitterion which is only slightly soluble in methanol. It was recrystallized from water and melted with decomposition at 404°. It is characterized by unusual thermal stability, showing gradual darkening only at temperatures above 370°.

Acridizinium Bromide Monohydrate (V). This was obtained in the course of the preparation of the anhydrous bromide I, as described above.

Dimer of Acridizinium Bromide (VI). This was prepared from the solid monomeric monohydrate of acridizinium bromide by irradiation with ultraviolet light for several days with occasional stirring of the solid as described by Bradsher, Beavers, and Jones.[6] These workers also presented evidence from boiling point elevation measurements in ethanol solutions of the dimeric state of the irradiated solid. Heating of the solid results in dissociation and some decomposition so that measurements on the anhydrous dimer could not be made.

12a,14a-Bis(azania)pentaphene Dibromide (VII). C. K. Bradsher of this department kindly provided a sample of this dibromide, the synthesis of which is described by Parham.[4]

Anthracene. Measurements were made with anthracene samples of three kinds: Eastman fluorescence grade, 480X, Eastman "hyperpure" grade 480H, and also with single crystals produced by the Harshaw Chemical Co.

B. Apparatus and Procedures. These were essentially as dedescribed in considerable *detail in an earlier publication.*[7] They need not be repeated here except to note minor modifications in the construction of the conductivity cell used in the present measurements. Most of the measurements, as in the work previously described, were carried out with samples consisting of compressed powder wafers 2.85 cm in diameter and varying in thickness from 0.8 to 2.0 mm. By repeated trials the pressures were determined which were required to obtain essentially void-free sample disks. These ranged from 340 atm in the case of anthracene to as high as 4100 atm for acridizinium bromide. The absence of significant voids was confirmed by comparing the calculated densities of the disks with the crystal densities of anthracene and acridizinium bromide. It was assumed that the pressures employed in the case of acridizinium bromide were sufficient for the other acridizinium compounds which were only available in smaller quantities from which to prepare the disks.

In the case of most of the materials void-free disks of 2.85-cm diameter were successfully prepared. A thin circular film of aluminum (1.9-cm diameter) was deposited at the center of both sides of the disks by evaporation of aluminum under high vacuum from a hot tungsten filament. The two circular films on opposite sides of the disk made contact with two massive circular copper blocks of the same diameter (1.9 cm) which were the contact electrodes of the cell assembly. A thin grounded copper ring, 1.5 mm thick, 6 mm high, and of 2.85-cm o.d., placed on the periphery of sample disk served as a guard ring. This ensured that the measurements gave values for the bulk conductivities between the 1.9-cm diameter electrodes and did not include surface conduction components.

In the cases where only limited amounts of material were available and smaller disks (1.27-cm diameter) or smaller areas (as in the case of anthracene single crystals) were being measured, a sample holder using small pools of mercury as the contact electrodes was employed. In this the sample is sandwiched between two square (25 × 25 mm) Teflon plates. The lower plate is 4.5 mm thick and has a circular well 6 mm in diameter in the center and 3 mm deep, which is filled with mercury just to the top. A circular guard ring of thin copper coil of 10-mm i.d. (o.d. 12.7 mm) is placed on the Teflon around the circular well and is grounded. The disk or lower face of the sample to be measured rests on the copper foil guard ring. The amount of mercury in the well is adjusted to contact the lower side of the sample in a circular area corresponding to the diameter of the well. The mercury does not extend out radially between the periphery of the well and the inside of the copper guard ring because of its surface tension and the very small clearance between the Teflon plate and the bottom of the sample disk. A second Teflon plate (3 mm thick) with a 6.0-mm diameter hole cut through its center rests on top of the sample disk, the two plates and the disk being held fimrly together by four grounded brass bolts at the corners of the Teflon plates. Mercury in a thin layer is poured into the circular hole (with the sample disk as its bottom) in the upper plate and constitutes the second electrode.

Results and Discussion

As in previous measurements,[6] polarization effects were noted. When a measuring voltage was applied to the sample, the current at first fell rapidly from a high initial value, continued to fall more slowly, and finally approached a constant or equilibrium value. In the acridizinium compounds measured, equilibrium was reached in times ranging from minutes to hours. Thus, it does not seem probable that the polarizations observed in these materials are due to a true dielectric relaxation involving the formation or rotation of dipoles. As the samples were disks pressed from powdered crystals, it is more probable that the polarization effects were associated with the interface contacts between the small crystals. Considerable data were taken on the polarization characteristics of these compounds which it is hoped will lead to better understanding of the phenomena involving the polarization effects. These will be presented in a future communication. In interpreting the present conductivity results, the values of the conductivity after attainment of equilibrium will be employed as these appear to be the least ambiguous. This is the viewpoint taken by Sutter and Nowick[8] in connection with polarization and conductivity measurements of "pure" NaCl single crystals.

Conductivities were determined over a range of temperatures from 55 to 105°. In all cases the variation with temperature followed the relation

$$\sigma = \sigma_0 \exp(-E/kT) \tag{1}$$

where σ is the conductivity, σ_0 a constant, E the activation energy, k the Boltzmann constant, and T the absolute temperature. Table I summarizes the conductivity data.

