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Conducting Salts of Cyclic Sulphonium Cations with 7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ): *X*-Ray Crystal Structure of 1-Methyl-1,4-dithianium TCNQ salt, $(MDT)_1^+ (TCNQ)_2^-$

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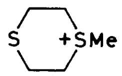
Cyclic sulphonium cations (**1**)—(**3**) form 1 : 2 salts with TCNQ which are organic conductors at room temperature ($\sigma_{r.t.}$ 1 × 10^{-3}—2.0 S cm^{-1}); the *X*-ray crystal structure of 1-methyl-1,4-dithianium TCNQ salt $(MDT)_1^+(TCNQ)_2^-$ (**1**) has been determined.

Salts of TCNQ remain at the forefront of research on organic materials that exhibit novel electronic and magnetic properties.[1,2] Close face-to-face overlap of the TCNQ molecules within the crystal lattice favours extensive intermolecular electron mobility and the formation of an energy band. The partial occupancy of this energy band is a prerequisite for high conductivity, and this usually arises as a result of incomplete charge transfer (ρ) from an electron donor molecule to TCNQ (*e.g.*, for TTF–TCNQ ρ = 0.57 electrons) or by crystallisation of a binary salt in a stoicheiometry other than 1 : 1, typically $(cation)_1^+(TCNQ)_2^-$. Ammonium and phosphonium cations have been widely studied as counterions for TCNQ anion salts and these materials provide classical examples of organic metals and organic semiconductors.[1—3]



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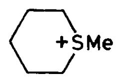

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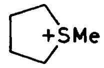

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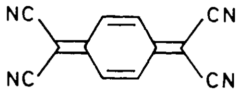

TCNQ

Table 1. Conductivity values for TCNQ salts.

Salt[c]	(1)	(2)	(3)
Cation : TCNQ	1 : 2	1 : 2	1 : 2
$\sigma_{r.t.}$/S cm^{-1}	2.0[a]	0.1[a]	1 × 10^{-3b}

[a] Single crystal, four-probe measurement, [b] Compressed pellet, two-probe measurement. [c] Salts (**1**)—(**3**) formed from cations (**1**)—(**3**) respectively.

We report that cyclic sulphonium cations form conducting, binary salts (**1**)—(**3**) with TCNQ. Saturated sulphur heterocycles have not been reported previously as cations for TCNQ salts, although unsaturated sulphur heterocycles are widely used as π-donors for complexes (*e.g.*, TTF–TCNQ).[1,2] This new series of salts (**1**)—(**3**) has been characterised by variable temperature conductivity measurements, magnetic suscepti-

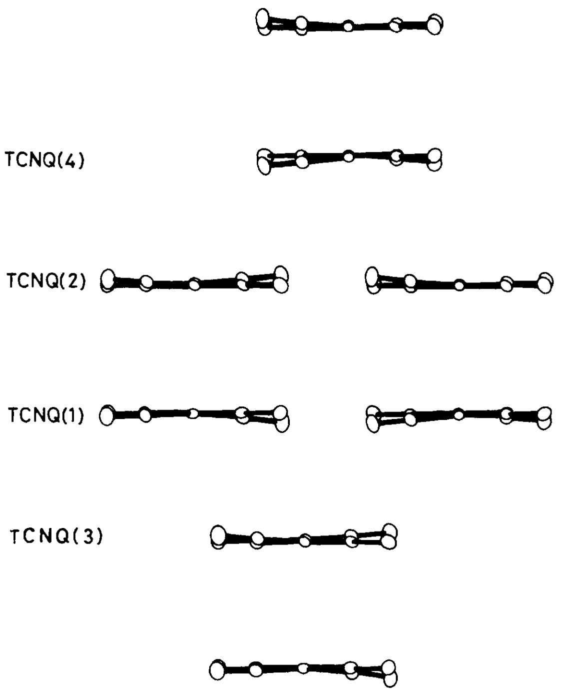

Figure 1. TCNQ dimers viewed down the long axis of the TCNQ molecules.

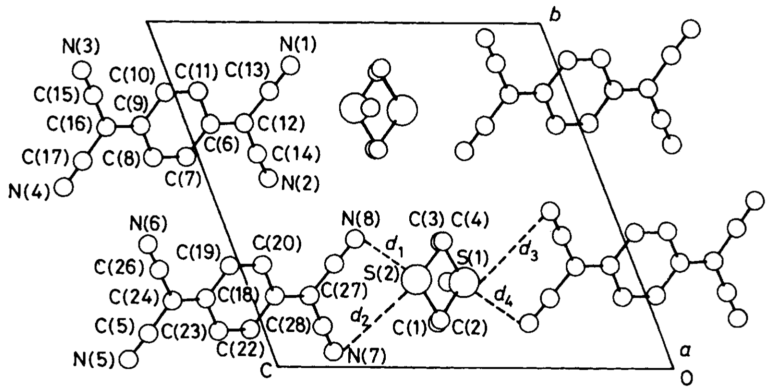

Figure 2. View along the crystallographic *a* axis. Non-bonded S · · · N distances: d_1 3.74, d_2 3.98, d_3 4.14, d_4 3.97 Å.

bility data and, for compound (**1**), single crystal *X*-ray analysis.

