

Organic Superconductors: Structural Aspects and Design of New Materials[†]

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..... we think, in concluding that the organic radicals in our amalgams are in the metallic state and, therefore, that it is possible to prepare composit metallic substances from non-metallic constituent elements—McCoy, H. N.; Moore, W. C. *J. Am. Chem. Soc.* 1911, 33, 273.

The majority of known organic materials¹ are electrical insulators, e.g., anthracene has an electrical conductivity, σ , less than $10^{-22} \Omega^{-1} \text{ cm}^{-1}$. A few organic systems are semiconductors, including perylene-*p*-chloranil ($\sigma \approx 10^{-8} \Omega^{-1} \text{ cm}^{-1}$) and certain doped organic dyes ($\sigma \approx 10^{-5} \Omega^{-1} \text{ cm}^{-1}$). An even smaller, but growing, number of organics are metallic in nature. The electrical conductivity of the metallic substances increases with decreasing temperature, and they comprise a class of intensely studied materials known as "organic metals" ($\sigma \approx 10-10^4 \Omega^{-1} \text{ cm}^{-1}$). Although metallic in nature, they have low conductivity compared to a metal such as copper. However, while some organic metals become superconducting (absence of electrical resistance) at low temperature, copper never does! The first organic metal, reported in 1954,² was a perylene-bromine complex (perylene-Br_x, $\sigma \sim 1 \Omega^{-1} \text{ cm}^{-1}$). While this finding may be considered as the first, a real burst in research on organic conductors did not occur until after the discoveries of the powerful π -molecular acceptor tetracyano-*p*-quinodimethane³ (TCNQ), in 1960, and sulfur-based tetrathiofulvalene⁴ (TTF), in 1970, and finally in 1972 their combination to form the π -molecular donor-acceptor complex TTF-TCNQ.^{5,6}

Many were surprised to learn that TTF-TCNQ had high metallic conductivity, rising to $\sim 10^4 \Omega^{-1} \text{ cm}^{-1}$ around 60 K, at which point a metal-semiconductor transition occurred.^{4,5} This discovery caused many chemists, physicists, and theoreticians to enter the field of organic metals.⁷ Until 1979, when the first organic superconductor was discovered,⁸ research focused on the synthesis of new TTF and TCNQ derivatives^{9,10} and other novel donor and acceptor systems.

In this Account we focus our discussion on Se- and S-based organic superconductors. We are especially concerned with the novel structural features that characterize these systems and allow the development of structure-property correlations. Such correlations provide considerable insight into the means whereby new conducting systems can be rationally designed.

At this early stage of development, it is important to point out that the crystal structures adopted by organic conductors play an extremely important role in determining their unusual physical properties. First, in most organic conductors the planar, or nearly planar, organic moieties have a pancake-like structure. The mode of

their stacking (directly overlapping, zigzag, herringbone, etc.), and the manner in which they communicate electronically in the solid, may or may not favor electron delocalization and high electrical conductivity.

TTF-TCNQ-like metals (segregated double stack, incomplete charge-transfer), possess an important structural feature. Because of the strong *intrastack* delocalization there are only *weak* interactions between the segregated stacks. This results in producing a highly anisotropic conductivity ($\sigma \approx 10^4 \Omega^{-1} \text{ cm}^{-1}$ at 54 K) in TTF-TCNQ.^{8,9} Without increased two- and three-dimensional electronic interactions *between* the segregated stacks, all of these materials would likely behave as quasi-one-dimensional conductors and have a tendency to undergo insulating transitions at low temperature. Such is the case for TTF-TCNQ; this material is metallic for $T > 54$ K, at which temperature^{8,9} a Peierls¹¹ distortion occurs. This transition involves a one-dimensional instability, a crystal lattice distortion, and a rapid decrease in electrical conductivity. It is known in TTF-TCNQ that a second transition occurs at lower temperature (38 K)^{12,13} and that the two anomalies are associated with the two different types of stacks. These results were derived from X-ray diffuse scattering^{14,15} and elastic neutron scattering

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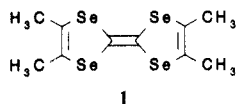
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studies.¹⁶ A large number of studies of TTF-TCNQ-like (segregated stack) systems were conducted before the need for increasing *interchain* communication was fully appreciated and eventually fulfilled with the synthesis of a true molecular organic superconductor.⁸ However, new materials have provided the concepts necessary to the development of organic superconductors.

