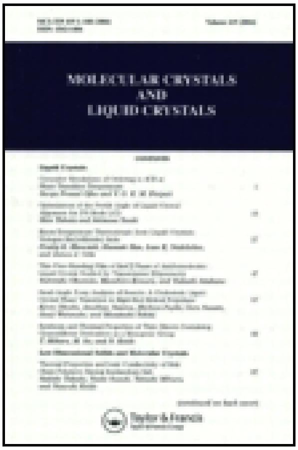

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Doping and Conduction in Organic Radical Ion Systems

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Doping and Conduction in Organic Radical Ion Systems

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There is a large class of organic compounds which form stable radical ions at room temperature, that is they have a single electron in the highest occupied molecular orbital and carry a negative (e.g., tetracyanoquinodimethane) or a positive charge (e.g., tetracene tetrasulphide). They undergo simple one electron oxidation and reduction reactions and in the solid state these different oxidation states have high resistivities, generally $> 10^{10}$ ohm cm. However, we have shown that the presence of small amounts ($< 1\%$) of other oxidation states as an impurity in an otherwise pure sample can increase the electrical conductivity by 5 or 6 orders of magnitude. The accompanying changes in the Seebeck Coefficient and activation energy for conduction are of the order of 1 mv/°C and 0.5 ev respectively. These results are explained by assuming a hopping model of conduction and by postulating the existence of a redox equilibrium in the solid state.

INTRODUCTION

There is now extensive evidence that the electronic conductivities of simple radical anion salts, especially of 7,7,8,8-tetracyanoquinodimethane, (TCNQ) (e.g. $M^+TCNQ^{\overline{\cdot}}$) are considerably increased, in most cases, by the addition of an equivalent of the corresponding neutral species from which the radical anion is derived. Such mixtures of valence states often form well defined chemical compounds of definite stoichiometry and are then called complex salts. Thus the stoichiometry $TCNQ^{\overline{\cdot}} : TCNQ^0 = 1:1$ is found in the complex salt with the quinolium ($Quin^+$) cation, $Quin^+ (TCNQ)_2{}^{\overline{\cdot}}$. These

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complex salts can show low, medium or high conductivity[1] and the mechanism of conduction has been discussed.[2,3] Other radical anions[4,5] also form complex salts such as that of 2,4,7-trinitro-9-dicyanomethylenefluorene with the 1,2,3-trimethylbenzimidazolium cation described by Dupuis and Neel.[6]

In simple salts the radical anions usually form stacks of dimer pairs between which electron transport occurs through the generation of a dianion as shown in Eq. (1),

$$\underset{M^+}{TCNQ^{\cdot-}} + \underset{M^+}{TCNQ^{\cdot-}} \longrightarrow \underset{M^+}{TCNQ^0} + \underset{M^+}{TCNQ^{2-}} \tag{1}$$

The Coulomb repulsion involved in creating the dianion restricts the conductivity which remains low. However, in a few simple salts such as that with the *N*-methylphenazinium cation ($NMP^+TCNQ^{\cdot-}$), in which the radical anions are equally spaced, the coulomb repulsion is reduced by polarisation of the counter ion so that a band structure is possible and these have high conductivities.

In complex salts the Coulombic repulsion is avoided because the neutral TCNQ molecules, by forming an integral part of the radical anion stack, permit electron transfer without the formation of dianions as shown in Eq. (2),

$$\underset{M^+}{TCNQ^{\cdot-}} + TCNQ^0 \longrightarrow \underset{M^+}{TCNQ^0} + TCNQ^- \tag{2}$$

Thus the activation energy for electron transport is much lower than in Eq. (1) and so the conductivity is higher.

Although complex salt formation usually increases conductivity the full advantage is sometimes offset by the work which has to be done against Coulombic attraction between the radical anion and its counter cation. For example in the case of $NMP^+TCNQ^{\cdot-}$ ($\sigma = 10^{+2}$ ohm^{-1} cm^{-1}) the complex salt $NMP^+(TCNQ)_2^{\cdot-}$ has a lower conductivity ($\sigma = 10$ ohm^{-1} cm^{-1}). In some TCNQ salts, for example those involving the poly-(2-vinylpyridinium) cation, $(PVPH)^+$, we have found that[7] the maximum conductivity is reached with a ratio of 0.5:1 $TCNQ^0/TCNQ^{\cdot-}$ respectively in compounds of structure $\{PVP\}_{0.7}$ $\{PVPH^+(TCNQ)_{1.5}{}^{\cdot-}\}_{0.3}$ and other examples have been given by Hadek *et al.*[8] The effect of adding increasing amounts of neutral TCNQ to a poly-(1-methyl-2-vinylpyridinium)TCNQ simple salt was studied by Lupinski *et al.*[9] who showed that the conductivity reached a maximum at a molar ratio of 0.33:1 and falls at higher concentrations of $TCNQ^0$. Thus the maximum in conductivity depends on the composition of the "complex" salt.

The above mechanism of charge transport in complex TCNQ salts is basically that proposed by LeBlanc[10] as modified by Eley *et al.*[11] The transfer of charge between neutral and radical ion species has been suggested by Klopffer and Rabenhorst[11] to be important in determining the conductivity of polymeric charge transfer complexes. Hadek[8] also emphasises that the presence of neutral molecules among radical anions and radical cations, formed by the interaction of oligoanilines with the acceptors, iodine, TCNQ, *p*-chloranil and *m*-dinitrobenzene is essential for easier transport of charge.

There are many examples of radical cation conductors. Kearns[12] regarded the presence of positive radical cations as the cause of conductivity in complexes of aromatics with halogens. The presence of only a small concentration (ca 1 %) of acceptor can lead to high conductivity as Uchida and Akamatu[13] have shown by doping violanthrene with iodine. The conductivity of violanthrene (10^{-14} ohm^{-1} cm^{-1}) increased to almost 10^{-5} ohm^{-1} cm^{-1} on adding iodine to give a mole ratio, violanthrene: $I_2 = 1:0.01$; it rose to 10^{-1} ohm^{-1} cm^{-1} at a ratio of 1:2 and fell to 10^{-2} ohm^{-1} cm^{-1} at 1:3. This system no doubt involves violanthrene radical cations and Roberts[14] has shown that it is probably a hopping conductor.

Radical cations as stable as the radical anion, $\mathrm{TCNQ}^{\dot{-}}$, are formed by even-numbered polyene systems. Honzl *et al.*[15] showed that aminium and polyaniline radical cations were conducting and the whole field of violene systems was opened up by Hünig.[16] Various violene structures were used as polymer building blocks by Manecke[17] and Kossmehl.[18] Litt[19] and Iida[20] studied conductivity in the phenothiazine radical cation and Gebus[21] used infra-red absorption to estimate the proportion of radical cation in the conductive C—T complexes of poly-(2-vinylphenothiazine) with various acceptors. Wudl *et al.*[22] reported high conductivity in the tetrathiofulvalene (TTF) radical cation salts and the salt $\mathrm{TTF}^{\dot{+}}$ $\mathrm{TCNQ}^{\dot{-}}$[23] has recently been studied intensively because of its metallic conductivity.[3, 24]

