

corresponds very closely to what is found in Na_xWO_3 ; even the 2-eV separation corresponds well to the shift expected for removal of one electron.

A detailed discussion of (1) the relationship between the electronic structure of the bronzes and XPS valence-band data, (2) the connection between XPS binding energies of W and Na core levels and spin-relaxation²⁰ and Knight-shift²¹ experiments, and (3) the implications of the detection of a unique W 4*f* doublet on conduction-electron delocalization will be published elsewhere. A more extensive investigation of the dependence of α on x and on the local environment is in progress.

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¹⁸The alternate interpretation of the W 4*f* spectrum in terms of separate contributions from W^{6+} and W^{5+} is not tenable for various reasons. The intensity ratios $[\text{W}^{5+}]/[\text{W}^{6+}] = x/(1-x)$ for the three samples range from 4.1 for $x = 0.805$ to 1.63 for $x = 0.620$. This is contrary to the data. Neither the x -dependent shift of the narrower line at smaller binding energy, nor the x -dependent change in the separation between the two sets of lines fits into this picture.

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dc Conductivity in an Isostructural Family of Organic Metals

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The tetracyano-*p*-quinodimethane salts of tetrathiafulvalene and its newly synthesized selenium analogs tetraselenafulvalene and *cis/trans*-diselenadithiafulvalene form an "isostructural" series of highly conducting organic salts. The electrical conductivity is remarkably similar and peaks at 59, 40, and 64°K, respectively. It is concluded that the conduction mechanism is of the same origin in spite of their varying molecular properties.

Considerable interest has been generated recently by the dc-conductivity properties of the crystalline organic charge-transfer salt tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ).¹⁻⁷ In order to understand this material

better we have synthesized the selenium analog of TTF, tetraselenafulvalene (TSeF)⁸ [Fig. 1(a)], and *cis/trans*-diselenadithiafulvalene (DSeDTF)⁹ [Figs. 1(b) and 1(c)]. In this paper we report conductivity measurements on the TCNQ

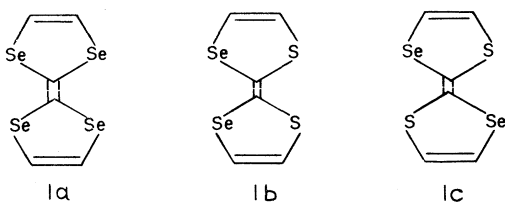


FIG. 1. The molecular structure of the constituents.

salts of these molecules. The new materials described here offer an approach for understanding TTF-TCNQ by changing the molecular properties while maintaining the crystal structure.

Prior attempts at varying the physical properties of TTF-TCNQ by the addition of substituents on either TTF or TCNQ have resulted in a change in crystal structure¹⁰ which obscures the electronic effect of the molecular modification. The x-ray diffraction patterns and unit-cell constants, which are listed in Table I for the TCNQ salts of TTF, DSeDTF, and TSeF, show these three materials to be isostructural. These parameters were determined by completely indexing the powder x-ray diffraction patterns consistent with the space group reported for TTF-TCNQ.¹¹ TSeF-TCNQ possesses a slightly larger unit cell than its sulfur analog, while the mixed sulfur-selenium derivative lies almost exactly in the middle of these values. Considering that the Van der Waals radius of selenium is 0.15 Å larger than that for sulfur, we find only a very small increase along the b_0 stacking axis in TSeF-TCNQ (0.05 Å) and DSeDTF-TCNQ (0.02 Å).

DSeDTF-TCNQ differs fundamentally from TTF-TCNQ and TSeF-TCNQ, since the less-symmetric DSeDTF molecule is capable of introducing disorder into the TCNQ salt. Proton NMR reveals the presence of approximately equal amounts of *cis* and *trans* isomers [Figs. 1(b) and

TABLE I. Unit-cell constants and conductivity results.

Parameter	TTF-TCNQ ^a	DSeDTF-TCNQ	TSeF-TCNQ
a_0 (Å)	12.298	12.405	12.514
b_0 (Å)	3.819	3.847	3.876
c_0 (Å)	18.468	18.486	18.511
β (deg)	104.5	104.3	104.2
σ ($\Omega^{-1} \text{ cm}^{-1}$)	500 ± 100	350 ± 100	800 ± 100
T_p (°K)	59 ± 1	64 ± 2	40 ± 1
ρ_2 [$10^{-8} \Omega \text{ cm} (\text{°K}^{-2})$]	2.2 ± 0.2	2.4 ± 0.3	1.6 ± 0.2
No. of samples	5	3	8

