Organic Conductors

Organic compounds synthesized recently, such as tetrathiofulvalenium—7,7,8,8-tetracyanoquinodimethanide (TTF-TCNQ), exhibit properties similar to metallic conductors over a wide temperature range although they consist solely of nonmetallic atoms. In addition, the compounds are "quasi-one-dimensional" with distinctive electrical, structural, and magnetic properties. Properties of some of the compounds in this class are described, with emphasis on the trends and distinctions produced by chemical and crystallographic modifications to the prototype TTF-TCNQ compound.

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Introduction

Traditionally, the term "electrical conductor" has been applied to solids composed of a metallic element or metallic alloys. Conversely, most organic compounds are insulators or semiconductors with room temperature conductivities below 10^{-8} mho/cm that decrease exponentially as the temperature is lowered. In the early 1960's, Melby and his co-workers at duPont[1] discovered that some salts of 7,7,8,8-tetracyanoquinodimethane (TCNQ) have electrical conductivities as high as 100 mho/cm. This is remarkable for an organic compound, although the value is low compared to that of a metal such as copper, whose room-temperature conductivity is 5×10^5 mho/cm. In 1964, Little of Stanford University[2] suggested that a linear chain of organic molecules that is surrounded by polarizable side chains could produce a high-temperature superconductor by means of electron interactions via polarization excitations. While Little's proposed organic system was somewhat different than the structure of the TCNQ salts, the similarities enhanced interest in those compounds.

[1] L. R. Melby, R. J. Harder, W. R. Hertler, W. Makler, R. E. Benson, and W. E. Mochel, "Substituted Quino-dimethans. II. Anion-Radical Derivatives and Complexes of 7,7,8,8-Tetracyanoquinodimethan," *J. Am. Chem. Soc.* **84**, 3374–3384 (1962).

[2] W. A. Little, "Possibility of Synthesizing an Organic Superconductor," *Phys. Rev. A* **134**, 1416–1424 (1964).

The first truly metallic organic compound was discovered in 1972 by Cowan and his co-workers at Johns Hopkins[3] when they synthesized tetra-thiofulvalenium—7,7,8,8-tetracyanoquinodimethanide (TTF-TCNQ). This material had a room temperature conductivity of 500 mho/cm, and the conductivity increased with decreasing temperature to a maximum of greater than 10^4 mho/cm at about 59 K. This conductivity is large enough to suggest that true metallic conduction is occurring. Moreover, the increase in conductivity as the temperature falls is characteristic of metallic conduction, where the increase is associated with decreased scattering from the crystal lattice (phonon scattering) at low temperatures. After these results were reported, a group at the University of Pennsylvania[4] announced in 1973 that giant peaks in the conductivity were observed near 60 K in a few samples of TTF-TCNQ. The peaks were attributed by that group to fluctuations toward a superconducting state that was suppressed by the appearance of a lattice distortion. Their claim caused great excitement among solid-state physicists, and significant efforts have been made in several laboratories to reproduce similar results[5]. These investigations have been negative, and the Pennsylvania data have been sharply criticized as being generated by experimental artifacts.

Despite their disappointment in not finding a high-temperature superconductor, investigators of organic conductors have made significant progress. A wide variety of organic charge-transfer compounds has been synthesized, progressing from TTF-TCNQ to hexamethylene-tetraselenaful-valenium tetracyanoquinodimethanide (HMTSF-TCNQ), the first organic compound found whose conductivity remains metallic at all temperatures[6]. The crystal structure and electrical properties of HMTSF-TCNQ are quite close to that of the quasi-one-dimensional inorganic polymer $(SN)_x$, which is a superconductor[7], at some temperature it can be expected that some organic metals of the HMTSF-TCNQ type will also become superconducting. One important attribute of these materials, unmatched by other intrinsic solids, is the ability to control chemically the electronic properties of the organic salts, allowing systematic synthesis of compounds ranging from insulators to good conductors[8].

Structure

High electrical conductivity can be a property of a purely organic compound that is characterized by a metallic energy-band system; i.e., many charge carriers in the conduction band at ordinary temperatures. The TCNQ molecule is an electron acceptor that can pick up electrons from other molecules and readily forms a charge-transfer complex with a donor molecule such as TTF. The structure of these molecules is shown in Fig. 1.

The physical properties of the organic compounds, including their electrical conductivity, are determined largely by their crystal structure. When a crystal of the compound TTF-TCNQ is grown, it forms a lattice consisting of parallel conducting chains of TTF and TCNQ molecular ions separately stacked along the crystallographic b axis[9]. The crystal structure of TTF-TCNQ projected along the conducting b axis is shown in Fig. 2, while the structure projected along the a axis is shown in Fig. 3. This crystal structure and all of the other observable physical properties of the compound are highly anisotropic. The highest occupied wave functions of the individual molecules are Π orbitals perpendicular to the plane of the molecules. The intermolecular spacing along each stack of molecules in the b direction is such that the Π orbitals overlap in that direction, allowing electrons to move freely from molecule to molecule along the stack. Hence, electronic conduction along parallel conducting chains of TTF

[3] J. Ferraris, D. O. Cowan, V. Walatka, and J. H. Perlstein, "Electron Transfer in a New Highly Conducting Donor-Acceptor Complex," *J. Am. Chem. Soc.* **95**, 948–949 (1973).

