

# From Organic Metals to Superconductors: Managing Conduction Electrons in Organic Solids<sup>†</sup>

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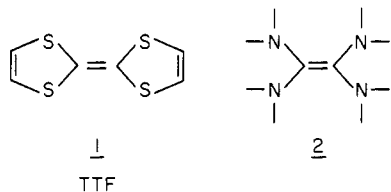
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New organic materials with remarkable electrical properties have been synthesized in recent years. One, an organic solid, has about half the electrical conductivity of manganese metal at room temperature ( $\sim 3000 \Omega^{-1} \text{ cm}^{-1}$ );<sup>1</sup> another, an organic crystal, can be coaxed to conduct electricity without resistance.<sup>2</sup> The existence of these compounds is in part due to accident but also due to arduous research in a few laboratories where strong collaboration between chemists and physicists is the rule. In this Account, we discuss the conduction of electricity in organic solids, especially the parameters required for metallic electron flow and the phenomena responsible for its permanent interruption (metal-to-insulator transitions) or perpetual flow (metal-to-superconductor transition). Although polymeric conductors will be mentioned, the protagonists will be single-crystal radical ion salts.

## TTF•TCNQ, the First Organic Metal

Organic metals,<sup>3</sup> either single crystal or polymers, are composed of radical ions. If one were to consider graphite organic, it would be the sole exception, since it is a *neutral* "organic" conductor. The radical ions are derived from donors ( $\pi$  bases) and acceptors ( $\pi$  acids) either by combination of the two or by oxidation of the donors (D) or reduction of the acceptors (A) independently to form salts of the type (D)<sub>m</sub>X<sub>n</sub> or (A)<sub>m</sub>M<sub>n</sub>, where X is an anion and M is a cation and *m* is larger than *n*.

We prepared tetrathiafulvalene (TTF; 1) in 1970<sup>4</sup> because we wanted to have an electron-rich olefin that was a better reducing agent than tetrakis(dimethylamino)ethylene (2). We reasoned that lowering of the



ionization potential of an electron-rich olefin could be achieved by lowering the electronegativity of the heteroatoms. Furthermore, in TTF there should be a "Huckel driving force", i.e., in contrast to 2, the less electronegative heteroatoms in TTF were made part of a potential aromatic sextet in a five-membered ring

Fred Wudl is probably the only (Bolivian) organic chemist in a physics department. He assumed his present position as Associate Director of the Institute for Polymers and Organic Solids at Santa Barbara last September after spending ca. 10 years at Bell Laboratories. Prior to his arrival there, and while being an Assistant Professor of Chemistry at SUNY—Buffalo, he discovered the electrical properties of TTF salts (the principal component of many organic metals, particularly TTF•TCNQ). He received his Ph.D. degree under the direction of Donald J. Cram and worked on the synthesis of vitamin B<sub>12</sub> in R. B. Woodward's group. His current interests are in synthesis of polymeric conductors, organic metals, and superconductors.

containing a double bond. However, after preparing TTF by known procedures,<sup>5</sup> we learned that it was a much poorer donor<sup>4</sup> than 2! An a posteriori rationalization for this result is that  $\pi$ -electron density in the central double bond is not increased nearly as much by sulfur substitution as compared to nitrogen because the former is a much poorer *resonance* lone-pair donor ( $\text{Me}_2\text{N}$ ,  $\sigma_p = -0.83$ ,  $\sigma^+ = -1.7$ ;  $\text{SMe}$ ,  $\sigma_p = 0.00$ ,  $\sigma^+ = -0.60$ ). It is also conceivable that there is actual electron density *withdrawal* by the sulfur atoms.<sup>6,7</sup> Even though 1 was found to be a poorer reducing agent than 2, radical cations derived from the former were found to be much more stable than those derived from the latter.

Coppens' finding<sup>8</sup> that TTF crystallized in stacks very much like those of tetracyanoquinodimethane (TCNQ), whose radical anion salts were known to be good electrical conductors, induced us to measure the electrical conductivity of TTF<sub>m</sub>Cl<sub>n</sub> ( $m = 1$ ,  $n = 0.9$ )<sup>4,9</sup> and TTF itself. Having established the TTF salts are highly conducting, it did not take long before the marriage of the young donor with the old acceptor took place. The exact location of the ceremony is somewhat obscure.<sup>10-12</sup> It is clear it was a fertile coupling as judged from the number of papers it generated between 1973 and the present. The sudden interest (1973-1975) in this solid

<sup>†</sup>This Account is dedicated to Don Cram in appreciation for instilling in his students, mostly by example, a maverick's approach to Organic Chemistry."

(1) Park, Y.-W.; Heeger, A. J.; Druy, M. A.; MacDiarmid, A. G. *J. Chem. Phys.* 1980, 73, 946.

(2) Bechgaard, K.; Jerome, D. *Sci. Am.* 1982, 247, 52.

(3) The term "organic metal" is a misnomer because these solids are neither ductile nor malleable; they are frail organic crystals or relatively brittle polymers. The only properties reminiscent of metals are high reflectivity and relatively low room-temperature resistivity, which decreases with decreasing temperature over a certain temperature range.

(4) Wudl, F.; Smith, G. M.; Hufnagel, E. J. *J. Chem. Soc., Chem. Commun.* 1970, 1453. Hunig, S.; Kiesslich, G.; Scheutzow, D.; Zahradnik, R.; Carsky, P. *Int. J. Sulfur Chem., Part C* 1971, 109.

(5) Prinzbach, H.; Berger, H.; Luttringhaus, A. *Angew. Chem., Int. Ed. Engl.* 1965, 4, 435.

(6) The importance of empty sulfur d orbitals in organosulfur compounds is one of continuing controversy. Coffen<sup>7</sup> and McIver<sup>8</sup> found independently that unless d orbitals are included in the molecular orbital calculations of TTF, neither spectroscopic<sup>7</sup> nor molecular structure<sup>8</sup> could be correlated with theory.

(7) Coffen, D. L.; Chambers, J. Q.; Williams, D. R.; Garrett, P. E.; Cauffman, N. D. *J. Am. Chem. Soc.* 1971, 93, 2258.

