# Organic Conductors. 2,3,6,7-Tetramethyl-1,4,5,8-tetraselenafulvalenium 2,5-Dimethyl-7,7′,8,8′-tetracyano-*p*-quinodimethanide

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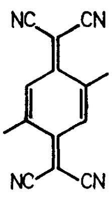
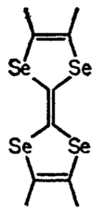
*Summary* 2,3,6,7-Tetramethyl-1,4,5,8-tetraselenafulvalene reacts with 2,5-dimethyl-7,7′,8,8′-tetracyano-*p*-quinodimethane to give a highly conducting organic solid.

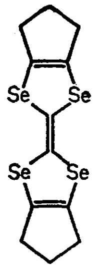
Highly conducting organic charge-transfer salts based on the prototype tetrathiafulvalene–tetracyano-*p*-quinodimethane (TTF–TCNQ)[1,2] are currently being investigated in order to evaluate the effect of changed molecular properties of donors and acceptors on the solid state properties of the resulting charge-transfer salts. So far the majority of these studies have concentrated upon modifying the molecular properties of the donor.[3–8]



2,5-DMTCNQ



TMTSF



HMTSF

We report the results of changing the acceptor properties by introduction of methyl substituents. 2,5-Dimethyl-7,7′,8,8′-tetracyano-*p*-quinodimethane (2,5-DMTCNQ)[9] differs from TCNQ by being larger, having a lower electron affinity, and by having a lower molecular symmetry ($C_{2h}$ as compared to $D_{2h}$). 2,5-DMTCNQ (like TCNQ) has no permanent dipole moment, however. A characteristic of the conducting solids formed by TCNQ is the occurrence of separate stacks of acceptor and donor molecules. 2,5-DMTCNQ carries the possibility of different stacking patterns. Stacks might be formed in a regular way in order to facilitate minimum steric repulsion of methyl groups of adjacent molecules. Alternatively, the methyl groups can be 'randomized' with resulting slight disorder in the lattice.[10]

2,5-DMTCNQ was prepared from 2,5-dimethylcyclohexane-1,4-dione[9] which was obtained by dimethylation of diethyl-2,5-dioxocyclohexane-2,4-dicarboxylate followed by hydrolysis and decarboxylation. It was purified by multiple recrystallizations followed by gradient sublimation on to Teflon.

Solution measurements suggest that 2,5-DMTCNQ is a poorer electron acceptor than TCNQ, since reduction in acetonitrile occurs at a potential *ca.* 0·15 V more cathodic. This should, however, be taken only as an indication of lower electron affinity, since it has been shown that half-wave potentials of TCNQ and related molecules depend strongly on electrode materials and solvent composition.[12]

The acceptor properties of 2,5-DMTCNQ were examined with four donors, TTF,[1] TMTTF,[3] TMTSF,[7] and HMTSF.[8] Their 1 : 1 charge transfer salts were obtained by slow evaporation of solvent from (preferentially) MeCN–$CH_2Cl_2$ solutions of the constituents. We have so far failed to obtain single crystals of TTF–2,5-DMTCNQ and TMTTF–2,5-DMTCNQ. The selenium-containing donors, however, yield crystals of reasonable quality.