While there is no direct evidence bearing on the nature and mobility of the charge carriers in these compounds, some inferences concerning these can be drawn from the data of Table I. The very low conductivity of the betaine IV with its zwitterion structure and the much higher conductivities found in the other three acridizinium salts (I–III) suggest that the conduction in the latter compounds is ionic. The fact that the bis(azania)pentaphene dibromide (VII) with five aromatic

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[5] C. K. Bradsher and J. C. Parham, *J. Heterocyclic Chem.*, 1, 30 (1964).

[6] C. K. Bradsher, L. E. Beavers, and J. H. Jones, *J. Org. Chem.*, 22, 1740 (1957).

[7] C. C. Gravatt and P. M. Gross, *J. Chem. Phys.*, 46, 413 (1967).

[8] P. H. Sutter and A. S. Nowick, *J. Appl. Phys.*, 34, 734 (1963).

Table I

Compound	σ_0, ohm^{-1} cm^{-1}	E, eV	σ (90°), ohm^{-1} cm^{-1}
Acridizinium bromide (I)	1.2×10^{4}	1.38	1.2×10^{-15}
Acridizinium perchlorate (II)	5.0×10^{8}	1.57	9.5×10^{-14}
Acridizinium anthraquinone-2-sulfonate (III)	8.0×10^{6}	1.62	2.5×10^{-16}
Betaine of 9-sulfoacridizinium hydroxide (IV) (zwitterion)	1.0×10^{-3}	1.07	5.8×10^{-18b}
Acridizinium bromide hydrate (V)			1.1×10^{-12c}
Acridizinium bromide dimer (hydrate) (VI)			5×10^{-13c}
12a,14a-Bis(azania)pentaphene dibromide (VII)			2.0×10^{-15}
Anthracene (polycrystalline)	10^{-1}–10^{-2}	1.0	7.5×10^{-16a}
Anthracene (single crystal)			$<3 \times 10^{-18b}$

[a] Measured at 80°. [b] Measured at 100°. [c] Measured at 25°.

rings has about the same conductivity as acridizinium bromide lends support to this conclusion.

Because of the large size of the acridizinium cation, it is probable that most of the current is carried by the bromide ion, either interstitially or through anion vacancies. The absolute magnitude of the conductivity is also consistent with an ionic mechanism. Thus Sutter and Nowick find a conductivity of 3×10^{-14} ohm^{-1}cm^{-1} at 90° for solid sodium chloride.[9]

In the third salt, acridizinium anthraquinone-2-sulfonate (III), the cation and anion are approximately the same in size. The anion is considerably larger than the bromide ion, and the conductivity of this salt (III) is lower than that of acridizinium bromide, though not as much as might have been anticipated from other data involving ion-size differences. Thus, for example, at 400° the conductivity of NaBr is 200 times greater than that of potassium bromide, the current being carried by the cations.[10] In this instance the two salts have the same crystal structure, whereas in the two acridizinium salts this may not be the case.

That ion size is not the only factor which must be considered is seen from the fact that the perchlorate II has a much higher conductivity than the bromide I. This suggests the possibility in this case of cation–anion interaction of the van der Waals type in view of the large polarizability of the perchlorate ion, resulting in an added electronic contribution to the conductivity.

The two remaining acridizinium compounds in Table I, the monohydrated bromide V and the dihydrated dimer of the bromide (VI), involve a quite different situation from that for the other compounds because of the inclusion of water of hydration in their crystal-lattice structure. As a consequence, conduction mechanisms involving the water molecule must be considered in the case of these two compounds. The conductivity at 25° of the acridizinium bromide monohydrate (V) was slightly larger than that of the dimer hydrate (VI). As disks of the dimer hydrate almost invariably broke on heating and also showed signs of decomposition, it was not possible to measure the conductivity of the anhydrous dimer—if indeed this form exists.

The conductivity of the acridizinium bromide monohydrate (V) was several thousand fold greater than that of the anhydrous salt. Furthermore, no polarization effect was observed on applying the charging potential to this compound. Determinations of the conductivity of acridizinium bromide as a function of its water content were carried out at room temperature (~25°). A sample was stored over silica gel for several days to reduce surface moisture without decomposition of the hydrate, and its conductivity was then measured. After drying in an oven for a short interval it was weighed and its conductivity remeasured. This was repeated until a total wight loss of 6.2% resulted. This is somewhat lower than the 6.48% weight loss which would correspond to complete dehydration of the hydrate to the anhydrous salt. In this way the data of Table II were developed. The numbers in the first column represent the successive order of the conductivity measurements.