(8) Reference 4 in Cooper, W. F.; Kenney, N. C.; Edmonds, J. W.; Nagel, A.; Wudl, F.; Coppens, P. *J. Chem. Soc., Chem. Commun.* 1971, 889.

(9) Wudl, F.; Wobschall, D.; Hufnagel, E. J. *J. Am. Chem. Soc.* 1972, 94, 670. The stoichiometry of TTFCl alluded to in this as well as ref 4, above, was in error; see: Scott, B. A.; LaPlaca, S. J.; Torrance, J. B.; Silverman, B. D.; Welber, B. *J. Am. Chem. Soc.* 1977, 99, 6631.

(10) Apparently TTF•TCNQ was prepared almost simultaneously at Monsanto, Johns Hopkins,<sup>11</sup> University of Pennsylvania,<sup>12</sup> and SUNY—Buffalo.

(11) Ferraris, J.; Cowan, D. O.; Walatka, V. V., Jr.; Perlstein, J. H. *J. Am. Chem. Soc.* 1973, 95, 948.

(12) Coleman, L. B.; Cohen, M. J.; Sandman, D. J.; Yamagishi, F. G.; Garito, A. F.; Heeger, A. J. *Solid State Commun.* 1973, 12, 1125.

was caused by two, almost simultaneous, events: the discovery of metal-like conductivity between room temperature and 56 K<sup>11,12</sup> and the report of "superconductivity" just above 56 K.<sup>12</sup> Of these, only the former survived scrutiny.

The following points summarize, perhaps in a simplified fashion, the salient features of single-crystal organic metals as we know them now.

1. The crystal lattice of organic metals consists of segregated stacks of planar ( $D_{2h}$ ) donors and planar ( $D_{2h}$ ) acceptors or radical ion stacks with closed-shell counterions ( $D_mX_n$  and  $A_mM_n$ ,  $m > n$ ).

2. The stacks must be partially charged, i.e., consist of neutral and charged molecules, as for example  $(TTF^{0.59+})(TCNQ^{0.59-}) = "TTF \cdot TCNQ"$ <sup>13</sup> or  $(TTF^{0.58+})(SCN^-)_{0.58} = TTF_{12}SCN_7$ .<sup>14</sup>

3. Organic metals are pseudo-one-dimensional conductors. This is a result of the structure; conductivity is highest along the stacking axis (in most cases, the long axis of the needle-shaped crystals) and lowest in the remaining two crystal axis directions. The anisotropy in electrical conductivity can be as high as a factor of 10<sup>3</sup>.

4. Organic metals are ground-state insulators and undergo a metal-to-insulator transition at a certain temperature ( $T_{MI}$ ). From a theoretical point of view,  $T_{MI}$  is a consequence<sup>15</sup> of point 3.

5. Substitution of selenium for sulfur in donors raises the room-temperature conductivity and lowers  $T_{MI}$ .<sup>16</sup>

6. Most  $D_mX_n$  solids are highly conducting and metallic, whereas  $A_mM_n$  crystals are not.

In neutral TTF, the interplanar separation between molecules along a stack is 3.62 Å, whereas in TTF·TCNQ this distance is reduced to 3.47 Å.<sup>17</sup> This occurs even though, on the average, slightly more than one out of every two TTF molecules in a stack bears a positive charge. Therefore, some kind of "intermolecular, intrastack bonding" must exist that acts as a cohesive interaction to overcome the cationic Coulomb repulsion.<sup>18</sup> Because of the relatively large distances (in terms of the usual covalent bond distances), the overlap in these "bonds" must per force be on the order of 0.1 eV or 2–3 kcal/mol.

The supermolecular orbital, or band, formed from all the molecular overlaps in a stack provides a mechanism for metallic delocalization of electrons along the stacks. According to Soos, this type of bonding is difficult to treat theoretically because it is in the boundary between

the correct applicability of VB and MO theories.<sup>19</sup> It has, so far, shown to be the case that the larger the heteroatoms of a donor molecule, the greater the "overlap" or the stronger the "intermolecular bonding" (larger bandwidth) and, hence, the higher the room temperature conductivity.

There are several mechanisms whereby conductivity of an organic metal would increase with decreasing temperature. First, cooling of a single crystal of an organic metal causes anisotropic contraction, i.e., shrinking along the stacking axis is more pronounced than along either of the other two crystal axes.<sup>20</sup> Consequently, intermolecular overlap (and conductivity) increases dramatically with decreasing temperature.

Second, the intermolecular overlap is so weak, it should be very sensitive to lattice vibrations, particularly along the stacking axis. As the crystal is cooled, the number of phonons (i.e., the amplitude of the lattice vibrations) decreases, better overlap is maintained, and electronic mean free path and conductivity go up. Finally, coherent coupling of the electronic motion to lattice vibrational modes (electron-phonon coupling, "collective mode") could result in a conductivity above that which would be expected from very narrow bandwidth metals such as TTF·TCNQ. In the early days of TTF·TCNQ, this was a controversial proposal until it was shown<sup>21</sup> that, unfortunately, these collective mode waves are easily "pinned" by lattice defects or Coulomb interactions with adjacent collective mode waves so that below  $T_{MI}$  they cannot move freely through the whole crystal and consequently cannot carry current. One theory<sup>21</sup> also predicts that as  $T_{MI}$  is approached, collective mode contributions to the conductivity are resistive rather than conductive or superconductive. More recently, spectroscopic results appear to lend support to a collective mode contribution to metallic conductivity just prior to the metal-to-insulator transition in TTF·TCNQ,<sup>22a,b</sup> but definitive experiments of the type performed on NbSe<sub>3</sub><sup>22c</sup> are still required to finally settle this controversy.

In summary, the relatively high room-temperature conductivities observed in organic metals can be ascribed to narrow-band formation by overlap of a combination of open-shell and closed-shell molecular orbitals. Metallic behavior, that is, decreasing resistivity with decreasing temperature, is most likely due to a combination of lattice contraction, decreasing lattice vibrations with decreasing temperature, and perhaps a "sliding" collective mode contribution described below.