Another major advance in organic metal research came with the discovery that in the charge-transfer complex of tetramethyltetraselenafulvalene, TMTSF, 1, and 2,5-dimethyl-TCNQ (under a pressure of 13 kbar) the electrical conductivity rises to $\sim 10^5 \Omega^{-1} \text{ cm}^{-1}$ at 10 K. The conductivity continues to rise even to the lowest temperatures attained.¹⁷ The structure of



TMTSF-DMTCNQ is somewhat similar to that of TTF-TCNQ in that it consists of alternating sheets of TMTSF and DMTCNQ stacks.¹⁸ However, the low-temperature electrical properties (under pressure) are spectacularly different (vide infra) and as yet not fully understood. At $T = 42 \text{ K}$ and ambient pressure there is a metal-semiconductor transition which is observed in conductivity¹⁹ and magnetic measurements.²⁰ A most surprising finding from the magnetic measurements was that the driving force for the transition resided solely in the *TMTSF donor stacks*. This was quite unlike most organic metals known at that time. The abrupt disappearance of the metal-semiconductor transition under pressure, the observation of the extremely high electrical conductivity with decreasing temperature, and the realization that the 42 K transition was undoubtedly associated with the TMTSF stacks, set the stage for Bechgaard^{8,21} to focus on the synthesis of new TMTSF charge-transfer salts containing only simple anions. These did *not* contain TCNQ-like electron acceptors, but rather monovalent charge-compensating anions such as PF_6^- , AsF_6^- , and ClO_4^- . With this change in direction came the synthesis and initial electrical characterization of what were to become the first molecular organic superconductors based on $(\text{TMTSF})_2\text{X}$ salts ($\text{X} = \text{PF}_6^-$, AsF_6^-) and which are discussed in the next section.^{8,21} Little did anyone realize at that time that while TMTSF single stacks might be expected to be largely one-dimensional in nature and might therefore be expected to show typical Peierls-type insulating transitions, they actually form a most unusual network of Se-Se interactions causing $(\text{TMTSF})_2\text{X}$ systems to be two- or three-dimensional (vide infra).

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Properties of $(\text{TMTSF})_2\text{X}$ Organic Superconductors

The $(\text{TMTSF})_2\text{X}$ [$\text{X} = \text{NO}_3^-$, PF_6^- , AsF_6^- , BF_4^-] organic metals were synthesized and characterized²¹ in 1979. These materials exhibit both unusually high electrical conductivities (at low temperature) of $\sim 10^5 \Omega^{-1} \text{ cm}^{-1}$, or, correspondingly low electrical resistivities, and low temperature ($\sim 12 \text{ K}$ for $\text{X} = \text{PF}_6^-$, AsF_6^- , and NO_3^-) metal-insulator transitions believed at that time to be Peierls transitions.²¹ Shortly thereafter, experiments aimed at the suppression of a possible Peierls transition through the application of hydrostatic pressure to $(\text{TMTSF})_2\text{PF}_6$ led to the first observation of superconductivity ($T_c \simeq 0.9 \text{ K}$) in an organic conductor.⁸ Very shortly after the discovery of pressure-induced superconductivity in $(\text{TMTSF})_2\text{PF}_6$, *ambient pressure* superconductivity was observed in $(\text{TMTSF})_2\text{ClO}_4$.^{22,23} At the time of this writing, superconductivity has been observed, and independently verified, in $(\text{TMTSF})_2\text{X}$ [$\text{X} = \text{PF}_6^-$, AsF_6^- , SbF_6^- , TaF_6^- , ReO_4^- , ClO_4^-].²⁴

Structural Aspects of $(\text{TMTSF})_2\text{X}$ Conductors

A knowledge of the crystal and molecular structures of the $(\text{TMTSF})_2\text{X}$ conductors provides key information for understanding their electrical properties and gives vital insight required for the design of new conducting materials. In terms of structure a most unusual feature of these systems is that they are all *isostructural*, belonging to the triclinic class (space group $P\bar{1}$).²⁵ In the crystal the nearly planar TMTSF molecules stack in a zigzag fashion forming a quasi-one-dimensional chain that parallels the axis (*a*) of highest conductivity (see Figure 1).²⁴

The lack of complete crystallographic regularity in the stacking motif is indicated in the varying *intrastack* Se-Se contacts given in Figure 1. Possibly most noteworthy of all the structural features found in these systems is the existence of Se-Se contact distances which are often considerably less than the sum of the van der Waals radii for Se, i.e., 4.0 Å (Pauling)²⁶ or 3.9 Å (Bondi),²⁷ respectively.²⁸ Another structural finding that implies that these systems are electronically two- or three-dimensional in nature is that there exists an infinite "sheet network"²⁹ of Se-Se interactions between TMTSF molecules extending in the *a-b* plane, and within these sheets there exist unusually short ($d < 4.0 \text{ Å}$) *interstack* Se-Se interactions (see Figure 2). However, the TMTSF molecules do not themselves form a complete three-dimensional network because the sheets are separated along *c* by the anions (X). The anions appear to play no direct role in the electrical conduc-