It is probable that the mechanism of conduction in radical cation salts is similar to that in TCNQ salts but in only a few cases have complex radical cation salts been reported. Evidence for complex salt formation comes mainly from charge transfer complexes. Matsunaga[25] found that the phenothiazine, (Phen.) salt, $\{\mathrm{Phen.}^0\ \mathrm{Phen.}^+\}\ \mathrm{Br_2I^-}$ had high conductivity and also showed[26] that the complex $\{\mathrm{DBPT}\}_2^{\dot{+}}$ $\mathrm{DDQ}^{\dot{-}}$ ($\sigma_{20} = 5.9 \times 10^{-2}$ ohm^{-1} cm^{-1}) had a higher conductivity than the simple salt $\mathrm{DBPT}^{\dot{+}}$ $\mathrm{DDQ}^{\dot{-}}$ ($\sigma = 10^{-4}$ ohm^{-1} cm^{-1}). Perylene forms a highly conductive complex $(\mathrm{Perylene})_2^{\dot{+}}$ $\mathrm{NiMNT}^{\dot{-}}$ with nickel maleonitrile dithiolate[27] which can be regarded as a complex radical cation salt. The first complex radical cation salt of TTF was formed[28] with the hexacyanobutadienide (HCBD) radical anion, $(\mathrm{TTF})_2^{\dot{+}}$ $\mathrm{HCBD}^{\dot{-}}$ ($\sigma = 10^{+3}$ ohm^{-1} cm^{-1}) and can be regarded also as a

C—T complex. It is significant that both Matsunaga[29] and Krikorian and Sneed[30] found that the conductivities of the C—T complexes of tetracene tetrasulphide (TTS) were highest when the neutral TTS was present in considerable excess.

We have found further evidence of complex salt formation between radical cations and neutral molecules, leading to increased conductivity. Furthermore doping a neutral molecule with low concentrations of radical cation, of the order of 10 ppm, produces considerable changes in its electrical properties. We have examined the electrical conductivity, activation energy, and Seebeck coefficient, of selected radical ion systems as a function of the relative concentration of two oxidation states and the results are discussed in terms of a hopping model of conduction.

EXPERIMENTAL

Electrical Experiments

Measurements of the electrical properties, viz resistivity, activation energy and Seebeck coefficient were carried out on polycrystalline compactions. Materials were first ground in a ball mill† and compacted at pressures of the order 700 kg/cm^2. Resistivities of less than 10^8 ohm cm were measured on rectangular compactions (15 × 3 mm) using a Fell four point probe[31] at 10^{-5} torr. Higher resistivities were measured using a two point probe at 60 volts and 10^{-1} torr. The resistivities measured using the two point probe are assumed to be bulk values. In the four point probe the temperature was variable over the range -20°C and $+80$°C using a Peltier cooling and heating device. Temperature variation of the two point probe was achieved by immersing the measuring cell in a water bath. The apparent activation energy for conduction was obtained by measuring four values of resistivity.

The Seebeck effect was measured using an evacuable metal cell of conventional design. Platinum foil electrodes and leads were used and the temperature difference across the sample was monitored using thermocouples formed by platinum/rhodium alloy wires welded to the electrode. For high resistance samples PTFE screening and sleeving was necessary for all electrical leads to prevent pick up problems. The Seebeck voltage was measured using a Vibron Electrometer Model 33B-2 with an output to a digital voltmeter which allowed remote readings and avoided noise due to changes in body capacitance. Compacted samples were 0.5 cm diameter and as thin as possible for high resistance samples.

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† Vibromill VM 100 obtained from: Beckman RIIC Limited, Glenrothes, Fife, Scotland.

Materials

TCNQ[32] and its lithium salt[33] were prepared using methods described in the literature. The experimental details for all other materials discussed in the text are given in the Appendix.

PREPARATION OF MIXTURES

Freeze Drying

This procedure was used for neutral/radical cation mixtures of DBBTA. A mixture of the two components in the correct proportions was dissolved in formic acid and the solution sprayed at 4–6 litres/min, with the aid of nitrogen, using an atomiser (Gallenkamp "all glass spray") into liquid nitrogen in a closed container. The atomiser was fitted with a heater and a thermometer and the temperature of the solution was adjusted to 15°C at 1 cm from the end of the atomiser. This was necessary to prevent the solution freezing in the atomiser. The nitrogen was allowed to boil off leaving a solid mixture of DBBTA and formic acid. The sample was then transferred to a cooled round bottomed flange flask fitted with a cold finger at a height of 5–10 cm above the surface of the sample and the flask maintained at a temperature of 5°C. The formic acid was removed by sublimation at a pressure of 0.1 torr over 16 hours. The residue which had a cotton wool like appearance was then transferred to a nitrogen glove box and evacuated for a further 2 hours at 10^{-6} torr before compacting for electrical measurements. Powder X-ray examination revealed only slight evidence of crystallinity in these samples, suggesting that the particle size is less than 500 Å.

Grinding

Ground mixtures were prepared using a ball mill.† The appropriate amount of the two components was mixed together and ground in an agate container for up to 2 hours. $Li^+ TCNQ^{\dot{-}}/TCNQ$ and $DBBTA^{\dot{+}}BF_4^-/DBBTA$ mixtures were ground dry while mixtures of the different oxidation states of BBDY were ground in the presence of one or two drops of acetic acid. Microscopic examination revealed a spread in particle size between 0.5 and 10 microns with an average at 1 micron.

Co-Crystallisation

Mixtures of DBBTA were also prepared by co-crystallisation of the two components (neutral/radical cation) from acetic acid. The two pure components

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† Vibromill VM 100 obtained from: Beckman RIIC Limited, Glenrothes, Fife, Scotland.

were mixed together and dissolved in refluxing acetic acid under nitrogen. The acetic acid was then removed by evaporation and the resulting solid dried under vacuum (5 torr) at 100°C with a nitrogen bleed. More dilute solutions down to 4 parts of radical cation in 10^8 of neutral material were prepared by diluting the one mole percent solution further with neutral precursor. Particles had a diameter of 1–4 microns.

RESULTS AND DISCUSSION

Table I summarises the results of preliminary measurements on a range of radical cation systems derived from violenes. With a few exceptions the conductivities are relatively high for organic materials. Our investigations suggest that the conductivity depends upon the method of preparation and also on the purity of the sample, since we invariably find that pure radical cations are less conductive than samples containing other oxidation states as impurities. For example the conductivity of the sulphate salt of DBBTA (3) varies between $\sigma_{20} = 4 \times 10^{-7}$ and 3×10^{-4} ohm^{-1} cm^{-1} depending upon the reaction time of DBBTA with ceric sulphate. We were also able to isolate a complex salt of DBBTA, which corresponds to $(\mathrm{DBBTA})_2^{+}\mathrm{BF}_4^{-}$, in the form of large single crystals, which had a conductivity $\sigma_{20} = 2 \times 10^{-3}$ ohm^{-1} cm^{-1}.

Similar behaviour was observed for tetracene tetrasulphide (TTS) (1). The conductivity of the analytically pure acetate salt ($\mathrm{TTS}^{+}\mathrm{CH_3COO}^{-}$) fell from $\sigma_{20} = 2 \times 10^{-3}$ to 8.7×10^{-7} ohm^{-1} cm^{-1} on further purification. Furthermore, we found that the conductivity of a vacuum (10^{-5} torr) sublimed sample of neutral TTS was 10^{-11} ohm^{-1} cm^{-1}, at 20°C measured prior to exposure to air, which confirms the value reported by Inokuchii[34] ($\sigma_{20} = 2.4 \times 10^{-11}$ ohm^{-1} cm^{-1}). It also supports Matsunaga's[29] suggestion that the high conductivity (σ_{20} approx. 10^{-4} ohm^{-1} cm^{-1}) widely reported for the neutral form of TTS is due to contamination with the radical cation.

