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Structure-Property Correlations in the Design of Organic Metals and Superconductors: An Overview

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Abstract. Molecular structure and, more importantly, molecular packing in organic superconducting salts $(TMTSF)_2X$, β-$(BEDT\text{-}TTF)_2X$ and κ-$(BEDT\text{-}TTF)_2X$ will be examined in the context of deducing structure-property correlations in these systems. Such an approach has been instrumental in the discovery of superconductivity at 10.4 K in κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$, and it will continue to serve as an important tool in the rational design of new organic superconductors with even higher superconducting transition temperatures.

1. Introduction

Since the first discovery of superconductivity in 1979 in a cation-radical salt of the organic donor TMTSF, four other molecular systems — BEDT-TTF, $Ni(dmit)_2$, DMET and MDT-TTF — have now yielded superconducting solids. While there are about 30 superconductors known to date derived from these organic/metalloorganic precursors, BEDT-TTF has yielded the largest number (at least 10) of ambient pressure superconductors as well as the one with the highest transition temperature [T_c = 10.4 K in κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$]. This rapid progress in less than a decade is remarkable and it clearly raises the level of optimism for the discovery of "high-T_c" organic superconductors, particularly in view of the recent explosive progress made in the area of oxide superconductors.

2.1 Molecular and Structural Design

The organic conducting and superconducting solids are comprised of "molecular building blocks", and their electronic bands are constructed from the overlap of molecular orbitals. Thus, a full understanding and control of the solid state properties rests primarily upon our ability to judiciously vary and control such parameters as molecular structure and molecular packing of these "building blocks" in the solid state. While the molecular design strategies for the preparation of electrically conducting solids are relatively well-understood [1], the structural design — our ability to induce molecules to pack in a desired and favorable (to achieve high conductivities and superconductivity) fashion — is still in its infancy. The preparation of a series of isostructural solids and the correlation of their properties with various identifiable molecular and structural parameters, then becomes a crucial structural design strategy, from which we can gain important insights as an aid to the development of new materials. We present here an overview of such efforts, successful especially in the β-$(BEDT\text{-}TTF)_2X$ series [2], which led to the discovery of the 10.4 K superconductor, κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$, with a distinctly different, nonstacking packing arrangement (the so-called κ-phase) of BEDT-TTF molecules. It is to be noted that no structure-property correlations yet exist for κ-phase salts. In the absence of such, we discuss some key molecular and structural parameters in known κ-phase salts and their relationship to the observed solid state properties. This analysis, we hope, will serve as a prelude to the development useful structure-property correlations in the κ-phase superconductors.

2.2 $(TMTSF)_2X$ and β-$(BEDT\text{-}TTF)_2X$ Series

In the $(TMTSF)_2X$ series of isostructural salts, the size of the anion dictates the packing density of TMTSF molecules. Thus, the inter- and intra-stack selenium-selenium network distances (critical parameters related to bandwidths and Fermi surfaces) have been correlated to the anion size by Williams *et al.* [3] and Kistenmacher [4]. This correlation can qualitatively rationalize the ambient pressure superconductivity in $(TMTSF)_2ClO_4$ while all other salts with anions larger than ClO_4^- require applied pressure to become superconducting.

The cation-radical salts of BEDT-TTF, while being more complex due to the formation of multiple stoichiometries and structural phases (sometimes even within the same "apparently single" crystal [5]), for the same anion [2], are an ideal case in point to illustrate the intricate relationship between the structure (i.e., packing scheme of molecules) and the solid state properties. There are four (α, β, θ and κ) structurally unique phases known of BEDT-TTF-triiodide salts with a 2:1 stoichiometry. While the α-phase is a metal with a metal-insulator transition at 135 K, the three remaining phases are ambient pressure superconductors with $T_c = 1.5$ K (8 K, 0.5 kbar), 3.6 K and 3.6 K respectively. The different packing arrangements of BEDT-TTF molecules in these four salts are shown in Figure 1. The transfer integral (t) between two molecules is well-known to vary significantly depending upon the intermolecular separation and their relative orientation [6]. Thus, the electronic bandwidths and the shapes of the Fermi surfaces depend heavily on the packing arrangement of BEDT-TTF molecules.

