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Organic superconductors: structure–property relations and new materials design

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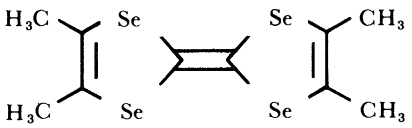
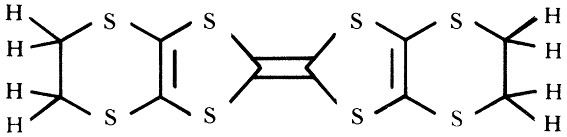
Most known organic materials are electrical insulators having extremely low electrical conductivities of $\sigma < 10^{-10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$. A small number of organic materials are semiconductors having, for classification purposes, conductivities of $\sigma \approx 10^{-10}$–$1\ \Omega^{-1}\ \mathrm{cm}^{-1}$. A very small, but growing, number of organic substances are metallic in nature, i.e. having conductivities that rise with decreasing temperature ($\sigma \approx 1$–$10^{10}\ \Omega^{-1}\ \mathrm{cm}^{-1}$). The latter systems comprise a class of intensely studied materials known as 'organic metals' of which fewer than ten can display the complete absence of electrical resistance at low temperatures, i.e. superconductivity ($\sigma \approx$ infinity). The known organic superconductors are novel, being derived from radical-cation donors and monovalent anions, X. The donors are derived from two kinds of molecules, neither of which contain any metallic elements. These are TMTSF (tetramethyltetraselenafulvalene) and BEDT-TTF (bis-ethylenedithiotetrathiafulvalene, or 'ET' in abbreviated form). Most of the $(\mathrm{TMTSF})_2\mathrm{X}$ and $(\mathrm{ET})_2\mathrm{X}$ conducting materials require applied pressure to induce superconductivity that is thus far observed at very low temperatures ($T_c \approx 1$–2 K). However, two materials, $(\mathrm{TMTSF})_2\mathrm{ClO}_4$ and $(\mathrm{ET})_2\mathrm{I}_3$ are ambient pressure organic superconductors ($T_c = 1.2$ and 1.4 K, respectively). Within each class the crystal structures have many similarities, the most important being a complex 'infinite sheet network' of short Se–Se interactions in $(\mathrm{TMTSF})_2\mathrm{X}$ and a 'corrugated sheet network' of short S–S interactions in $\mathrm{ET}_2\mathrm{X}$. In this paper we discuss structure–property relations of the $(\mathrm{TMTSF})_2\mathrm{X}$ salts, and of the $(\mathrm{ET})_2\mathrm{X}$ salts as far as is known. In addition, we attempt to provide insight and guidelines for the synthesis of new highly conducting anionic derivatives of TMTSF and ET. It appears that while highly conducting $(\mathrm{TMTSF})_2\mathrm{X}$ materials can be designed before synthesis, the onset of superconductivity depends heavily on the presence of anion order in the crystal, which is a parameter not easily controlled. For the $(\mathrm{ET})_2\mathrm{X}$ systems the structural disorder apparent at 298 and 125 K may persist to very low temperature, making it difficult to correlate structural order with superconductivity as is the case for $(\mathrm{TMTSF})_2\mathrm{X}$ systems.

Introduction

The longstanding search for superconductivity in an organic system containing no metallic elements ended successfully in 1980 with the discovery of this phenomenon, induced by an applied pressure with critical temperature $T_c = 1.2$ K, in the Se-based radical-cation salt $(\mathrm{TMTSF})_2\mathrm{PF}_6$. (TMTSF, **1**, is tetramethyltetraselenafulvalene; Jerome *et al.* 1980.) Similarly, pressure-induced superconductivity ($T_c \approx 2.0$ K) was discovered very recently in S-based $(\mathrm{BEDT\text{-}TTF})_2\mathrm{ReO}_4$. (BEDT-TTF, **2**, is bis-ethylenedithiotetrathiafulvalene and is commonly abbreviated as 'ET'; Parkin *et al.* 1983.)



TMTSF (1)



BEDT-TTF or ('ET') (2)

For $(TMTSF)_2PF_6$ an applied pressure of 10–12 kbar† was necessary to suppress a metal–semiconductor transition occurring at *ca.* 12 K, while in $(ET)_2ReO_4$ pressure (*ca.* 4 kbar) was also required to inhibit a metal–insulator transition observed at a much higher temperature (81 K) and at ambient pressure. Shortly after the discovery of superconductivity in $(TMTSF)_2PF_6$, identical electrical behaviour was observed in *slow-cooled* $(TMTSF)_2ClO_4$, but at ambient pressure with $T_c = 1.2$ K (Bechgaard *et al.* 1981). Only very recently has a preliminary report appeared indicating that ambient pressure superconductivity has been observed in $(ET)_2I_3$ with $T_c = 1.4$–1.5 K (Yagubskii *et al.* 1984). This unusual finding has been confirmed independently (Williams *et al.* 1984*b*; Crabtree *et al.* 1984).

To date, superconductivity has been observed and independently confirmed in what are now known as the Bechgaard salts $(TMTSF)_2X$, where $X = TaF_6^-$, AsF_6^-, PF_6^-, SbF_6^-, ReO_4^-, and ClO_4^- (Bechgaard 1982). All $(TMTSF)_2X$ systems except $X = ClO_4^-$ require pressure to promote superconducting transitions, and although pressure suppresses metal–semiconductor transitions in $(TMTSF)_2X$, where $X = BF_4^-$ and NO_3^-, these salts never become superconducting but remain metallic to temperatures near $O(10^{-3}\ \mathrm{K})$ (see figure 1) (Bechgaard *et al.* 1980). Among the $(ET)_2X$ salts, only $(ET)_2X$, $X = ReO_4^-$ and I_3^- have been reported to exhibit superconductivity and while the former salt requires pressure, this has been confirmed in the latter at ambient pressure.