[4] L. B. Coleman, M. J. Cohen, D. J. Sandman, F. G. Yamagishi, A. F. Garito, and A. J. Heeger, "Superconducting Fluctuations and the Peierls Instability in an Organic Solid," *Solid State Commun.* **12**, 1125–1132 (1973).

[5] G. A. Thomas, A. N. Bloch, D. O. Cowan, T. O. Poehler, et al., "Electrical Conductivity of Tetrathiafulvalenium-Tetracyanoquino-dimethanide (TTF–TCNQ)," *Phys. Rev. B* **13**, 5105–5110 (1976).

[6] A. N. Bloch, D. O. Cowan, K. Bechgaard, R. E. Pyle, and T. O. Poehler, "Low-Temperature Metallic Behavior and Resistance Minimum in a New Quasi-One-Dimensional Organic Conductor," *Phys. Rev. Lett.* **34**, 1561–1564 (1975).

[7] R. L. Greene, P. M. Grant, and G. B. Street, "Superconductivity in Polysulfur Nitride $(SN)_x$," *Phys. Rev. Lett.* **34**, 577–579 (1975).

[8] A. W. Bloch, D. O. Cowan, and T. O. Poehler in *Energy and Charge Transfer in Organic Semiconductors* (ed. K. Masuda and M. Silver), Plenum Press, New York, 167–174 (1974).

[9] T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, "The Crystal and Molecular Structure of the Organic Conductor Δ$^{2,2'}$-bis-1,3-dithiolium 7,8,8-Tetracyano-p-quinodimethanide (TTF-TCNQ)," *Acta Crystallogr.* **B30**, 763–769 (1974).
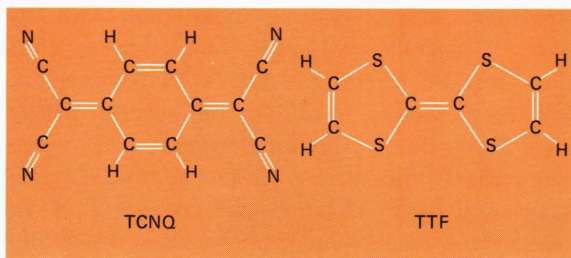
Fig. 1—Structure of TTF and TCNQ molecules.
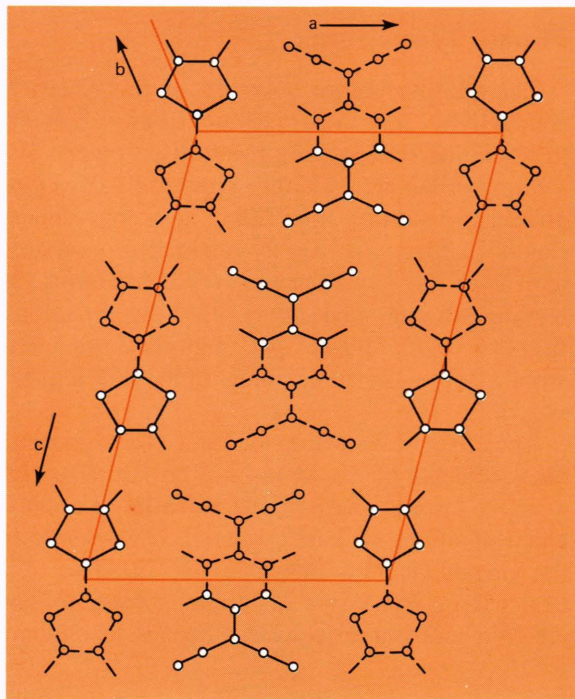
TCNQ   TTF

Fig. 2—Crystal structure of TTF-TCNQ projected along the b axis.

and TCNQ molecules occurs primarily along the b axis. The weaker interaction between chains of unlike molecules along the a axis is important in establishing the Fermi level of the system so that the highest energy band is partially filled; this is necessary for metallic behavior. The highly anisotropic crystal structure of such compounds as TTF-TCNQ and the high electrical conductivity in one crystallographic direction have caused these materials to be characterized as "one-dimensional metals."