It is evident, therefore, that the conductivities quoted in Table I are unlikely to represent intrinsic values characteristic of the pure material. Furthermore, we feel that many of the resistivities reported in the literature for these or similar materials may be misleading and should be viewed with suspicion.

As a result of these preliminary observations we investigated in more detail the dependence of the electrical properties of some representative radical ion systems on the relative concentrations of the various oxidation states.

The electrical properties of mixtures containing the reduced (neutral) form and the radical cation fluoroborate salt of DBBTA (3) are shown in Figures 1, 2 and 3. The major changes in resistivity as shown in Figure 1 are

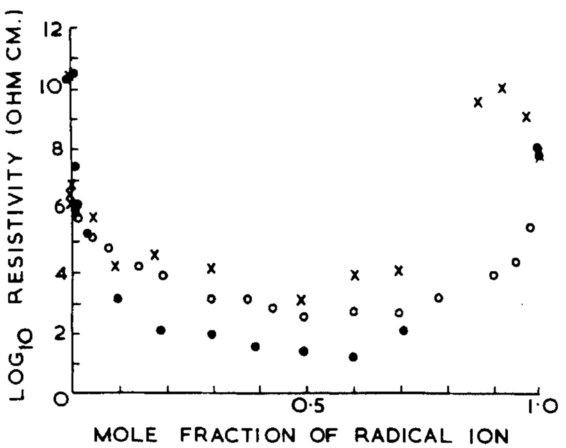


FIGURE 1 DBBTA Log_{10} resistivity vs mole fraction (neutral/radical cation mixtures) as a function of sample preparation: (×) co-crystallisation, (○) grinding, (●) freeze drying.

confined to the two extremes of the concentration range. The effect of low concentrations of radical cation can be seen more clearly in Table II, thus the addition of 100 ppm to the pure reduced form of DBBTA produces a decrease in resistivity of four decades. Doping the neutral species in this way increases the carrier concentration and as shown in Figure 2 substantially decreases the activation energy for conduction. Figure 3 shows a corresponding reduction in the thermopower which remains positive over the entire concentration range. The peaks in resistivity and activation energy at roughly 90% radical cation for the co-crystallised samples probably arise from trace quantities of the dication as an impurity.

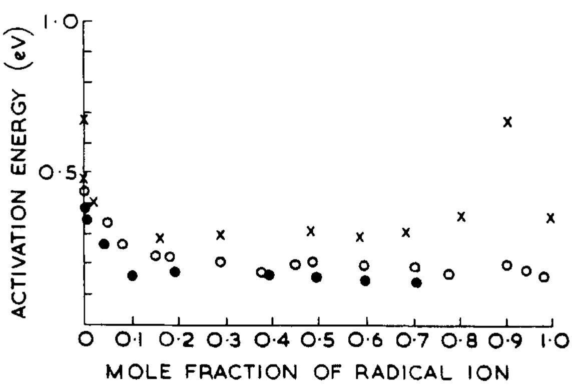
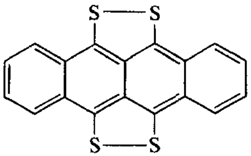
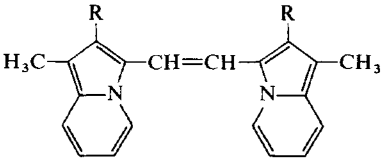
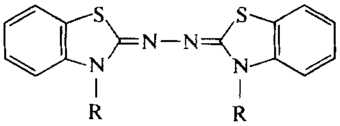
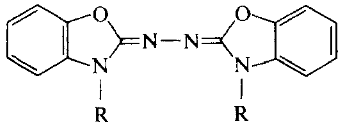
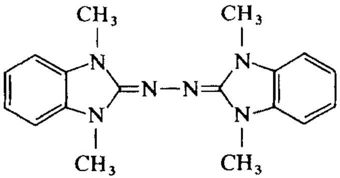
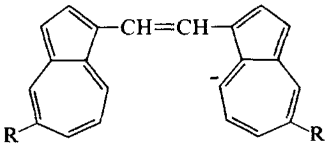
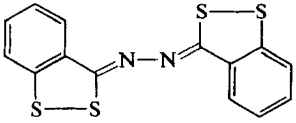


FIGURE 2 DBBTA Activation energy for conduction vs mole fraction (neutral/radical cation mixtures) as a function of sample preparation: (×) co-crystallisation, (○) grinding, (●) freeze drying.

TABLE I

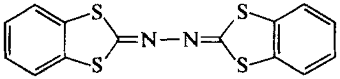
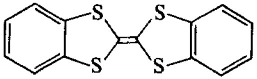
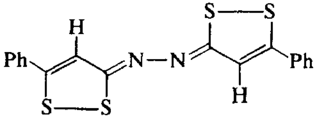
Summary of preliminary investigations of the electrical properties of some violene radical cation systems

Name and structure of neutral material	Counter ion	Activation energy (eV)	Conductivity at 20°C (ohm^{-1} cm^{-1})	Reference
1. Tetracene tetrasulphide (TTS)	Neutral		10^{-11}	34
	HSO_4^-		1×10^{-2}	40
	CH_3COO^-		2.2×10^{-3}	41(A)
	CH_3COO^- (Recryst.)	0.41	8.8×10^{-7}	(A)
2. Substituted indolizyl ethylene 				
R = CH_3	ClO_4^-		6.4×10^{-5}	(B(i))
	BF_4^-	0.22	1.2×10^{-4}	43, 42, 48
R = Ph	BF_4^-		5.5×10^{-7}	27(B(ii))
3. NN'Dialkyl bis (benzthiazolinylidine)azine (DBBTA) 				
R = CH_3	Neutral	0.67	2.3×10^{-10}	49 (E)
	BF_4^-		3.6×10^{-8}	
	Complex 1 : 1, BF_4^-		1.9×10^{-3}	
	$SO_4^=$		$10^{-4} - 10^{-7}$	

4. NN′Dimethyl bis (benzoxazolinylidine)azine  R = CH_3	Neutral	1.1	6×10^{-16}	
	1 : 1 mixture	0.17	3×10^{-4}	(C)
	Br_3^-	0.52	1.2×10^{-11}	
5. Bis (1,3-dimethyl benzimidazolinylidine)azine 	Neutral		1×10^{-11}	51
	1 : 1 mixture		1×10^{-5}	(F)
	BF_4^-		7×10^{-9}	
6. Isopropyl guaiazulenyl ethylene  R = Isopropyl	ClO_4^-		2.7×10^{-5}	42, 52
7. Bis (benzo-1,2-dithiolinylidine)azine 	Neutral		$<10^{-8}$	47
	BF_4^-	0.1	3×10^{-1}	
	Br^-	0.06	8×10^{-1}	(G)
	$SO_4^=$	0.26	3.8×10^{-7}	

(*Table continued*)

TABLE I (*Continued*)

Name and structure of neutral material	Counter ion	Activation energy (eV)	Conductivity at 20°C ($ohm^{-1} cm^{-1}$)	Reference
8. Bis (benzo-1,3-dithiolinylidine)azine 	Neutral		$<10^{-8}$	47
9. Bis (benzo-1,3-dithiolinylidine) (BBDY) 	Neutral Br$^-$	0.86 0.17	3.2×10^{-11} 3.4×10^{-1}	47 (H)
10. Bis (5-phenyl-1,2-dithiolinylidine)azine 	Neutral Br$^-$	 0.18	$<10^{-8}$ 8.6×10^{-2}	 (D)

Letters refer to the appropriate section in the Appendix.
Figures are references to the literature.

