TOWARD CRYSTAL DESIGN IN ORGANIC CONDUCTORS AND SUPERCONDUCTORS

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1. Introduction

The vast majority of organic solids are electrical insulators with electrical conductivity values on the order of $10^{-20}$ to $10^{-15} \ \Omega^{-1} \text{cm}^{-1}$. This property is of course exploited in many everyday applications. Two principal reasons are responsible for this fact: (1) The highest occupied molecular orbital (HOMO) of most organic molecules is completely filled, and there is a significant energy difference to the lowest unoccupied molecular orbital (LUMO). (2) Organic solids are usually molecular, i.e., they do not possess a system of covalent bonds extending over macroscopic distances. Therefore the quantum mechanical interactions between the HOMOs of adjacent molecules are small. The valence band formed by these interactions remains therefore very narrow. Similarly, the conduction band arising from the interactions between the LUMOs is also small, and the band gap is essentially that of the free molecule. This holds even in the case of conventional polymers, e.g. polyethylene, that are o-bonded.

Electrical conduction may be classified in a number of types. The two main ones are activated and metallic, see Table 1.

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<thead>
<tr>
<th>Temperature Dependence</th>
<th>Activated</th>
<th>Metallic</th>
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<td>(lowering T)</td>
<td>lower conductivity</td>
<td>higher conductivity</td>
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<tr>
<td>Band Situation</td>
<td>Filled valence band, empty conduction band</td>
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<td>Fermi Level</td>
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Activated behavior is found in semiconductors, of which insulators are an extreme case. Semiconductors with appreciable conductivities ($10^{-10}$ to $10^{-2} \ \Omega^{-1} \text{cm}^{-1}$) at room
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(temperature) are obtained by shrinking the HOMO–LUMO gap, e.g., with the use of extensive $\pi$-bonding, sometimes including heteroatoms with lone pair electrons. Examples of this kind are polyacetylene, polyaniline, polyaromatics, and in the extreme case, graphite. Conductivity is governed by an activated term, $e^{-\Delta E/2kT}$, given by the band gap, $E_g$, and a pre-exponential factor which is more difficult to calculate. Conductivity may be increased by a reduction of the band gap, or by the introduction of impurity states within the gap.

In contrast, in a metal the Fermi level intersects a band, and the electrons possessing the proper momentum are able to delocalize freely. In a real system, conduction is not infinite, but reduced by scattering with other electrons, vibrations, and impurities. The temperature dependence of the resistivity (inverse of conductivity) is usually approximated by an power law with a small exponent ($2$–$3$). Partial band filling is achieved by the oxidation of electron donor molecules or the reduction of electron acceptor molecules to their respective radical ions and crystallization with charge-compensating counter-ions. It is also possible to combine electron donors and acceptors leading to spontaneous electron transfer. Provided these entities are spatially separated, e.g., in segregated stacks or layers, metallic conduction can occur within these substructures. Of necessity, the metallic properties of charge transfer salts will be low-dimensional, or at least highly anisotropic. In practice, this is also the case with most organic radical ion salts (see below).

Superconductivity is a special low-temperature regime of some metals and a sought-after property in our research program. It arises as a cooperative effect from the pairing of conduction electrons of opposite momentum (Cooper pairs) and is mediated in the conventional (Bardeen-Cooper-Shrieffer) theory by phonons. The detailed nature of the superconducting state in organic and many inorganic systems is the subject of current scientific debate.

Electrical conduction in organic solids was predicted in 1911 by McCoy and Moore [1]. It was achieved experimentally in 1954 when perylene was complexed with bromine [2]. Little in 1964 [3] predicted superconductivity in organic solids, which triggered more intense activity in the field. Milestones include the synthesis of the acceptor molecule tetracyano-$p$-quinodimethane (TCNQ) [4] and tetrathiafulvalene (TTF), see Figure 1. These were combined in 1972 to the charge transfer salt (TTF)(TCNQ), which was the first organic solid to show metallic conductivity over an extended temperature range [5, 6]. Superconductivity was found below 0.3 K in the polymer (SN)$_x$ in 1975. In the late 1970s, effort shifted to the exploration of the cation radical salts of TTF derivatives. Finally, superconductivity was observed in several salts of tetramethyltetraselenafulvalene (TMTSF) with simple anions such as ClO$_4^-$ and PF$_6^-$ [7]. Many more superconductors were found among the radical cation salts of a different TTF derivative, bis(ethylenedithio)tetrafulvalene (BEDT-TTF or ET), first synthesized by Mizuno et al. [8]. The salts of this donor molecule have been the subject of our research program for a number of years, and we have found the organic salts with
the highest superconducting transition temperatures ($T_c$), i.e., $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br ($T_c = 11.6$ K at ambient pressure) [9] and $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Cl ($T_c = 12.5$ K at 0.3 kbar applied pressure) [10]. Only the radical anion salts of C$_{60}$ with alkali metal cations have recently achieved higher $T_c$s among molecular solids. The field has been reviewed in books [11, 12] and monographs [13].