Electrical Conductivity

The physical property that sets TTF-TCNQ and other members of its family apart from other organic compounds is its electrical conductivity. A typical set of results of the temperature dependence for TTF-TCNQ is shown in Fig. 4. The average conductivity at room temperature, σ_{RT}, is about 500 mho/cm, and the conductivity increases with decreasing temperature to a maximum value of about 10^4 mho/cm near 59 K $(\sigma_{max}/\sigma_{RT} \approx 20)$[3]. At lower temperatures, there is a metal-to-insulator transition, and the compound becomes a small band-gap semiconductor.

The large value of the electrical conductivity implies a qualitative difference between the conduction mechanisms in TTF-TCNQ and in organic compounds previously studied. From simple energy-band theory, there is a relationship between the conductivity σ and the mean free path λ for a one-dimensional conductor
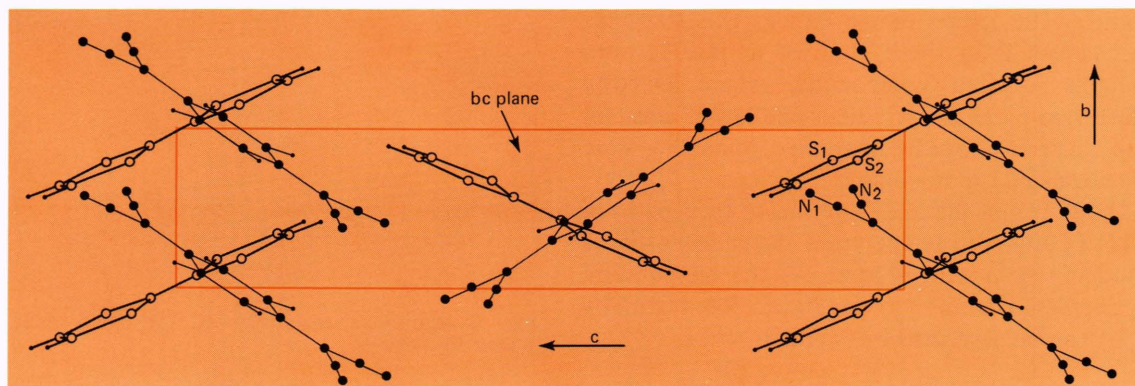
$$\lambda = \frac{h\sigma}{4Ne^2},$$

Fig. 3—Crystal structure of TTF-TCNQ projected along the a axis. (S_1, S_2, N_1, and N_2 are sulfur and nitrogen atoms.)
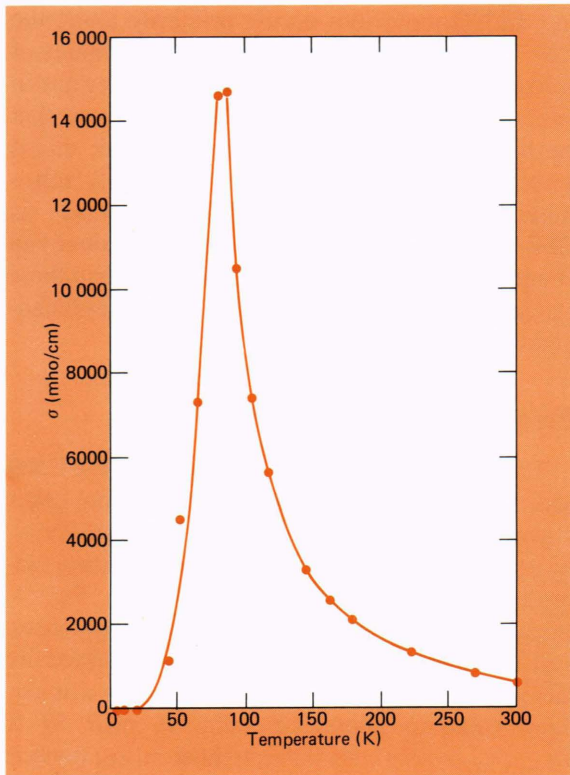
Fig. 4—Electrical conductivity of TTF-TCNQ.

ture dependence can be compared with the $\gamma = -1$ dependence for the conductivity of ordinary metals, where the decreased resistivity at low temperatures is due to diminished phonon scattering. Below the temperature of the conductivity maximum, 59 K, the conductivity decreases sharply. Detailed measurements of the temperature dependence show several discontinuous changes in the conductivity at 53 K and 38 K (Fig. 5).

Phase Transitions

The sharp changes observed in the electrical conductivity and the transition from a metallic to insulating state are the result of a "Peierls distortion" of the crystal lattice structure[10]. This type of lattice distortion arises only in a "one-dimensional" lattice where the interactions between molecules are strong in one crystallographic direction and very weak in the other two directions. In normal, more isotropic, materials the interatomic forces in three dimensions stabilize the system.