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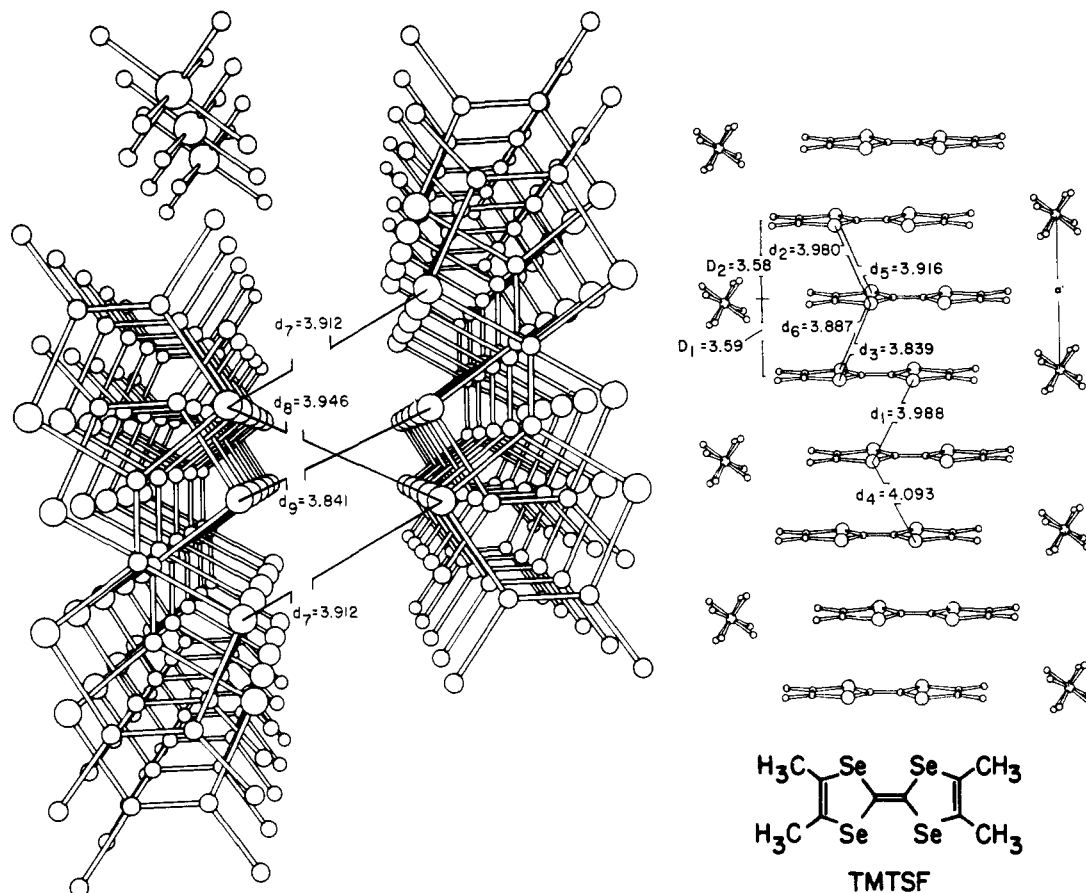


Figure 1. Illustration of the crystal structure of the conductor $(\text{TMTSF})_2\text{BrO}_4$ viewed down the stacking direction (left) and showing the zigzag stacking of TMTSF molecules (right-side view). Not all of the oxygen atom positions of the anion, which result from crystallographic disorder, are shown. Note the Se-Se contacts ($d \approx 3.9\text{--}4.0$ Å) and that there is no dimerization in the TMTSF stack.

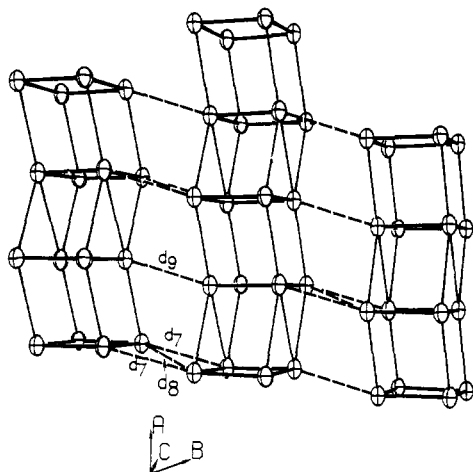


Figure 2. A view of the "infinite sheet network" of short Se-Se interactions found in all $(\text{TMTSF})_2\text{X}$ conductors.²⁹ The interstack distances d_7 , d_8 , and d_9 are also shown in Figure 1.

tivity, which occurs *through* the network of Se-Se interactions, but as we will see later, they indirectly moderate the electrical properties (*vide infra*). The existence of the short Se-Se interactions was first noted by Thorup²⁸ et al. and described in terms of an infinite "sheet network" (see Figure 2) by Williams et al.²⁹ The room-temperature crystal structures of $(\text{TMTSF})_2\text{X}$, $\text{X} = [\text{PF}_6^-]$,²⁸ $[\text{AsF}_6^-]$,³⁰ $[\text{ReO}_4^-]$,³¹ $[\text{FSO}_3^-]$,²⁹ $[\text{BF}_4^-]$,³²

$[\text{ClO}_4^-]$,²³ $[\text{BrO}_4^-]$,²⁹ $[\text{NO}_3^-]$,³³ and $[\text{CF}_3\text{SO}_3^-]$,³⁴ have now been reported.

