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Stabilization of the Organic Metallic State: The Properties of Two Substituted Tetraselenafulvalenes and Their TCNQ Salts

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Stabilization of the Organic Metallic State

The Properties of Two Substituted Tetraselenafulvalenes and Their TCNQ Salts

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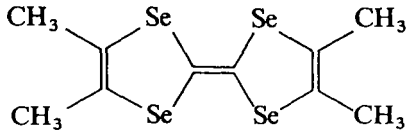
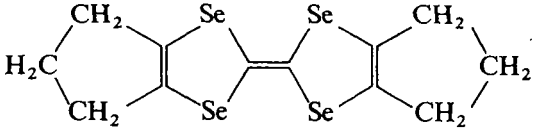
Results are described for two new one-dimensional organic conducting solids. 2,3,6,7-Tetramethyl-tetraselenafulvalene-TCNQ (1 : 1) crystallizes in a triclinic structure and undergoes a metal-to-insulator transition at low temperature. Introduction of a new substituent pattern leaves the electronic properties of the donor unchanged, but 2,3;6,7-bis-(trimethylene)- tetraselenafulvalene crystallizes in a nearly orthorhombic structure and retains metallic properties to 0.07 K.

Selenium analogues of the quasi one-dimensional organic conductor TTF–TCNQ[1,2] has attracted much attention recently. TSF–TCNQ[3] is isostructural with TTF–TCNQ and exhibits parallel properties. Two other tetraselenafulvalenes TMTSF[4] and HMTSF[5] which appear electronically indistinguishable, both form conducting TCNQ compounds of triclinic and nearly orthorhombic structure respectively.



TMTSF



HMTSF

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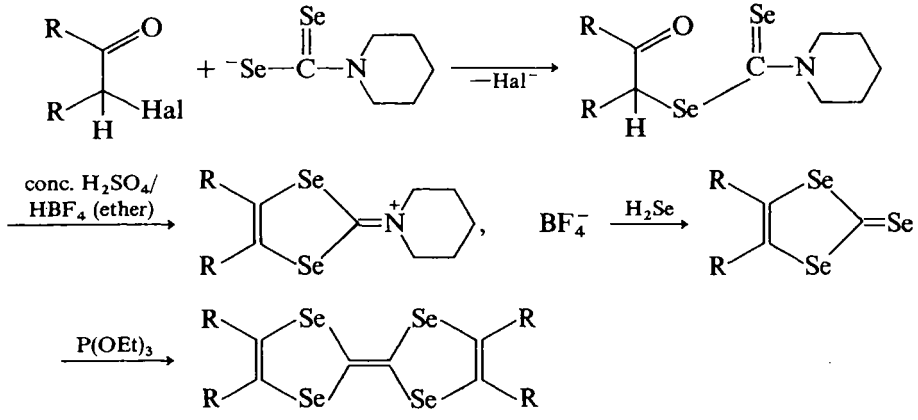
SYNTHESIS

TMTSF and HMTSF have been prepared[4–6] by the following procedure:



$$R = CH_3 \quad \text{or} \quad R + R = -CH_2-CH_2-CH_2-$$

The *electronic structures* of the two donors appear as should be expected to be quite similar. Their electronic absorbtion spectra are nearly superimposable, (λ_{max}, log ε, TMTSF:304 nm, 4.21, 365 nm(sh), 3.2, 500 nm, 2.18 and HMTSF 301 nm, 4.14, 370 nm(sh), 3.1, 498 nm, 2.22). Furthermore, the solution oxidation potentials of the two donors as determined by cyclic voltammetry are identical within experimental error. The vapor pressure of HMTSF is too low to allow determination of gas-phase ionization potentials but a PES determination of TMTSF provides a value of 6.58 eV.[7] Interestingly, tetraselenafulvalenes have slightly higher IP's than their sulfur counterparts, a feature which is reflected both in the gas phase and in solution. (See Table I.)

TABLE I

Ionization potentials

Compound	$E^1_{1/2}$[a]	$E^2_{1/2}$[a]	IP_{PES} eV
HMTSF	+0.55	+0.92	—
TMTSF	+0.54	+0.93	6.58[7]
TMTTF[b]	+0.36	+0.86	6.42[7]

[a] Volts *vs.* SCE at Pt button electrode in CH_2Cl_2/*n*-Bu_4NBF_4 (0.2 M).
[b] Tetramethyltetrathiafulvalene.

Based on the similarity of the electronic structures of TMTSF and HMTSF it is reasonable to assume that the different solid state properties of their 1:1 compounds with TCNQ are solely determined by the crystal structure.

STRUCTURES

TMTSF–TCNQ (1:1) can be obtained in two different crystal structures.[8] A "red" orthorhombic, insulating form is dominated by mixed stacks of donor and acceptor molecules, whereas a "black," triclinic conducting form exhibits the separate chains of donor and acceptor molecules characteristic of conducting organic solids. The somewhat larger non-planar HMTSF give rise to a nearly orthorhombic, conducting HMTSF–TCNQ (1 : 1) compound, with a lower density of chains per unit area than TMTSF–TCNQ, as well as some long range disorder.[9]

CONDUCTIVITY

A detailed account of the physical properties of TMTSF–TCNQ[8] and HMTSF–TCNQ[10] has been given elsewhere. The conducting form of TMTSF–TCNQ has a conductivity σ_{RT} of 1200 $(\Omega cm)^{-1}$ and undergoes the metal-to-insulator transition, also characteristic of previously known fulvalenium–TCNQ salts near 65 K. HMTSF–TCNQ, however, behaves as a metal throughout the accessible temperature range. HMTSF–TCNQ

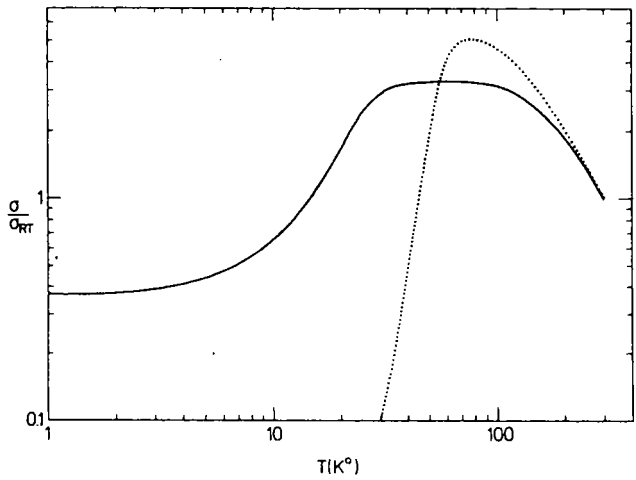


FIGURE 1

displays the largest high temperature ($\sigma_{300} \sim 2000\ (\Omega cm)^{-1}$) and low temperature ($\sigma_{0.07} \sim 800\ (\Omega cm)^{-1}$)[11] a conductivity of any organic substance reported so far. A logarithmic plot of the normalized conductivities of TMTSF–TCNQ (dotted line) and HMTSF–TCNQ (full line) vs temperature is given in Figure 1. Thus a slight change of geometry of the donor molecule can effect a suppression of the insulating state. It is, however puzzling that the sulfur analogue[11] of HMTSF–TCNQ appears to be isomorphous, but undergoes a metal-to-insulator transition at 50 K.

Preliminary results obtained for 1 : 1 compounds of both TMTSF and HMTSF with the acceptor TNAP[12] have indicated that the metallic state is stable at very low temperature. Crystal growth is however rather difficult, and crystals investigated were of rather poor quality.

Acknowledgement

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