Organic Superconductors—New Benchmarks

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Recent advances in the design and synthesis of organic synthetic metals have yielded materials that have the highest superconducting transition temperatures ($T_c \approx$ 13 kelvin) reported for these systems. These materials have crystal structures consisting of alternating layers of organic donor molecules and inorganic anions. Organic superconductors have various electronic and magnetic properties and crystal structures that are similar to those of the inorganic copper oxide superconductors (which have high T_c values); these similarities include highly anisotropic conductivities, critical fields, and short coherence lengths. The largest number of organic superconductors, including those with the highest T_c values, are charge-transfer salts derived from the electron donor molecule BEDT-TTF or ET [bis(ethylenedithio)-tetrathiafulvalene]. The synthesis and crystal structures of these salts are discussed; their electrical, magnetic, and band electronic structure properties and their many similarities to the copper oxide superconductors are treated as well.

SUPERCONDUCTIVITY WAS DISCOVERED (*1*) IN 1911 IN THE metal Hg (transition temperature T_c = 4.15 K). By coincidence, during the same year it was speculated (*2*, p. 293) that "it is possible to prepare composite metallic substances from nonmetallic constituent elements." Thus, the concept of a "synthetic metal," that is, a material exhibiting metallic electrical conductivity (increasing electrical conductivity with decreasing temperature) but not containing any metal atoms, was born. Although many of the organic charge-transfer salt superconductors described in this article do contain metal atoms in an anion constituent, their role is one of charge compensation, not electrical conduction. In this article we review organic superconductivity (*3–8*), a rapidly growing research field that is now only one decade old, and discuss many of the novel properties associated with these materials. We also discuss how superconductivity can be found in materials composed of elements that are normally electrical insulators.

Although most organic substances are insulators, a class of organic substances known as "organic metals" or "synthetic metals" exhibit metallic conductivity. The magnitude of the conductivity of most organic metals is ordinarily much less than that of a metal such as elemental Cu, but some of these synthetic metals become superconducting at low temperatures, whereas Cu does not. The real impetus to the investigation of synthetic metals arose after the seminal discoveries of the electron acceptor tetracyano-*p*-quinodimethane (TCNQ) in 1960 (*9*) and the electron donor tetrathiafulvalene (TTF) in 1970 (*10–13*) and their combination in 1972 to form the π-molecular donor-acceptor complex TTF-TCNQ (*14, 15*). TTF-TCNQ has anisotropic conductivity arising from segregated stacks of TTF and TCNQ molecules. The metallic conductivity (σ) along the stacking direction increases with decreasing temperature to $\sigma \cong 10^4$ S cm^{-1} (S cm^{-1} = ohm^{-1} cm^{-1}) near 60 K (compared to the value for Cu of ~10^6 S cm^{-1} at room temperature), below which a metal-insulator Peierls (*16*) transition occurs because of a lattice distortion and localization of the conducting electrons. Peierls (*17*) and Fröhlich (*18*) have shown that a one-dimensional (1-D) conductor inherently favors a lattice distortion that opens a band gap at the Fermi level. In a three-dimensional (3-D) material, however, the elastic restoring forces of the lattice overcome the distortion when the temperature exceeds the Peierls transition temperature (above which the material is metallic).

The first organic superconductor, quasi–1-D $(TMTSF)_2PF_6$ (T_c = 0.9 K at P = 12 kbar), was discovered in 1979 and required high pressure to suppress a metal-insulator antiferromagnetic ordering transition (spin density wave, SDW) at ~16 K (*19*). This transition arises when the on-site electron-electron Coulomb repulsion exceeds the stabilization gained from delocalization. The electrons are localized to reduce the Coulomb repulsion, and the ground state is that of an antiferromagnetically coupled insulator, known as a Mott-Hubbard insulator (*20, 21*). The substitution of simple monovalent charge-compensating anions (such as PF_6^-, SbF_6^-, ClO_4^-) for TCNQ in TMTSF organic metals (Bechgaard salts) led to the rapid development of additional TMTSF organic superconductors. Organic superconductors have been derived from several different organic electron donor molecules, including TMTSF, BEDT-TTF (or ET), DMET, MDT-TTF, BEDO-TTF, TTF, and the metal-organic acceptor complexes $[M(dmit)_2]^{2-}$ (Fig. 1). Ten years after the discovery of the first organic superconductor, they now total almost 40 (Table 1), and T_c values have increased an order of magnitude to just below 13 K.

In this article we focus on the organic systems based on ET that have yielded both the largest number of organic superconductors and those with the highest T_c values known to date. The TMTSF systems have been extensively reviewed elsewhere (*22–24*), whereas insufficient data now exist for a full review of the materials based on DMET, MDT-TTF, BEDO-TTF, and the $[M(dmit)_2]^{2-}$ anion.

Synthesis

Several review articles have given detailed descriptions of the strategies and methodologies pertaining to the synthesis of the organic donor and acceptor molecules that constitute organic metals

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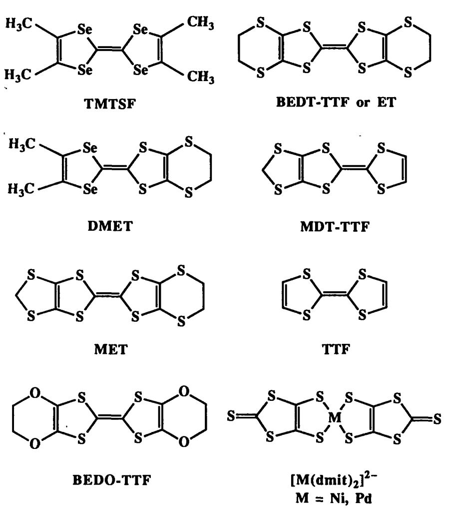


Fig. 1. Molecular components of organic superconductors.

Table 1. Organic superconductors and their critical temperatures.