It was not until after our temperature-dependent (298, 125 K) crystal structure studies had been conducted on $(\text{TMTSF})_2\text{X}$, $\text{X} = [\text{BrO}_4^-]$, $[\text{FSO}_3^-]$,²⁹ $[\text{ClO}_4^-]$, $[\text{PF}_6^-]$, $[\text{AsF}_6^-]$,³⁵ and $[\text{H}_2\text{F}_3^-]$ ³⁶ that the ramifications of the anisotropic structural changes in the *interstack* Se-Se network (see Figure 2), and their relationship to pressure-induced superconductivity in some derivatives, were revealed.³⁷ Although all Se-Se contact distances are about 3.9–4.0 Å at room temperature, this is certainly not the case as the temperature is decreased. Surprisingly, as observed by use of the 125 K data, there is a marked change in interstack Se-Se distances with the *interstack* distances becoming shorter than the *intrastack* separations. At 125 K the ratio of the decrease in *interstack* to *intrastack* Se-Se distances is nearly 2:1 when compared to the room-temperature distances. Therefore, the distances between the vertical "chains" shown in Figure 2 decrease, on the average, by twice as much as the distances between the stacks of TMTSF

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molecules.^{35,37} Thus, one would expect this to lead to considerably increased interchain electronic delocalization through the Se-Se network as the temperature is lowered if the orbital overlap is favorable. Although it has been suggested³⁸ (from the limited data available at the time) that the TMTSF stacks are considerably dimerized, which might in turn cause electron localization and decreased conductivity, the reverse is actually true.³⁹

The magnitude of the structural changes with temperature (298 K \rightarrow 125 K) in terms of the interstack Se-Se distances (d_7 , d_8 , and d_9 in Figure 2)³⁷ reveals that certain of these interatomic separations may be up to 0.3 Å smaller than the van der Waals sum. Theoretical calculations have shown that considerable Se-Se bonding interactions are involved in the cases of these shortened separations.⁴⁰

Structure-Property Correlations in (TMTSF)₂X Systems

A significant finding is that the Se-Se sheet-network distances are also anion dependent and vary systematically with the anion size. Because of the isostructural nature of these conductors, these observations allow correlations^{37,41} to be drawn between crystallographic unit cell volumes and the average [$d_{av} = (2d_7 + d_9)/3$] interstack Se-Se distances (see Figure 3). Inspection of Figure 3 reveals that the minimum values of V_c and d_{av} center around those for the sole ambient pressure organic superconductor (TMTSF)₂ClO₄ and that they are very nearly the same for X = FSO₃⁻ and BF₄⁻. It is most noteworthy that the incipient (pressure is required) superconductors [X = TaF₆⁻, SbF₆⁻, PF₆⁻, AsF₆⁻, ReO₄⁻] all have $d_{av} > d_{av}$ for X = ClO₄⁻. From these structural findings the conclusion may be drawn that when the incipient superconductors are placed under pressure⁴² the Se-Se network contracts in a predictable fashion until its geometry closely approximates that in (TMTSF)₂ClO₄. At this point a superconducting transition is "structurally" favored.³⁷ This discussion represents only a partial explanation of the relationship between structure and superconductivity in (TMTSF)₂X conductors because of anion-ordering phenomena that occur at low temperature in these systems.

The final utility of the correlations given here is in their application in designing new TMTSF conductors which would, hopefully, have unit cell volumes, and properties, very nearly the same as those found for (TMTSF)₂ClO₄. The unit cell volume, and corresponding value of d_{av} resulting from insertion of any given monovalent anion into the (TMTSF)₂X lattice, can be predicted with a fair degree of certainty as described elsewhere.³⁷ This approach has been used in

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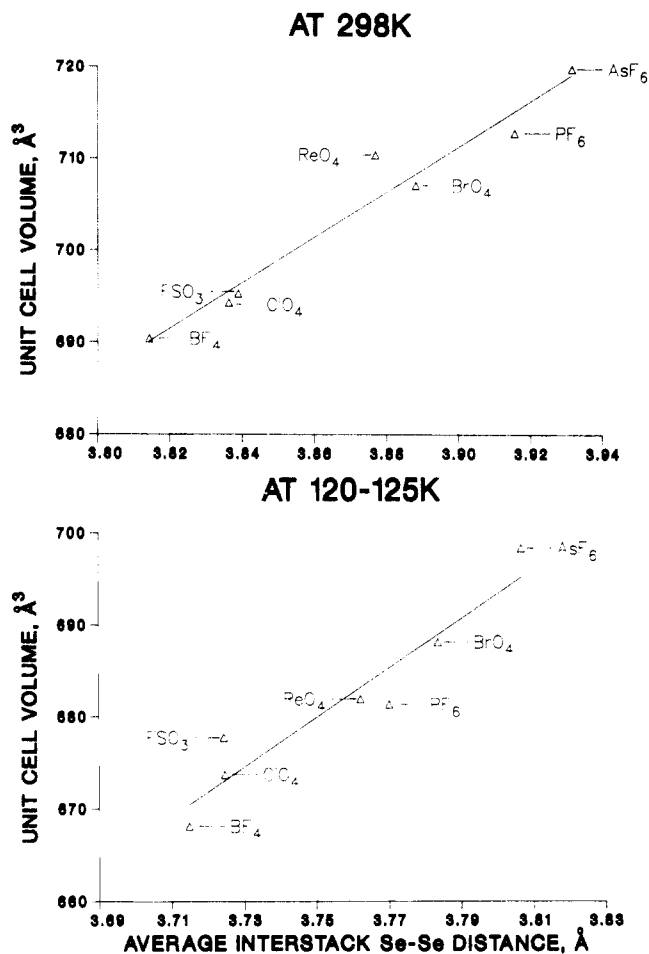