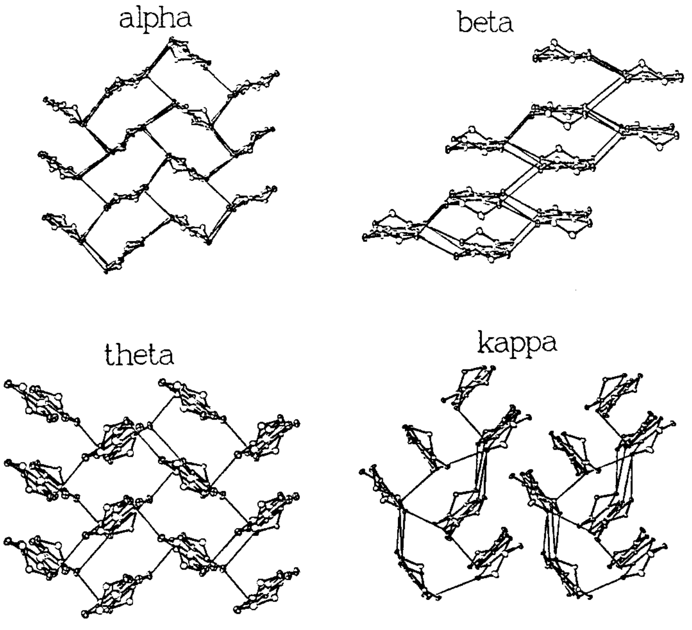

Figure 1. Packing schemes of BEDT-TTF molecules in α, β, θ and κ phases of $(BEDT\text{-}TTF)_2I_3$.

The isostructural β-(BEDT-TTF)$_2X$ superconductors, where $X^- = I_3^-$, AuI_2^-, and IBr_2^-, with T_c = 1.5 K (8 K at 0.5 kbar), 4.9 K and 2.8 K respectively, provided the first opportunity to develop meaningful structure-property correlations in organic superconductors. These correlations (Figure 2) revealed a plausible way to prepare new superconductors with higher T_c's by simply going to longer (than I_3^-) linear anions. As evident in Figure 3, if the same structure is retained, the longer anions, which reside in a cavity created by -CH_2- units, will induce the BEDT-TTF molecules to pack less densely (than when $X^- = I_3^-$). This would result in narrower bandwidths (due to reduced orbital overlaps) and higher density of states at the Fermi level, and hence a higher T_c. The negative pressure dependance (–1K/kbar) of T_c's in β-(BEDT-TTF)$_2X$ superconductors, i.e., suppression of T_c with applied pressure, also qualitatively lends support to this working hypothesis [7]. Realistically, however, there must be a limit to which this can be accomplished, since structural changes and dimensionality crossover (e.g., from 2-D to 1-D) may ensue at a certain longer anion length.

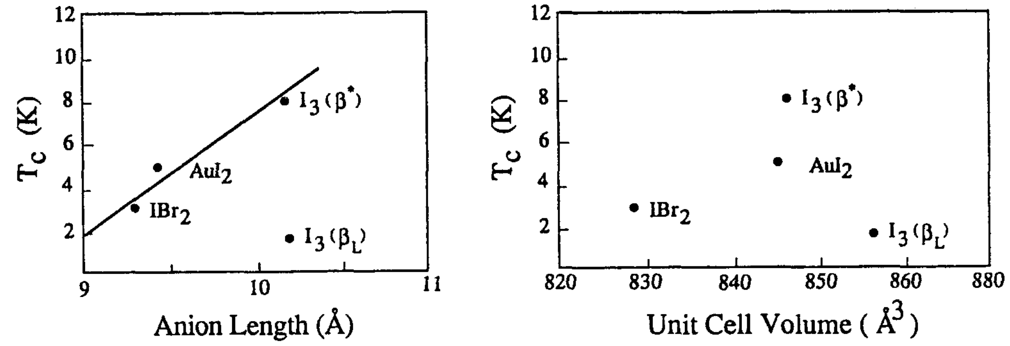

Figure 2. Plots of T_c vs. anion length (left) and T_c vs. unit cell volumes (right) in β-(BEDT-TTF)$_2$X salts, where X = I_3, AuI_2 and IBr_2.