Compound	T_c† (K)	Reference
	TMTSF compounds	
$(TMTSF)_2PF_6$	0.9 (12 kbar)	(*19*)
$(TMTSF)_2AsF_6$	1.1 (12 kbar)	(*100*)
$(TMTSF)_2SbF_6$	0.4 (11 kbar)	(*100*)
$(TMTSF)_2TaF_6$	1.4 (12 kbar)	(*100*)
$(TMTSF)_2ReO_4$	1.3 (9.5 kbar)	(*100*)
$(TMTSF)_2FSO_3$	2.1 (6.5 kbar)	(*101, 102*)
$(TMTSF)_2ClO_4$	1.4	(*100*)
	ET compounds	
$(ET)_2ReO_4$	2.0 (4.5 kbar)	(*103*)
β-$(ET)_2I_3$‡	1.4	(*42*)
β^*-$(ET)_2I_3$§	8.0 (0.5 kbar)	(*43, 44, 50*)
γ-$(ET)_3(I_3)_{2.5}$	2.5	(*104*)
θ-$(ET)_2I_3$	3.6	(*105, 106*)
κ-$(ET)_2I_3$	3.6	(*107*)
α_t-$(ET)_2I_3$	7–8	(*39, 40*)
(α/β)-$(ET)_2I_3$	2.5–6.9	(*108*)
β-$(ET)_{1.96}(MET)_{0.04}I_3$	4.6	(*109*)
β-$(ET)_2IBr_2$	2.8	(*45*)
β-$(ET)_2AuI_2$	4.98	(*46*)
κ-$(ET)_4Hg_{3-\delta}Cl_8$	1.8 (12 kbar); 5.3 (29 kbar)	(*33, 110*)
κ-$(ET)_4Hg_{2.89}Br_8$	4.3; 6.7 (3.5 kbar)	(*111–113*)
$(ET)_2Hg_{1.41}Br_4$	2.0	(*114*)
α-$(ET)_2[(NH_4)Hg(SCN)_4]$	1.15	(*115*)
$(ET)_3Cl_2{\cdot}2H_2O$	2.0 (16 kbar)	(*116*)
κ-$(ET)_2Cu(NCS)_2$	10.4	(*55*)
κ-$(ET)_2Ag(CN)_2{\cdot}H_2O$	5.0	(*59*)
κ-$(ET)_2Cu[N(CN)_2]Br$	11.6	(*56*)
κ-$(ET)_2Cu[N(CN)_2]Cl$	12.8 (0.3 kbar)	(*57*)
	DMET compounds	
$(DMET)_2Au(CN)_2$	0.8 (5 kbar)	(*117*)
$(DMET)_2I_3$	0.47	(*118*)
$(DMET)_2IBr_2$	0.59	(*118*)
$(DMET)_2AuCl_2$	0.83	(*119*)
$(DMET)_2AuI_2$	0.55 (5 kbar)	(*119*)
$(DMET)_2AuBr_2$	1.0 (1.5 kbar)	(*120*)
κ-$(DMET)_2AuBr_2$	1.9	(*62*)
	Other compounds	
κ-$(MDT\text{-}TTF)_2AuI_2$	4.5	(*121, 122*)
β_m-$(BEDO\text{-}TTF)_3Cu_2(SCN)_3$	1.06	(*123*)
$(TTF)[Ni(dmit)_2]_2$	1.6 (7 kbar)	(*124*)
$Me_4N[Ni(dmit)_2]_2$	5.0 (7 kbar)	(*125*)
α'-$(TTF)[Pd(dmit)_2]_2$	6.42 (20.7 kbar)	(*126*)
α-$(TTF)[Pd(dmit)_2]_2$	1.7 (21.75 kbar)	(*126*)

†At ambient pressure in those entries where no pressure is indicated in parentheses.
‡Also referred to as β_L-$(ET)_2I_3$. §Also referred to as β_H-$(ET)_2I_3$.

and superconductors (*8, 25–30*). To produce crystals of organic metals, one oxidizes the organic electron donor molecules and crystallizes them with charge-balancing anions in a one-step technique termed "electrocrystallization." The electrocrystallization is a slow, continuous process that enables one to carry out the reaction (oxidation or reduction) electrolytically near the electrodes. This process also purifies the products, which grow simultaneously as crystals on the appropriate electrode. Typically, an H-configuration cell with Pt electrodes is used with the donor molecule (ET, 1 eq) in the working electrode compartment and a supporting electrolyte (NBu_4X salt >10 eq, where X is a monovalent anion such as PF_6^- or ClO_4^- and Bu is *n*-butyl) in both the working and auxiliary electrode compartments (*31, 32*). With a constant current of ~1 μA cm^{-2}, the crystal growing process can typically take 2 weeks to several months. Slowly grown crystals are usually suitable for single-crystal x-ray structural studies and various other physical property measurements.

The charge-balancing anions or electrolytes used during electrocrystallization fall into two categories: (i) isolated anions, such as simple halides (Cl^-, Br^-), tetrahedral (ClO_4^-, ReO_4^-), octahedral (PF_6^-, AsF_6^-), planar [NO_3^-, $AuCl_4^-$, $C_5(CN)_5^-$], and linear anions (I_3−, IBr_2^-); and (ii) polymeric anions, such as $[Ag_4(CN)_5^-]_n$, $[Hg_3Cl_8^{2-}]_n$, $[Cu(NCS)_2^-]_n$, $[(NH_4)Hg(SCN)_4^-]_n$, and $\{Cu[N(CN)_2]Br^-\}_n$. Except for the polymeric anions, the anionic species are usually well defined in solution, and the product stoichiometry is predictable to some extent. The polymeric anions, however, are generally the product of rearrangement or in situ formation (or both) under equilibrium conditions in solution. For instance, the $(ET)Ag_4(CN)_5$ and κ-$(ET)_4Hg_3Cl_8$ salts are the products when ET is electrocrystallized with $Ag(CN)_2^-$ and $HgCl_3^-$ anions, respectively (*33, 34*). On the other hand, κ-$(ET)_2Cu[N(CN)_2]Br$ (T_c = 11.6 K) can be prepared from CuBr and $N(CN)_2^-$ or $Cu[N(CN)_2]$ and Br^- (*35*).