### The Metal-to-Insulator Transition

The metal-to-insulator transition has been thoroughly explored in organic metals. As already mentioned, a one-dimensional metal is theoretically unstable relative to an insulating "ground state". Close examination using diffuse X-ray<sup>14,15</sup> and neutron scattering of several organic and inorganic systems in the metallic state

(13) Megtert, S.; Pouget, J. P.; Comes, R. *Ann. N.Y. Acad. Sci.* 1978, 313, 235 and references therein.

(14) Thomas, G. A. In "The Physics and Chemistry of Low Dimensional Solids"; Alcacer, L., Ed.; Reidel: Holland, 1980; p 31.

(15) This is known as the Peierls transition as treated in the following: Schultz, T. D. in ref 14, p 1. Chaikin, P. M. *Ann. N.Y. Acad. Sci.* 1978, 313, 128. Emery, V. J. In "Chemistry and Physics of One-Dimensional Metals"; Keller, H. J., Ed.; Plenum Press: New York, 1977; p 1. "Highly Conducting One Dimensional Solids"; Devrese, J. T.; Eurard, R. P.; Van Doren, V. E., Ed.; Plenum Press: New York, 1979.

(16) This has been found to be correct for the fulvalene series. So far, hexamethylenetetrafulvalene (HMTTF),<sup>60</sup> the first tetrafulvalene has failed to produce single-crystal organic metals (Wudl, F.; Aharon-Shalom, E.; Liao, P. unpublished results; Saito, G.; Enoki, T.; Inokuchi, H.; Kumagai, H.; Tanaka, J. *Chem. Lett.*, in press). In polymers, increase in conductivity on going from poly(phenylene sulfide) to poly(phenylene selenide) was not observed (Sandman, D. J.; Stark, J. C.; Rubner, M.; Acampora, L. A.; Samuelson, L. A.; Foxman, B. M. *Mol. Cryst. Liq. Cryst.* 1983, 93, 293.

(17) Kistenmacher, T. J. *Ann. N.Y. Acad.* 1978, 312, 333.

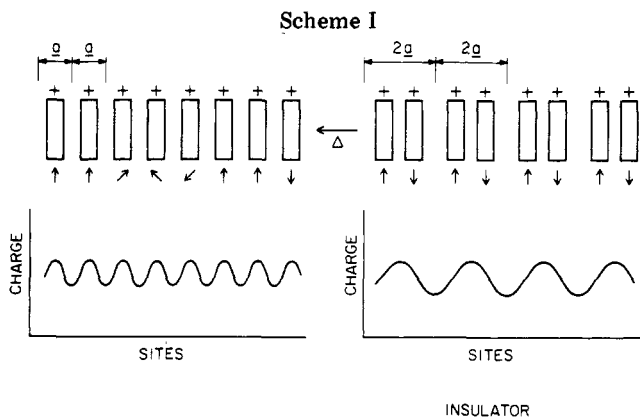
(18) Bloch, A. Proceedings of the International Colloquium on the Physics and Chemistry of Synthetic and Organic Metals, Les Arcs, France, 1982 and unpublished results, 1980.

(19) Soos, Z. G. *J. Chem. Educ.* 1978, 55, 546.

(20) Schultz, A. J.; Stucky, G. D.; Blessing, R. H.; Coppens, P. *J. Am. Chem. Soc.* 1976, 98, 3194.

(21) Lee, P. A.; Rice, T. M.; Anderson, P. W. *Phys. Rev. Lett.* 1973, 31, 462.

(22) (a) Tanner, D. B.; Cummings, K. D.; Jacobsen, C. S. *Phys. Rev. Lett.* 1981, 47, 579. (b) Heeger, A. J. *Comments Solid State Phys.* 1979, 65. (c) Fleming, R. M.; Moncton, D. E.; McWhan, D. B. *Phys. Rev. B* 1978, 18, 5560.

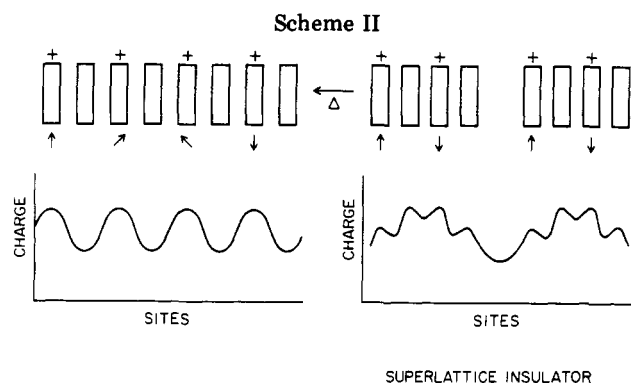


(above  $T_{MI}$ ) and in the insulating state (below  $T_{MI}$ ) revealed that there are several mechanisms that can drive metal-to-insulator transitions in one- and two-dimensional solids.<sup>23</sup>

The phenomena responsible for turning off electronic flow are, in general, due to a combination of electronic and lattice vibrational energies. Visualize a one-dimensional array of charged molecules undergoing a periodic displacement in one-dimension. There will be alternating regions in the lattice that have higher and lower charge densities, i.e., a charge-density wave (CDW) will be generated (see Scheme I). This is known as the Peierls instability.

The degree of instability of a one-dimensional metallic band depends on the amount of band filling, e.g., number of neutral and radical ionic species in a stack. For example, in an exactly half-filled band there are no neutral molecules in the stack.<sup>24,25</sup> Thus each molecule has an unpaired spin, and there is an electronic driving force for spin pairing. The molecules in a stack tend to dimerize and form a "covalent bond", thereby doubling the unit cell (if the original unit cell dimension ( $a$ ) was the width of one molecule (cf. Scheme I), the new unit cell dimension would be  $2a$ ). Associated with the "covalent bond" of the dimerized state are bonding and antibonding bands. The energy gap between the bonding and antibonding bands leads to semiconducting behavior and is responsible for the loss of free electrons and the loss of metallic electrical conductivity. Also, in the case of a half-filled band, the periodicity of the charge-density wave is commensurate with the lattice periodicity. When the period of the charge-density wave is commensurate with the lattice periodicity, the CDW is "pinned" and stops sliding so the material becomes an insulator.