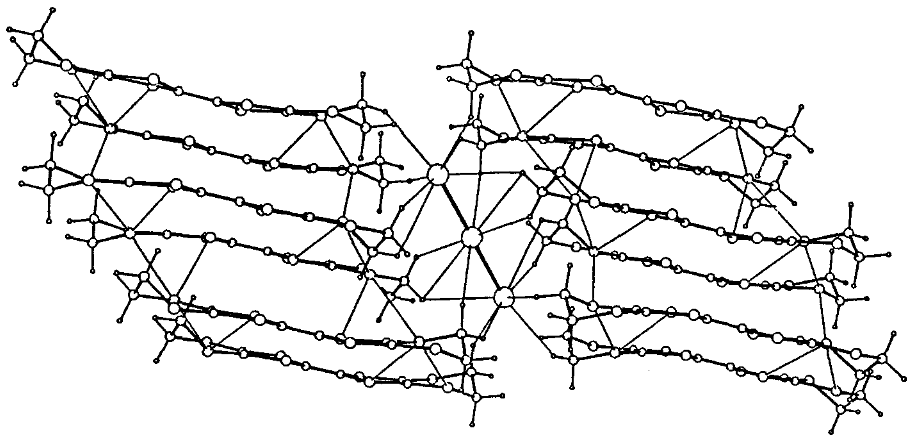

Figure 3. Structure of β-(BEDT-TTF)$_2X$ salts from the perspective of the anion.

The superconducting (T_c = 10.4 K) cation-radical salt of BEDT-TTF with $Cu(NCS)_2^-$ counterion, first prepared by Japanese scientists [8] along a similar line of reasoning (in their case, "the effective volume" of BEDT-TTF), however, was shown to consist of not β-type but κ-type packing arrangement for BEDT-TTF molecules [9,10]. This unique packing motif does not consist of interacting stacks of molecules, as in β-$(BEDT\text{-}TTF)_2X$ salts, but rather interacting dimers which are arranged nearly orthogonal to each other. This arrangement is still conducive to the formation of 2-dimensional $S\cdots S$ networks and the electronic band-structure calculations also reveal a 2-dimensional Fermi surface in this compound [10,11,12]. The 2-dimensional Fermi surface has also been recently verified experimentally by Shubnikov-de Haas oscillations observed in this salt [12,13]. Moreover, the anion in this case is not a linear, isolated species, but consists of a polymeric network involving tri-coordinated Cu(I). Thus, a new type of molecular packing arrangement has recently come to be recognized as a structure type that can also yield superconducting solids.

2.3 κ-$(BEDT\text{-}TTF)_2X$ Series

The κ-type structure, first observed in a non-superconducting but metallic salt $(BMDT\text{-}TTF)_2Au(CN)_2$ [14], has now been found in superconducting salts derived from three other donor systems — BEDT-TTF, MDT-TTF and DMET (see Table 1). There are five BEDT-TTF salts which are known to possess the κ-type structure, but no structure-property relationships, e.g., T_c vs. unit cell volume, have been elucidated yet (Figure 4). As can be seen in Table 1, κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ and κ-$(BEDT\text{-}TTF)_2I_3$ [15] are ambient pressure superconductors, while κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$ [16] requires applied pressure for superconductivity and κ-$(BEDT\text{-}TTF)_2Ag(CN)_2{\cdot}H_2O$ [17] is metallic to 150 K. Yet another salt $(BEDT\text{-}TTF)_4Hg_{2.89}Br_8$, an ambient pressure superconductor (T_c = 4.3 K), is reported to be similar to κ-$(BEDT\text{-}TTF)_4Hg_3Cl_8$, but with two incommensurate BEDT-TTF sublattices, and its full structural details are presently not available [18]. Consequently, it will not be included in the following discussion.

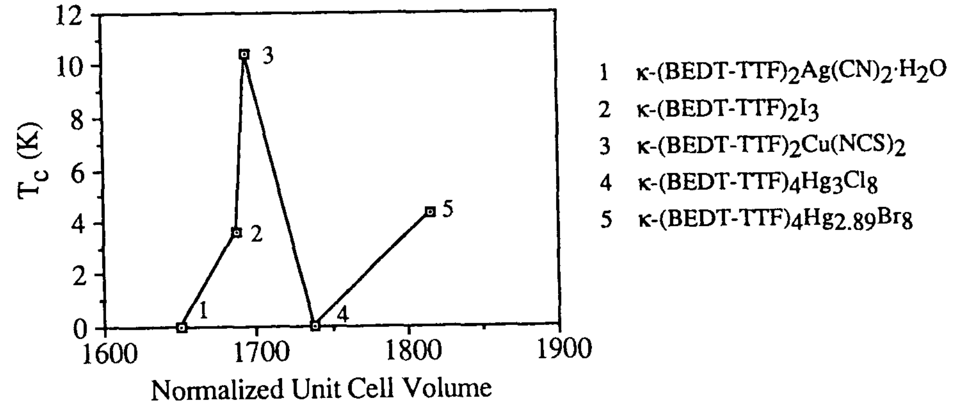

Figure 4. A plot of T_c vs. Normalized unit cell volumes of known κ-phase salts derived from BEDT-TTF.