TABLE II

Electrical properties of mixtures of the neutral and radical cation forms of DBBTA prepared by co-crystallisation

Mole fraction of radical cation in the mixture	Log_{10} Resistivity (ohm. cm. at 20°C)	Activation energy (eV)	Seebeck coefficient (mv/°C)
0	10.36	0.67	
4×10^{-8}	10.10		
7.7×10^{-7}	6.64	0.48	+1.46
5.6×10^{-6}	6.87	0.41	+1.60
9.2×10^{-4}	6.4	0.4	+0.7
0.01	6.10	0.4	+0.79
0.18	4.53	0.22	+0.1
0.30	4.18	0.25	+0.13
0.49	3.08	0.26	+0.11
0.61	3.38	0.214	+0.11
0.70	3.86	0.26	+0.08
0.84	9.46	0.32	+0.088
0.92	9.85	0.58	+0.05
0.93	9.50		+0.08
0.99	8.82		
1.00	7.75	0.311	+0.18'

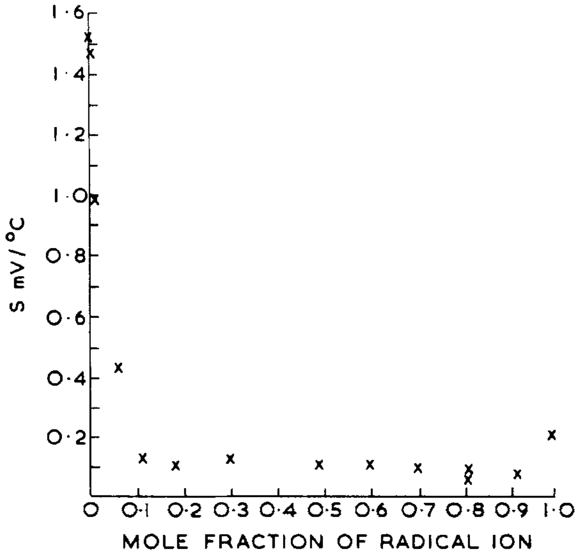


FIGURE 3 DBBTA Seebeck coefficient vs mole fraction (neutral/radical cation mixtures, prepared by co-crystallisation).

It is possible to explain the qualitative features of these results by assuming a hopping model of conduction, which is suggested by the relatively low values of charge carrier mobility (approx. 10^{-2} cm^2 V^{-1} sec^{-1} for both carriers) obtained from drift mobility measurements[35] on single crystals of the neutral forms of DBBTA (3) and the structurally similar DBBOA (4). Furthermore, activation energies obtained from the temperature dependence of the Seebeck coefficient for mixtures of DBBTA^0 and DBBTA$^{\dot{+}}$ and for several other radical ion systems were consistently lower than those obtained from the temperature dependence of the resistivity. Similar observations have been reported[36] for TTS. According to Bransky *et al.*[37] this observation is consistent with a hopping model of conduction.

In mixtures containing the neutral and radical cation forms of the same molecule we assume that charge transport takes place by the transfer of electrons between molecules in different valence states, i.e. a redox process of the type

$$\begin{pmatrix} + \\ 0 \end{pmatrix}_1 + \begin{pmatrix} 0 \\ 0 \end{pmatrix}_2 \longrightarrow \begin{pmatrix} 0 \\ 0 \end{pmatrix}_1 + \begin{pmatrix} + \\ 0 \end{pmatrix}_2 \qquad (3)$$

$$\begin{pmatrix} + \\ 0 \end{pmatrix} = \text{radical cation} \qquad \begin{pmatrix} 0 \\ 0 \end{pmatrix} = \text{neutral}$$

Although not shown in Eq. (3) each radical cation is associated with a negative counter ion which does not take part in the conduction process, but merely serves to preserve electroneutrality, unlike the situation in charge transfer complexes. The major effect of the counter ion is to provide an electrostatic potential which influences the energetics of the electron transfer process in a way which will be discussed.

We postulate that a neutral species, capable of forming radical cations, has a very low intrinsic conductivity and that conduction is due to the presence of electronegative impurities which oxidise the host material, forming the radical cation species, and thus allowing conduction by the redox process described in Eq. (3) above. With the addition of increasing amounts of electronegative impurity the conductivity should rise to a maximum and then decrease since the conduction mechanism requires both the radical cation and neutral species. The same arguments apply to the dicationic species, $\binom{+}{+}$, which also has a low intrinsic conductivity. The appropriate expression for the conductivity of a mixture of neutral and radical cation is thus

$$\sigma = N\begin{pmatrix} + \\ 0 \end{pmatrix}\begin{pmatrix} 0 \\ 0 \end{pmatrix}e\mu$$

where N is the number of molecules per cm^3, $\binom{+}{0}$ and $\binom{0}{0}$ are the mole fraction of radical cation and neutral species respectively and μ is an effective mobility which may be activated. The equilibrium concentrations of the two oxidation states are determined by the following equations, where x^- represents the counter ion.

Dissociation $[(x^-)\binom{+}{0}] \xrightarrow{k_1} (x^-) + \binom{+}{0}$

Disproportionation $2\binom{+}{0} \xrightarrow{k_2} \binom{+}{+} + \binom{0}{0}$

$$k_1 = \frac{(x^-)\binom{+}{0}}{[(x^-)\binom{+}{0}]} \qquad k_2 = \frac{\binom{+}{+}\binom{0}{0}}{\binom{+}{0}^2}$$

The value of k_1 which affects the radical cation concentration, is expected to influence the conductivity as shown by the theoretical curves in Figure 4. k_2 will also influence the conductivity at high radical ion concentration by determining the concentration of the various oxidation states which are involved in the mechanisms (3) and (4) below

$$\binom{+}{0}_1 + \binom{+}{+}_2 \longrightarrow \binom{+}{+}_1 + \binom{+}{0}_2 \tag{4}$$

Species with a high equilibrium constant for disproportionation will therefore be expected to exhibit a relatively high conductivity at high radical cation

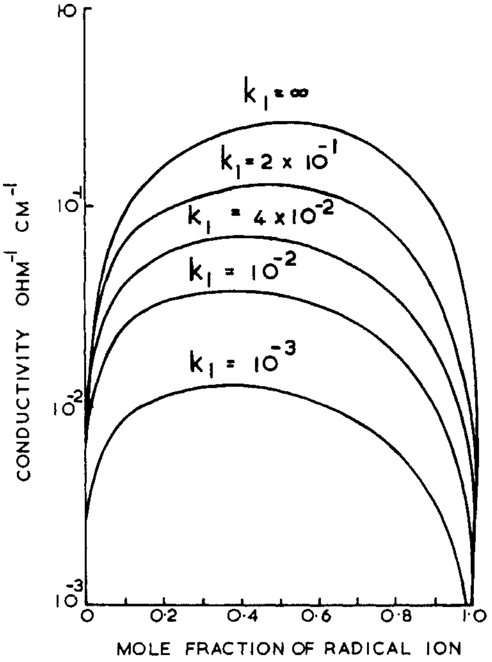


FIGURE 4

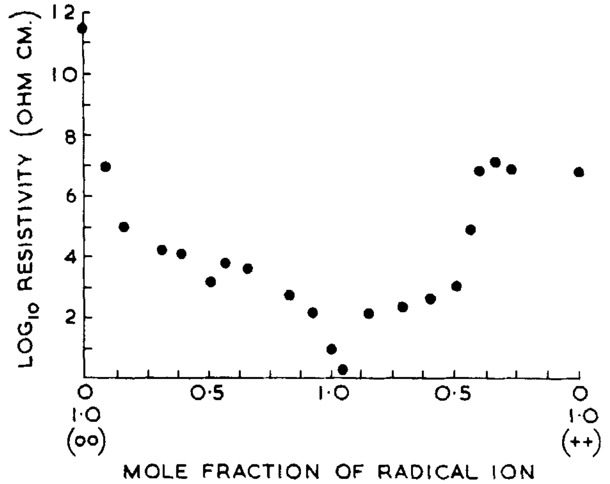


FIGURE 5 BBDY Log_{10} resistivity vs mole fraction of radical ion (for mixtures of: neutral/radical cation; radical cation/dication, prepared by grinding).