When one introduces neutral molecules in the stack, the resulting band is less than half-filled. Since the CDW periodicity is no longer commensurate with the lattice, the energy gained by going to a distorted structure is less favorable. This is because the buildup of charge between molecules is weaker than the dimerized half-filled case and the transition to a distorted phase takes place at relatively low temperatures. In this case a metallic state is allowed between room temperature and the lattice distortion temperature,  $T_{MI}$ . If



enough neutral molecules are introduced into the stack so that half the total molecules in the stack are neutral, the charge transfer is again an integer, i.e., one electron per two molecules. Thus a commensurate CDW can be achieved if the molecules move from their uniform lattice position to form a superlattice with period  $4a$ . This is shown schematically in Scheme II for a quarter-filled band where the stack consists of equal numbers of neutral and ionic molecules.

For TTF-TCNQ the CDW and the underlying lattice periodicities are truly incommensurate since the charge per stack is nonintegral, i.e., 0.59. However, a driving force still remains to order the charge-density waves on different stacks relative to each other, a three-dimensional effect.<sup>15</sup> In the case of TTF·TCNQ, this forces the molecules in the stacks to form a very large superlattice below  $T_{MI}$ .

Sometimes there is a mismatch in cation and anion periodicity in a  $D_mX_n$  type crystal. In that case, the anion periodicity may drive a solid-state phase transition of the donor sublattice. Yet another, similar type of phase transition, with more dramatic consequences, conversion of one lattice type to another, can be CDW driven as has been observed in TTF $_m$ X $_n$  ( $X = \text{SCN}$ ,  $\text{SeCN}$ ;  $m = 1$ ,  $n = 0.58$ ).<sup>15</sup> In this case, the room-temperature, metallic crystal is tetragonal and the crystal is monoclinic below  $T_{MI}$ .

Prior to 1981, it was thought that CDW-driven metal-to-insulator transitions were the rule in all low-dimensional solids. As usual, a couple of other mechanisms were left to be discovered: spin-density waves (SDW) and anion ordering.

In 1979, Bechgaard<sup>26</sup> grew a series of tetramethyltetraselenafulvalene (TMTSF) salts of stoichiometry TMTSF $_2$ X ( $X = \text{univalent, complex anion but not halide}$ ). These salts exhibited high room-temperature conductivities and low  $T_{MI}$ 's ( $\sim 11$  K for several cases). It was later discovered that the metallic states could be reestablished by application of pressure or by application of an electric field<sup>27</sup> on the order of  $\sim 0.1$  V/cm. The field effect, coupled with electron spin resonance and magnetic susceptibility measurements as well as the absence of charge-density waves, induced Lee to interpret these observations in terms of a spin density wave driven transition.<sup>27</sup> It was later confirmed that the spins order antiferromagnetically,<sup>28</sup> alternating spin

(23) DiSalvo (DiSalvo, F. J. in "Chemistry and Physics of One-Dimensional Metals"; Keller, H. J., Ed.; Plenum Press: New York, 1977; p 369) discussed CDW's in two-dimensional solids.

(24) There is another reason for anticipating that half-filled one-dimensional bands should lead to insulators rather than conductors; on-site Coulomb repulsion discussed thoroughly by Torrance.<sup>25</sup>

(25) Torrance, J. B. *Acc. Chem. Res.* 1979, 12, 79.

(26) Bechgaard, K.; Andersen, J. R. in ref 14, p 247.

(27) Walsh, W. M., Jr.; Wudl, F.; Thomas, G. A.; Nalewajek, D.; Hauser, J. J.; Lee, P. A.; Poehler, T. O. *Phys. Rev. Lett.* 1980, 45, 829. Scott, J. C.; Pedersen, H. J.; Bechgaard, K. *Ibid.* 1980, 45, 2125.

(28) Walsh, W. M., Jr.; Wudl, F.; Aharon-Shalom, E.; Rupp, L. W., Jr.; Vandenberg, J. M.; Andres, K.; Torrance, J. B. *Phys. Rev. Lett.* 1982, 49, 885.

up and spin down. This magnetic order interrupts metallic electron flow by introducing an energy gap in the electronic band. In two cases ( $X = \text{PF}_6^-$  and  $\text{AsF}_6^-$ ), there appears to be no lattice distortion associated with the loss of conductivity.<sup>29</sup>

For years, the emphasis by chemists and physicists interested in organic metals was to stabilize the metallic state down to low temperature by somehow thwarting the metal-insulator transition. While that research has taken several different directions,<sup>30</sup> the one that had the most spectacular result was application of pressure.

### Organic Superconductors

The first organic system where  $T_{\text{MI}}$  could be systematically lowered with pressure was  $\text{TMTSF-DMTCNQ}$  (TM-DM).<sup>31</sup> There was also a suggestion that this compound's high-pressure metallic state may have "superconducting fluctuations", that is, a precursor to bulk superconductivity,<sup>57</sup> because there was a strong magnetic field dependence of the conductivity.<sup>31</sup> On the basis of this result it was found through the collaboration of Bechgaard and Jerome that not only did pressure eliminate the metal-to-insulator transition in  $\text{TMTSF}_2\text{PF}_6$  but it caused the latter to show a sudden loss of resistivity at 0.9 K and 12 kbar,<sup>32</sup> a strong indication of a metal-to-superconductor transition. Shortly after the French preliminary report, the group at Bell Labs proved conclusively that the phenomenon responsible for sudden loss of resistivity was a transition into the superconducting state.<sup>33</sup> It is still not clear how a moderate pressure prevents CDW or SDW formation and the associated loss of metallic behavior, particularly since at lower pressures there is coexistence of resistive and superconducting trends in the same crystal.<sup>34</sup>

In order to test whether the  $(\text{TMTSF})_2\text{X}$  salts are BCS type superconductors,<sup>35</sup> we prepared<sup>36</sup>  $\text{TMTSF-d}_{12}$ . The conventional type of superconductivity arises from the interaction of electrons with phonons. Thus, increasing the isotopic mass of elementary superconductors causes the transition temperature,  $T_c$ , to go down. Indeed, in collaboration with Schwenk et al.,<sup>37</sup> it was discovered that  $T_c$  of  $(\text{TMTSF-d}_{12})_2\text{ClO}_4$  is .95 K compared to 1.09 K for  $(\text{TMTSF})_2\text{ClO}_4$  under the same conditions.<sup>38</sup> The deuterated material makes possible neutron-scattering experiments aimed at the direct observation of spin-density waves. So far, attempts to observe neutron scattering from spin-density waves in  $(\text{TMTSF-d}_{12})\text{PF}_6$  at atmospheric pressure have

failed<sup>39</sup> presumably because of the suspected weak scattering by SDW's, which requires especially large crystals.