Synthetic metals that are based on ET donor molecules commonly form many crystallographic phases during electrocrystallization. The most complicated case is the ET-I_3 system, for which as many as 14 different phases have been reported, although the α- and β-$(ET)_2I_3$ phases predominate (*36, 37*). Under slow growth conditions (current density <1.5 μA cm^{-2}) with dry tetrahydrofuran as the solvent, pure β-phase (superconductor) materials can be grown (*38*). However, under rapid growth conditions with a high current density (10 μA cm^{-2}) and a small amount of water or oxidant added, more than 90% of the product is α-phase (a semimetal with a metal-to-insulator transition T_{MI} = 135 K). The α-$(ET)_2I_3$ phase is a kinetically favored product, whereas the β-phase is the thermodynamically more stable product. In addition, some phases in the ET-I_3 system can be interconverted in the solid state. For instance, the α- and θ-$(ET)_2I_3$ and ϵ-$(ET)_2(I_3)(I_8)_{0.5}$ phases can be converted at 100°C to α_t-$(ET)_2I_3$ (α_t denotes transformed α), with T_c near 7 K (*39–41*).

Crystal Structures of Superconducting ET Salts

The β-$(ET)_2X$ *salts.* The β-$(ET)_2X$ family of compounds consists of an isostructural series of salts with linear, triatomic anions [X^--I_3^-, T_c = 1.4 K at ambient pressure (*42*), 8 K at 0.5 kbar (*43, 44, 50*)], IBr_2^- [T_c = 2.8 K at ambient pressure (*45*)], and AuI_2^- [T_c = 4.8 K at ambient pressure (*46*)]. Isostructural superconducting salts are important because their study can lead to useful structure-property relations (see below). These salts are all triclinic (space group $P\bar{1}$) with one formula unit (two ET molecules) per unit cell (*45–47*). These salts are layered superconductors, and the repeat unit contains one layer of the conducting donor molecules (general crystallographic position) and one layer of anions. The latter are located on inversion symmetry centers. The donor molecule packing is shown in Fig. 2. All of the molecules are oriented parallel to each other, and a distinctive stacking axis exists along the unit cell diagonal direction. All short S···S intermolecular contacts (drawn in Fig. 2) are located between molecules on neighboring stacks and form a honeycomb-like pattern that provides the pathways for the conduction electrons in the donor molecule layers.

Whereas the IBr_2^- and AuI_2^- salts retain their structure upon cooling, the I_3^- compound undergoes a phase transition to an incommensurately modulated structure at 175 K (*48, 49*). The transition to the modulated phase can be suppressed by modest external stress of 0.5 to 1 kbar (*43, 50, 51*), and the resulting so-called β_H- or β^*-phase (*52, 53*) has a much higher T_c ($\cong$8 K) than the modulated β_L-phase (T_c = 1.4 K). One can also obtain the β^*-phase by prolonged annealing of the β_L-phase at temperatures less than 125 K (*54*).

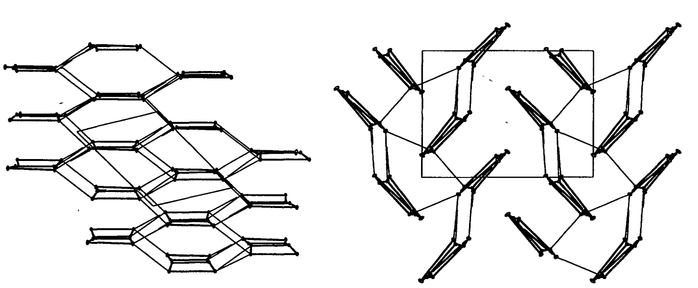
The κ-phase salts. The recently discovered organic superconductors with the highest T_c values found to date, κ-$(ET)_2Cu(NCS)_2$ [T_c = 10.4 K (*55*)], κ-$(ET)_2Cu[N(CN)_2]Br$ [T_c = 11.6 K (*56*)], and κ-$(ET)_2Cu[N(CN)_2]Cl$ [T_c = 12.8 K at 0.3 kbar (*57*)], are all members of the κ-phase series. The κ-family of salts shows more variability among its members than the β-$(ET)_2X$ family, both in composition and details of the crystal packing. All κ-phase salts have face-to-face molecular dimers, which are oriented approximately at right angles with respect to their neighbors, forming a two-dimensional (2-D) conducting S···S network (Fig. 2). A few unsymmetrical donor molecules, such as MDT-TTF and DMET (Fig. 1), also exhibit this packing pattern in some of their superconducting salts (Table 1). However, not all κ-phase salts are isostructural because of variations in the number of donor molecule layers in the unit cell (one or two) and the presence or absence of a center of inversion at the center of the donor dimer. The salts κ-$(ET)_2Cu(NCS)_2$ (*58*) and κ-$(ET)_2Ag(CN)_2(H_2O)$ (*59, 60*) are noncentrosymmetric and have one layer per cell, κ-$(ET)_2I_3$ (*61*) and κ-$(DMET)_2AuBr_2$ (*62*) are centrosymmetric and have one layer per cell, and all other κ-phase compounds contain two centrosymmetric layers in the unit cell.

Electrical Conductivity and Superconductivity

The metallic conducting state of organic synthetic metals is like that of an ordinary metal: σ increases with decreasing temperature and is describable as the transport of conduction band electrons. In ET salts, the conduction band originates from weak S···S interactions at distances at or near the sum of the van der Waals radii and not from the presence of metal atoms with strongly overlapping orbitals. Because organic molecules in their neutral state have an even number of electrons, charge transfer is an essential requirement, but not a guarantee, for the production of a partially filled valence band (conduction band). As a consequence of the charge transfer, the mechanical properties of these "organic metals" are more like those of an ordinary salt than those of a metal: they are not malleable materials because the cohesive interactions are largely due to the electrostatic (ionic) and van der Waals forces rather than the "metallic bonding" interactions of ordinary metals.