Figure 3. A plot of observed unit cell volumes (298 and 125 K) vs. the average interstack Se-Se distances for (TMTSF)₂X metals indicating a fairly linear correlation between the two.³⁷

the synthesis^{43,44} of (TMTSF)₂PO₂F₂ with predicted $V_c = 675.6 \text{ Å}^3$ (125 K) and measured $V_c = 676.9 \text{ Å}^3$ (125 K) compared to that observed for (TMTSF)₂ClO₄ at the same temperature, viz., $V_c = 673.7 \text{ Å}^3$. However, even though the ClO₄⁻ and PO₂F₂⁻ anions are of similar size, (TMTSF)₂PO₂F₂ undergoes a metal-insulator transition⁴⁴ at ~ 137 K due to structural disordering of the anion because of weak $-\text{CH}_3 \cdots \text{F}_2\text{O}_2\text{P}$ hydrogen bond formation.⁴³ This phenomenon is not easily controlled, thereby making the rational synthesis of new (TMTSF)₂X systems somewhat difficult.

Weak Anion-Methyl Group Interactions

An unusual aspect of the crystal structures of (TMTSF)₂X systems, which may be related to observed "anion ordering" transitions, is the finding of intimate contact between the peripheral atoms of the anions and the H atoms of the methyl groups of TMTSF.⁴⁵ Indeed, the anions in these systems reside in a "methyl group H atom cavity." For example, the immediate nearest-neighbor environment about the disordered octahedral AsF₆⁻ anion in (TMTSF)₂AsF₆ reveals a nearly isotropic (symmetric) sea of H atoms with no short H-F separations.⁴⁵ In contrast, the tetrahedral

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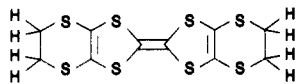
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ClO_4^- anion in $(\text{TMTSF})_2\text{ClO}_4$ resides in an *asymmetric* H atom environment, with numerous short H-O contacts. These $\text{H}_2\text{C}-\text{H}\cdots\text{OClO}_3^-$ interactions result in a "pinning" of the ClO_4^- anion, which may be associated with a "sluggish" anion ordering transition observed at 24 K (resulting from *slow cooling* of the sample), and which is a *necessary prerequisite* to the development of superconductivity in the ClO_4^- derivative.^{46,47} Thus, in these systems it is strongly believed that crystallographic order is required in order to reduce electron scatter which tends to destroy superconductivity. By comparison, rapidly cooled samples of $(\text{TMTSF})_2\text{ClO}_4$ may not become superconducting because, apparently, the ClO_4^- anions remain in a frozen disorder.⁴⁷ We have suggested that the array of anion-ordering phenomena observed in $(\text{TMTSF})_2\text{X}$ systems may arise from precursor methyl group ordering followed by anion ordering due to C-H \cdots anion interactions.⁴⁵ Variable-temperature NMR studies (H and ^{13}C) should shed light on this suggestion. If this is the case, the synthesis of new anionic derivatives suggests that these weak interactions must be taken into consideration.

Finally, it should be noted that the origin of the unit cell volume- d_{av} correlations discussed in a previous section are likely the result of the "sponginess" of the Se-Se interactions between TMTSF molecules in these systems. With increased anion size, and concomitant expansion of the methyl group H atom cavity through methyl group and anion interactions, the Se atoms are simply pushed farther apart resulting in the systematic changes between d_{av} and anion size.

Sulfur-Based Organic Superconductors

The discovery of superconductivity in a Se-based organic donor system containing simple charge compensating monovalent anion acceptors has greatly stimulated studies of promising S-based systems. One such donor system is bis(ethylenedithio)tetrathiafulvalene⁴⁸ (abbreviated to BEDT-TTF, **2**, and commonly referred to (herein also) as "ET"). In 1982, it was



reported⁴⁹ that $(\text{ET})_2\text{ClO}_4(1,1,2\text{-trichloroethane})_{0.5}$ is metallic over the temperature range 298 K \rightarrow 1.4 K. Again, a complex network of very short *interstack* contacts (S-S in this case and with distances less than the van der Waals radius sum of 3.6 Å, Bondi²⁷) was also observed⁵⁰ (vide infra). Thus, for the first time metallic conductivity to a temperature as low as 1.4 K was observed in a S-based organic donor system. The discovery of superconductivity in a different anionic derivative of ET, i.e., $(\text{ET})_2\text{ReO}_4$ soon followed.⁵¹ In this case, as is commonly observed in most of the TMTSF family of materials, pressure (>4 kbar) was required to