With all previously studied organic metals, the metal-to-insulator transition was found to be driven by CDW formation. In  $\text{TMTSF}_2\text{X}$  ( $X = \text{PF}_6^-$  and  $\text{AsF}_6^-$ ) the conductivity loss is SDW driven. In order to determine if there was a structure-related reason for this profound difference in mechanism, we scrutinized a large-scale model of the three-dimensional structure containing several units cells of  $(\text{TMTSF})_2\text{AsF}_6$ . We observed several aspects of the structure which, in conjunction with molecular properties of  $\text{TMTSF}$  or  $\text{TMTTF}$ , the sulfur analogue, led us to several general conclusions.<sup>40</sup> First, unlike organic metals based on  $\text{TCNQ}$ , in both  $(\text{TMTSF})_2\text{PF}_6$  and  $\text{AsF}_6^-$  the metallic properties and superconductivity are very likely due to selenium intermolecular orbital overlap and not to carbon  $p-\pi$  overlaps. Indeed, the intermolecular distances are larger than the sum of the van der Waals radius of carbon but shorter than that for selenium. Second, the electronic character of  $(\text{TMTSF})_2\text{X}$  salts should be two dimensional because there are several close *interstack* selenium contacts ( $\sim 3.9$  Å) of the same order of magnitude as *intrastack* selenium distances. It should be noted in this context that deviation from one-dimensional electronic character tends to suppress the CDW instability.<sup>23</sup> A third conclusion was based on the expected poor overlap between Se 4p and carbon 2p orbitals. Because of this the electronic structure of the radical cation derived from  $\text{TMTSF}$  is quite different from that of its sulfur analogue. Thus in the former the ionic site could be localized on a particular selenium atom in the radical cation. Finally, because of this localization, we concluded that anions play an important role through Coulomb interactions or ion pairing. The resulting charge neutralization and, in some cases, anion-cation bonding, as in  $(\text{TMTSF})_2\text{ReO}_4$  (vide infra), lead to radical cations that tend to behave as organic radicals and hence form singlet pairs.

We have recently found electron density between molecules in the stacks of  $(\text{TMTSF})_2\text{AsF}_6$  (and  $\text{PF}_6^-$ ) and, more significantly, electron density between only one out of a possible four *interstack* selenium contacts. Not only was this finding a direct proof of the two-dimensional character of these salts but also a direct confirmation of a quantum mechanical calculation<sup>41</sup> of the electronic structure.

In order to test the significance of Coulomb interactions we embarked on the preparation of  $(\text{TMTSF})_2\text{FSO}_3$  in order to compare its properties with  $(\text{TMTSF})_2\text{ClO}_4$ . The latter had just been shown to be a superconductor at atmospheric pressure.<sup>42</sup> The reasons for this comparative study were that the two anions were tetrahedral, of roughly the same molecular weight ( $\text{FSO}_3^-$ , 99.06 mol;  $\text{ClO}_4^-$ , 99.45 mol), and roughly

(29) Pouget, J. P.; Moret, R.; Comes, R.; Bechgaard, K.; Fabre, J. M.; Giral, L. *Mol. Cryst. Liq. Cryst.* **1982**, *70*, 129. Moncton, D.; Thomas, G. A., private communication.

(30) Wudl, F. In "The Physics and Chemistry of Low-Dimensional Solids"; Alacer, L., Ed.; Reidel: Holland, 1980; p 265. Wudl, F. *Pure Appl. Chem.* **1982**, *54*, 1051.

(31) Jerome, D. In "The Physics and Chemistry of Low-Dimensional Solids"; Alacer, L., Ed.; Reidel: Holland, 1980; p 123.

(32) Jerome, D.; Mazaud, A.; Ribault, M.; Bechgaard, K. *J. Phys. Lett.* **1980**, *41*, L-95.

(33) Andres, K.; Wudl, F.; McWhan, D. B.; Thomas, G. A.; Nalewajek, D.; Stevens, A. L. *Phys. Rev. Lett.* **1980**, *45*, 1449.

(34) Greene, R. L.; Engler, E. M. *Phys. Rev. Lett.* **1980**, *45*, 1587.

(35) To date, all known superconductors behave according to the Bardeen-Cooper-Schrieffer (BCS) theory of superconductivity. Other theories have been proposed as possible mechanisms for superconductivity,<sup>2</sup> but these have not been realized.

(36) Wudl, F.; Aharon-Shalom, E.; Bertz, J. H. *J. Org. Chem.* **1981**, *46*, 4612.

(37) Schwenk, H.; Neumaier, K.; Andres, K.; Wudl, F.; Aharon-Shalom, E. *J. Phys. Colloq. (Orsay, Fr.)* **1983**, *C3*, 1041.

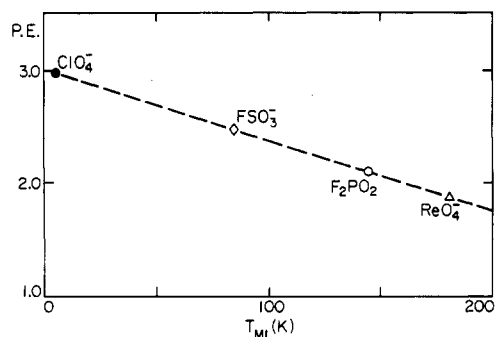
(38) The fact that the  $\text{TMTSF-d}_{12}$  is only 99.5% D (see ref 35) would also, unfortunately, have an effect of lowering  $T_c$ , but we do not know by how much. Lowering of  $T_c$  may also be due to a "pressure" effect (C-D is shorter than C-H): Andres, K., private communication.