The effect of distorting the lattice through small displacements of the atoms can be visualized for a simple lattice. The periodic potential of a linear chain of atoms of lattice spacing b gives rise to the energy diagram shown in Fig. 6a. The electron energy $E(p)$ is a quadratic function of the electron momentum p except near the boundary
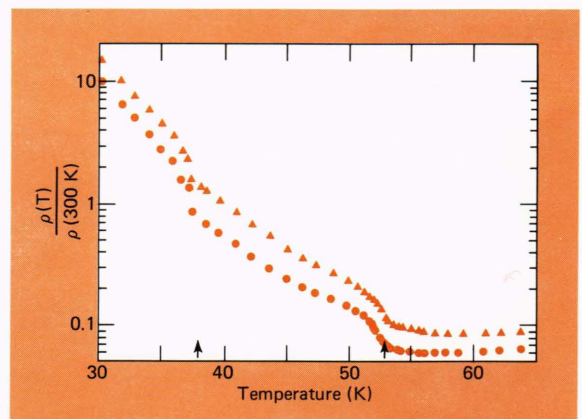
where N is the number of conducting chains per unit cross-sectional area, e is the electronic charge, and h is Planck's constant. At temperatures near the conductivity maximum, the mean free path of about 4 nm is equivalent to more than ten b-axis lattice constants, where the lattice spacing is 0.382 nm. The proper description of electron transport under these conditions is an energy-band picture where electrons in a band propagate through the lattice and occasionally collide with defects or the lattice. This transport mechanism is in sharp contrast to that in non-metallic organic compounds, where electron mean free paths are less than one lattice constant and electrons move by hopping or tunneling from one localized site to another.

Aside from the electron mean free path of TTF-TCNQ, the temperature dependence of its conductivity is also unique. As the temperature is decreased from 300 to 70 K, the resistivity $\rho(T)$ can be described by the relation

$$\rho(T)/\rho(300\ K) = a + BT^{\gamma} \quad ,$$

where $\gamma = 2.3 \pm 0.1$. This very strong tempera-

Fig. 5—Electrical resistivity of TTF-TCNQ near the phase transitions.

[10] R. E. Peierls, *Quantum Theory of Solids*, Oxford Press, London, 108–114 (1955).

of the interval

$$-\frac{h}{2b} < p < \frac{h}{2b}.$$

All available electron states are filled up to the Fermi energy E_F, which is in the middle of the band, so that the crystal is a metal. If the chain of atoms is distorted by displacing each atom slightly, with the displacement repeated each rth atom, the translational symmetry of the lattice will be reduced, and the new unit cell of the lattice will contain r atoms. Figure 6b shows the energy band for the case where r = 2. The effect of the distortion that occurs near the edge of the Fermi distribution is to displace downwards energy states that are occupied and to raise states that are empty. The result is a net reduction of the energy. The crystal has become an insulator with the filled band separated by an energy gap from the next higher band and with no continuous way to change the momentum of the electrons.

For the one-dimensional metal with a partly filled band, the regular chain structure will never be stable, since distortions will always occur with a break near the Fermi energy. This lattice distortion was predicted by Peierls in 1955 for one-dimensional metals and has now been observed in several highly anisotropic, near-one-dimensional conductors. The lattice distortion is observable not only by its effect on the optical and electrical properties[11], but also directly by X-ray studies of the periodicity of the lattice.

The existence of a "superlattice" with a periodicity of rb should be directly apparent in X-ray diffraction photographs at low temperatures. Attempts to observe this phenomenon in TTF-TCNQ before 1975 were unsuccessful due to the very low scattered radiation intensity from the superlattice. Finally, in 1975, X-ray studies indicated a superlattice structure with a periodicity of 3.7 b along the conducting chain at T = 20 K; the scattering from the superlattice became diffuse at T = 40 K and very faint at 55 K. [12] Recently, neutron-scattering measurements have provided more details associated with the transitions showing that the periodicity of the complete three-dimensional lattice below the 20 K transition is 4 a $\times$ 3.7 b $\times$ c.[13] Neutron-scattering studies show the superlattice scattering to be constant up to 38 K where it drops sharply and then decreases smoothly to zero at 54 K.

Material Modifications

Peierls distortions of the lattice that lead to metal-insulator transitions are peculiar to highly anisotropic, one-dimensional systems. These transitions do not exist in more isotropic systems since the interchain coupling suppresses the instabilities. However, many organic systems are highly anisotropic, and retaining the nearly one-dimensional character may be important in realizing good organic metals or possibly superconductors.