Crystals of the salts (**1**)—(**3**) were prepared (30—50% yield) by mixing the appropriate sulphonium methiodide and TCNQ in a 1 : 1 or 1 : 2 molar ratio in hot acetonitrile, followed by slow cooling of the solution to 0 °C. The stoicheiometry of the salts (**1**)—(**3**) (1 : 2 cation : TCNQ) was determined by elemental analysis. Room temperature conductivity values are given in Table 1. The conductivity was measured over the temperature range 300—80 K; all three salts show typical semiconductor behaviour, *i.e.*, there is a steady decrease in conductivity as the temperature is lowered. The $\sigma_{r.t.}$ value for the salts (**1**) and (**2**) is notably higher than that for most TCNQ salts of ammonium and phosphonium cations ($\sigma_{r.t.}$ 10^{-2}—10^{-5} S cm^{-1}).[1a,2]

We have determined the *X*-ray crystal structure of the salt (**1**), the most highly conducting member of the series.† The TCNQ molecules form discrete pairs (dimers) (Figure 1); the intra-dimer [TCNQ(1)–TCNQ(2)] separation between the mean planes of the TCNQ rings is 3.2 Å and the intra-dimer overlap is of the 'ring-over-bond' type. This intra-dimer configuration is common and is known[4] to maximise the attractive interactions within a pair of TCNQ ions, $(TCNQ)_2^-$. However, there is essentially no inter-dimer face-to-face overlap: the slipped inter-dimer configuration, with only very weak interaction between TCNQ(1) and TCNQ(3) and between TCNQ(2) and TCNQ(4), is most unusual. This leads to a 'brick wall' stacking of TCNQ dimers within the lattice (Figure 1), as opposed to columnar stacking that is a feature of the vast majority of TCNQ salts.[1] The cavities formed by this structure are occupied by the methyldithianium cations. Non-bonded S · · · N distances are slightly asymmetric (Figure 2). However, all such distances are greater than the sum of the respective van der Waal's radii, *viz.* 3.35 Å.[5] The overall features of the structure of the salt (**1**) are reminiscent of the −160 °C structure of the 1 : 2 salt *N*-methyl-*N*-ethyl-morpholinium TCNQ, $(MEM)_1^+$-$(TCNQ)^{2-}$, where weak, slipped, inter-dimer interaction is also found.[6] However, at room temperature, $(MEM)_1^+(TCNQ)_2^-$ has a quite different structure.[7] The MEM salt has been thoroughly studied because of the unusual paramagnetic properties (a spin Peierls transition) observed at low temperatures.[8]

The three sulphonium TCNQ salts (**1**)—(**3**) are strongly paramagnetic. The temperature dependence of the spin susceptibility has been studied by e.s.r. spectroscopy (300—90 K) and by using a Faraday balance (300—4.2 K). The data for the salts (**2**) and (**3**) are consistent with Curie-Weiss behaviour, typical of many cation TCNQ salts. On the other hand, data for the salt (**1**) are strikingly different: between 300 and 4.2 K the data are well fitted by a Bonner-Fischer susceptibility, whereas below 6 K there is a sharp drop in the total susceptibility which may be due to a spin Peierls transition analogous to the 20 K transition in $(MEM)_1^+(TCNQ)_2^-$. Detailed magnetic data for salt (**1**) will be published separately.[9]

In conclusion, we have demonstrated that cationic sulphur heterocycles offer considerable potential in the area of novel, conducting organic molecules.

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† *Crystal data* for (**1**): $(C_5H_{11}S_2)^+2(C_{12}H_4N_4)^{\frac{1}{2}-}$, $M = 543.64$, triclinic, space group $P\bar{1}$, $a = 7.970(4)$, $b = 13.010(2)$, $c = 14.169(2)$ Å, $\alpha = 68.28(1)$, $\beta = 93.48(3)$, $\gamma = 86.90(4)°$, $U = 1357.7(7)$ Å^3, $Z = 2$, $F(000) = 562$, Mo-K_α radiation (graphite monochromator), $\lambda = 0.71069$ Å, μ(Mo-K_α) = 110.7 cm^{-1}, $D_c = 1.330$ g cm^{-3}; 4785 independent reflections, 3026 with $I > 1.5\sigma(I)$ used, direct methods, SHELXS-84, $R = 0.060$, $R_w = 0.059$. Non-hydrogen atoms refined anisotropically, all hydrogen atoms placed in calculated positions (C–H = 0.96 Å, $U = 0.10$ Å^2); 355 parameters refined. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.