The very recent discovery of superconductivity in Se- and S-based organic systems is remarkable not only because of its novelty, but also because it may prove possible to systematically change, and even increase, T_c by varying portions of the organic donor system or the anion. By the use of the vast array of synthetic tools available to the preparative chemist, it appears likely that a large number of new electronically interesting materials will continue to be produced for the foreseeable future. To understand and then modify the electrical properties of these organic systems, it has been found invaluable to study their crystal and molecular structures, especially as a function of temperature. These structural data, and the patterns that emerge, provide the vital insight needed to partly unravel the wide variety of electrical properties exhibited by the organic metals. We now turn to a discussion of what is known of the relations between crystal structure and electrical properties of the $(TMTSF)_2X$

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† 1 kbar = 10^8 Pa.

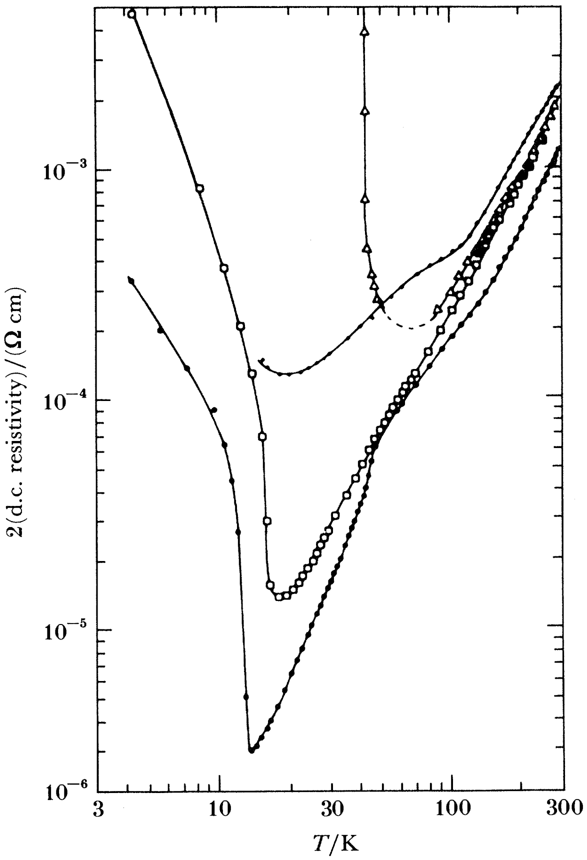

FIGURE 1. Ambient pressure electrical conductivities of $(TMTSF)_2X$, where X = univalent anion; open squares, PF_6^-; open triangles, BF_4^-; larger circles, NO_3^-; smaller circles, AsF_6^-.

and $(ET)_2X$ systems and will especially focus on (i) the question of why pressure is required to promote superconductivity in the $(TMTSF)_2X$ materials and (ii) the role the anion plays in moderating the electrical properties of the $(TMTSF)_2X$ salts. These same questions will be addressed, to a lesser extent because of the lack of available data, to the $(ET)_2X$ salts.

STRUCTURE-PROPERTY CORRELATIONS IN $(TMTSF)_2X$ AND $(ET)_2X$ CONDUCTORS

It is important to appreciate at the outset that in most organic conductors, planar (such as $(TMTSF)_2X$) or nonplanar (such as $(ET)_2X$) radical-cation molecules stack by direct overlap, zig-zag overlap, herringbone, and so on, to form π-overlapped systems. This frequently results in columnar arrays of face-to-face stacked organic moieties with concomitant electron delocalization up and down the stack, resulting in high electrical conductivity in the (*intra*stack) direction. However, if delocalization is not extensive in the off-stack *inter*stack directions, a feature that increases the 'dimensionality' of the system, there is a marked tendency toward low temperature Peierls-type insulating or semiconducting transitions (Peierls 1964).

In the Se-based TMTSF systems, the Se p-orbital extends further out of the molecular plane than that in the S-based TTF materials. When molecular stacking occurs in the former system, the result is larger intermolecular overlap integrals than in the S-based systems, and the increased longitudinal overlap causes an increased bandwidth and more efficient reduction (screening) of repulsive electron–electron interactions (Jerome & Schultz 1982).