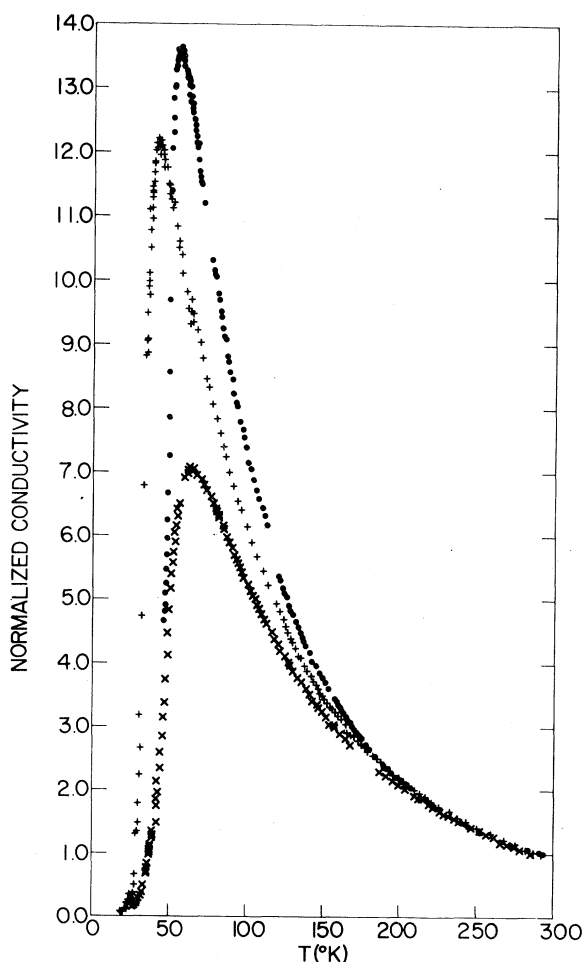
^aRef. 11.

1(c)] in neutral DSeDTF.⁹ The *cis* isomer has a permanent electric dipole moment, while the *trans* isomer has a quadrupole moment.

Single-crystal, four-contact, dc-conductivity measurements on the three isostructural systems have been carried out as a function of temperature. To ensure current homogeneity, the current contacts were capped at the ends of the crystal and the voltage contacts were wrapped around the sample.⁵

The most important experimental observation of this work is that the temperature dependence of the electrical conductivities of the three systems show remarkably similar behavior (Fig. 2). In spite of the significant changes in the molecular properties of the donor, both the crystal structure and the sharply peaked temperature dependence of the conductivity remain similar.

Within the context of the overall similarity between the three members of this isostructural

FIG. 2. Normalized conductivity $\sigma/\sigma(295\text{°K})$ of (●) TTF-TCNQ, (+) TSeF-TCNQ, and (×) DSeDTF-TCNQ.

family it is interesting to examine the differences which do exist.¹² In transmission, thin crystals of TSeF-TCNQ and DSeDTF-TCNQ have a magenta red and a deep orange color, respectively, as opposed to the yellow color of TTF-TCNQ. The metallic state in TSeF-TCNQ is stabilized to $\sim 40^\circ\text{K}$, the lowest temperature reported to date for any organic solid (compared to $\sim 59^\circ\text{K}$ for TTF-TCNQ, Table I and Fig. 2). The potentially disordered system, DSeDTF-TCNQ, has its peak conductivity at $\sim 64^\circ\text{K}$ which is higher than T_p in either TTF-TCNQ or TSeF-TCNQ, or their average, 50°K . This is also contrary to the suggestion that disorder might stabilize the metallic state to lower temperatures.²

In order to compare the resistivity in the temperature range above T_p we have chosen to fit the data by two dominant terms of the simple power-series expansion $\rho = \rho_0 + \rho_2 T^2$. We find that all samples are fitted reasonably well (Fig. 3) over the limited temperature range $T_p < T \leq 250^\circ\text{K}$, as found previously for TTF-TCNQ.^{1,3,13} By using thin and narrow samples we have found good reproducibility in ρ_2 for each compound, contrary to the previous finding.¹ This strongly indicates that ρ_2 measures an intrinsic property of the system. Having made this two-parameter fit we can use ρ_2 to compare TTF-TCNQ measured in different laboratories and the different members of the isostructural family reported here.

First, considering TTF-TCNQ, we have fitted the data from a number of different laboratories by $\rho = \rho_0 + \rho_2 T^2$ and find (in units of $10^{-8} \Omega \text{ cm}/^\circ\text{K}^2$) $\rho_2 = 2.7,^1 1.8,^3 2.5,^4 2.9,^5$ and 2.2 (Table I).¹⁴ These values provide a measure of the consistency with which TTF-TCNQ can be prepared and measured.