Research in the field has thus emphasized modifications to organic systems by molecular substitutions that gradually alter the interchain coupling or dimensionality of the compounds. TTF-TCNQ is a particularly useful prototype in this process because of the amenability of the TTF donor molecule to chemical modification.
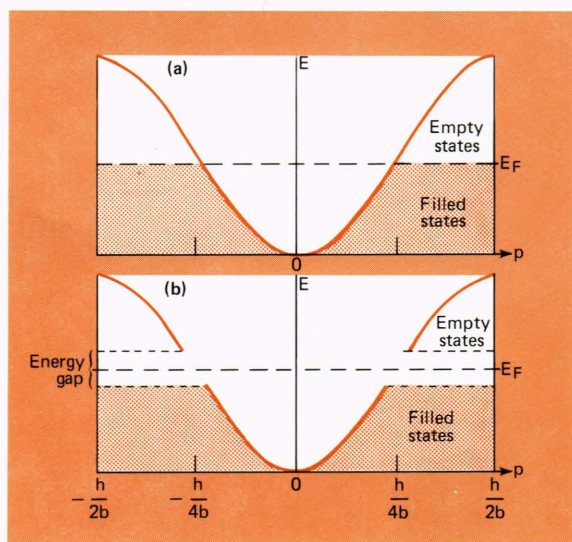

Fig. 6—Energy versus momentum curves for electrons in a periodic potential associated with a linear chain of atoms.
(a) Original undistorted lattice.
(b) Peierls distortion of crystal lattice.

[11] T. O. Poehler, A. N. Bloch, J. P. Ferraris, and D. O. Cowan, "Far-Infrared Photoconductivity in TTF–TCNQ," *Solid State Commun.* **15,** 337–340 (1974).
[12] F. Denoyer, F. Comes, A. F. Garito, and A. J. Heeger, "X-Ray-Diffuse-Scattering Evidence for a Phase Transition in Tetrathiafulvalene Tetracyanoquinodimethane (TTF TCNQ)," *Phys. Rev. Lett.* **35,** 445 (1975).
[13] R. Comes, S. M. Shapiro, G. Shirane, A. F. Garito, and A. J. Heeger, "Neutron-Scattering Study of the 38 and 54 K Phase Transitions in Deuterated Tetrathiafulvalene-Tetracyanoquinodimethane (TTF–TCNQ)," *Phys. Rev. Lett* **35,** 1518–1521 (1975).

Some of the variations are illustrated in Fig. 7. Some or all of the sulfur heteroatoms can be replaced by selenium while the terminal protons can be replaced by a variety of substituent groups. Likewise, new acceptor molecules such as TNAP, whose structure is shown in Fig. 7, can be substituted for TCNQ. In studying the role of interchain coupling, it is desirable to maintain the electronic structure of the molecule and intrachain stacking patterns as nearly constant as possible while introducing steric factors that will induce changes in the crystal structure.

The donor molecule (TTF) of the salt has been modified by two methods. First, the terminal protons on TTF can be replaced by electronically inert, but physically bulky substituent groups. For example,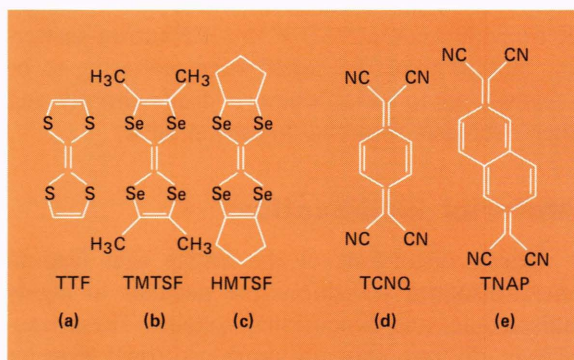 adding methyl groups gives the tetra-methyl derivative TMTTF-TCNQ[14]. This molecule is too large to be accommodated by the crystal structure of TTF-TCNQ and thus forces a rotation of each molecular stack about its axis (Fig. 8). The rotation weakens the interchain coupling along the a axis and makes TMTTF-TCNQ more one dimensional than its parent compound. The properties of TMTTF-TCNQ and other TCNQ salts are listed in Table 1. The typical room-temperature conductivities σ_{RT}, the ratio of the maximum conductivity to the room-temperature value σ_{max}/σ_{RT}, the temperature T_{max} of the conductivity maximum, and the critical transition temperature T_c are given for a number of compounds. Also given are the shifts in the spectroscopic splitting factor (g factor) of ESR lines measured along the three principal crystallographic directions, together with typical spin resonance linewidths ΔB measured in these samples. Within a given class of compounds, the resonance linewidths serve as a sensitive measure of the dimensionality of a system.

A second modification to the donor molecule consists of replacing the sulfur heteroatoms by selenium to form TSF, TMTSF, or HMTSF. The arrangement of interchain contacts in TCNQ salts

Fig. 7—Prototype molecules and some modifications.

