Many highly conducting organic and organometallic "synthetic metals" have been prepared recently. Approximately 20 are bulk superconductors with superconducting transition temperatures \(T_c\) of \(10\) to \(10^2\) K. About half of the known organic superconductors require pressures (up to \(10^2\) kbar) to suppress low temperature phase transitions that may occur prior to the onset of superconductivity. The \((\text{BEDT-TTF})_2X\), \(X = \text{monovalent anion, system has yielded the largest number (\(>8\)) of ambient pressure organic superconductors. The linear anions which yield ambient pressure \((\text{BEDT-TTF})_2X\) superconductors are \(X = I_3^-, IBr^-,\) and \(AuI_2^-\) and the \(T_c\)'s range from \(1.5\) K \((I_3^-)\) to \(2.8\) K \((IBr^-)\) to \(5\) K \((AuI_2^-)\), respectively. The \(I_3^-\) system is novel because at pressures \(\approx 10^2\) kbar the \(T_c\) is increased to \(\approx 8\) K. The unusual electrical properties exhibited by \((\text{BEDT-TTF})_2I_3\) conductors are due to a two-dimensional network of \(S\cdots S\) interactions existing in the solid phases and which arise from novel stacking patterns associated with the \((\text{BEDT-TTF})_2X\) electron-donor molecules. In these materials the anions reside in \(H\)-atom cavities created by the \(-CH_2\) groups of the \((\text{BEDT-TTF})_2\) molecules. Thus, by varying the length of the anion it is possible to systematically vary the intra- and inter-stack \(S\cdots S\) interactions and, in turn, the \(T_c\)'s. The \((\text{BEDT-TTF})_2X\) systems are very sensitive to anion disorder which appears to inhibit the onset of superconductivity.

When tetrathiofulvalene, TTF, is the electron donor molecule and \(Ni(dmft)_2\) the anion, the first known organometallic superconductor \((\text{BEDT-TTF})_2Ni(dmft)_2\) is formed with \(T_c = 6.25\) K at \(p = 7\) kbar.

Recently derived structure-property relationships for the \((\text{BEDT-TTF})_2X\) and \((\text{BEDT-TTF})_2Ni(dmft)_2\) systems will be discussed.

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\text{BEDT-TTF}
\]

\[
\text{Ni(dmft)}_2^n
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07.X.5 CRYSTAL AND ELECTRONIC STRUCTURES OF ORGANIC SUPERCONDUCTORS BASED ON MULTI-SULFUR-MOLECULES. By Kayao Kobayashi, Department of Chemistry, Faculty of Science, Toho University, Funabashi, Chiba 274, Japan.

Most of the organic conductors are regarded to be one-dimensional (1D) systems, which are not suitable for designing new molecular superconductors because of their strong CDW instabilities. We have synthesized various molecular conductors having multi-dimensional intermolecular interactions. The present paper is to describe the molecular designs of some molecular superconductors including new superconductors, \(\alpha\) - and \(\kappa\) -ET_2I_3.

Black crystals of \(\alpha\) - and \(\kappa\) -ET_2I_3 were prepared electrochemically from the tetrahydrofuran solution using mixed electrolyte of \((n-But)_4NI_3\) and \((n-But)_4NHClO_4\). X-ray diffraction patterns of \(\alpha\)-type salt can be classified into two types (type-I and type-II). The molecular arrangement of ET and the "averaged position" of the \(I_3^-\) anions could be easily obtained by examining the type-I reflections. The type-II reflections indicate that the crystal is composed of the domains where the \(I_3^-\) arrangement is ordered. Superconducting (SC) transition temperature \((T_c)\) is 3.6 K. Magnetic field effect on the resistivity showed the strong 2D nature, which is confirmed by the tight-binding band calculation. The SC state of \(\alpha\)-ET_2I_3 seems to be very sensitive to the crystal imperfection. The brittleness of the crystal and the unique domain structure may be responsible for the variety of the SC behaviors (3D, partial 2D, no SC).

Crystal of \(\kappa\)-ET_2I_3 belongs to monoclinic system. \(\alpha\) is 3-4 K. Similar to \(\alpha\)-type salt, \(\kappa\)-type salt can be regarded as a layered metal. Electronic band structure calculation gave 2D round Fermi surface.

07.X.6 STRUCTURAL PHASE TRANSITIONS IN ORGANIC SUPERCONDUCTORS. By R. Moret, R. Savy and J.-P. Fouret, Laboratoire de Physique des Solides, Université Paris Sud, Orsay, France.

The study of the structural properties of organic conductors and superconductors has always played a key role in the progress towards a better understanding of these materials. This is mainly due to the remarkable interplay of transport and structural properties which is observed. For instance when the temperature is reduced, structural phase transitions of various types occur in most of these compounds leading either to a nonconducting state or to a conducting and possibly superconducting state at low temperature.

There is a significant evolution in the nature of the phase transitions which have been studied over 15 years of interest for the organic conductors. This evolution is related to a change in the dimensionality of the corresponding compounds, going from quasi-1D in the seventies with TTF-TCNQ and its family to quasi-2D at present with some \((\text{BEDT-TTF})_2\) salts.

In the case of \(\text{TTF-TCNQ}\) and related compounds the Peierls instability and the formation of charge density waves govern the structural behaviour and they reflect the quasi-1D character of the lattice. In the more recent charge transfer salts of the type \((\text{TMTSF})_2X\) the Peierls instability does not prevail because the 1D character is weaker. In place, we observe structural phase transitions which involve an orientational ordering of the anions \(X\), in the case of non-centrosymmetric ones. With the \((\text{BEDT-TTF})_2X\) family (and \(\alpha\) \((\text{BEDT-TTF})_2I_3\) where \(T_c\) reaches \(8.1\) K) the 2D character is even stronger and new structural effects compete with superconductivity (such as commensurate, in \((\text{BEDT-TTF})_2\)BeO_4, or incommensurate, in \(\alpha\) \((\text{BEDT-TTF})_2I_3\), modulations).

These properties will be reviewed with emphasis on new results.