Semiconducting 1,2-Dithiolylium Charge-transfer Salts

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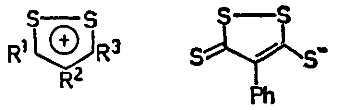
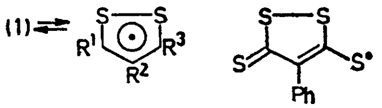
Summary 1,2-Dithiolylium 5-thioxo-1,2-dithiole-3-thiolates are shown to be charge-transfer salts with semiconducting electrical properties.

IN the search for conducting and semiconducting organic compounds interest has been focused so far on the 1,3-dithiole system, where the most efficient organic conductor, the complex of tetrathiafulvalene and tetracyanoquinodimethane has been found.[1] The corresponding selena-analogue has recently been described[2]. Until now, however, it has not been possible to prepare the tetrathiafulvalene analogue in the 1,2-dithiole series.[3]

We now report the preparation and properties of the semiconducting charge-transfer salts (**1**). Their conductivity is probably due to the action of the thiolate anion as an electron donor which gives rise to the neutral radical (**2**). Such charge-transfer salts with an ionic ground state and an excited state consisting of two neutral radicals are well known.[4]


(1)


(2)

The specific d.c. resistance ρ_{20} was *ca.* 10^7—10^8 ohm cm for 3,5-diphenyl-1,2-dithiolylium 4-phenyl-5-thioxo-1,2-dithiole-3-thiolate (AD) whereas corresponding salts derived from 3-phenyl-1,2-dithiolylium salts and 3,4-diphenyl-1,2-dithiolylium salts were found to be insulators.

Table

U.v. and visible spectral data for 3,5-diphenyl-1,2-dithiolylium perchlorate, the thiolate anion and the corresponding charge-transfer salt

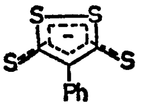
A$^+$,ClO$_4^-$	λ_{max}=247		375	
	ϵ =8·800		29·300	
Me$_2$NH$_2^+$,D$^-$	λ_{max}=242	306		420
	ϵ =11·200	9·800		28·700
A$^+$,D$^-$	λ_{max}=242	318	378	418
	ϵ =26·200	15·000	38·900	32·900

[a] Spectral data measured in MeCN, concentration *ca.* 1·3 × 10^{-5} mol l^{-1}.

This is in good agreement with the observation that 3-phenyl and 3,4-diphenyl-1,2-dithiolylium perchlorates have reduction potentials in acetonitrile of −0·45 and −0·46 V respectively,[5] whereas 3,5-diphenyl-1,2-dithiolylium perchlorate is reduced to the stable dithiolyl radical at −0·27 V.[6]

To avoid random potentials due to asymmetric orientation in the crystal it is essential that the ions are highly symmetrical. Both ions in (**1**) (R^1 = R^3 = Ph, R^2 = H) possess C_{2v} symmetry, as the negative charge in the anion is probably delocalised, so that the true structure of the anion is best represented as (**3**).

The compounds could also have structure (**4**) which could be in equilibrium with the radical species. It is well known[6] that such 'dimers' are easily formed. Structure (**4**), however, seems unlikely on the basis of the u.v.–visible spectral data (Table) which are more consistent with a charge transfer salt.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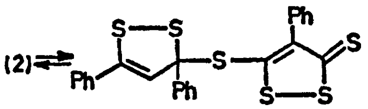
(4)

The salts were obtained in analytically pure state by mixing the dithiolylium perchlorate in acetonitrile with a solution of the anion[7] in acetonitrile at room temperature.

It has not been possible to grow single crystals suitable for d.c. resistance measurements. The resistance was measured from pellets compacted at room temperature under a pressure of 7·500 kg cm^{-2}. The size of the pellets was 2 × 2 × 13 mm.

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