[14] J. P. Ferraris, T. O. Poehler, A. N. Bloch, and D. O. Cowan, "Synthesis of the Highly Conducting Organic Salt: Tetrathioful-valenium-Tetracyano-p-quinodimethanide," *Tetrahedron Lett.* **27**, 2553–2556 (1973).
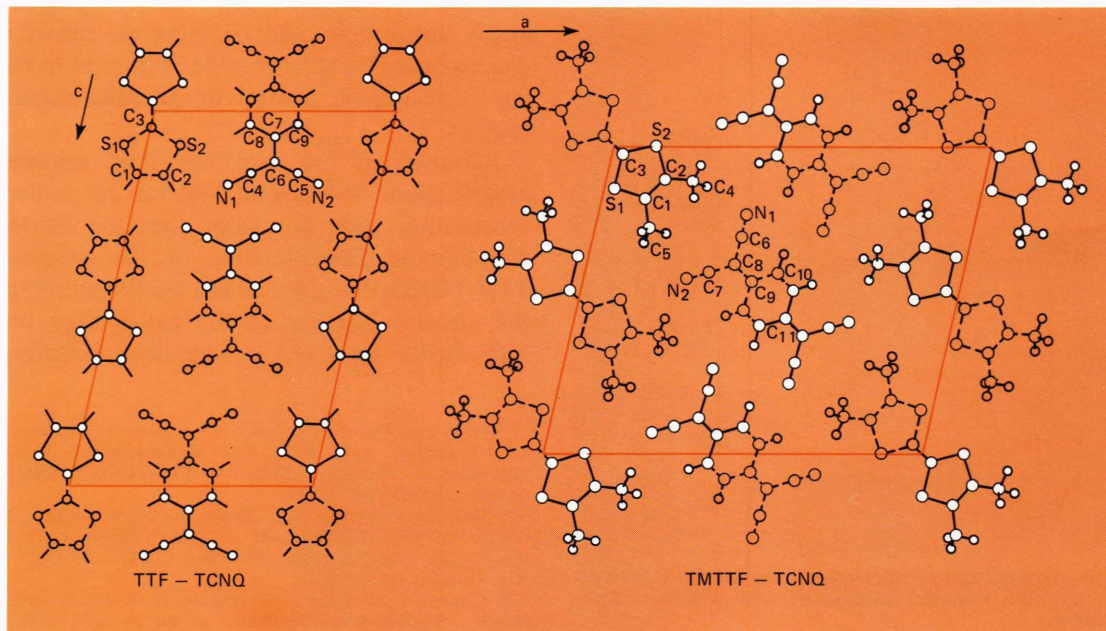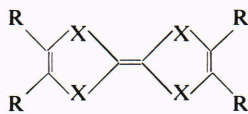
Fig. 8—Comparison of structures of TTF-TCNQ and TMTTF-TCNQ projected along their conducting axes.

Table 1

PROPERTIES OF ORGANIC CONDUCTING COMPOUNDS
CONSTRUCTED FROM VARIOUS DONOR MOLECULE—TCNQ COMBINATIONS

Compound	R	X	σ_{RT} (mho/cm)	σ_{max}/σ_{RT}	T_{max}	T_c	$\Delta g \times 10^4$ (300 K)	ΔB (gauss) (300 K)
TTF	—H	S	500	20	59	53,38	20, 40, −2	6
DMTTF	2—H,2—CH₃	S	50	25	≈50	≈35 (broad)	37, 2	5
TMTTF	—CH₃	S	350	15	60	34	37, 37, 1	3–4
HMTTF	—CH₂CH₂CH₂—	S	500	4	80	50, 40	≈40	11
DTDSF	—H	2 S, 2 Se	500	7	64	≈45 (broad)	≈100	250
TSF	—H	Se	800	12	40	28	≈100	500–650
TMTSF	—CH₃	Se	1200	6	61	57	88, −30	100
HMTSF	—CH₂CH₂CH₂—	Se	2000	3.5	No transition		Not observable	

of these molecules is qualitatively unchanged, but, because of the greater spatial extent of Se and the shorter Se-N interchain separations, the interchain coupling is considerably larger. From crystallographic structural studies, HMTSF-TCNQ, which is the largest of these molecules, is found to adopt a lattice structure that is the most two dimensional of all the materials in the series. That the coupling in the a direction is not strong enough to prevent some disorder in this direction is evidenced by diffuse streaking in X-ray photographs. Scanning electron micrographs

Fig. 9—SEM picture of HMTSF-TCNQ (magnification 2000). This is a top view showing evidence of macroscopic layering.

(Fig. 9) show evidence of nacroscopic layering in the same direction.