concentration. This mechanism is used to explain the results obtained from a study of BBDY (9). Again the resistivity, Figure 5, drops off rapidly with increasing mole fraction, however the minimum in the curve is observed close to the 100% radical cation, rather than at 50:50 as for DBBTA, showing a decrease of 12 orders of magnitude compared to the resistivity of the neutral material. As the mole fraction of dication in the mixture increases the resistivity is observed to increase as expected on the basis of our model. The activation energy for conduction, Figure 6, is observed to be

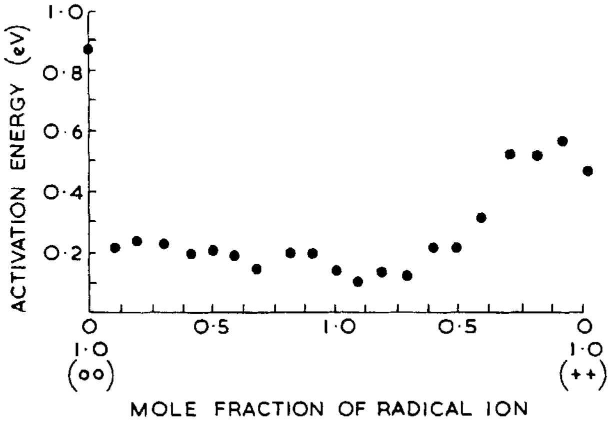


FIGURE 6 BBDY Activation energy for conduction vs mole fraction of radical ion (for mixtures of: neutral/radical cation: radical cation/dication, prepared by grinding).

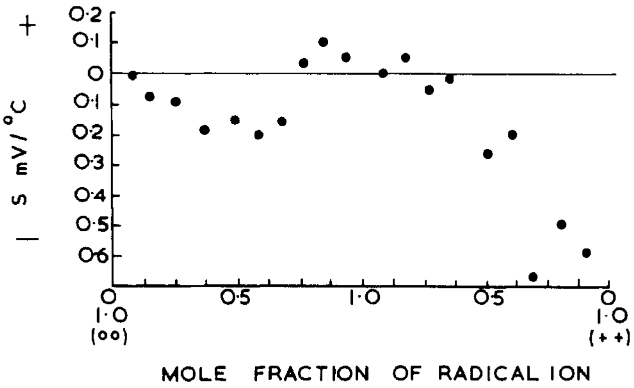


FIGURE 7 BBDY Seebeck coefficient vs mole fraction of radical ion (for mixtures of: neutral/radical cation; radical cation/dication, prepared by grinding).

constant over the major portion of the graph, even for the pure radical cation, only increasing at the two extremes.

The main features of the Seebeck coefficient results for BBDY, Figure 7, and also for DBBTA, Figure 3, can be explained on the basis of the following model. In an idealised mixed system assuming a mole fraction $\binom{+}{0}$ of mobile radical cations added to the neutral species $\binom{0}{0}$, the Seebeck coefficient can be expressed as[38]

$$S = \frac{k}{e}\left[\ln\frac{\binom{0}{0}}{\binom{+}{0}} + \frac{E}{kT}\right] \tag{5}$$

where $\ln[\binom{0}{0}/\binom{+}{0}]$ is an entropy of mixing term and E/kT is associated with the energy transported by the charge carriers. For roughly equal concentrations of neutral and radical cation species, E is obtained from the temperature dependence of the Seebeck coefficient. This is shown in Figure 8 for DBBTA, $\binom{0}{0}:\binom{+}{0} = 0.4:0.6$, which gives $E = 0.033$ eV.

It can be seen from Table III that values of S calculated from Eq. (5) are in reasonable quantitative agreement with the experimental values for DBBTA in the low radical cation concentration range. As we increase the radical cation concentration Eq. (5) predicts a zero crossing of S and a high negative value as the simple salt is approached. This is not observed even though the salt has a high resistivity and is unlikely to disproportionate to any great extent to produce the added complication of the dicationic species. The apparently complicated behaviour of the observed S for BBDY is, however, in qualitative agreement with that predicted by Eq. (5). If we consider mixtures of $\binom{+}{0}$ and $\binom{0}{0}$ as one system and mixtures of $\binom{+}{0}$ and $\binom{+}{+}$ as a separate system we would expect the behaviour shown in Figure

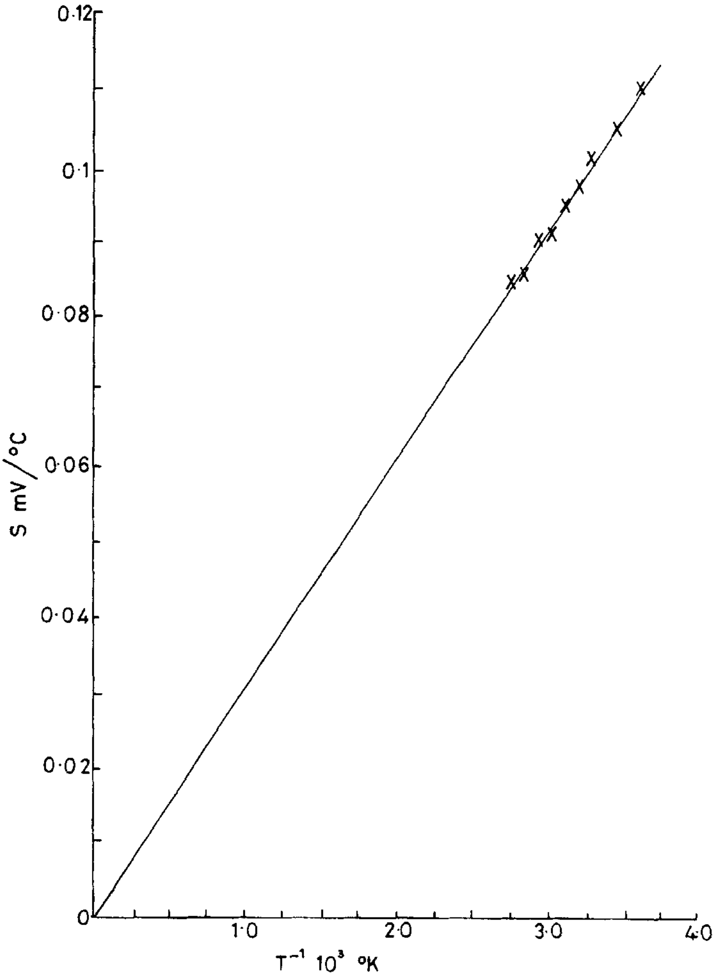


FIGURE 8 Temperature dependence of Seebeck coefficient for DBBTA, mixtures prepared by co-crystallisation.