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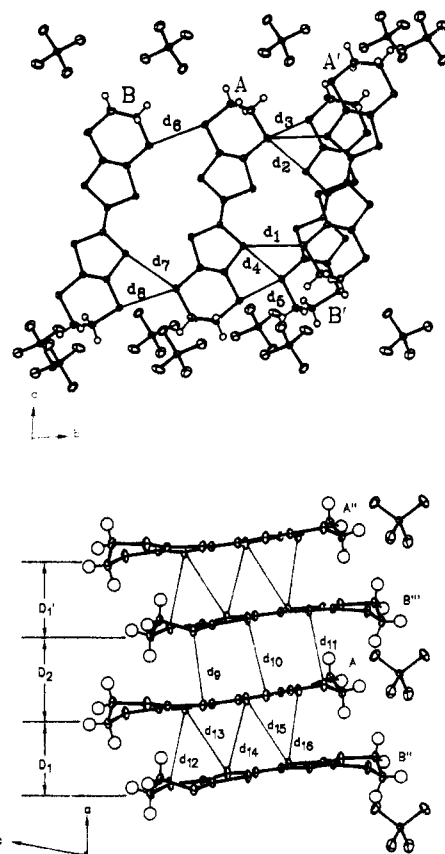


Figure 4. View of the intermolecular S-S interactions in $(\text{ET})_2\text{BrO}_4$. The upper part indicates the interstack S-S contact distances less than the van der Waals sum of 3.60 Å (298/125 K): $d_1 = 3.581$ (2)/3.505 (2), $d_2 = 3.499$ (2)/3.448 (2), $d_3 = 3.583$ (2)/3.483 (2), $d_4 = 3.628$ (2)/3.550 (2), $d_5 = 3.466$ (2)/3.402 (2), $d_6 = 3.497$ (2)/3.450 (2), $d_7 = 3.516$ (2)/3.434 (2), and $d_8 = 3.475$ (2)/3.427 (2) Å. The S-S contact distances, d_9-d_{16} (lower part) are, by contrast, all longer than 3.60 Å even at 125 K. In addition the loose zigzag molecular packing of ET molecules is such that they are not equally spaced, $D_1 = 4.01/3.95$ Å and $D_2 = 3.69/3.60$ Å. Almost identical S-S distances and interplanar spacings are observed in $(\text{ET})_2\text{ReO}_4$ at both 298 and 125 K.

suppress a metal-insulator transition that occurred at 81 K prior to the onset of superconductivity at ~ 2 K.

Whereas the only structural parameters reported for $(\text{ET})_2\text{ReO}_4$ were the triclinic unit cell parameters (space group $P\bar{1}$) and unit cell volume ($V_c = 1565$ Å³ at 298 K), the published structural description indicated that the structure is similar to the $(\text{TMTSF})_2\text{X}$ system. Very recently we reported⁵² that the structure of $(\text{ET})_2\text{BrO}_4$ is isostructural with that of $(\text{ET})_2\text{ReO}_4$, and notable structural differences, compared to $(\text{TMTSF})_2\text{X}$ systems, are as follows: (i) whereas the TMTSF molecule is always found to be nearly planar, the ET moiety is decidedly nonplanar with the $-\text{CH}_2$ groups protruding out of the molecular plane (see Figure 4) and (ii) the ReO_4^- anion is ordered at ambient temperature. The Re atom does *not* reside at a center of symmetry in this case. The ordered anion is probably significant as a required precursor to a superconducting transition, an explanation which is consistent with that recently observed for $(\text{TMTSF})_2\text{ClO}_4$.⁴⁷

Perhaps the most surprising structural feature of the $(\text{ET})_2\text{X}$ systems, compared to the known $(\text{TMTSF})_2\text{X}$

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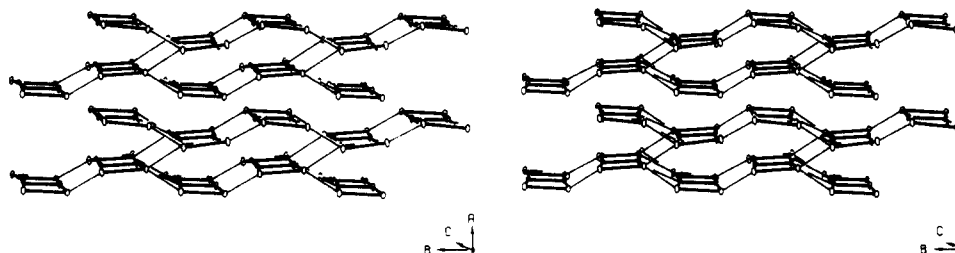


Figure 5. The stereoview "corrugated sheet network" of short *interstack* S...S interactions ($d < 3.60$ Å) observed in $(\text{ET})_2\text{X}$, X = ReO_4^- and BrO_4^- (125 K).⁵² Note that the ET molecules are nonplanar and are decidedly nonparallel in the quasi-stacking direction. Similar S-S networks, but which are more highly developed, are common to all β - $(\text{ET})_2\text{X}$, X = I_3^- , I_2Br^- , and AuI_2^- systems.