$(TMTSF)_2X$ SUPERCONDUCTORS

An unusual feature of the $(TMTSF)_2X$ systems is that they possess identical triclinic crystal structures (space group $P\bar{1}$) in terms of molecular packing. The presence of the centre of symmetry often requires that the anion, which 'resides' at that site, be crystallographically disordered. Electron conduction occurs largely through a network of intra- and interstack intermolecular Se–Se interactions, and although the anions play no obvious role in this process, they do produce extremely subtle changes in the electrical properties that we shall consider shortly. The crystal structures derived from ambient temperature X-ray diffraction data ($(TMTSF)_2X$; $X = NO_3^-$, ClO_4^-, ReO_4^-, PF_6^-, TaF_6^- and $CF_3SO_3^-$) have been described by Thorup *et al.* (1983) while those at low temperature ($T = 125$ K; $X = H_2F_3^-$, AsF_6^-, PF_6^-, ClO_4^-, BrO_4^-, BF_4^- and FSO_3^-) have been described by Williams *et al.* (1983*b*). As indicated in figure 2 (redrawn from Bechgaard 1982), the basic architectural features of the $(TMTSF)_2X$ systems involve a network of Se–Se interactions derived from (i) zig-zag columnar stacking of the nearly planar TMTSF molecules parallel to the high conductivity *a*-axis and (ii) infinite two-dimensional molecular sheets that lie perpendicular to *a* and extend in the *a*–*b* plane. At room temperature the intermolecular inter- and intrastack Se–Se distances, shown in the left and right sides of figure 2 respectively, are all similar, having distances of 3.9–4.9 Å† compared with the Se-atom van der Waals radius sum of 4.0 Å (Pauling 1960). However, at 125 K, these distances (figure 2) are generally less than 4.0 Å. Furthermore, as the temperature is decreased (from 298 down to 125 K) rather unusual changes occur; for example, the ratio of the decrease in the interstack: intrastack Se–Se distances is not unity but is approximately 2:1, indicating rather anisotropic structural changes (Williams *et al.* 1982; Beno *et al.* 1982). Thus, the distances between the vertical 'chains' in the 'infinite sheet network' of Se–Se interactions shown in figure 3 decrease, on the average, by twice as much as between TMTSF molecules in each stack. Calculations reveal that this leads to increased interchain bonding and electronic delocalization through the Se-atom network as temperature is decreased (Whangbo *et al.* 1983; Grant 1983). It is important to note that at 298 and 125 K there appears to be little, if any, dimerization in the TMTSF stacks, a process that would result in electron localization and decreased electrical conductivity (Williams *et al.* 1983*c*). As indicated above, the major structural changes occurring upon cooling involve the interstack Se–Se distances d_7, d_8 and d_9 in figure 3. The Se–Se distances are anion dependent, vary systematically with the anion size, and therefore correlations between crystallographic unit cell volumes (that reflect anion size) and interstack Se–Se distances can be derived (Williams *et al.* 1983*b*). As shown in figure 4 for $T = 125$ and 298 K, there is a striking correlation between unit cell volume V_c and the average interstack Se–Se distance $[d_{avg} = (2d_7 + d_9)/3]$ and these structural changes correlate well with the observation of pressure-induced superconductivity in most $(TMTSF)_2X$ systems.

The linear correlation given in figure 4 is important for three reasons.

(i) The minimum values of V_c and d_{avg} centre around that for ClO_4^-. Note that the ClO_4^-, FSO_3^-, and BF_4^- salts have only insignificant structural differences at $T = 125$ K

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† $1\ Å = 10^{-10}\ m = 10^{-1}$ nm.

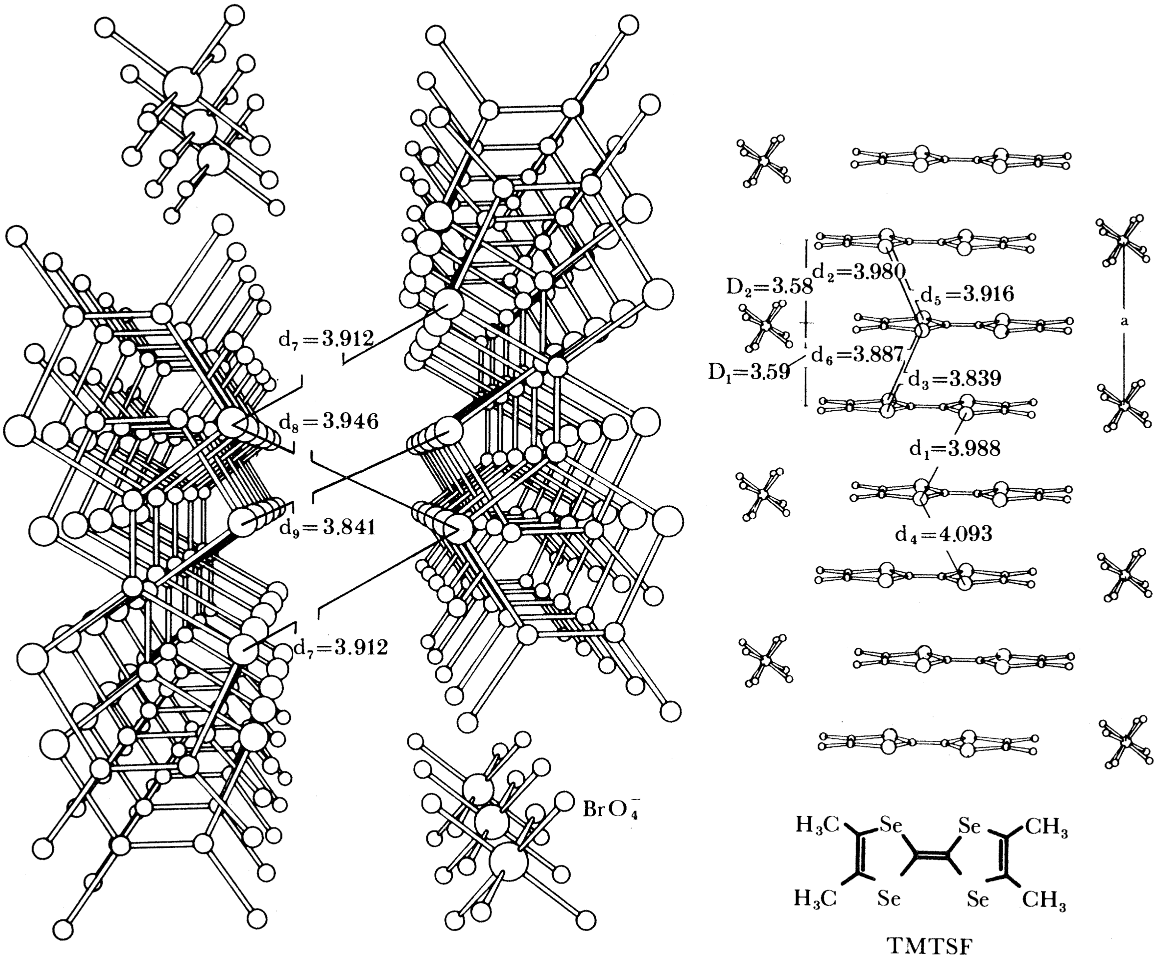

FIGURE 2. Schematic illustration of the structure of $(TMTSF)_2BrO_4$ at 125 K showing intermolecular Se–Se interstack (left) and intrastack (right) separations (in Å). Note that most distances are less than the van der Waals radius sum of Se of ≈ 4.0 Å.