The room-temperature conductivities of the ET-based organic metals are typically less than 100 S cm^{-1}. For example, $\sigma \approx$ 50 S cm^{-1} at 300 K for crystals of the β-$(ET)_2I_3$ (*42*) and κ-$(ET)_2Cu[N(CN)_2]Br$ (*56*) salts. These values are a factor of $\sim 10^{-4}$ of the conductivities of ordinary metals such as Cu. Furthermore, in contrast to the isotropic conductivity of ordinary elemental metals, the conductivities of the organic metals are highly anisotropic because of the layered nature of the materials. Most of the ET-based superconductors are 2-D conductors because the conductivity is approximately isotropic within the layers of the ET donor molecules but smaller by a factor of $\sim 10^3$ in the perpendicular direction. This anisotropic behavior correlates well with the S···S networks found in the crystal structures, in which the anion arrays are more or less "electronically inert" spacers between the 2-D layers of the organic donor molecules. The crystal structures and chemical stoichiometry also account for the small conductivities. The transfer of one electron from $(ET)_2$ to X, giving $(ET)_2{}^+X^-$, leaves one unpaired conduction electron associated with $(ET)_2{}^+$ within a typical unit cell volume of 800 to 900 Å^3 per formula unit. This yields a conduction electron density of $\sim 10^{21}$ cm^{-3}, which is several orders of magnitude smaller than that of an ordinary metal. Furthermore, the large number of atoms, ~50 to 60 per formula unit, serve as a large number of electron scatterers from vibrational motions (phonons). Thus, these organic metals are expected to have conduction electrons of both lower number density and lesser mobility than those of ordinary metals.

The resistivity of a single-crystal specimen of β-$(ET)_2I_3$ (Fig. 3A) decreases monotonically with decreasing temperature below 300 K, much like that of an ordinary metal, and then exhibits a superconducting transition beginning at 1.6 K (*63*). The superconducting transition width from onset to completion is rather broad, $\Delta T \approx 1$ K, which is typical of some organic superconductors. This broadness is generally attributed to sample inhomogeneities. The temperature of the resistive transition midpoint is traditionally defined as the "resistive T_c." The abrupt drop in resistance near 8 K in Fig. 3A is now well recognized (*37*) as the signature of a small amount of the crystallographically ordered phase β^*-$(ET)_2I_3$, which is stabilized in bulk quantities under an applied stress and exhibits a T_c near 8 K, (see above).


β-$(ET)_2X$ network

κ-$(ET)_2Cu(NCS)_2$ network

Fig. 2. ET molecule network in β- and κ-type organic superconductors. Thin lines indicate short intermolecular contacts, and the unit cell boundaries are also indicated.

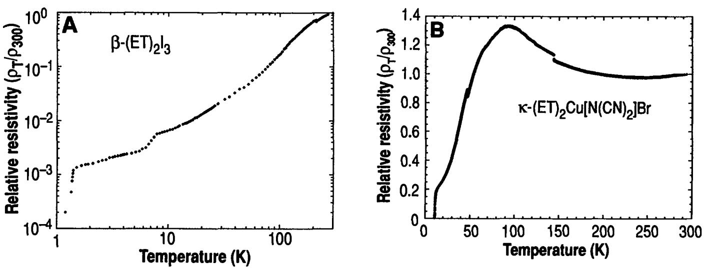


Fig. 3. Relative resistivity as a function of temperature. (**A**) Single-crystal specimen of β-$(ET)_2I_3$ at ambient pressure and zero applied field. The figure is a log-log plot to enhance the structure at low temperatures (note the drop near 8 K). (**B**) Single-crystal specimen of κ-$(ET)_2Cu[N(CN)_2]Br$ at ambient pressure and zero applied field. The abrupt slight increases in resistance near 145 and 45 K likely represent the development of microcracks in the specimen, a typical phenomenon found in crystals of organic charge-transfer salts.

The resistivity of κ-$(ET)_2Cu[N(CN)_2]Br$ (Fig. 3B) shows a novel feature of a different nature: a maximum in the resistivity (*56*). The resistance is weakly metallic just below 300 K, becomes semiconductive near 250 K, and then becomes strongly metallic below 100 K. The resistive peak is a common feature of most of the κ-phase superconducting salts, but its origin is not yet fully understood. The κ-$(ET)_2Cu(NCS)_2$ superconductor, which has been studied in considerable detail, has a resistive peak that can be suppressed by the application of either hydrostatic pressure (*64*) or tensile stress (*65*). In the low-temperature metallic state at ambient pressure, κ-$(ET)_2Cu[N(CN)_2]Br$ undergoes a resistive superconducting transition with onset at 12.5 K, midpoint at 11.6 K, and completion at 10.5 K (*56*). These values represent the current temperature record for an ambient pressure organic superconductor. However, the Cl-analog salt κ-$(ET)_2Cu[N(CN)_2]Cl$, which is nonsuperconducting at ambient pressure, attains a higher T_c of ~12.8 K (midpoint, 0.2 K transition width) when subjected to a slight applied pressure (*57*) (see below). At ambient pressure, this Cl^- salt undergoes a metal-insulator transition at 40 to 50 K. Electron spin resonance (ESR) measurements of the linewidth, spin susceptibility, and g value near the transition are consistent with SDW formation (*66*). This result illustrates the delicate competition between insulating and superconducting electronic ground states in many organic conductors. This competition can sometimes be mediated in favor of a superconducting ground state by the use of applied pressures, as in the κ-$(ET)_2Cu[N(CN)_2]Cl$ salt.

Although resistive measurements are important in the characterization of the superconducting transition, inductive measurements involving the detection of the diamagnetic properties of a superconductor are essential in the establishment of the existence of bulk (volume) superconductivity (an ideal superconductor is a perfect diamagnet with volume magnetic susceptibility of $-1/4\pi$). Numerous inductive studies have confirmed that the organic superconductors are indeed bulk superconductors (Fig. 4). Moreover, heat capacity measurements near T_c designed to study the heat capacity anomaly expected for a second-order phase transition from the normal to the superconducting state have confirmed the bulk nature of the superconductivity (*67, 68*).

Many different studies of organic superconductors based on ET and other organic donor molecules have established that these materials are superconducting in the conventional sense of exhibiting both zero resistance and magnetic flux expulsion (Meissner effect). However, the question of the mechanism of superconductivity in these materials remains open. The mechanism of conventional superconductors is that of the Bardeen, Cooper, and Schrieffer (BCS) theory (*69, 70*), in which the superconducting electrons are paired in zero net momentum and spin states (Cooper pairs) by weak interactions (weak-coupling superconductors) of the conduction electrons with the lattice modes (that is, phonons). Recent heat capacity studies (*67, 68*) have indicated that if electron-phonon coupling is involved in organic superconductors, it is a rather strong coupling for the compounds with the higher T_c values.