structures, is that there exist (mainly) short *interstack* S-S interactions, rather than short *intrastack* S-S separations, and little or no columnar stacking.^{50,52} Thus, the *interstack* S-S interactions are sufficiently strong that the TMTSF-like (face to face) columnar stacking is not favored and, rather the ET molecules are arranged in a side by side fashion to form two-dimensional sheets. The side by side *interstack* S-S contact distances are quite short [3.3–3.7 Å in $(\text{ET})_2\text{ClO}_4(\text{C}_2\text{H}_3\text{Cl}_3)_{0.5}$.⁵⁰ This two-dimensionality in S-S interactions is also manifest in the anisotropy of the electrical conductivity which for $(\text{ET})_2\text{ClO}_4(\text{C}_2\text{H}_3\text{Cl}_3)_{0.5}$ is $\sim 10^2$ – 10^3 higher in the sheet than in the "columnar" direction. Finally, there exists a "corrugated sheet network"⁵² of very short *interstack* S-S distances ($d < 3.60$ Å) in these systems as shown in Figure 5 for $(\text{ET})_2\text{BrO}_4$. As might be expected, the S-S network is the main pathway for electrical conduction in all of the $(\text{ET})_2\text{X}$ systems discussed herein. The absence of significant columnar stacking is also reported for α - $(\text{ET})_2\text{PF}_6$ (triclinic, a semiconductor),⁵³ β - $(\text{ET})_2\text{PF}_6$ (orthorhombic, metal-insulator transition at 297 K),⁵⁴ $(\text{ET})_2\text{AsF}_6$ (monoclinic, semiconductor at 298 K \rightarrow 125 K),⁵⁵ and $(\text{ET})_2\text{InBr}_4$ (triclinic, a semiconductor).⁵⁶

During 1983 our group worked with Strem Chemical Co., Inc., to make the TMTSF and ET organic donors commercially available.⁵⁷ During that same period we were able to perfect the crystal growth procedure (electrocrystallization)⁵⁷ required for the synthesis of $(\text{ET})_2\text{X}$ materials. This was necessary because while the $(\text{TMTSF})_2\text{X}$ systems typically yield only one phase during electrocrystallization, the ET systems frequently produce from two to five different phases all with differing crystallographic and electrical properties. This occurs while often yielding crystals with the same stoichiometry. Separating these materials is an art in itself and is often best accomplished in a nondestructive or nondamaging fashion by use of ESR line-width measurements.⁵⁸

In early 1984 a major breakthrough occurred with the finding, for the first time in an $(\text{ET})_2\text{X}$ system, of *ambient pressure* superconductivity ($T_c \approx 1.5$ K) in β - $(\text{ET})_2\text{I}_3$.⁵⁹ Another 2:1 phase, α - $(\text{ET})_2\text{I}_3$, is grown si-

multaneously during electrocrystallization, but it has a different crystal structure and a metal-insulator transition at 135 K.⁶⁰ However, the α - and β - $(\text{ET})_2\text{I}_3$ systems are easily separated by their room-temperature ESR peak-to-peak line widths of ~ 90 and ~ 20 G, respectively.⁵⁸ Our extensive experience with the ET system allowed us to be the first to confirm ambient pressure superconductivity in β - $(\text{ET})_2\text{I}_3$.^{61–64} The crystal structure^{61,65–67} of β - $(\text{ET})_2\text{I}_3$ reveals that it, like $(\text{ET})_2\text{ReO}_4$ and $(\text{ET})_2\text{BrO}_4$, contains a "corrugated sheet network"⁶¹ of short *interstack* S-S contacts sandwiched between *sheets* of linear-symmetric I_3^- anions. However, the *intrastack* S...S distances are usually > 3.60 Å in length while the similar *interstack* distances are < 3.60 Å. Our previous finding of the methyl group H atom "cavities", which encapsulate the anion in $(\text{TMTSF})_2\text{X}$ materials, prompted us to search for a similar structural feature in β - $(\text{ET})_2\text{I}_3$. This revealed that the anion is completely surrounded by H atoms from the CH_2 groups of the ET molecule.^{68,69} This crucial piece of structural information caused us to realize that the S-S *interstack* distances in the β - $(\text{ET})_2\text{X}$ materials can be systematically altered simply by changing the length of the anion. This led us to synthesize the isostructural β - $(\text{ET})_2\text{IBr}_2$,⁷⁰ which contains the linear-symmetric $(\text{Br-I-Br})^-$ anion and which has a much *higher* ambient pressure superconducting transition temperature (2.7 K) than β - $(\text{ET})_2\text{I}_3$.⁷¹ The

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IBr_2^- anion is approximately 7–8% shorter than I_3^- , and this causes the comparable interstack S–S distances to shorten in a similar fashion ($d_{\text{S-S}} < 3.60 \text{ \AA}$) resulting in a very two-dimensional sheet network of chalcogenide interactions. This two-dimensionality is also observed in the electrical properties of $\beta\text{-(ET)}_2\text{I}_3$ ^{59,63,64} and $\beta\text{-(ET)}_2\text{IBr}_2$.^{70,71} Thus, it appeared that a decrease in the anion length resulted in an increased T_c , at ambient pressure, but this idea was soon to be reversed (vide infra).

To test the effects of anion *disorder* on the electrical properties and to guide us in preparing new materials, we synthesized $\beta\text{-(ET)}_2\text{I}_2\text{Br}$, which contains the *asymmetric*, and crystallographically disordered, $(\text{I-I-Br})^-$ anion with a length *intermediate* between that of I_3^- and IBr_2^- .⁷² We found that the ESR determined electrical conductivity increased down to $T = \sim 10 \text{ K}$, but then leveled off between 1 and 10 K, and the salt never became superconducting at ambient pressure down to 0.45 K. Thus, anion disorder appears to inhibit the onset of superconductivity in the $\beta\text{-(ET)}_2\text{X}$ systems as it does in $(\text{TMTSF})_2\text{ClO}_4$ and should be avoided in synthesizing new systems. However, we have not observed any cooling rate effects in the $\beta\text{-(ET)}_2\text{X}$ materials.