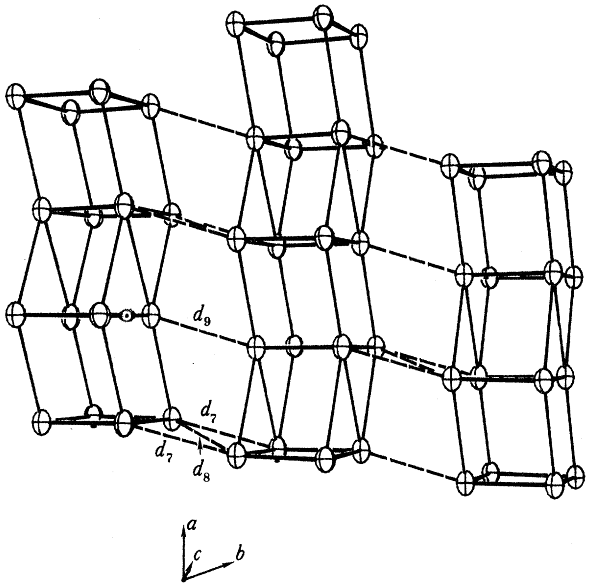

FIGURE 3. The 'infinite sheet' network of Se–Se interactions in $(TMTSF)_2X$ organic metals showing the interstack distances (d_7, d_8, d_9) between vertical chains.

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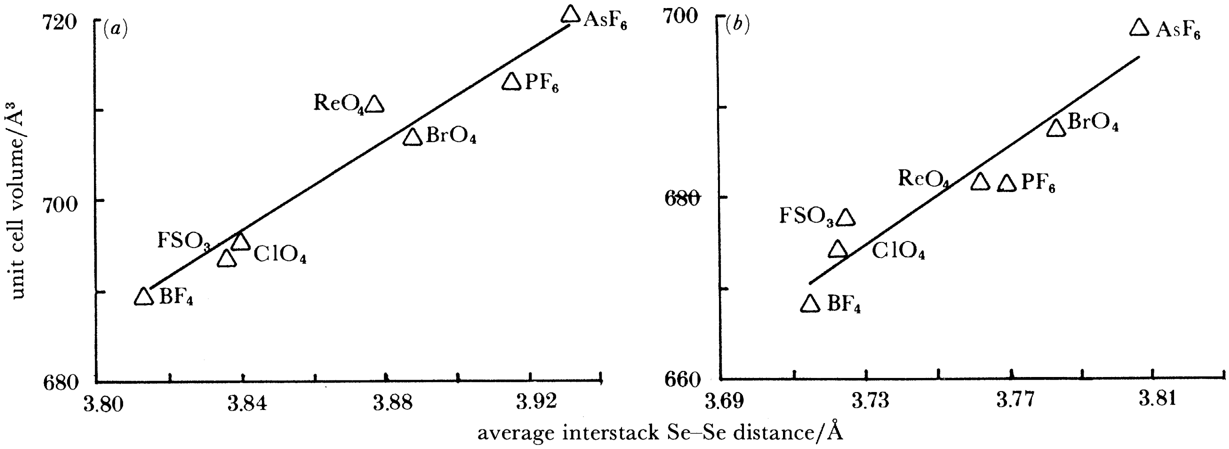

FIGURE 4. Linear correlation between unit cell volume (V_c) and average interstack Se–Se distance in $(TMTSF)_2X$ metals. (*a*) At 298 K; (*b*) at 120–125 K.

(d_{avg} = 3.715–3.725 Å). This suggests the existence of very similar Se-atom network geometry and low temperature electrical properties if, in the absence of transitions such as anion ordering, these structural trends continue down to $T \approx 1$ K. However, if the anion is too small, or if the geometry is different from octahedral or tetrahedral (e.g. NO_3^- and $H_2F_3^-$ are planar), then the interchain network rearranges slightly, with d_{avg} often becoming greater than that for the ClO_4^- derivative, and the precise configuration associated with $(TMTSF)_2ClO_4$ is likely to be destroyed.

(ii) The $(TMTSF)_2X$ systems that require pressure to induce superconductivity ($X = TaF_6^-$, SbF_6^-, AsF_6^-, PF_6^-, ReO_4^-), which should decrease d_{avg}, all have d_{avg} values above that of ClO_4^- in figure 4. Therefore, under an applied pressure it appears that the entire Se–Se sheet network shrinks in a predictable fashion until the structural architecture associated with the superconducting state, perhaps best exemplified by $(TMTSF)_2ClO_4$, is achieved.

(iii) It is now possible to predict the anion size required to produce a $(TMTSF)_2X$ derivative with a tailored unit cell volume–d_{avg} combination because one may accurately predict unit cell volumes (V_{cp}) based on the anion chosen. Thus for any given monovalent octahedral or tetrahedral anion, one may calculate V_{cp} by using the equations $V_{cp} = 2.741\,V + 645.00$ ($T = 298$ K) or $V_{cp} = 1.743\,V + 642.40$ ($T = 125$ K). The derived anionic volume, V, is $(r_i + 2r_0)^3$, in arbitrary units, where r_i = radius of the inner ion and r_0 = radius of the outer atom (Williams *et al.* 1983*b*).