(39) Kjems, K.; Moncton, D., unpublished results found that the  $(\text{TMTSF-d}_{12})_2\text{PF}_6$  crystals were too small for detection of neutron scattering by relatively low-intensity spin-density waves.

(40) Wudl, F. *J. Am. Chem. Soc.* **1981**, *103*, 7064.

(41) Grant, P. M. *Phys. Rev. B* **1982**, *26*, 6888.

(42) Bechgaard, K.; Carneiro, K.; Rasmussen, F. B.; Olsen, M.; Rindorf, G.; Jacobsen, C. S.; Pedersen, H.; Scott, J. C. *J. Am. Soc. Chem. Soc.* **1981**, *103*, 2440.



**Figure 1.** Plot of Pauling electronegativity (P.E.) of the central atom of the complex anions  $\text{ClO}_4^-$ ,  $\text{FSO}_3^-$ ,  $\text{F}_2\text{PO}_2^-$ , and  $\text{ReO}_4^-$  vs.  $T_{\text{MI}}$  of their TMTSF salts at atmospheric pressure.

the same size (S–O, 1.44 Å; Cl–O, 1.41 Å). The only differences between the anions are that  $\text{FSO}_3^-$  has a dipole moment<sup>43</sup> and sulfur is less electronegative than chlorine.

Fortunately for our comparative study, the salt  $(\text{TMTSF})_2\text{FSO}_3$  turned out to be isomorphous to its  $\text{ClO}_4^-$  sibling. Also, about the same time, Parkin et al. have collected data on another tetrahedral anion salt,  $(\text{TMTSF})_2\text{ReO}_4$ .<sup>44</sup> Much more recently, we prepared  $(\text{TMTSF})_2\text{F}_2\text{PO}_2$ ,<sup>45</sup> because we assumed the new anion may have even a larger dipole moment than  $\text{FSO}_3^-$ . All  $(\text{TMTSF})_2\text{X}_T$  ( $\text{X}_T$  = tetrahedral anion) salts are metals at room temperature and below, but all become semiconductors and insulators between 180 and 4 K.<sup>46</sup> The  $T_{\text{MI}}$ 's of the  $\text{FSO}_3^-$  and  $\text{ReO}_4^-$  salts reflect a sharp, first-order transition at 86 and 180 K, respectively.

According to our suggestion of the influence of anions on the electronic character of these salts (vide supra), the salt with the more nucleophilic anion should have a higher  $T_{\text{MI}}$ . Figure 1 shows a plot of Pauling electronegativity of the central atom of oxo and oxofluoro tetrahedral anions ( $\text{ClO}_4^-$ ,  $\text{ReO}_4^-$ ,  $\text{FSO}_3^-$ , and  $\text{F}_2\text{PO}_2^-$ ) vs.  $T_{\text{MI}}$  of their  $(\text{TMTSF})_2\text{X}_T$  salts. This figure represents the first correlation between a physical, solid-state property of a series of organic metals and a fundamental chemical property of their constituents.<sup>47</sup> This corre-

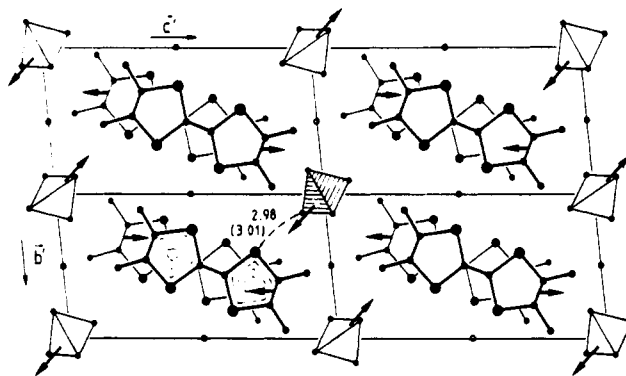
(43) Haddon, R. C.; Raghavachari, K., unpublished results calculated a dipole moment of 0.56 D for  $\text{FSO}_3^-$ .

(44) Parkin, S. S. P.; Jerome, D.; Bechgaard, K. *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 213.

(45) Wudl, F. *Bull. Am. Phys. Soc.* **1983**, *28*, 400. Cox, S.; Boysel, R. M.; Moses, D.; Wudl, F.; Chen, J.; Ochsenbein, S.; Heeger, A. J.; Walsh, W. M., Jr.; Rupp, L. W., Jr. *Solid State Commun.* **1984**, *49*, 259.

(46) Takahashi et al. (Takahashi, T.; Jerome, D.; Bechgaard, K. *J. Phys. Lett.* **1982**, *43*, 565), among others, have found that the observation of the onset of superconductivity or the observation of a  $T_{\text{MI}}$  (~4–5 K) prior to superconductivity depends on the rate of sample cooling.

(47) The only exception to this correlation is the  $\text{BrO}_4^-$  salt, which is reported to have a  $T_{\text{MI}}$  of ~250 K (Tomic, S.; Pouget, J. P.; Jerome, D.; Bechgaard, K.; Williams, J. M. *J. Phys. (Orsay, Fr.)* **1983**, *44*, 375). This result, however, should be taken with some suspicion since  $\text{BrO}_4^-$  is very unstable and  $\text{BrO}_3^-$  may have been incorporated into the lattice. The metal-to-insulator transition in the perchlorate salt appears at ~18 K below the anion-ordering transition.<sup>50a</sup> One possible explanation is that the "anion ordered" perchlorates do not interact with the selenium atoms in the same way as  $\text{ReO}_4^-$  and  $\text{FSO}_3^-$  because the symmetry of the ordered states of the perchlorate and the latter two anions are different. Therefore, in the ordered state the perchlorate salt cannot become an insulator. In the quenched state (disordered anions), there is more flexibility; upon cooling to ca. 5 K, the oxygen-selenium interatomic distance decreases until these atoms bond and convert the metal to an insulator. The  $\text{BF}_4^-$  salt has a  $T_{\text{MI}}$  of 40 K (Pauling electronegativity of boron is 2.0). This salt was not incorporated in Figure 1 because, (1) it is not an oxyanion; oxygen's valence is two, fluorine's is one, and (2) one cannot write a resonance structure with a localized negative charge on a peripheral atom as can be done with all the anions in Figure 1. Thus with  $\text{BF}_4^-$  one cannot have a directed "bond" from oxygen to selenium and therefore would not expect this salt to fit in the above plot.