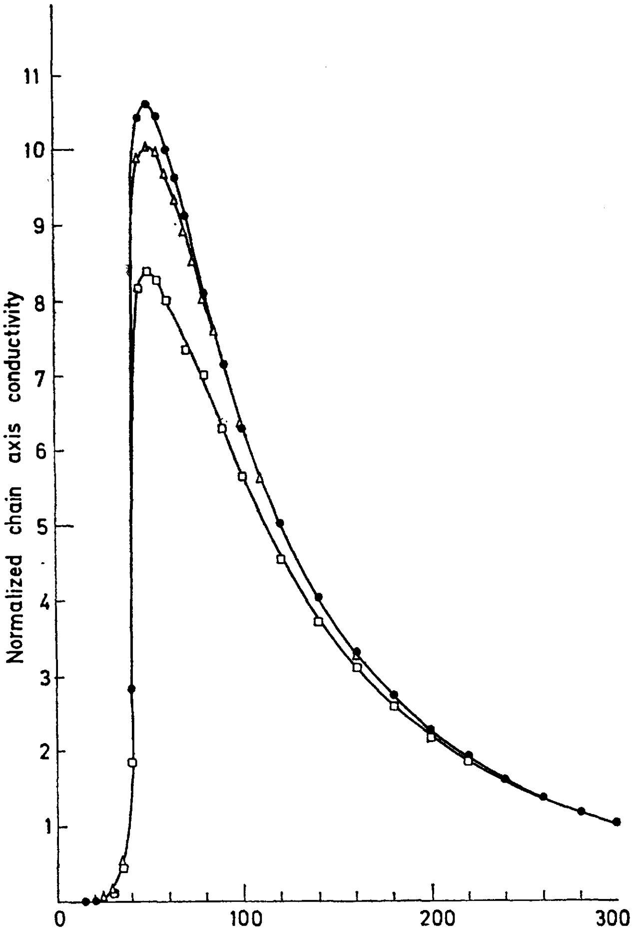


Figure. Normalized *a*-axis conductivity of three separately grown crystals of TMTSF–2,5-DMTCNQ.

TMTSF–2,5-DMTCNQ (1 : 1) was obtained as black needles of typical dimensions 3 × 0·02 × 0·06 mm. Four-probe d.c. conductivity measurements indicate a room temperature conductivity of at least 300 $\Omega^{-1}$ cm$^{-1}$ rising to a maximum value of *ca.* 3000 $\Omega^{-1}$ cm$^{-1}$ at 50 K (Figure). Below this temperature, the crystals undergo a metal–insulator transition as usually seen in these materials.[1,2]

TMTSF–2,5-DMTCNQ crystallizes in a triclinic lattice. The unit-cell constants are $a = 3{\cdot}94$, $b = 8{\cdot}12$, $c = 18{\cdot}9$ Å, $\alpha = \beta = 97{\cdot}5$, $\gamma = 91{\cdot}4°$. The short axis ($a$) is parallel to the needle axis and is recognized from previously investigated conducting TCNQ salts.

It is of interest to compare crystal and solid-state data for TMTSF–2,5-DMTCNQ with those for the conducting form of TMTSF–TCNQ.[13] Both structures are triclinic and the crystals show comparable conductivity data. In TMTSF–2,5-DMTCNQ the transition temperature is lower, however, by *ca.* 20°. This could arise from disorder effects[2,4,6,10] (*vide supra*), or indicate that solid-state data are mainly dominated by the actual crystal structure and less by electronic properties of donors and acceptors. TMTSF–2,5-DMTCNQ has a unit cell volume approximately 10% larger than TMTSF–TCNQ thereby probably reducing interchain coupling markedly.

The observed stabilization of the 'metallic' region deserves comparison with recent results obtained for TTF–TNAP[14] (TNAP = 11,11′,12,12′-naphtho-2,6-quinodimethane). TNAP has the same low symmetry ($C_{2h}$) as 2,5-DMTCNQ, but TTF–TNAP is not metallic in the high-temperature range and the conductivity drops sharply at 185 K.

The sensitivity of molecular properties to small structural changes is illustrated by the results obtained for HMTSF–2,5-DMTCNQ (1:1). This salt crystallizes as long needles which appear red in reflected light. Four-probe d.c. measurements show that the crystals are insulating, $\sigma_{\mathrm{RT}} < 10^{-8}$ $\Omega^{-1}$ cm$^{-1}$.

Preliminary structural data for this salt indicate a structure consisting of mixed stacks, and we have not so far been able to observe any polymorphism as previously found for TMTSF–TCNQ.[13]

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