The methodology given here is of practical use because for any imaginable octahedral or tetrahedral anion the unit cell volume can be predicted with some certainty before synthesis of the desired derivative. Therefore, the search for new superconducting $(TMTSF)_2X$ derivatives should centre around those with unit cell volumes similar to that of $(TMTSF)_2ClO_4$ [V_c = 694.3 Å³ (298 K) and 673.7 Å³ (125 K)]. From the equations given above, an excellent candidate for superconductivity appeared to be $(TMTSF)_2PO_2F_2$ [V_c = 675.6 Å³, (125 K)]. However, $(TMTSF)_2PO_2F_2$ has been prepared (Cox *et al.* 1984; Eriks *et al.* 1984) and possesses an insulator transition, ascribed by Cox *et al.* (1984) to its dipolar nature, at the surprisingly high temperature of 137 K. Pressure does not suppress the transition, and it seems likely that it never will because of the surprising discovery of an inherent anion disorder in the structure even below the 137 K transition, previously thought to be an 'anion-ordering' transition (Eriks *et al.* 1984). This will be discussed shortly.

It is clear that the anion 'size' criteria described herein are only part of the complex relation between structure and properties that governs superconductivity in $(TMTSF)_2X$ materials. We must now turn to the role the anion plays in these systems to shed some understanding on their unusual temperature-dependent electrical behaviour.

THE ROLE OF THE ANION IN $(TMTSF)_2X$ SUPERCONDUCTORS

The key to understanding the role of the anion, and its effects on the electrical properties of the $(TMTSF)_2X$ materials, appears to centre around the anion disorder–order transitions that occur at various temperatures as revealed by X-ray diffuse scattering studies. In this respect $(TMTSF)_2ClO_4$ appears to be the model material for probing the effects of anion disorder–order in these systems. Very recently it has been discovered that a 'sluggish' phase transition at 24 K in slow-cooled (R = 'relaxed state') $(TMTSF)_2ClO_4$ is due to anion ordering (Gubser *et al.* 1982; Takahashi *et al.* 1982; Pouget *et al.* 1983), while in rapidly cooled specimens (Q = 'quenched state') the higher temperature (disordered) anion configuration remains frozen in place. Surprisingly, samples in the Q state either do not become superconducting, or have a severely depressed T_c, indicating that the anion-ordered R state is a necessary precursor to the superconductivity in $(TMTSF)_2ClO_4$. The main implication of these findings is that completely ordered materials may be required in the $(TMTSF)_2X$ systems for them to exhibit superconductivity. It also appears that the anion-ordering phenomena observed in many $(TMTSF)_2X$ compounds is associated with, or follows, precursor methyl-group ordering because of anion–methyl-group interactions that occur at low temperature in these materials (Beno *et al.* 1983). Very recently it has been observed that the peripheral atoms of the anions, namely F of AsF_6^- and PF_6^-, and O of ClO_4^-, are involved in weak van der Waals interactions with the H-atoms of the methyl groups (weak H–bonds?). For example, the immediate nearest-neighbour environment about the disordered octahedral AsF_6^- anion in $(TMTSF)_2AsF_6$ reveals a nearly isotropic (symmetric) sea of H-atoms, arising from the discovery that in these materials the anion resides in a 'methyl-group H-atom cavity' (Beno *et al.* 1983; Williams *et al.* 1983*a*). By contrast, the tetrahedral ClO_4^- anion in $(TMTSF)_2ClO_4$ possesses a very asymmetric methyl-group H-atom environment as shown in figure 5.

This asymmetric distribution of oxygen atom to methyl-group H-atom ($H_2C–H\cdots OClO_3^-$) interactions results in a 'pinning' of the anion that appears to be associated with the anion-ordering phase transition occurring at 24 K. On the basis of these results for $(TMTSF)_2ClO_4$ it again seems likely that an ordered crystal lattice may be a necessary prerequisite to superconductivity in $(TMTSF)_2X$ superconductors. This observation takes on special meaning when attempting to explain why $(TMTSF)_2NO_3$ and $(TMTSF)_2PO_2F_2$ do not exhibit superconductivity even under pressure down to very low temperatures. The answer to this behaviour appears to centre around the very recent findings that the NO_3^- (Emge *et al.* 1984*a*) and $PO_2F_2^-$ (Eriks *et al.* 1984) anions adopt disordered anion configurations at 125 K, which are likely to be retained even to the lowest temperatures. For $(TMTSF)_2PO_2F_2$ this configuration is observed even below the 137 K phase transition. This is the first case in which disorder has been observed below the metal–insulator transition and the large displacement of the anion from the centre of symmetry (P$\cdots$P site separation 0.76 Å) is shown in figure 6.

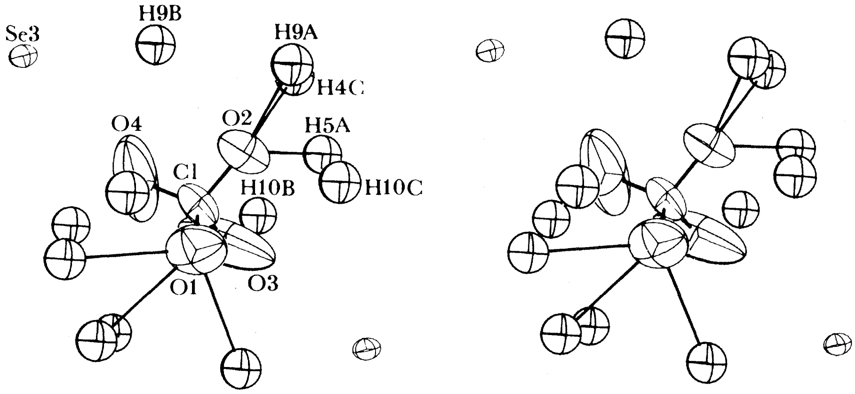

FIGURE 5. Stereoview of the ordered ClO_4^- environment ($T = 125$ K) in $(TMTSF)_2ClO_4$, showing short $H_2C\text{–}H\cdots OClO_3^-$ hydrogen-bonding interactions ($O\cdots H < 3.0$ Å) that pin the anion.