9*a*. However the ($^{+}_{0}$) species disproportionates and at the nominal 100% ($^{+}_{0}$) point there is an appreciable concentration of ($^{0}_{0}$) and ($^{+}_{+}$) which leads to two conduction mechanisms with opposite thermopowers. The behaviour in this region will be typical of compensated semiconductors with a net zero thermopower at some point and we would expect the Seebeck coefficient for the combined systems to have the general features shown in Figure 9*b*. This is in reasonable agreement with the results for BBDY, Figure 7, where the Seebeck coefficient is tending to go positive at low

TABLE III

Comparison of observed and theoretical values of Seebeck coefficient for DBBTA mixtures prepared by co-crystallisation

Mole fraction of radical cation in the mixture	Seebeck coefficient mv/°C	
	Observed	Calculated from equation (5)
7.7×10^{-7}	1.46	1.21
5.6×10^{-6}	1.60	1.04
9.2×10^{-4}	0.70	0.60
1×10^{-2}	0.79	0.40
0.18	0.10	0.13
0.30	0.13	0.07

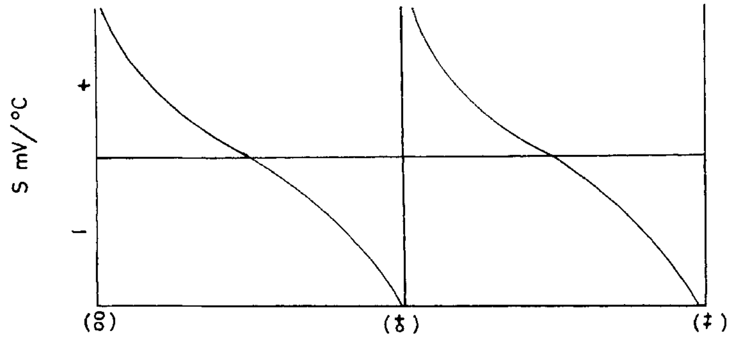


FIGURE 9*a* Seebeck coefficient predicted by equation (5).

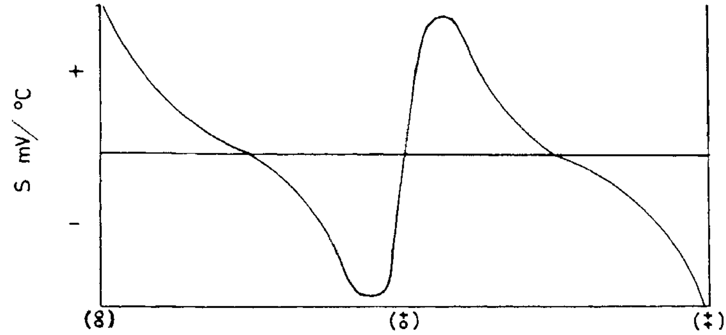


FIGURE 9*b* Seebeck coefficient predicted by equation (5) but including compensation.

radical cation concentrations, becomes negative as the dication is approached and has a zero point in the region of the 100% radical cation.

The doping behaviour discussed for radical cations is also observed for organic molecules which form radical anions. Figures 10 and 11 show the resistivity and activation energy respectively for mixtures of lithium TCNQ and neutral TCNQ. The change in conductivity is more gradual than the previous systems falling to a minimum at or near the 100% radical anion. The change in the activation energy is also not as marked and is approximately constant for most of the concentration range. This behaviour is

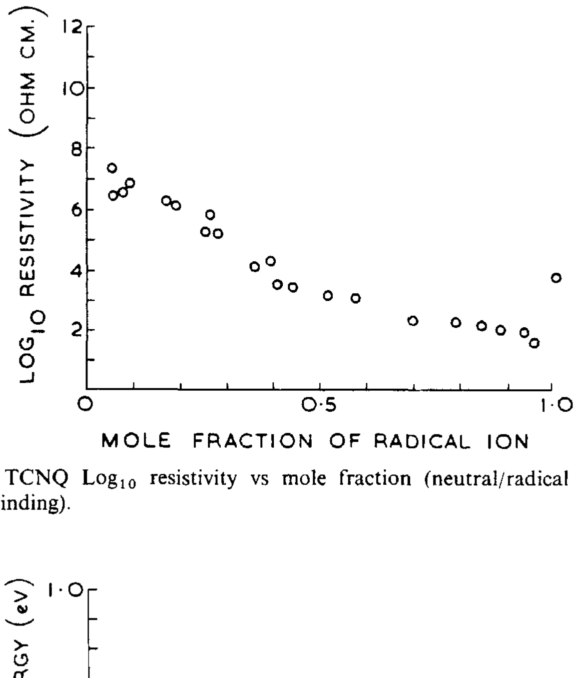


FIGURE 10 TCNQ Log_{10} resistivity vs mole fraction (neutral/radical anion mixtures. prepared by grinding).

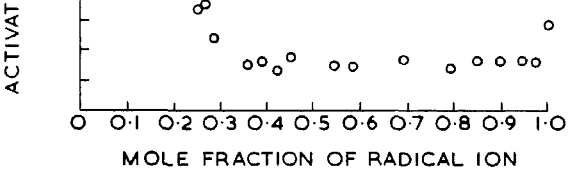


FIGURE 11 TCNQ Activation energy for conduction vs mole fraction (neutral/radical anion mixtures, prepared by grinding).

similar to that observed for BBDY suggesting the importance of the disproportionation constant k_2 in determining the electrical properties of pure TCNQ radical anion.

It was mentioned earlier that the counter ion is important in determining the activation energy for conduction. Its influence probably arises from the following mechanism. The electrostatic field due to a counter ion causes an energy distribution as shown in Figure 12*a*. At low concentrations the potential wells do not overlap and the radical cation associated with each counter ion is trapped and requires activation to $E_{\max}$ for d.c. conduction. A radical cation has an energy $E_{\max}$ when located at a site midway between two counter ions. If the counter ions are a distance R apart then

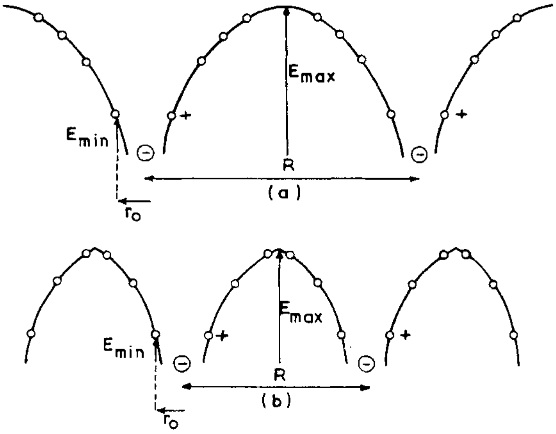


FIGURE 12*a*, *b* Activation energy for conduction.

$$E_{\max} = \frac{e^2}{\pi\varepsilon\varepsilon_0 R}$$

As the concentration of counter ions increases, the Coulomb wells begin to overlap and the energy barrier is reduced as shown in Figure 12*b*.

Assuming that the minimum in energy $E_{\min}$ corresponds to the transfer of an electron between the counter ion and the nearest donor site then

$$E_{\min} \doteqdot -\frac{e^2}{4\pi\varepsilon\varepsilon_0}\left(\frac{1}{r_0} + \frac{1}{R - r_0}\right)$$

where r_0 is the distance between the counter ion and the nearest donor site. The activation energy for conduction is therefore given by

$$\Delta E = E_{\max} - E_{\min} = \frac{e^2}{4\pi\varepsilon\varepsilon_0}\left(\frac{1}{r_0} + \frac{1}{R - r_0} - \frac{4}{R}\right)$$

This relationship does not apply if there is substantial interaction between a counter ion and a donor site which effectively deepens the well. This expression yields $\Delta E \sim 1$ eV for $r_0 \simeq 5$ Å, $\varepsilon = 3$ and $R \gg r_0$ and is thus of reasonable magnitude. ΔE is halved when $R \simeq 6r_0$ which corresponds to a radical cation concentration of approximately one mole percent and is in reasonable agreement with the observed trends. The constant activation energy measured over the major part of the concentration range is thought to be that of the redox process itself and is not explained by this mechanism.