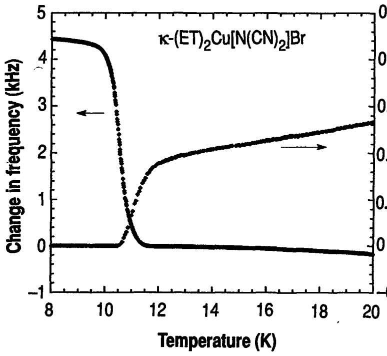


Fig. 4. The superconducting transition of κ-$(ET)_2Cu[N(CN)_2]Br$ at ambient pressure and zero applied field as determined by radio-frequency penetration depth measurements (left axis) and resistivity measurements (right axis).

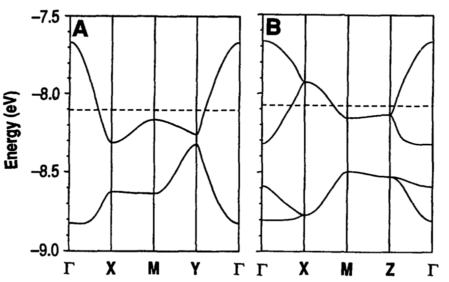


Fig. 5. Dispersion relations of (**A**) the highest two occupied bands of β-$(ET)_2I_3$ and (**B**) the highest four occupied bands of κ-$(ET)_2Cu[N(CN)_2]Br$.

Band Electronic Structures

Because of their large and structurally complex crystallographic unit cells, the band electronic structures of organic synthetic metals and superconductors have largely been examined by the extended Hückel tight-binding (EHTB) method (*71, 72*) or its simplified version (*73*). EHTB calculations show that the metallic properties of $(ET)_2X$ salts arise from partially filled bands that are essentially composed of the highest occupied molecular orbitals (HOMOs) (*30, 74*) of the donor molecule. These conclusions are supported by first-principles self-consistent field band calculations that make use of adequate nonspherical potentials, which are crucial in describing low-symmetry, covalently bonded systems such as those constituting the organic salts.

EHTB band calculations reveal that the electronic structures of the β-phase superconductors are similar (*72, 75*), as are those of the κ-phase superconductors (*75–78*). Figure 5 shows the dispersion relations of the bands calculated (*75*) for β-$(ET)_2I_3$ (A) and κ-$(ET)_2Cu[N(CN)_2]Br$ (B). The dashed lines refer to the Fermi level, e_f, appropriate for the formal oxidation state $(ET)_2{}^+$. Table 2 lists the electronic densities of states, $n(e_f)$, calculated at the Fermi level for a number of β- and κ-phase salts (*75–78*). The $n(e_f)$ values are similar within the β-phases and within the κ-phases. Each κ-phase has two partially filled bands, but each β-phase has one partially filled band. Nevertheless, the overall width of the partially filled band or bands is nearly the same in the β- and κ-phases. Thus, the $n(e_f)$ values of the κ-phases are about twice those of the β-phases.

The Fermi surfaces associated with the partially filled bands of β-$(ET)_2I_3$ and κ-$(ET)_2Cu[N(CN)_2]Br$ (*75*) are shown in Fig. 6. These Fermi surfaces consists of closed loops, so that all β- and κ-phases are predicted to be 2-D metals. This prediction is consistent with available experimental results, except that the κ-phase salts κ-$(ET)_2Cu(NCS)_2$ and κ-$(ET)_2Cu[N(CN)_2]Br$ exhibit a resistivity maximum in their resistivity versus temperature plots. The origin of this resistivity maximum is not understood yet, although several explanations have been proposed (*65, 79–81*).

Crystallographic Disorder and Its Effects on Organic Superconductors

A feature of the ET materials that sets them apart from inorganic superconductors is the occurrence of different conformations of the organic molecules and the relation of these conformations to lattice softness, disorder, and therefore T_c. β-$(ET)_2I_3$ illustrates these effects best because it has three distinct structural phases (β-, β_L, and β^*) (see above). At ambient pressure and room temperature one of the two ethylene groups of the ET molecule exhibits random disorder such that the terminal ethylene groups, when viewed along

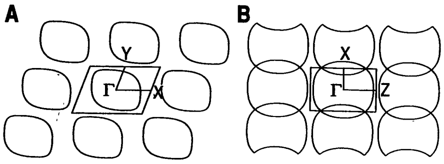


Fig. 6. Fermi surfaces calculated for (**A**) β-$(ET)_2I_3$ and (**B**) κ-$(ET)_2Cu[N(CN)_2]Br$.

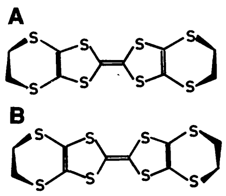


Fig. 7. Schematic views of two possible ethylene group arrangements of ET: (**A**) eclipsed and (**B**) staggered, where the C–S and C–C bonds of the ethylenedithio units are represented by wedges to distinguish the C atoms lying above and below the molecular π-framework.

the central C═C double bond, are either eclipsed or staggered (Fig. 7) (*47*). Among all the other β-$(ET)_2X$ salts, where $X^- = IBr_2^-$, I_2Br^-, and AuI_2^-, the ET molecules adopt an ordered eclipsed conformation. A second structural phase, designated β_L for low T_c, occurs upon cooling β-$(ET)_2I_3$ below 175 K; below this temperature incommensurate satellite reflections appear in the x-ray and neutron diffraction patterns (*48*). We have shown that these reflections are due to (i) displacive modulations of the positions of the I_3^- anions and the ET molecules as rigid groups and (ii) modulation of the above-mentioned conformational disorder (*49, 82*). Upon further cooling β_L-$(ET)_2I_3$ becomes superconducting at 1.4 K. T_c decreases with applied pressures of ~0.5 to 1 kbar, at which point T_c jumps from ~1 K to ~8 K (*43, 50*). We examined the neutron diffraction structure of β-$(ET)_2I_3$ under a range of applied pressures and found no satellite reflections above 0.5 kbar (*51*). This third structural phase of β-$(ET)_2I_3$, designated β^* (or β_H for high T_c), which has been fully characterized by neutron diffraction at 4.5 K and 1.5 kbar (*52*) and x-ray diffraction at room temperature and 9 kbar (*53*), is completely ordered with the ET molecule in the staggered ethylene group conformation. Thus, a completely ordered structure is accompanied by a higher T_c.

