

Figure 2. Structure of TMTSF (tetramethyltetraselenafulvalene)

Bechgaard Salts: Quasi One Dimensional Superconductors

The first organic superconductors consisted of planar TMTSF donors (**3**) (Figure 2) and monovalent anion acceptors with the general formula $(\text{TMTSF})_2\text{X}$, where X is either an octahedral or tetrahedral anion such as PF_6^- , AsF_6^- , SbPF_6^- , TaF_6^- , NbF_6^- , ClO_4^- , or ReO_4^- . These charge transfer salts, also known as the Bechgaard salts, consist of segregated, stacked sheets of donors and acceptors. Several of these complexes require an applied pressure (5-12 kbar) to suppress a metal to insulator transition.^{2a} When the octahedral anions were replaced by a tetrahedral anion, perchlorate, superconductivity was observed at ambient pressure.^{2c} Researchers proposed that the use of the smaller tetrahedral anion could mimic the effect of pressure through closer packing of the solid. Critical temperatures of 1-2 K have been reported for the Bechgaard salts.² The critical temperature of a material (T_c) is the temperature below which a substance becomes superconducting.

The electrical conductivity in the Bechgaard salts is highly anisotropic and occurs primarily along the stacking axis of the donor molecules. The spacing between the molecules within a stack is smaller than the sum of the van der Waals radii of the Se atoms. The conductivity perpendicular to the stacking axis is several orders of magnitude lower. The orbital overlap of the π -orbitals is not as good within each layer, which leads to the anisotropic conductivity (Figure 3).

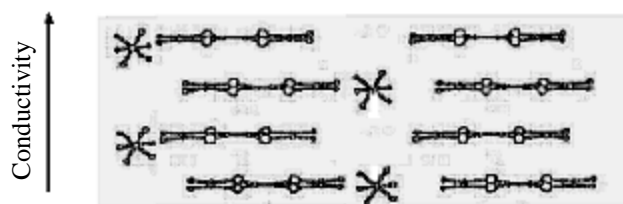
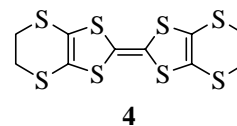


Figure 3. Structure of quasi one dimensional superconductor, $(\text{TMTSF})_2\text{PF}_6$

Quasi Two Dimensional Systems

Further research led to the identification of a new class of organic superconductors. A new donor, BEDT-TTF (**4**) [bis(ethylenedithio)tetrathiafulvalene], was synthesized which contains eight sulfur atoms whereas the TMTSF donor only contains four selenium atoms per donor (Figure 4).

Four of the sulfur atoms are located at the peripheries of the donor, which allow for better orbital overlap between stacks of donors compared to within the stacks



(Figure 5). The donor molecule, ET, is nonplanar due to the ethylene groups, which prevent good overlap along the stacking axis.

Figure 4. Structure of BEDT-TTF (ET)



Figure 5. (a) Donor stack interactions in a quasi 1D superconductors (b) Donor stack interactions in a quasi 2D superconductor

Within the family of the quasi two-dimensional superconductors, the compositions are remarkably different. Several different structural phases are possible including the β -phase with a honeycomb-like appearance and the κ -phase, which consists of twisted dimers of donors. Dozens of superconducting charge transfer complexes containing the BEDT-TTF donor have been uncovered. Linear, tetrahedral, and polymeric anions have all been used as acceptors in these salts. In a comparison of linear anions, only centrosymmetric anions would produce superconductivity. Complexes such as β -(BEDT-TTF)₂X where X is I₃⁻, Br-I-Br⁻, and I-Au-I have all shown superconductivity with critical temperatures of 1.5, 2.7, and 4.9 K, respectively. When X is I-I-Br⁻, superconductivity is not detected, possibly due to a more disordered system.¹³ Disorder within charge transfer salts appears to suppress superconductivity. Critical temperatures of the ET salts increase with increasing anion length. This trend has been attributed to a higher density of states caused by less interaction between the donor molecules. The highest critical temperatures for the two dimensional charge

transfer salts have been obtained with polymeric anions such as κ -(ET)₂Cu(NCS)₂ ($T_c = 10.4$ K),^{3c-d} κ -(ET)₂Cu[N(CN)₂]Br ($T_c = 11.6$ K),^{3e} and κ -(ET)₂Cu[N(CN)₂]Cl ($T_c = 12.8$ K at 0.3 kbar).^{3f}

Other donors have been synthesized including oxygen-containing donors such as BEDO-TTF (**5**) [(bisethylenedioxy)tetrathiafulvalene]¹⁴ and unsymmetrical donors like DODHT (**6**) [(1,4-dioxane-2,3-diylidithio)dihydro-tetrathiafulvalene] (Figure 6).¹⁵ Although lighter atoms (compared to selenium or sulfur) were predicted to yield higher T_c superconductors, none of the oxygen containing donors have yielded high critical temperatures. Unfortunately, no further advancements have been made in the search for a higher critical temperature for quasi two dimensional organic superconductors.

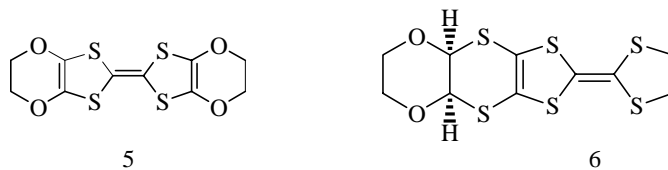


Figure 6. Structure of BEDO-TTF (**5**) and DODHT (**6**)

Fullerenes and Nanotubes

Although C₆₀ is an insulator with a band gap of 1.7 eV, doping of this three dimensional system with alkali metals produces superconductivity with critical temperatures up to 40 K. The general formula for these superconductors is A₃C₆₀ where A is an alkali metal.⁴ Superconductivity has also been observed in single-walled nanotubes with critical temperatures up to 15 K.⁷

The scientists at Bell Laboratories have performed promising research with the use of a field-effect-transistor to yield extremely high critical temperatures in fullerenes.⁵ The field-effect-devices provide both n (electron doped) and p (hole doped) channel activity by injecting charge (or holes) into a fullerene crystal. Higher critical temperatures have been observed for hole doped C₆₀ due to the higher density of states in the conduction band (five-fold degenerate HOMO versus three-fold degenerate LUMO in C₆₀). Intercalation of CHBr₃ into hole doped C₆₀ has led to the highest critical temperature reported for an organic superconductor ($T_c = 117$ K).^{5c}

Field-Effect-Devices

Field-effect transistors have also been used to detect superconductivity in other systems such as acenes. Anthracene, tetracene, and pentacene have all shown superconductivity with critical temperatures between 2 and 4 K. The critical temperature increases with decreasing number of π electrons. This trend has been predicted by computations, which show that the critical temperature increases with decreasing number of π electrons.⁸ The trend has also been observed in fullerene cages (C_{60} versus C_{70}).⁶

Exciting advances have been made in the world of organic superconductors through the recent discovery of superconductivity in polythiophene⁹ and oligomers of poly-phenylenevinylene¹⁰ with the use of a field-effect-device to introduce charge. Although only modest critical temperatures have been found in these systems ($T_c = 2-4$ K), the future of this field looks extremely promising for the identification of other plastics with superconducting properties.

Conclusion

The highest critical temperature obtained for an organic superconductor is 117 K which was found for hole doped C_{60} intercalated with $CHBr_3$. This value is not far from the highest critical temperature ever reported (138 K, $Hg_{0.8}Tl_{0.2}Ba_2Cu_3O_{8.33}$).¹⁶ The search for higher critical temperatures in organic superconductors and additional types of superconducting plastics appears promising.

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