The room-temperature dc conductivity of HMTSF-TCNQ is the largest of any known organic substance, with a typical value of 2200 mho/cm. When the material is cooled below 300 K, the resistivity drops rapidly. However, below 100 K, the curve flattens and passes through a broad minimum between 75 K and 45 K, where the conductivity is about 3.5 times its room-temperature value. With further cooling, the resistivity rises again, but measurements to below 1 K yield values in the metallic range. Careful measurements indicate a weak phase transition at 32 K, but apparently the two-dimensional nature of the compound stabilizes it against a metal-insulator transition. The normalized temperature-dependent resistivities of HMTSF-TCNQ and of other compounds are shown in Fig. 10. At low temperatures, most of the conductivities behave as if the compounds are semiconductors with a temperature-dependent conductivity $\sigma(T)$ that decreases from a value σ_0 near the transition temperature according to

$$\sigma(T) = \sigma_0 \exp(-\Delta/kT)$$

with an activation energy Δ of about 0.01 eV (corresponding to an energy gap of approximately 0.02 eV). The consistent value of the activation energy might be construed to arise from a common impurity except for the fact that chemical[15]

[15] R. V. Gemmer, D. O. Cowan, A. N. Bloch, and T. O. Poehler, "Chemical Purity and the Electrical Conductivity of TTF–TCNQ," *J. Org. Chem.* **40**, 3544–3547 (1975).
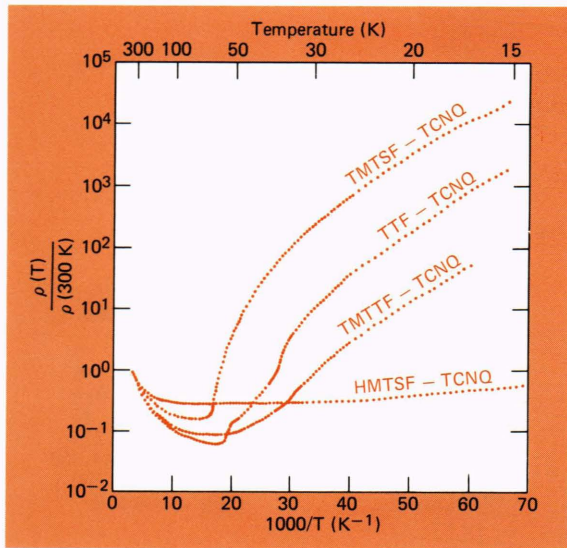
Fig. 10—Temperature-dependent resistivities of some organic conductors.

Magnetic Resonance Studies

ESR is a very sensitive technique for exploring the properties of the organic conductor. Resonance experiments have been exploited as a measure of local susceptibilities and of temperature-dependent conductivity. ΔE, the splitting of the ground-state energy level of an atom in a magnetic field B, is given by

$$\Delta E = g_s \mu_b M_s B \quad ,$$

where $M_s = \pm \frac{1}{2}$ and μ_b is the Bohr magneton. The g factor for a simple electron is $g = 2.00232$. Spin-flip transitions occur when the system resonantly absorbs energy E from a microwave magnetic field of frequency ν, where

$$E = h\nu = g_s \mu B \quad .$$

The g values have been measured as a function of temperature by X-band microwave absorption at a frequency ν near 10 GHz for a variety of organic compounds. The principal values of g for TTF-TCNQ at 300 K are $g_a = 2.006$, $g_b = 2.0025$, and $g_c = 2.008$. The b-axis value corresponds to the free electron value, while the values in the other crystallographic directions correspond to a weighted average of the ionic values ($g_{TTF+} = 2.008$, $g_{TCNQ-} = 2.0025$). The observation of a single absorption line with a unique g value is indicative of strong interchain coupling. By contrast, in weakly coupled insulating compounds, separate resonance lines associated with each ionic value would be observed.

The behavior of the c-axis g values of TTF-TCNQ as a function of temperature is shown in Fig. 11. A sharp change is observed in the temperature range where the material is undergoing phase transition from the high-temperature conducting regime where the TTF and TCNQ spins contribute equally to the resonance, to the insulating regime where only the TTF has appreciable magnetization. Most organic conductors show a similar behavior, with an averaged g value in the conducting regime followed by a sharp transition to either the anion or cation value at low temperature.

A resonant absorption of radiation at a frequency ν will occur in a field B with an absorption linewidth T_1^{-1}, where

$$T_1^{-1} = \frac{\Delta \nu}{2\pi} = 2\pi g_s \mu_b \Delta B / h \quad .$$

In isotropic conductors, the linewidth is proportional to the product $(\Delta g)^2 \tau^{-1}$ where Δg is the g shift away from the free electron value due to spin-orbit coupling and τ^{-1} is the scattering rate characterizing the phonon part of the resistivity. In simple metals, the phonon scattering rate is often so large that the line is too broad to observe. In purely one-dimensional metals, the scattering mechanisms are ineffective, so that sharp spin-resonance absorption lines can be observed for values of τ that would obliterate the
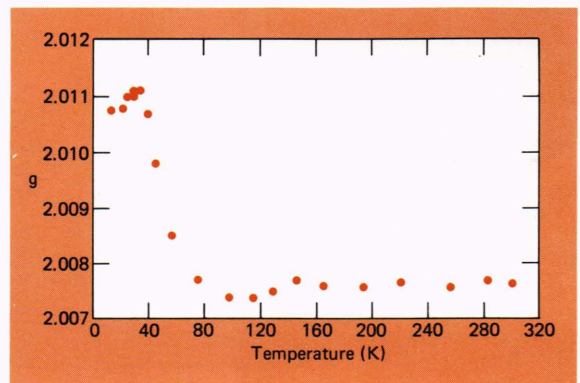