Second, the values of ρ_2 for the three isostructural compounds are nearly the same (Table I). Neither the replacement of TTF with TSeF which differs in mass, ionization potential, polarizability, etc., nor the disorder introduced by DSeDTF significantly changes the nearly quadratic dependence of resistivity on temperature or its absolute value. This similarity indicates a common origin for the conduction in all three systems.

It is of course interesting to compare the normal samples reported here and by most workers (conductivity peaks ≤ 20 times room-temperature values) with the University of Pennsylvania "super" TTF-TCNQ samples (conductivity peaks of 40, 50, and 150 times room-temperature values).⁵ The super samples differ from the normal ones only in the transition region. At higher temperatures the super samples also follow $\rho_0 + \rho_2 T^2$, with

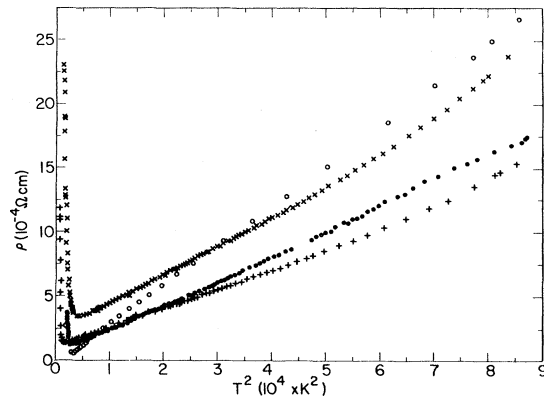


FIG. 3. The absolute resistivity of (○) TTF-TCNQ, data taken from Ref. 5, (●) TTF-TCNQ measured by authors, (+) TSeF-TCNQ, and (×) DSeDTF-TCNQ.

$\rho_2 \approx 2.9$, just as for normal samples (Fig. 3). However, just above the transition, the resistivity drops significantly below the T^2 curve, giving rise to the giant conductivity peak. We conclude that whatever the mechanism giving rise to the apparent giant conductivity it is dominant only in a transition region near the conductivity-peak temperature; that is, the giant peak is not an outgrowth of the high-temperature T^2 behavior observed in all samples. Similar, although much weaker, deviations from the T^2 behavior in the transition region have been observed in some of our samples.

Many authors have proposed possible theories for the conductivity behavior of TTF-TCNQ or for ideal one-dimensional systems. At present it is not clear if any actually apply to TTF-TCNQ.¹⁵ At the risk of increasing the possible theories, we would like to consider electron-electron scattering as a possible resistivity mechanism in these systems.¹⁶ It is well known that in transition metals where there are narrow d bands degenerate with broad s bands, $e-e$ scattering contributes a T^2 term to the resistivity at low temperatures. An even more favorable situation may be present in TTF-TCNQ where narrow tight-binding bands prevail, and the bandwidths of TCNQ and TTF chains are not necessarily the same. Because of the small Fermi energy, $E_F \sim 0.2 \text{ eV}$,¹⁷ and inefficient screening in pseudo-one-dimensional systems, Thomas-Fermi screening length of $\sim 7 \text{ \AA}$,¹⁸ $e-e$ scattering between the two bands may give a large contribution to the resistivity. In the free-electron approximation the mean free path for $e-e$ scatter-

ing, L_{e-e} , is¹⁹

$$1/L_{e-e} = 4\pi n \lambda_{sc}^2 (k_B T / E_F)^2,$$

where n is electron density and k_B is the Boltzmann constant. The expected value for TTF-TCNQ is $L_{e-e} \sim 2 \times 10^{-2} / T^2$ cm compared to the experimental value $L_{e-e} \sim 1 \times 10^{-3} / T^2$ cm derived by using ρ_2 of Table I. This reasonable agreement is encouraging, considering the simplicity of the free-electron approximation²⁰ as compared with the complexities of these organic systems.

In conclusion, we have studied a new isostructural family of organic metals which display widely varying molecular properties, and found remarkably similar single-crystal dc-conductivity behavior. It is apparent that in these systems the dc conductivity is governed by a common process, possibly electron-electron scattering.

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¹³Another method of fitting the data is the three-parameter fit $\rho = \rho_0 + AT^\lambda$ used by Groff, Suna, and Merrifield (Ref. 7) on four samples. By suitable normalization they are able to determine $\lambda = 2.33$ independently from the fit by ρ_0 or A . We do not find any reason to prefer either our choice of $\lambda = 2$ in a two-parameter fit or their three-parameter fit, but rather caution that either fit is made over a limited temperature range.

¹⁴It should be noted that since ρ is related to the measured resistance by an effective area-to-length ratio, A/l , uncertainties in A/l caused by internal breaks or finite contact size will be reflected in ρ . This effect may explain the variation in ρ observed in early experiments.

¹⁵Some of the theories are referred to in Ref. 5.

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