Just as we were working to prepare new isostructural $\beta\text{-(ET)}_2\text{X}$ derivatives containing linear-symmetric anions with lengths less than that of IBr_2^- , Russian⁷³ and, shortly thereafter, Japanese⁷⁴ scientists reported that $\beta\text{-(ET)}_2\text{I}_3$ also becomes superconducting, but under a slight pressure of $\sim 1.3 \text{ kbar}$, with a much higher T_c of $\sim 7\text{--}8 \text{ K}$. This was not altogether surprising because two groups had previously observed a large increase in electrical conductivity in the $\beta\text{-(ET)}_2\text{I}_3$ derivative at $\sim 7\text{--}8 \text{ K}$ at *ambient pressure*.^{59,63} However, the report of a pressure-induced T_c of $\sim 7\text{--}8 \text{ K}$ radically altered our thinking and synthesis effort.

We have come to believe that the $T_c \approx 1.5 \text{ K}$ first observed in $\beta\text{-(ET)}_2\text{I}_3$ at ambient pressure is abnormally depressed from the (pressure-induced) $T_c = 7\text{--}8 \text{ K}$ value likely because of a structural "modulation" we previously reported.^{67–69} This structural modulation causes local atomic displacements (from the average crystal structure positions) of ~ 0.28 and 0.12 \AA in the I_3^- anions and ET molecules, respectively. This effect arises because partial $-\text{CH}_2$ *disorder* is observed in $\beta\text{-(ET)}_2\text{I}_3$ due to $-\text{CH}_2$ group interactions with the I_3^- anion. It seems possible (to us) that the $-\text{CH}_2$ groups may become more highly ordered under the slight 1.2 kbar pressure due to anisotropic shearing of the S–S sheet network which could provide more "space" in the crystal structure for the I_3^- anion.⁷⁶ The higher crystallo-

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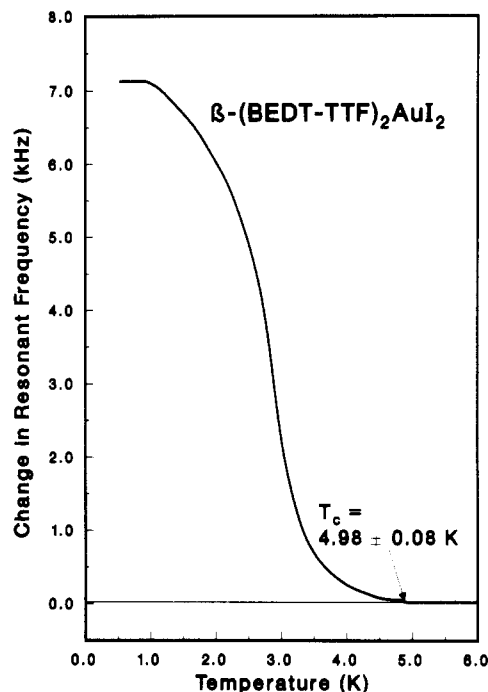


Figure 6. Radio frequency field penetration depth measurement indicating an onset temperature for bulk superconductivity, at ambient pressure, of $4.98 \pm 0.08 \text{ K}$ in $\beta\text{-(ET)}_2\text{AuI}_2$.⁷⁵ This is the highest transition temperature recorded for an organic superconductor at ambient pressure.

graphic order thus achieved would be consistent with a higher T_c . At any rate, this novel finding caused us to reverse our previous approach of using ions shorter than IBr_2^- . Therefore, we have set out to synthesize $\beta\text{-(ET)}_2\text{X}$ salts with linear-symmetric anions of greater length than IBr_2^- , but shorter than I_3^- , which we hoped would increase T_c beyond the 2.7 K we found in $\beta\text{-(ET)}_2\text{IBr}_2$ and yet avoid an I_3^- anion type structural modulation. Our first attempt met with considerable success: viz., we discovered that $\beta\text{-(ET)}_2(\text{I-Au-I})$ becomes superconducting at ambient pressure with the highest such T_c reported to date, i.e., 5 K (see Figure 6).⁷⁵ Thus, for the first time, an ambient pressure organic superconductor has been found to have a transition temperature above that both of liquid helium (4.2 K) and the first superconductor, Hg metal. This is the first case of metal atom replacement of the central atom of the I_3^- anion, and it promises to afford a new means for the synthesis of new ambient pressure organic superconductors with even higher transition temperatures.

Concluding Remarks

As we have discussed in this Account, organic superconductivity has now been realized in a number of Se- and S-based materials. In this way the quotation from McCoy and Moore in the epigraph on the title page, made in the same year as the discovery of superconductivity in Hg, has been fulfilled. Indeed, the future for the synthesis of new $(\text{ET})_2\text{X}$ conductors and superconductors appears extremely bright!

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