Table 1. Intra-dimer Overlap Patterns, Intra-dimer Distances and Ethylene Endgroup Conformations in Known κ- or κ-like Salts

Compound	T_c	Overlap Pattern*	Intra-Dimer Distance, Å	Ethylene Conformation#
(BEDT-TTF)$_2$Cu(NCS)$_2$	10.4 K	B o R	3.35	S,S
(BEDT-TTF)$_2$I$_3$	3.6 K	B o R	3.35	E,E
(BEDT-TTF)$_4$Hg$_3$Cl$_8$	1.8 K (12 kbar) 5.3 K (39 kbar)	B o R	3.6	S,S
(BEDT-TTF)$_2$Ag(CN)$_2$·H$_2$O	Non S.C. (Metal to 150 K)	B o R	3.7	E,S
(BMDT-TTF)$_2$Au(CN)$_2$	Non S.C. (T_{MI} 76 K)	B o B	3.6	–
(MDT-TTF)$_2$AuI$_2$	4.5 K	B o R	3.35	–
(DMET)$_2$AuBr$_2$	1.9 K	B o R	--	–

* B o R = Bond over Ring; B o B = Bond over Bond
\# S = Staggered; E = Eclipsed

We have examined intra-dimer overlap patterns (bond-over-ring or bond-over-bond), intra-dimer distances and conformations of ethylene end groups (eclipsed or staggered) of BEDT-TTF molecules in these κ-phase materials. This analysis has shed light on the question of why some κ-phase salts are superconducting, while some are not.

In the κ-(BEDT-TTF)$_2X$ salts, the observed overlap pattern of the BEDT-TTF molecules forming the dimer is bond-over-ring type. This type of overlap is common to almost all segregated stack charge-transfer salts and is most likely due to inhomogeneous charge distributions on the radical cation and radical anion species [1,19]. The intra-dimer separations, however, show quite a variation: they are 3.35Å in both κ-(BEDT-TTF)$_2$-Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$I$_3$, and are 3.6 Å and 3.7 Å, in κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ and κ-(BEDT-TTF)$_2$Ag(CN)$_2$·H$_2$O, respectively. Since a smaller intra-dimer separation translates into a larger transfer integral and better electron delocalization, the absence of ambient pressure superconductivity in κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ and κ-(BEDT-TTF)$_2$Ag(CN)$_2$·H$_2$O can be reconciled with the larger intra-dimer distances. Furthermore, the superconducting transitions at 1.8 K and 5.3 K, under 12 kbar and 39 kbar pressure respectively, for κ-(BEDT-TTF)$_4$Hg$_3$Cl$_8$ can also be understood in terms of intra-dimer distances possibly becoming smaller under pressure. A similar reasoning would then predict κ-(BEDT-TTF)$_2$Ag(CN)$_2$·H$_2$O to also become superconducting under pressure, but this compound has been reported to undergo a destructive phase transition (crystal shattering) when cooled below 150 K [20]. Therefore, a short intra-dimer distance (3.35 Å) appears to be critical for superconductivity.

Finally, some comments on the conformations of ethylene endgroups. Both the molecules forming the dimers in κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ have ethylene groups in the staggered conformations, but they are both eclipsed in κ-(BEDT-TTF)$_2$I$_3$. The staggered conformation is the one found in the high-T_c (8 K) state of β-(BEDT-TTF)$_2$I$_3$ [21], which has been shown to result in "softer" anion–CH$_2$ contacts and hence a larger electron-phonon coupling constant (λ) than in other superconducting β-type salts with the eclipsed conformations [22]. Neutron diffraction studies on both κ-(BEDT-TTF)$_2$Cu(NCS)$_2$ and κ-(BEDT-TTF)$_2$I$_3$ are needed to probe how the two different ethylene conformations are associated with the "hardness" or "softness" of anion–CH$_2$ contacts and to the observed T_c's in these salts. Difficulty in obtaining large, good quality single crystals suitable for such studies is the major stumbling block for clarifying this important question.