**Figure 2.** Taken directly from Figure 3a of ref 49 (reprinted with permission from the authors. Copyright American Physical Society, 1982). Displacement pattern for the molecules of  $(\text{TMTSF})_2\text{ReO}_4$  at  $T \sim 150$  K (ca. 30 K below  $T_{\text{MI}}$ ). View along  $\bar{a}$  and labels  $b'$  and  $c'$  are the projections of  $\bar{b}$  and  $\bar{c}$ . The Re atoms are omitted and the  $b$ - $c$  plane of oxygen tetrahedra is located above the TMTSF molecules. The arrow lengths are proportional to the displacement values. Some intermolecular distances are given along with the RST average-structure values (in parentheses).

lation supports the notion that the higher the electronegativity of the central atom of a tetrahedral oxyanion, the lower the transition temperature of a  $(\text{TMTSF})_2\text{X}_T$  salt regardless of size and symmetry of the anion.<sup>47,48</sup>

The solid-state phase transition that occurs at  $T_{\text{MI}}$  is driven by anion ordering. At room temperature, there are two ways in which a tetrahedral anion can fit in the octahedral holes created by the methyl groups of the TMTSF's in the crystal structure of  $(\text{TMTSF})_2\text{X}$ . Since there are three degrees of freedom per anion, there are eight possible ways ( $2^3$ ) to arrange these anions relative to each other at the four corners of a unit cell.<sup>48b</sup> At room temperature, there is a random distribution of positions of the anions relative to each other, but at  $T_{\text{MI}}$  they order in one particular way, and this causes a true rearrangement of molecules in the unit cell.

If we consider a room temperature unit cell of dimensions  $a$ ,  $b$ ,  $c$  ( $a$ , stacking direction;  $b$ , interstack direction; and  $c$ , stack-to-anion direction), the ordering of  $\text{ReO}_4^-$  and  $\text{FSO}_3^-$  at  $T_{\text{MI}}$  causes formation of a new unit cell of dimensions  $2a$ ,  $2b$ , and  $2c$  and ordering of  $\text{ClO}_4^-$  generates a unit cell of  $a$ ,  $2b$ ,  $c$  dimensions. The structure of the  $\text{ReO}_4^-$  salt was determined above and below  $T_{\text{MI}}$ , and the rearrangements that occur are depicted in Figure 2.<sup>49</sup> As can be seen, the more "economic" phase ( $2a$ ,  $2b$ ,  $2c$ ) has one of the  $\text{ReO}_4^-$  oxygens in very close proximity of a neighboring selenium atom. The new Se–O distance is shorter than the sum of Se and O van der Waals radii<sup>50a</sup> by 0.44 Å! It should not be surprising then, in view of this structural change, that  $T_{\text{MI}}$  can be proportional to the nucleophilicity of the anion. With a very nonnucleophilic anion, such as perchlorate, the transition is "softer", i.e., occurs at lower temperature with relatively minor

(48) It is very surprising that the big difference in size between  $\text{ClO}_4^-$  and  $\text{FSO}_3^-$  on the one side and  $\text{ReO}_4^-$  on the other is overridden by this electronic effect. Emery has reached a similar conclusion on the effect of electronegativity (Emery, V. J., lectures at UCSB).

(49) Moret, R.; Pouget, J. P.; Comes, R.; Bechgaard, K. *Phys. Rev. Lett.* **1982**, *49*, 1008. Rindorf, G.; Solig, H.; Thorup, N., private communication.

(50) (a) Oxygen radius,<sup>51</sup> 1.52 Å; selenium radius,<sup>51</sup> 1.90 Å; sum, 3.42 Å; experimental,<sup>49</sup> 2.98 Å. (b) Pouget, J. P.; Shirane, G.; Bechgaard, K.; Fabre, J. M. *Phys. Rev. B* **1982**, *27*, 5203.

perturbation of the unit cell.<sup>50b</sup> Unlike the  $\text{FSO}_3^-$ ,  $\text{F}_2\text{PO}_2$ , and  $\text{ReO}_4^-$ , the soft  $\text{ClO}_4^-$  transition does not appear to obliterate the metallic state. Consequently, pressure is not required to restore metallic conductivity and transition to the superconducting state occurs at atmospheric pressure.

The transition to the insulating phase of  $(\text{TMTSF})_2\text{X}_T$  can be removed with pressure. The pressure range (6–25 kbar) is of the same order as that required to convert other  $(\text{TMTSF})_2\text{X}$  salts to superconductors. The surprising result is that the  $\text{FSO}_3^-$  salt has a  $T_c$  of 2.5 K, approximately twice the transition temperature recorded to date for any organic superconductor. Since the only difference between  $\text{FSO}_3^-$  on the one hand and  $\text{ReO}_4^-$  and  $\text{ClO}_4^-$  on the other is symmetry ( $C_{3v}$  vs.  $T_D$ ), we interpreted<sup>52</sup> the increase in  $T_c$  in terms of a favorable interaction between the superconducting Cooper pairs and the array of dipoles due to  $\text{FSO}_3^-$ .