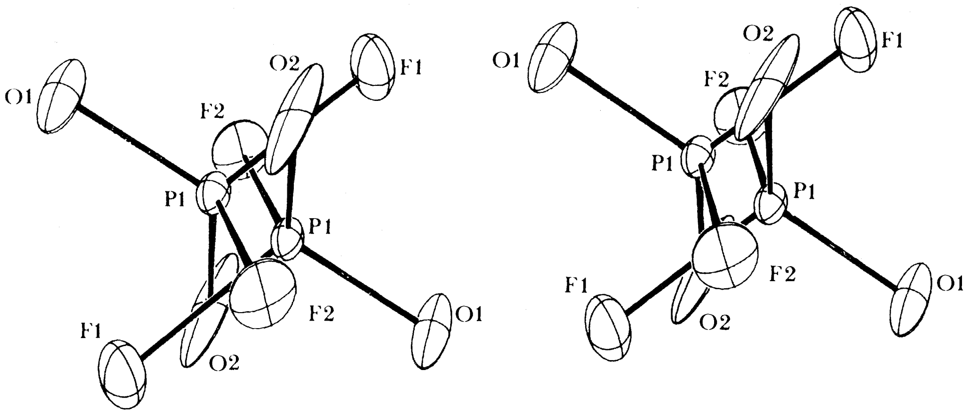

FIGURE 6. Stereoview of the disordered dipolar $PO_2F_2^-$ anion configuration ($T = 125$ K) in $(TMTSF)_2PO_2F_2$, observed below the 137 K 'anion-ordering' phase transition.

$(ET)_2X$ CONDUCTORS

Very recently, pressure-induced superconductivity ($p > 4$ kbar, $T_c \approx 2.0$ K) has been reported in $(ET)_2ReO_4$ (Parkin *et al.* 1983). The preliminary structure, determined at room temperature only, suggested certain similarities with the well-known $(TMTSF)_2X$ derivatives, i.e. 'zig-zag' stacks of ET molecules, with ReO_4^- anions dispersed between them and only the 'possibility' of interchain S–S interactions. However, the structure of the ReO_4^- salt appeared to be very different from the trichloroethane (TCE) solvated salt $(ET)_2ClO_4(TCE)_{0.5}$ because an X-ray structural study revealed a complex network composed only of very short ($d < 3.60$ Å) interstack S–S contact distances when compared with the van der Waals radius sum of S of 3.6 Å (Kobayashi *et al.* 1983). These structural differences were surprising in that the ReO_4^- derivative appeared to lack significant interchain coupling arising from short S–S interactions, which reduces dimensionality in a system and generally leads to a metal–insulator transition in organic metals. However, very recent multiple-temperature (298 and 125 K) X-ray and n.m.r.–e.s.r. studies of $(ET)_2ReO_4$ and an isostructural $(ET)_2BrO_4$ derivative have revealed a number of novel features (compared with $(TMTSF)_2X$); also that the previous structural description of Parkin *et al.* (1983) of $(ET)_2ReO_4$ requires considerable revision, as follows.

(i) In agreement with the earlier work the ET molecules are non-planar, but, surprisingly, the ET moieties are not evenly spaced in a columnar array as for $(TMTSF)_2X$.

(ii) Even after lattice shrinkage and contracted S–S distances (from 298 down to 125 K) there are no significantly short intrastack S–S interactions at 125 K (d_9–d_{16} > 3.6 Å, see figure 7*b*); therefore highly overlapped zig-zag columnar stacking of molecules does not occur (in contrast to $(TMTSF)_2X$ structures) and the structure is similar to that of $(ET)_2ClO_4\,(TCE)_{0.5}$.

(iii) At $T = 125$ K there exists a 'corrugated sheet' network (see figure 8) of very short interstack S–S interactions (d_1–d_8 < 3.60 Å, see figure 7*a*) actually very similar to that in the $(ET)_2ClO_4(TCE)_{0.5}$.

(iv) All atoms, including hydrogen, were located, and the ET molecules are completely ordered.

(v) In both the ReO_4^- and BrO_4^- salts the anion is ordered (Williams *et al.* 1984*a*).