Table II. Acridizinium Bromide Monohydrate Conductivity *vs.* Weight Loss on Drying

	Conductivity, ohm^{-1} cm^{-1}	Wt loss, %
1	1.1×10^{-12}	0
2	5×10^{-14}	0.35
3	3×10^{-14}	0.65
4	9.5×10^{-15}	1.35
5	6×10^{-15}	1.85
6	2.6×10^{-15}	3.50
7	(2.2×10^{-12})	(1.40)
8	1.4×10^{-15}	3.85
9	4×10^{-16}	6.20

From a plot of the data of Table II, the conductivity, except for the rapid decrease between measurements 1 and 2, appears to depend exponentially on the water content. The sample was stored over silica gel for 3 hr between measurements 6 and 7. About half of the weight loss was regained, but the conductivity rose to a value slightly greater than that found initially before any drying. On further drying, the low conductivities shown by measurements 8 and 9 resulted. This behavior strongly suggests the presence of adsorbed surface water, initially, and upon rehydration, which makes a large contribution to the total conductivity. As water is regained, it is first adsorbed at crystal surfaces and subsequently diffuses to hydration sites. That the effect is a significant one is evident from the large change in conductivity between measurements 1 and 2 in Table I though the loss involved is only about 1 mg in a total disk weight of about 300 mg.

It is probable that two mechanisms are operative in producing this enhancement of the conductivity by the adsorbed water film. Firstly the adsorbed water network can act as a conductor in the same sense as liquid water and possibly does so independently of the solid substrate. In the second place adsorbed water could provide conductive "bridges" at particle interfaces, effectively reducing intercrystalline contact resistances.

Presumptive evidence that conduction through a water film was one of the modes involved is provided by an experiment in which a sample of acridizinium bromide was exposed to a high humidity until its conductivity was increased by a factor of 500–1000 over that of the dessicator-dried material referred to in Table II. The currents observed in this case were relatively quite

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(9) See ref 8, p 740, Figure 10.

(10) "American Institute of Physics Handbook," 2nd ed, D. Gray, Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1963, Section 9, pp 65–66.

large (~10^{-6} A). After about 2 min a red spot appeared on the solid acridizinium bromide at the cathode. In aqueous solution, when acridizinium bromide is treated with alkali, a red "pseudo-base" of uncertain structure is formed which disappears on addition of acid.[11] A drop of dilute acid discharged the red color on the sample disk. It therefore appears that there was electrolysis of the adsorbed water with H_2 liberation at the cathode resulting in a local excess of hydroxyl ion which reacted with the acridizinium ion to produce the red "pseudo-base." Attempts to reverse the formation of the "pseudo-base" by reversal of the sign of the applied potential were unsuccessful. Apparently no local excess of hydrogen ions can be generated in this way, because the protons are more mobile than the hydroxyl ions. It thus appears that conduction in such adsorbed water films is due primarily to proton transfer.

It is, however, difficult without additional evidence to exclude other effects which may also play a role in the conduction process such as the possible increase, in the presence of adsorbed moisture, of the mobility of charge carriers already present as proposed for NaCl single crystals by Simkovich.[12] Evidence for electrolysis is difficult to obtain if the conductivities are low, as in the case of anhydrous acridizinium bromide ($\sigma = 1.2 \times 10^{-15}$ ohm $^{-1}$ cm^{-1} at 90°). Unambiguous evidence for this could best be obtained by measurement of mass transfer but this is hardly feasible in the case of the anhydrous bromide. By using high temperatures and with fields of 10^4 V/cm, currents of 10^{-10} A could be obtained. For currents of this magnitude it is estimated that the sample would show a weight loss of 1 mg in about 3 years if the current was carried by bromide ions.

Despite such an estimate, an attempt was made to obtain evidence for electolysis in anhydrous acridizinium bromide. A current of about 10^{-10} A was passed through a sample placed between two sheets of silver for 1 month in the hope that the current transport might produce some visible change in either of the electrodes which could be attributed to a reaction of the bromide ion and the silver. No change was observed.

In the case of equilibrium conductivity measurements of polycrystalline anthracene samples, activation energies of 1.0 ± 0.1 eV were found for all grades of anthracene studied including a ground sample of a Harshaw single crystal.

All measurements on anthracene were carried out in a nitrogen atmosphere, and no significant differences were observed in the conductivities of polycrystalline samples made from the three grades of anthracene. However, the equilibrium conductivity determinations on anthracene single crystals with mercury electrodes and a guard ring in the small sample holder previously described gave very small values regardless of the direction through the crystal in which the field was applied. An upper limit to the equilibrium conductivity was 3×10^{-18} ohm^{-1} cm^{-1} in any crystal direction at 100°. The equilibrium conductivity of a polycrystalline sample from ground material from the same single crystal was 7.5×10^{-16} ohm^{-1} cm^{-1} at 80°, a value about three orders of magnitude higher considering the difference in temperature in the two measurements. In another recent investigation of a single crystal of anthracene where a guard ring was used, the upper limit of conductivity was placed at 10^{-15} ohm^{-1} cm^{-1} at 180°.[13]

In many earlier measurements on single crystals, no guard rings were employed. In view of the large differences found here between measurements on a polycrystalline sample and on the single crystal, it would appear that the use of a guard ring may be of considerable importance to avoid surface conduction effects in single-crystal measurements.

Acknowledgments. The authors wish to thank Professor Charles K. Bradsher of this department for help and advice in connection with the synthesis and purification of the acridizinium compounds. They also recall with gratitude the privilege they had on a number of occasions of discussing various aspects of this work with Professor Peter Debye.

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