Fig. 11—Temperature dependence of g values for TTF-TCNQ along the c axis.

and magnetic studies to be described show that the samples are relatively free of impurities.
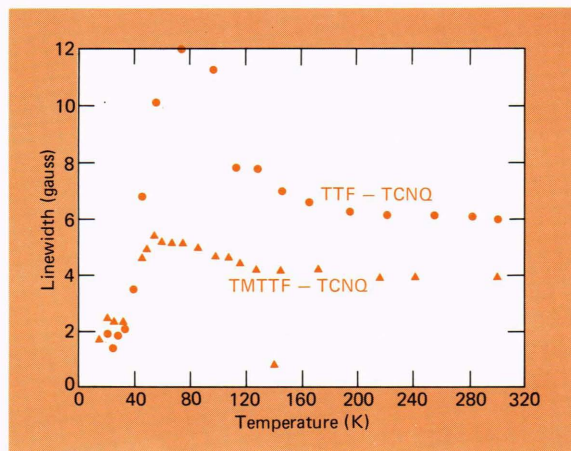
Fig. 12—EPR linewidths of TTF-TCNQ and TMTTF-TCNQ along the c axis.

line in an isotropic metal. As the interchain coupling is increased within a series of compounds, so is the amount of spin-flip scattering and hence the linewidth. The variation of the resonance linewidth of TTF-TCNQ with temperature in Fig. 12 shows increased coupling as the temperature is decreased below 300 K. A sharp transition from the metallic regime with strong interchain coupling to the insulating regime with a narrow line is observable below 60 K. The room-temperature dependence of linewidths on $(\Delta g)^2$ is experimentally established and the linewidths in Table 1 suggest the trends described above[16,17].

The compound HMTSF-TCNQ, which possesses the highest dimensionality in the series, is the only member of the class in which no spin-resonance signal is observed, implying a line-width substantially larger than 1000 G. The combination of magnetic experiments, crystallographic studies, and conductivity measurements has disclosed the interplay between structure, dimensionality, interchain coupling, and the electronic properties of the major organic conductors.

Summary

The extraordinary instabilities and fluctuation effects characteristic of a hypothetical one-dimensional metal are rapidly quenched as the effective dimensionality is increased. Hence we should expect that the physics of a nearly one-dimensional conductor should be especially sensitive to the effective interchain coupling. This is particularly true in two-band organic systems based upon the prototype TTF-TCNQ, where the one-electron band structure in the undistorted state is nominally semimetallic.

These observations suggest a way to adjust systematically the electronic properties. By adding saturated substituent groups to the molecular components of two-band organic systems, it is possible to control molecular size and interchain spacing without appreciably affecting the electronic structures of the molecule, the interchain stacking patterns and distances, or the effective radii of the conducting strands. While the details of the interchain coupling apparently have little effect on the temperature dependences of the high-temperature conductivity and magnetic susceptibility, or on the low-temperature semiconducting gap, they dominate the evolution of the metal-to-insulator transition. As the dimensionality is lowered, for example, the multiple phase transitions of TTF-TCNQ give way to a single very weak transition (TMTTF-TCNQ), with indications that the width of the critical region may approach the magnitude of the transition temperature itself. Conversely, with increased interchain coupling, the metal-to-insulator transition is suppressed, and the semimetallic band structure fully established. The result is HMTSF-TCNQ, whose electronic properties appear midway between those of TTF-TCNQ and a conventional semimetal. The crucial role of dimensionality in this system is emphasized by contrast with the more conventional TMTSF-TCNQ, which differs from HMTSF-TCNQ only in interchain coupling.

The development of HMTSF-TCNQ not only underscores the physical importance of higher dimensionality but illuminates the chemical means for attaining it. For example, preliminary studies indicate that the analogous series of compounds based on the electron acceptor TNAP (Fig. 7e) displays a wider range of electrical behavior than does the TCNQ sequence. It may not be overly optimistic to look forward to the emergence of a class of higher dimensional organic conductors that is much broader and more versatile electrically than the materials we have developed so far.

[16] T. O. Poehler, J. Bohandy, A. N. Bloch, and D. O. Cowan, "ESR Studies of TCNQ and TNAP Salts," *Bull. Am. Phys. Soc.* **21**, 287–288 (1976).
[17] A. N. Bloch, T. F. Carruthers, T. O. Poehler, and D. O. Cowan, *Chemistry and Physics of One-Dimensional Metals* (ed. H. J. Keller), Plenum Press, New York, 47–85 (1977).