These observations and others demonstrate the effect of disorder on T_c. In the case of $(TMTSF)_2ClO_4$ at room temperature, the perchlorate anion is located on a crystallographic inversion center that imposes crystallographic disorder (*83*). When one cools this compound at a slow rate, the anions are allowed to order; this ordering causes the appearance of x-ray (*84*) and neutron (*85*) superlattice reflections and a superconducting transition at ~1 K (*83*). However, rapid cooling freezes in the disorder and leads to a low-temperature metal-insulator transition (*86*). Among the β-$(ET)_2X$ salts, where X^- = centrosymmetric I_3^-, IBr_2^-, AuI_2^-, or noncentrosymmetric I_2Br^-, the anions are also located on crystallographic inversion centers. Among these, only β-$(ET)_2I_2Br$ is not a superconductor, which is due to the crystallographic twofold disorder imposed by symmetry on the noncentrosymmetric I–I–Br⁻ anion (*87, 88*). Within the new isostructural series κ-$(ET)_2Cu[N(CN)_2]X$, $X^- = Cl^-, Br^-$, or I^-, only the I^- analog is not a superconductor, again because of static conformational disorder of one ethylene group on the ET molecule (*78*). Thus, it appears that random crystallographic disorder introduces random potentials that disrupt the formation of Cooper pairs and suppress superconductivity in organic conducting systems.

Table 2. Density of states, $n(e_f)$, values calculated for the β- and κ-phase salts of ET.

Salt	$n(e_f)$ [e^-/(eV unit cell)]
β-$(ET)_2IBr_2$	3.69
β-$(ET)_2AuI_2$	3.48
β^*-$(ET)_2I_3$	3.53
β-$(ET)_2I_3$	3.66
κ-$(ET)_2Cu(NCS)_2$	7.39
κ-$(ET)_2Cu[N(CN)_2]Cl$	7.26
κ-$(ET)_2Cu[N(CN)_2]Br$	7.27
κ-$(ET)_2Cu[N(CN)_2]I$	7.79

Returning to β-$(ET)_2I_3$, we find the normal ordered β-type structure in the β_L-phase is modulated and T_c (1.4 K) is suppressed. Thus, it appears that the intermediate level of ordering due to the incommensurate modulation only partially suppresses T_c in β_L-$(ET)_2I_3$, but, because the modulation does have long-range periodicity and is not a completely random disorder, superconductivity can occur. If one removes the modulation by applying stress, the ordered β^*- or β_H-phase with $T_c \cong 8$ K results.

Lattice Softness and Superconductivity

Within the BCS theory (*69, 70, 89, 90*) of superconductivity, T_c is related to the Debye temperature θ and the electron-phonon coupling constant λ as follows:

$$T_c \cong \theta \exp\left(-\frac{1+\lambda}{\lambda-\mu^*}\right) \qquad (1)$$

where μ^*, a Coulomb pseudopotential, is a small correction term of the order of 0.1. In a "weak coupling" BCS limit, Eq. 1 is simplified as $T_c \propto \theta \exp(-1/\lambda)$, which shows that the T_c increases with λ. For a lattice of atoms with mass M possessing a phonon spectrum effective for electron-phonon coupling, λ is expressed as (*89*).

$$\lambda = \frac{n(e_f)\,\langle I^2\rangle}{M\langle\omega^2\rangle} \qquad (2)$$

where $\langle\omega^2\rangle$ is the square of the phonon frequencies averaged over the phonon band and $\langle I^2\rangle$ is an electron-phonon matrix element averaged over the Fermi surface. For an isostructural family of superconductors, the $n(e_f)$ values are nearly the same (Table 2), and the $n(e_f)\langle I^2\rangle$ terms are expected to be similar (*91*). Therefore, the difference in their λ values, and hence their T_c values, is largely governed by the $M\langle\omega^2\rangle$ term. The latter has the dimension of a force constant, so a large λ value, and therefore a large T_c, results when the lattice has soft phonons (*75, 91, 92*). The phonon frequencies crucial for superconductivity are of the order of $\sim 8k_BT_c$ (*93, 94*), where k_B is the Boltzmann constant. Such low-frequency phonons are associated with the translational and librational modes of vibrations. For organic salts, the phonons are intermolecular vibrations and therefore are strongly influenced by short intermolecular C–H···donor and C–H···anion contacts. In general, softer intermolecular phonons are expected when the C–H···donor and C–H···anion contacts lengthen and the interactions weaken (*75, 91, 92*).

Lattice Softness Versus T_c in β-$(ET)_2X$ ($X^- = I_3^-, AuI_2^-, IBr_2^-$)

The variation in the T_c values of β-$(ET)_2X$ ($X^- = I_3^-, AuI_2^-, IBr_2^-$) as a function of applied pressure P (*44, 95*) is shown in Fig. 8. For β-$(ET)_2X$ ($X^- = AuI_2^-, IBr_2^-$) the T_c decreases with increasing P. For $P < 0.5$ kbar, the T_c of β-$(ET)_2I_3$ decreases as well with increasing P. As described above, at $P \cong 0.5$ kbar, the T_c of β-$(ET)_2I_3$ jumps to ~8K [β^*-$(ET)_2I_3$] and then decreases as P increases further. The electronic structures of the β-$(ET)_2X$ ($X^- =$