### Recent Results and Outlook

Electrons in crystalline organic metals flow along supermolecular orbitals made up of molecular orbitals from molecules arranged in columns. The metallic electronic band structure associated with these giant orbitals is unstable and subject to the formation of an energy gap by phase transitions. The phenomena responsible for the phase transitions are due to electron-phonon interactions (CDW), magnetic interactions (SDW), or "mechanical" (anion ordering) interactions.<sup>53</sup>

In a few cases, the metallic state can be preserved by hydrostatic pressure. The most prominent example is the tribe of  $(\text{TMTSF})_2\text{X}$  salts where a majority of members become superconductors at moderate pressure. In a family of this tribe  $[(\text{TMTSF})_2\text{X}_T]$ , there are two exceptions;  $\text{X}_T = \text{ClO}_4^-$  is the only superconductor at atmospheric pressure and  $\text{X} = \text{FSO}_3^-$  is the only organic superconductor with a  $T_c$  close to 3 K (under pressure). In this family,  $T_{MI}$  is directly related to the electronegativity of the anion so that the electron flow interruption temperature is, in principle, controllable.

Very recently, the salt  $(\text{BEDTTTF})_2\text{ReO}_4$  ( $\text{BEDTTTF} = \text{bis}(\text{ethylenedithiotetrathiafulvalene})$ ) was found to be a superconductor at 1.5 K and 7 kbar.<sup>54</sup> This result is significant because in the crystal structure

of this salt there are essentially the same intra- and interstack chalcogen-chalcogen interactions as in the  $(\text{TMTSF})_2\text{X}$  salts,<sup>53,54</sup> and the observation of superconductivity is no longer limited to an organoselenium donor.

The most pressing problem in organic superconductors research is to raise  $T_c$ . In this regard, three questions come to mind. (1) Can organic superconductors be expected to have  $T_c$ 's of 30 K or higher? This is the most controversial topic in the field,<sup>5,57</sup> and its resolution hinges on the reproducibility of two key experiments.<sup>57,58</sup> (2) Will the tellurium analogues have a higher or lower  $T_c$ ?<sup>59</sup> The answer should be forthcoming since there already exist three tetratellurafulvalenes.<sup>60</sup> (3) Does the superconductivity in  $(\text{TMTSF})_2\text{X}$  and  $(\text{BEDTTTF})_2\text{ReO}_4^-$  arise from the BCS mechanism? We have a hint from deuterium isotope effect experiments (vide supra) that the former may be BCS superconductors.<sup>38</sup> A more definitive experiment would be to prepare pure  $^{80}\text{Se}$  and pure  $^{76}\text{Se}$   $(\text{TMTSF})_2\text{ClO}_4$  and compare their  $T_c$ 's. Pure  $^{76}\text{Se}$   $(\text{TMTSF})_2\text{ClO}_4$  should have a much sharper, higher  $T_c$  than the currently studied samples because naturally occurring elemental selenium is a veritable soup of isotopes ( $\sim 1\%$   $^{74}\text{Se}$ ,  $\sim 9\%$   $^{76}\text{Se}$ ,  $\sim 7.5\%$   $^{77}\text{Se}$ ,  $23.5\%$   $^{78}\text{Se}$ ,  $\sim 50\%$   $^{80}\text{Se}$ , and  $\sim 9\%$   $^{82}\text{Se}$ ). Unfortunately, pure selenium isotopes, while available, are very expensive.

As far as the future of organic metals and superconductors is concerned, there are several different aspects of electronic solid-state organic systems to be pursued: organic ferromagnets,<sup>56</sup> three-dimensional organic metals,<sup>29</sup> polymeric organic conductors that do not require doping to be metallic and polymeric organic superconductors. The latter are probably quite far in the future since polymeric organic metals are still in their infancy and organic superconductors have barely been born.

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(55) Grant, P. M. *Bull. Am. Phys. Soc.* **1983**, *28*, 445 (paper H.F.4). There are additional chalcogen-chalcogen interactions in the  $\text{BEDTTTF}(i)$  salt due to the peripheral sulfurs (cf. Kobayashi, H.; Kobayashi, A.; Sasaki, Y.; Saito, G.; Enoki, T.; Ionkuchi, H. *J. Am. Chem. Soc.* **1983**, *105*, 297).

(56) Breslow, R. *Pure Appl. Chem.* **1982**, *54*, 927.

(57) Jerome, D. *Bull. Am. Phys. Soc.* **1983**, *28*, 399 (paper G.B.2).

(58) Greene, R. L. *Bull. Am. Phys. Soc.* (paper G.B.3).

(59) If the tellurium analogues are BCS superconductors, they would be expected to have lower  $T_c$ 's than the selenium analogues for the following reasons: (1) Te is heavier than Se, (2) Te orbitals are more diffuse; therefore, the bandwidth (intermolecular overlap) will be larger and the density of states near the Fermi level will be lower. The lower the density of states (according to BCS), the lower the  $T_c$ . Also,  $T_c$  is 2.4–5.1 K at 38–55 kbar, whereas  $T_c$  of Se is 6.75–6.95 K at 130 kbar.

(60) Wudl, F.; Aharon-Shalom, E. *J. Am. Chem. Soc.* **1982**, *104*, 1154. Lerstrup, K.; Talham, D.; Bloch, A.; Poehler, T.; Cowan, D. *J. Chem. Soc., Chem. Commun.* **1982**, 336.

(51) Bondi, A. *J. Phys. Chem.* **1964**, *68*, 441.

(52) (a) Laco, R. C.; Wolf, S. A.; Chaikin, P. M.; Wudl, F.; Aharon-Shalom, E. *Phys. Rev. B* **1983**, *27*, 1947. (b) K. Andres and H. Schwenk recently found that  $\text{TMTSF}_2\text{FSO}_3$  exhibits a Meissner effect (private communication).

(53) What I mean by "mechanical" is equivalent to the statement by Bruinesma and Emery: "This behavior is quite unlike a Peierls transition, since it is the result of strong coupling between electrons (of the stack) and anions rather than an instability of the electron gas". Bruinesma, R.; Emery, V. J. *Proceedings of the International Colloquium on the Physics and Chemistry of Synthetic and Organic Metals*, Les Arcs, France, 1982. *J. Phys. Colloq. (Orsay, Fr.)* **1983**, *C3*, 115.

(54) Parkin, S. S. P.; Engler, E. M.; Schumaker, R. R.; Lagier, R.; Lee, V. Y.; Scott, J. C.; Greene, R. L. *Phys. Rev. Lett.* **1983**, *50*, 270.