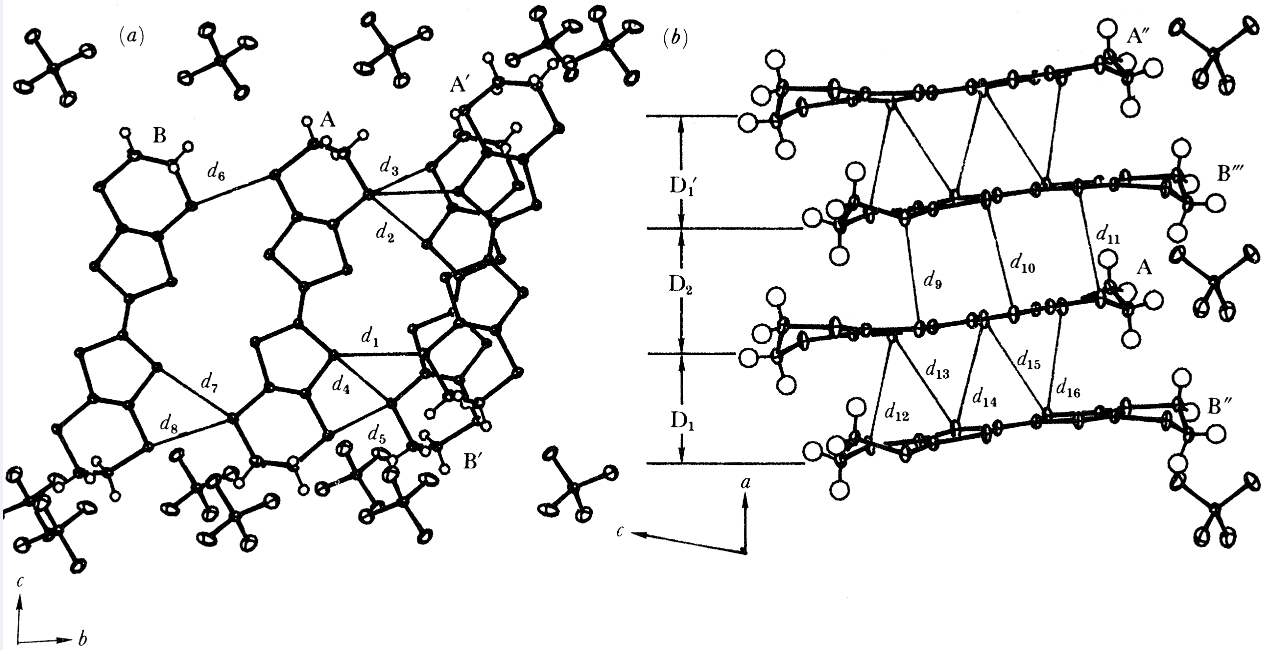

FIGURE 7. View of the intermolecular S–S interactions in $(ET)_2X$, where X = BrO_4^- or ReO_4^- for $T = 125$ K. (*a*) The interstack interaction distances (d_1–d_8) are all less than the van der Waals radius sum of S (*ca.* 3.60 Å). (*b*) The intrastack separations (d_9–d_{16}) are all larger than 3.60 Å. The opposite findings ($d_{\text{intra}} < d_{\text{inter}}$) are observed in $(TMTSF)_2X$ systems. The ET molecules are also not equally spaced ($D_1 > D_2$).

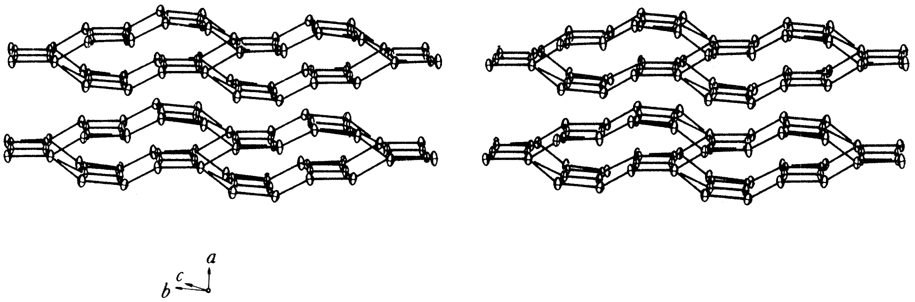

FIGURE 8. Stereoview of the two-dimensional 'corrugated sheet' network of short (d < 3.60 Å, $T = 125$ K) intermolecular interstack S–S interactions in $(ET)_2X$, where X = ReO_4^-, BrO_4^-.

This latter feature is reminiscent of the R-state (ordered anion and lattice) in $(TMTSF)_2ClO_4$ as a necessary prerequisite to superconductivity. Although $(ET)_2X$, $X = ReO_4^-$ and BrO_4^- are strictly isostructural, the BrO_4^- salt undergoes a magnetic transition at 6 K and pressure studies will soon reveal whether it can be made superconducting (Azevedo *et al.* 1984).

Very early in 1984 a report appeared in which two phases of $(ET)_2I_3$ ('flakes' and needle crystals) are stated to be the first ambient pressure S-based organic superconductor (four-probe resistivity measurement, $T_c \approx 1.4$–1.5 K) (Yagubskii *et al.* 1984). In an accompanying structure report, in which little detail is presented, it is noted that interstack S–S bonding is significant in terms of shortened S–S contacts ($d < 3.70$ Å) while the intrastack S–S distances all exceed the van der Waals radius sum for S (Kaminskii *et al.* 1984). Thus, in agreement with the structural findings for $(ET)_2ReO_4$ and $(ET)_2BrO_4$, the compound $(ET)_2I_3$ (where the I_3^- ion is linear) is a member of a new structural class of $(ET)_2X$ systems with extended two-dimensional networks of S–S interactions (Williams *et al.* 1984*a*). R.f. penetration depth measurements (Crabtree *et al.* 1984) sensitive to the exclusion of an applied r.f. field from a superconducting sample by persistent shielding currents, have confirmed that a different crystal morphology (distorted hexagon-shaped crystals, Williams *et al.* 1984 *b*) of $(ET)_2I_3$ is an ambient pressure superconductor. The critical temperature (T_c) for bulk superconductivity determined from these inductive measurements is 1.40 ± 0.02 K. These measurements show a broad superconducting transition that is incomplete down to 0.44 K (see figure 9). Measurements of the critical magnetic fields by r.f. penetration depth studies indicate a low value for the lower critical field and a value near 600 Oe† for the upper critical field for bulk superconductivity in the distorted hexagon-shaped crystals, as shown in figure 10.

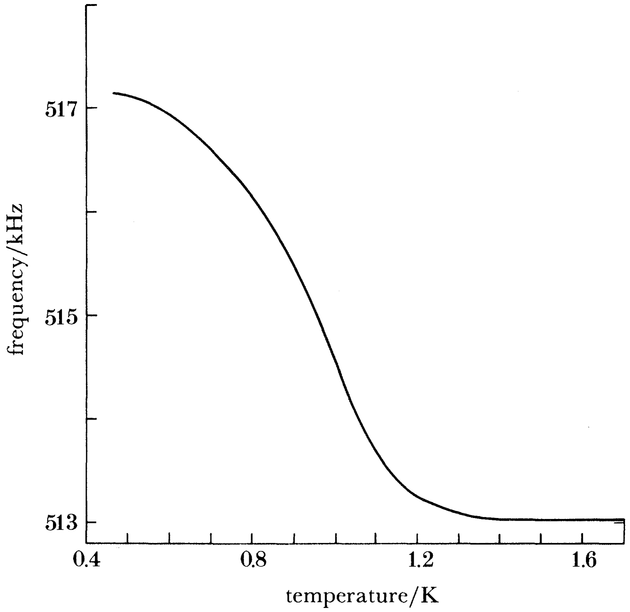

FIGURE 9. Resonant frequency of the r.f. coil for distorted-hexagon shaped crystals of $(ET)_2I_3$ as a function of temperature in zero applied field after a fast cooldown.