I_3^-, AuI_2^-, IBr_2^-) salts are similar. Consequently, the pressure- and anion-dependence of the T_c in β-$(ET)_2X$ materials originate not from their electronic structures but from factors related to their crystal lattice softness (*91, 92*). As shown in Fig. 9, each anion of β-$(ET)_2X$ ($X^- = I_3^-$, AuI_2^-, IBr_2^-) is enclosed in a CH_2 group H pocket made up of 12 ET donor molecules, in which each terminal halogen atom of X^- is surrounded by a total of six ethylene groups. This packing of the donor molecules around the anions gives rise to intermolecular C–H···donor and C–H···anion contacts that are shorter than would be expected from the sums of the van der Waals radii. The shortest C–H···H and C–H···anion (at the terminal halogen) contact distances found for β-$(ET)_2X$ ($X^- = I_3^-$, AuI_2^-, IBr_2^-) (*91, 92*) are listed in Table 3. These C–H···H and C–H···anion distances increase in the following order: β-$(ET)_2IBr_2$ < β-$(ET)_2AuI_2$ < β*-$(ET)_2I_3$. Thus the lattice softness increases in the same order, which is consistent with the increase in T_c. At ambient pressure, β-$(ET)_2I_3$ has unfavorably short C–H···H and C–H···I contacts. The structural modulation of β-$(ET)_2I_3$ discussed earlier, which occurs below 175 K (*49, 51*), reflects the presence of structural strain (*82*) that leads to a small λ and hence a low T_c. Adoption of an ordered staggered ethylene group arrangement by the ET molecules (for $P > 0.5$ kbar) makes the lattice of β*-$(ET)_2I_3$ particularly soft because in this arrangement the C–H···H and C–H···anion contacts are slightly longer (weaker) than those in β-$(ET)_2I_3$ (*52, 91*). A further increase in P beyond 0.5 kbar in β*-$(ET)_2I_3$ makes the lattice stiffer and again lowers T_c, as in the case of β-$(ET)_2X$ ($X^- = AuI_2^-$, IBr_2^-).

Table 3. Shortest C–H···H and C–H···anion contact (with the terminal halogen atom) distances in β-$(ET)_2X$ salts. The symbols E and S refer to the eclipsed and staggered arrangements of the ethylene groups, respectively.

Salt	C–H···H (Å)	C–H···anion (Å)
β-$(ET)_2IBr_2$	2.17	2.89
β-$(ET)_2AuI_2$	2.22	2.97
β*-$(ET)_2I_3$	2.26	3.01
β-$(ET)_2I_3$	2.15(S)	2.84(E)

Lattice Softness Versus T_c in the κ-$(ET)_2Cu[N(CN)_2]X$ ($X^- = Cl^-, Br^-, I^-$) Salts

The newly discovered, highest T_c κ-phase salts κ-$(ET)_2Cu[N(CN)_2]X$ ($X^- = Cl^-, Br^-$) are isostructural and are only the second such series to be discovered. They differ in their superconducting properties; the Br^- salt is an ambient-pressure superconductor with T_c = 11.6 K (*56*), and the Cl^- salt becomes a superconductor under a slight applied pressure of 0.3 kbar (T_c = 12.8 K) (*57*). The I^- salt is not a superconductor (*66*) even under pressures up to ~5 kbar. The crystal structures of κ-$(ET)_2Cu[N(CN)_2]X$ ($X^- = Cl^-, Br^-, I^-$) determined at ~127 K reveal (*66, 78*) that the ethylene groups of the ET donor molecules are ordered and have an eclipsed arrangement in the Cl^- and Br^- salts. In the I^- salt, however, one ethylene group of the ET molecule is crystallographically disordered into a statistical distribution of eclipsed and staggered arrangements with a 2:1 ratio (*66, 78*). The short C–H···donor and C–H···anion contacts found for the 127 K structures of κ-$(ET)_2Cu[N(CN)_2]X$ ($X^- = Cl^-, Br^-, I^-$) are listed in Table 4. The short C–H···anion contacts are primarily associated with the dicyanamide, $[N(CN)_2]^-$, anions of the polymeric anion chains. The short intermolecular contacts of κ-$(ET)_2Cu[N(CN)_2]X$ ($X^- = Cl^-, Br^-$) are similar except that the C–H···H contacts are more strained (shorter) in the Cl^- salt than in the Br^- salt. An applied pressure of ~0.3 kbar (required to induce superconductivity) in κ-$(ET)_2Cu[N(CN)_2]Cl$ might induce a slight twisting or slipping of the donor molecules, thereby reducing the unfavorable C–H···H strain and possibly even making the lattice softer than the lattice of κ-$(ET)_2Cu[N(CN)_2]Br$; this reasoning would explain the higher T_c of the Cl^- salt in comparison to the Br^- analog.

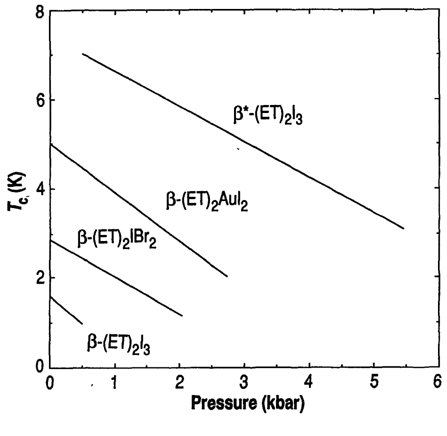


Fig. 8. Pressure dependence of the T_c of β-$(ET)_2X$ ($X = I_3^-$, AuI_2^-, IBr_2^-).

In κ-$(ET)_2Cu[N(CN)_2]I$, both the staggered and the eclipsed arrangements of the ethylene groups cause strongly strained intermolecular contacts (Table 4). The extent of this strain might be reduced if disorder were introduced in the ethylene group arrangements. An immediate consequence of such disorder is the resulting random potential, which also prevents superconductivity (see above) in the cases of $(TMTSF)_2ClO_4$ and β-$(ET)_2I_2Br$.