In the preceding discussion it was assumed that homogeneous mixing of the two components is achieved at a molecular level. While this might be the case with the freeze drying technique, microscopic examination shows that it is certainly not true for co-crystallisation or grinding. However it is clear that our results, particularly those obtained for DBBTA, show that freeze drying does not offer a significant improvement over the other techniques, and that all three are in reasonable agreement with the proposed molecular model for conduction. This is a particularly interesting result when one considers that the mixtures prepared by co-crystallisation or grinding consist of separate, approximately 1 micron diameter, particles of the two components.

A possible explanation is that during the ball milling which precedes compaction there is an exchange of molecules between the surfaces of the particles. This results in a molecular mixture at the surface of the particles which forms a conducting network through the sample. In the absence of a homogeneous bulk mixture this matrix model explains why very low levels of dopant viz 10 ppm are effective in bringing about significant changes in electrical properties.

A similar model has been discussed for polymer particles coated with small particles of metal.[39] In this system a precipitous decrease in resistivity is observed around 5 and 30% v/v of conducting material depending on the ratio of polymer/metal particle size ratio.

CONCLUSIONS

The addition of only trace quantities of a radical ion to its corresponding neutral material can produce significant changes in the electrical properties of the host. Comparison of the electrical resistivity of different radical ion systems for example, is only sensibly carried out by referring to values measured for complex salts (1 : 1, neutral : radical ion) which are much less sensitive to composition than either the neutral species or simple salts. The general features of the observed dependence of the electrical properties on the concentration of the various oxidation states, exhibited by both radical cations and radical anions, follow the behaviour expected for electron transfer between molecules in different valence states and are similar to those found for mixed valency inorganic compounds.[53]

The very large changes in the electrical properties with the addition of only 10–100 ppm of radical ion in systems where molecular mixing is not obtained is accounted for by the presence of a conducting network through the sample which is formed during ball milling. These results probably represent for organic materials the closest approach to conventional semiconductor doping. However until the "doping" of organic radical ion systems is as controllable and reproducible as their inorganic counterparts detailed investigations and precise theory are impossible.

Acknowledgements

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APPENDIX

PREPARATION OF MATERIALS

Neutral materials which have been previously described were made by the methods given in the appropriate references of Table I.

The structure numbers refer to Table I.

(A) **Tetracene tetrasulphide** (TTS) (1)

The radical cation acetate salt ($TTS^{+}CH_3COO^{-}$)[40,41] was purified by concentrating a solution of the salt in methanol (1 vol), acetic acid (2 vol) using a slow stream of nitrogen. (Found: C, 52.80; H, 2.90; S, 21.65%. Calculations for $C_{20}H_{11}O_2S_4 3H_2O$; C, 52.75; H, 2.70; S, 22.75%). The material had a conductivity $\sigma_{20} = 2.2 \times 10^{-3}$ ohm^{-1} cm^{-1}. A second purification reduced the conductivity to 8.8×10^{-7} ohm^{-1} cm^{-1}.

(B(i)) 1,2-Di-(3′-(1′,2′-dimethyl indolizyl))-ethylene (DDIE) (2, *R* = CH_3)

The radical cation perchlorate salt[42,43] ($DDIE^{\dot{+}}ClO_4^{-}$) was crystallised from ethanol. (Found: C, 63.6; H, 5.4; N, 6.9; Cl, 8.8. Calculations for $C_{22}H_{22}N_2ClO_4$, C, 63.5; H, 6.0; N, 6.7; Cl, 8.5%.) The fluoroborate salt, ($DDIE^{\dot{+}}BF_4^{-}$) crystallised from ethanol. (Found: C, 67.3; H, 6.03; N, 6.6; B, 2.45; F, 17.46. $C_{22}H_{22}N_2BF_4$ requires C, 67.3; H, 6.08; N, 6.52; B, 2.38; F, 17.72%.)

(B(ii)) 1,2-Di-(1′-methyl-2′-phenyl indolizyl)-ethylene (DMPIE) Radical cation fluoroborate (2, *R* = C_6H_5)

1-Methyl-2-phenyl indolizine[44] (20.8 g, 0.1 M) was dissolved in the minimum of ethanol and brought to boiling point. An excess of fluoroboric acid (12 g, 40%) was added. A blue fluorescent solution resulted and on cooling colourless crystals of 1-methyl-2-phenyl indolizinium fluoroborate (XIVa) were formed. This was recrystallised from ethanol. (25.5 g, 86.4%, m.p. 130°C). 1-Methyl-2-phenyl indolizinium fluoroborate (29.4 g, 0.1 M) was dissolved in the minimum of boiling ethanol and glyoxal monohydrate (3.8 g, 0.05 mol) was added. A black solution formed after a minute. After a further four minutes boiling the solution was cooled and a black precipitate formed. This was recrystallised from ethanol (10 g, 38.2%). No crystalline structure could be seen from the recrystallised product and under the microscope it had the appearance of a coagulated suspension. m.p., decomp. > 230°C. (Found: C, 73.76; H, 5.16; N, 4.91; F, 12.95. $C_{32}H_{28}N_2BF$ requires C, 73.75; H, 4.2; N, 5.5; F, 13.6%.)

(C) NN′-Dimethyl-bis-(benzoxazolinylidine)-azine (DBBOA) (4)

Dimethyl sulphate (3.05 g, 0.024 M) purified by neutralisation with sodium bicarbonate followed by distillation, was mixed with 2-methylmercaptobenzoxazole (4 g, 0.024 M) and the mixture was heated for 2½ hours at 100°C. The clear solution became opaque and viscous. The viscous oil, N-methyl-2-methylmercaptobenzoxazolium methosulphate, (7.05 g, 0.024 M) was dissolved in warm methanol (50 ml) cooled to room temperature and hydrazine hydrate (0.65 g, 0.013 M) was added over one minute. Triethylamine (10 g, 0.1 M) was then added quickly and the reaction mixture was stirred for one hour. Methyl mercaptan was evolved and a white precipitate obtained. The product was recrystallised from chloroform (2.4 g) m.p. 242–5°C. (Found: C, 65.4; H, 4.96; N, 19.4. $C_{16}H_4N_4O_2$ requires C, 65.3; H, 4.76; N, 19.05%.) The radical cation salt ($DBBOA^{\dot{+}}Br^-$) was prepared as follows. A solution of 0.5% bromine in chloroform was added to a solution of 3-methylbenzoxazolin-2-one azine (XXI) (1.0 g) in chloroform (25 ml) until the precipitation of a royal blue solid was complete. The precipitate was filtered off, washed once with chloroform and dried in vacuum. (Yield: 1.2 g, 66%), m.p. 152–3°C. (Found: C, 35.35; H, 2.65; N, 11.4; Br^-, 44.80. $C_{16}H_{14}N_4O_2Br_3$ requires C, 35.4; H, 2.58; N, 10.8; Br^-, 44.3%.)