Both the low value of the lower critical field and the broad superconducting transition in zero field found in $(ET)_2I_3$ are qualitatively similar to the same observations in $(TMTSF)_2X$

† 1 Oe ≈ 79.58 A m^{-1}.

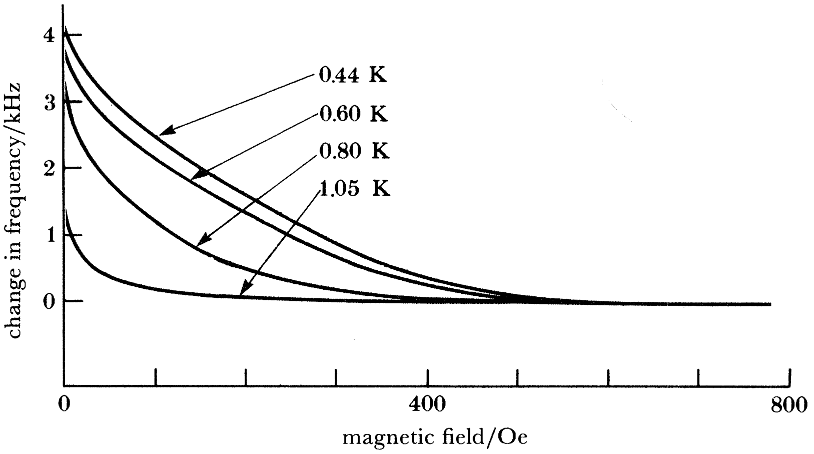

FIGURE 10. Change in resonant frequency from the empty coil value for distorted-hexagon crystals of $(ET)_2I_3$ as a function of applied field at various temperatures.

metals. The investigators have emphasized, however, that the inductive measurements of T_c and the critical fields may be influenced by the small dimensions of the crystals employed, because penetration depths in organic superconductors are typically rather large. There is also a question of possible strong anisotropy in the critical fields that has not yet been explored. In the same investigation (Crabtree *et al.* 1984), the needle-shaped crystals of $(ET)_2I_3$ grown in benzonitrile solvent (as was used by Yagubskii *et al.* 1984), gave the same T_c and critical fields as those measured for the distorted hexagon morphology. As a consequence of these investigations, one can conclude that $(ET)_2I_3$ is the first S-based ambient pressure superconductor and is only the second presently known ambient pressure organic superconductor. The room temperature crystal structure has also been determined with high resolution and is in agreement with the previous work in terms of the intrastack S–S distances all having $d > 3.60$ Å (shortest distance 3.759(1) Å), but with much shorter interstack separations (the four shortest interstack distances range from 3.574(1) Å to 3.599(1) Å, Williams *et al.* 1984*b*). The resulting corrugated sheet network of intermolecular interstack S–S interactions ($d < 3.60$ Å) is shown in figure 11.

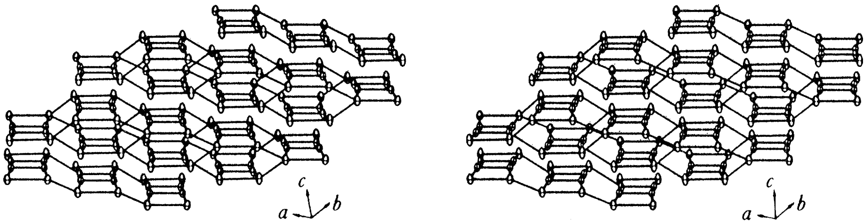

FIGURE 11. Stereoview of the corrugated sheet network of interstack S–S interactions ($d < 3.60$ Å) found in the unique ambient pressure organic superconductor, $(ET)_2I_3$ at 298 K. The network is more complete (closed) than that found in $(ET)_2X$, where $X = ReO_4^-$, BrO_4^- at the same temperature.

Thus the chalcogenide atom network is quite different from that found in $(TMTSF)_2X$ organic metals, but is remarkably similar to that found in $(ET)_2X$, where $X = BrO_4^-$, ReO_4^-. Preliminary X-ray investigations at 125 K reveal satellite reflections for all zones of diffraction vectors, indicating the presence of a complex modulated superstructure for at least the I_3^- anions

(Emge *et al.* 1984*b*). Finally, it appears that the $(ET)_2X$ systems having the same structural type as $(ET)_2X$ ($X = ReO_4^-$, BrO_4^-, and I_3^-) hold the promise of a rich variety of electrical properties including potentially new superconductors. An area of special interest to us involves the replacement of the central C═C double bond in the ET molecule with a metal atom, such as Pt, which may allow the synthesis of conducting salts possessing the features of both inorganic and organic conductors, i.e. both metal-atom chains and extended chalcogen atom networks.

Conclusions

Over the period of about five years approximately eight organic radical cation–anion systems, six based on Se and two on S, have been shown to exhibit superconductivity. The transition temperatures are in the range of 1–2 K and appear to be rising. New derivatives with novel physical and structural properties are being reported constantly and, indeed, the future appears most promising!

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Note added in proof (28 *November* 1984). The highest superconducting transition temperatures yet obtained for any organic system (at ambient pressure or otherwise) have recently been reported for $(ET)_2IBr_2$ with $T_c = 2.7$ K and higher at *ambient pressure* (Williams *et al.* 1984*c*).

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