Isotope Effect on T_c

When the H atoms of the ET molecule are replaced with deuterium (D) atoms, the resulting ET-d_8 molecule has a higher mass. According to the preexponential term θ of Eq. 1, the isotope substitution of D for H should lower the T_c, because the smaller vibrational frequencies associated with the isotope substitution should decrease the Debye temperature θ. Thus, the D for H substitution should lower the T_c if λ is unaffected by the substitution. However, this assumption is not necessarily valid (*75*). The C–D bond has a smaller stretching frequency than does the C–H bond, so that during the stretching vibration the D-atom displacement from the equilibrium position is smaller than that expected for the H-atom displacement. Therefore, the C–D bond is effectively shorter than the C–H bond as far as the C–H(D)···donor and C–H(D)···anion contact interactions are concerned (*75*). Conse-

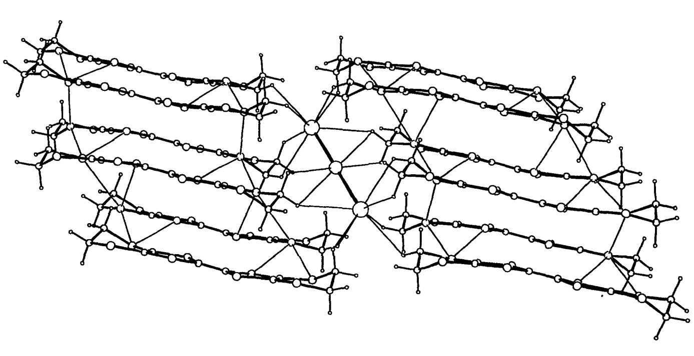


Fig. 9. Perspective view of a single AuI_2^- anion surrounded by CH_2 groups in the H pocket made up of 12 ET molecules in β-$(ET)_2AuI_2$.

quently, the D for H substitution may provide a softer lattice and lead to a larger λ value, thereby increasing the T_c according to the exponential term of Eq. 1. Thus, an isotope substitution such as D for H should decrease the T_c according to the preexponential term θ but may increase the T_c according to the exponential term $\exp[-(1+\lambda)/(\lambda-\mu^*)]$ (*75*). It appears likely that when the latter dominates, the isotope substitution of D for H increases T_c [from 10.4 to 10.8 K for κ-$(ET)_2Cu(NCS)_2$]. The interplay of these terms may explain why the T_c of deuterated κ-$(ET)_2Cu[N(CN)_2]Br$ is smaller than that of the hydrogen form, whereas the T_c of deuterated κ-$(ET)_2Cu[N(CN)_2]Cl$ is greater than that of the H form (*66*).

Similarities Between Organic and Inorganic Cuprate Superconductors

It is, perhaps, crucial to the eventual understanding of the mechanism of organic superconductivity to consider the similarities between the organic superconductors and the ceramic copper oxide high-T_c superconductors such as $YBa_2Cu_3O_{7-\delta}$. Both have layered crystal structures and exhibit a competition between insulating and superconducting ground states. Furthermore, both have very large upper critical magnetic fields, H_{c2}, which are the magnetic fields at which the superconductor is restored to its normal metallic state. These magnetic fields are highly anisotropic (*96*, *97*), and the anisotropy is similar to that of the normal state conductivities. In addition, both materials have small and anisotropic superconducting coherence lengths, ξ, which are measures of the spatial extent of the superconducting electron pairs in a spatially varying magnetic field (*98*). We have recently shown for κ-$(ET)_2Cu[N(CN)_2]Br$ that for superconductivity within the plane for the ET donor layers $\xi_\parallel \approx 37$ Å and for superconductivity perpendicular to the plane $\xi_\perp \approx 4$ Å (*97*). The latter quantity is remarkable because it is much smaller than the distance (~15 Å) between the organic conducting layers, which suggests that superconductivity in the direction perpendicular to the plane of the donor layers may involve Josephson tunneling of superconducting electrons between layers of the organic donor molecules. The fact that the unoccupied bands of the insulating anion layers lie close to the Fermi level might facilitate electron tunneling, and hence electrical conduction, along the direction perpendicular to the donor molecule layers (*74*, *75*). Similarly, in the high-T_c copper oxide superconductors, the CuO_2 layers are metallic and are separated by the rock-salt layers and the layers of Ba or rare-earth cations. In most cuprate superconductors, the rock-salt and the cation layers are insulating, and their unoccupied bands lie close to the Fermi level of the CuO_2 layer $d_{x^2-y^2}$ bands (*99*). One of the many highly motivating questions of organic superconductor research today is whether the electron pairing mechanism that causes superconductivity is the same as that of conventional metallic superconductors or that of the high T_c ceramic oxide superconductors; the mechanism may also be unique to organic materials. Now that "high-T_c" superconductivity is known to exist in the novel copper oxides there is every reason to expect it to occur in additional systems, including the organic superconductors (Fig. 10).

Table 4. Shortest C–H···donor and C–H···anion contact distances (Å) found in the 127 K structures of κ-$(ET)_2Cu[N(CN)_2]X$ ($X^- = Cl^-$, Br^-, I^-). The symbols E and S refer to the eclipsed and staggered arrangements of the ethylene groups, respectively.

Class	Contact	$X^- = Cl^-$	$X^- = Br^-$	$X^- = I^-$
C–H···donor	C–H···H	2.08	2.15	1.99(S)
	C–H···S	2.77	2.77	2.58(E)
C–H···anion	C–H···N	2.66	2.69	2.55(S)
	C–H···C	2.72	2.74	2.71

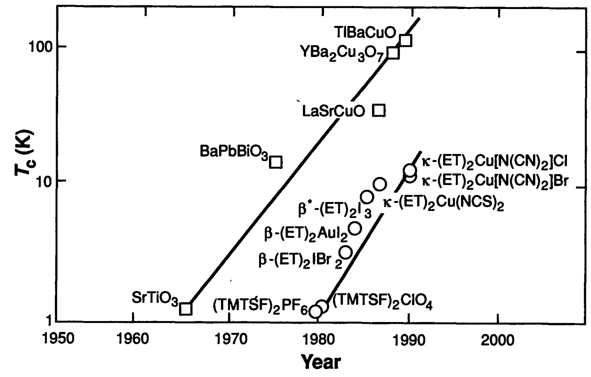


Fig. 10. A plot of T_c versus year of discovery for inorganic oxide (□) and organic superconductors (○).

Note added in proof: Superconductivity in the fullerene (C_{60}) compound, K_xC_{60}, has been reported (*99a*) (T_c = 18 K) and confirmed (*99b*) (T_c = 18.0 ± 0.1 K). The T_c for Rb_xC_{60} is 28.6 ± 0.1 K (*99c*). These new findings ("molecular superconductors") forge a link bewtween organic and inorganic superconductors and open a promising new area of superconductivity research.

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