(D) **Bis-(5-phenyl-1,2-dithiolinylidine)-azine** (BPDA) (10)

3-Methythio-5-phenyl-1,2-dithiolium methosulphate (3.4 g, 10 m mol) was reacted with hydrazine hydrate (1 g, 20 m mol) in acetic acid (50 ml) at room temperature for 48 hours. The red solid obtained (1.0 g) was purified by dissolving in concentrated sulphuric acid and reprecipitating with water m.p. 284–8°C. (Found: C, 55.76; H, 3.26; N, 7.12; S, 31.71%. $C_{18}H_{12}N_2S_4$ requires C, 56.26; H, 3.13; N, 7.29; S, 33.3%.) Oxidation of BPDA (0.6 g) was carried out using excess bromine (1 g) in chloroform (50 ml) to give a grey solid. (Found: C, 36.95; H, 2.07; N, 4.68; Br, 32.28%. $C_{18}H_{12}N_2S_4 2Br^-$, ($BPDA^{\ddagger}$ $2Br^-$) requires C, 38.36; H, 2.22; N, 5.18; Br, 29.61; S, 23.7%.)

(E) **NN-Dimethyl-bis-(2-benzthiazolinylidine)-azine** DBBTA (3, $R = CH_3$)

2-Methylmercaptobenzthiazole (100 g, 0.56 mol) was heated for 2 hours at 110–120° with dimethyl sulphate (69 g, 0.56 mol) and the resulting solid dissolved in methanol (400 ml). The solution was stirred vigorously and hydrazine hydrate (13.3 g, 99–100%) added dropwise. Methyl mercaptan was evolved and a precipitate began to form. After 5 minutes, triethylamine (77 ml) was added over a period of 20 minutes. The mixture became warm (40°) and, on completion of the addition, was cooled on ice. The resultant precipitate was filtered off, washed with methanol, dried and recrystallised from dimethylformamide to give colourless plates (73.1 g) m.p. 256–8°C. (Found: C, 59.2; H, 4.38; N, 17.41; S, 20.05%. $C_{16}H_{14}N_4S_2$ requires C, 58.9; H, 4.3; N, 17.2; S, 19.65%.)

Radical cation; Simple fluoroborate salt ($DBBTA^{\dot{+}}$) BF_4^-

A solution of DBBTA (1.7 g, 5 m mol) in methylene chloride (60 ml) and acetic anhydride (10 ml) was mixed with a solution of lead tetracetate (2.2 g, 5 m mol) in methylene chloride (30 ml) and acetic anhydride (5 ml) at room temperature. After adding a cold mixture of fluoroboric acid (15 ml), methylene chloride (60 ml) and acetic anhydride (50 ml) the solution was stirred at room temperature for 48 hours. The blue precipitate was collected and crystallized from acetonitrile to give blue needles (0.4 g) m.p. 191°C. (Found: C, 46.13; H, 3.35; N, 13.44. $C_{16}H_{14}N_4S_2BF_4$ requires C, 46.49; H, 3.39; N, 13.56%.)

Radical cation; sulphate

Oxidation of DBBTA using ceric sulphate in 66% sulphuric acid at 25°C for various periods of time failed to give a product corresponding to the pure radical cation sulphate. However a range of materials was obtained with variable analyses and with conductivities of between 3×10^{-4} and 4×10^{-7} ohm^{-1} cm^{-1}.

Radical cation. Complex fluoroborate salt $(DBBTA)_2^{+}$ BF_4^-

A solution of lead tetracetate (4.43 g, 10 m mol) in dry dimethyl formamide (200 ml) was added dropwise during 2 minutes to a stirred solution of DBBTA (7.52 g, 20 m mol) in dry dimethyl formamide at 60°C. Sodium fluoroborate (7.2 g, 70 m mol) in dimethyl-formamide (70 ml) was added and after stirring for 2 hours at 0°C the blue precipitate was collected and crystallised from formic acid to give blue-violet crystals (5.6 g). (Found: C, 52.69; H, 4.01; N, 15.24; S, 18.37. $C_{32}H_{28}N_8S_4BF_4$ requires C, 52.23; H, 3.81; N, 14.78; S, 17.42%.) X-ray diffraction showed the material to be only partly crystalline.

(F) Bis-(1,3-dimethyl-benzimidazolinylidine)-azine BDBIA (5)

The neutral material[46] had a m.p. 256–258°C. (Found: C, 66.8; H, 6.42; N, 26.3. Calculations for $C_{18}H_{20}N_6$, C, 67.5; H, 6.25; N, 26.5%.)

The radical cation salt ($BDBIA^{+}BF_4^-$, m.p. 292–93°C, was obtained by comproportionation of the neutral and dication forms of BDBIA in deoxygenated acetonitrile. (Found: C, 52.87; H, 5.53; N, 20.99. $C_{18}H_{20}N_6BF_4$, requires C, 53.0; H, 4.91; N, 20.62%.) A range of mixtures of the neutral/radical cation, neutral/dication were prepared and their electrical properties investigated.

(G) Bis-(benzo-1,2-dithiolinyldine)-azine (BBDA) (7)

The neutral compound[47] was obtained as orange crystals from dimethyl acetamide m.p. 246–8°C. (Found: C, 51.23; H, 2.44; N, 8.2; S, 38.47. Calculations for $C_{14}H_{18}N_2S_4$, C, 50.62; H, 2.41; N, 8.44; S, 38.56%.) Three radical cation salts were prepared. The fluoroborate was prepared by the reaction of BBDA with lead tetra-acetate and 40% aqueous fluoroboric acid in acetic anhydride and appeared to be a mixture of the neutral and radical cation forms. (Found: C, 43.95; H, 2.3; N, 7.2; S, 32.09. $C_{14}H_{18}N_2S_4BF_4$ requires C, 40.19; H, 1.91; N, 6.69; S, 30.58%.) The bromide was obtained as a mixture with neutral material by treating a suspension of neutral BBDA (2.2 m mol) in acetic acid with a large excess of bromine (18 m mol). (Found: C, 46.09; H, 2.22; N, 7.32; S, 33.51; Br, 8.79%. $(C_{14}H_{18}N_2S_4)_3(C_{14}H_{18}N_2S_4Br)_2$ requires C, 46.00; H, 2.2; N, 7.7; S, 35.00; Br, 9.00%.)

It was reduced to neutral BBDA on attempted recrystallisation from dimethyl acetamide. The sulphate was prepared by oxidation with ceric sulphate in concentrated sulphuric acid. (Found: C, 46.55; H, 2.34; N, 7.46. $(C_{14}H_8N_2S_5)_2SO_4$ requires C, 44.21; H, 2.11; N, 7.37%.)

(H) 2,2'-Bis-(4,5-benzo-1,3-dithiolinylidine) BBDY (9)

Recrystallisation of BBDY[47] from chloroform gave a product with m.p. 239–41°C (Lit.[47] 242.5–243°C). (Found: C, 54.29; H, 2.70; S, 43.02;. Calculations for $C_{14}H_8S_4$, C, 55.26; H, 2.63; S, 42.13%.) The bromide radical cation salt was prepared as a purple solid by oxidation of BBDY (0.608 g) in chloroform (100 ml) with 10.6 mls of Br_2/chloroform solution (0.0945 M). (Found: C, 40.98; H, 2.21; S, 34.25; Br, 23.62. $C_{14}H_8S_4Br$ requires C, 43.75; H, 2.08; N, 33.34; Br, 20.80%.) Oxidation with a large excess of bromine gave a dark red solid. (Found: C, 21.72; H, 1.21; S, 16.92; Br, 60.30. $(C_{14}H_8S_4)^{2+}2Br_3^-$ requires C, 21.4; H, 1.02; S, 16.3; Br, 61.53%.)