2.4 Other κ-Phase Salts

Besides BEDT-TTF, three other donor systems have also yielded cation-radical salts with κ-like structures. $(BMDT\text{-}TTF)_2Au(CN)_2$, first reported by Nigrey and coworkers [14], is the only metallic salt derived from BMDT-TTF thus far, and it undergoes a metal-semiconductor transition at 76 K. Application of pressure drives the transition to lower temperatures, but no superconductivity is observed up to 9000 psi (0.6 kbar) of pressure [23]. Unlike BEDT-TTF salts, the dimer molecular pair in this salt has a rarely-observed bond-over-bond overlap pattern, and the intra-dimer separation is much larger (3.6 Å). Despite the larger separation, extended Hückel calculations reveal much larger transfer integrals in this dimer, owing to better orbital overlap attainable through the bond-over-bond overlap [11]. However, weaker dimer-dimer interactions and "hard" anion–CH_2 interactions are probably the reasons for the absence of superconductivity in this salt [11].

The ambient pressure superconductors derived from unsymmetrical donors, $(MDT\text{-}TTF)_2AuI_2$ [24,25] and $(DMET)_2AuBr_2$ [26], are quite interesting in that they have now clearly established that molecular symmetry is not essential for superconductivity. The overlap patterns in both these salts are bond-over-ring type, which is not due to the slipped packing pattern (as in BEDT-TTF salts) but rather due to the intrinsic asymmetry of the donor molecules. This may be an important consideration in the design of molecular dimers, which are the building blocks of κ-phase materials. In other words, unsymmetrical donors are possibly well-suited for the structural design of κ-phase materials. Coincidentally, the intra-dimer separation in $(MDT\text{-}TTF)_2AuI_2$ is 3.35 Å, same as that found in κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ and κ-$(BEDT\text{-}TTF)_2I_3$!

It is noteworthy that ambient pressure superconductors with the highest T_c in the three donor systems, BEDT-TTF, MDT-TTF and DMET, all have the κ-type structures. The negative pressure derivative of T_c, (dT_c/dP), of κ-$(BEDT\text{-}TTF)_2Cu(NCS)_2$ is the largest (–3 K/kbar) recorded to date for any superconductor [27]. With the proper choice of anions, it is possible to enlarge the crystallographic unit cell in these salts to mimic the "negative pressure" effect and achieve higher superconducting transition temperatures. Thus, it is clear that κ-phase salts are very promising materials in the structural design of new superconductors.

3. Concluding Remarks

While the structure-property correlations in the κ-phase materials are still evolving at this point, it is our contention that structural subtleties discussed in the previous section have brought into focus their close relationship to the observed solid state properties. Obviously, more cation-radical salts of this structure type remain to be synthesized and studied, so that fully developed and useful structure-property correlations can be realized.

Finally, we consider the question of whether it is possible to "engineer" κ-type structures. Several approaches to build molecular dimers, the basic units of κ-phase materials, are deemed possible. As discussed earlier, unsymmetrical donors are good candidates in this regard. Secondly, transition metal-dithiolate chelate compounds are potential molecular components to build dimeric units, as shown by our recent work on $Ni(dsit)_2$ complexes [28]. Here, the square-pyramidal coordination of the transition metal ion by chalcogen atoms appears to favor a dimeric structure. There are numerous examples in the literature which illustrate this point. Synthesis of TTF-type compounds with a cyclophanelike structure is another way to engineer dimers, but this avenue is synthetically very challenging and laborious.

Inducing the potential molecular dimer units to pack in the desired κ-type structure is, however, not very straight forward. Molecular modelling studies may be a useful computational aid in this regard [19], but progress in this area has not been forthcoming because of the enormity of the problem beyond the dimer level. Resorting to trial-and-error methods using a variety of counterions, with a large dose of chemical "intuition", appears to be the only viable approach at this time. It may also be important to choose counterions which form "soft" donor-anion and acceptor-cation interactions, so that the "soft" phonon modes may give rise to strong electron-phonon coupling and hence higher superconducting transition temperatures.

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