Figure 1. Typical electron donor and acceptor molecules.

2. Cation Radical Salts, a Type of Organic Conductors

Cation radical salts are composed of the radical cations of an electron donor molecule and charge-compensating counter anions. Most of the electron donor molecules (Figure 1) studied to date are related to TTF, and ET has achieved a prominent position with well over 200 salts characterized and the largest number of superconductors. The search for new superconductors encompasses on one hand the search for new donor molecules, and on the other the search for novel anions. In both cases, a more-or-less trial-and-error method is employed, and the field could use a more systematic approach.

The vast majority of ET salts are layered, i.e., the crystal structure is composed of layers of densely packed radical cations alternating with layers of anions, see Figure 2. Anisotropic properties thus result: the electrical conductivity is highest within the plane (often by several orders of magnitude), and in the superconductors, the critical field (field required to suppress superconductivity) is much higher when it is applied parallel to the plane than perpendicular to it. The stoichiometry of many ET salts with monovalent anions is 2:1, thus on average only one of every two ET molecules is oxidized. In 1:1 salts, the unpaired electrons tend to be localized (Mott insulator). Other stoichiometries, e.g., 3:2 and (insulating) 1:2 have also been observed.
These salts are crystallized by an electrochemical method from an electrolyte solution containing neutral donor molecules and an excess of a suitable salt of the desired anion. Organic solvents such as 1,1,2-trichloroethane or tetrahydrofuran are frequently employed, thus anion salts with large organic counterions (e.g., tetra-n-butylammonium) are commonly used in order to achieve good solubility. Under constant-current conditions with applied potentials of a few volts, the donor molecules are oxidized and precipitate with the anions in solution. The occurrence of partial oxidation states is explained by the association of neutral donor molecules with cation radicals prior to the crystal growth process. After a few weeks, the salts are harvested as black, shiny, ca. millimeter size, and (usually) air-stable crystals. Standard characterization methods include single crystal X-ray diffraction analysis, ESR spectroscopy (temperature and angle dependent), electrical conductivity (temperature dependent), magnetic susceptibility (search for large diamagnetic signal in the superconducting state), and Raman spectroscopy. Physicists have subjected these crystals to a host of further experimental probes that are beyond the scope of this article.

3. ET-Based Superconductors

The first ambient-pressure organic superconductor based on the electron donor molecule ET was $\beta$-(ET)$_2$I$_3$ with $T_c = 1.5$ K [14]. In quick succession, two more salts of ET with linear, triatomic anions were found to be superconducting, $\beta$-(ET)$_2$IBr$_2$ ($T_c = 2.8$ K) [15] and $\beta$-(ET)$_2$AuI$_3$ ($T_c = 4$–$5$ K) [16]. At about the same time, it was realized that these two salts had to be compared with the high-pressure phase $\beta$*-$(\text{ET})_2$I$_3$ (obtained by cooling at ca. 1.5 kbar pressure) with $T_c = 7$–$8$ K [17, 18]. Without applied pressure, $\beta$-(ET)$_2$I$_3$ undergoes a phase transition at 175 K to an incommensurately modulated structure which is not observed in the other compounds [19]. These three salts represented the first isostructural series of ET-based
superconductors, and they varied primarily in the size of the anion, thus the volume of the unit cell which increases in the order IBr\textsuperscript{2-} < AuI\textsuperscript{2-} < I\textsuperscript{−}. ET salts with other linear triatomic anions were not superconducting, either because the anion was too small to form an isostructural salt, e.g., ICl\textsuperscript{2−} and AuCl\textsuperscript{2−}, or because it did not possess a center of inversion, e.g., I\textsubscript{2}Br\textsuperscript{−}. The crystal structure of the β-salts contains the anion on a center of inversion. Therefore, non-centrosymmetric anions are disordered, and the random potentials generated by the disorder are usually (but not always!) sufficient to suppress superconductivity [20].

The unit cell volume has a direct connection to the electronic properties since it scales inversely with the width of the conduction band. Furthermore, in the context of standard Bardeen-Cooper-Schrieffer (BCS) theory [21, 22], the McMillan equation [23]

\[ T_c \propto e^{-\lambda}, \quad \text{with} \quad \lambda \propto \left\langle \omega^2 \right\rangle / n(e_F) \]

relates the superconducting transition temperature via the electron-phonon coupling constant (\( \lambda \)) to the density of states at the Fermi level, \( n(e_F) \), which is largest when the band with is narrow. \( \left\langle \omega^2 \right\rangle \) is the mean-square coupling vibration frequency. Thus, keeping all other parameters constant, the isostructural salt with the largest cell volume should have the highest \( T_c \). At that time, it was predicted that “puffing up the lattice” with the use of longer linear anions, e.g., Cu(NCS)\textsubscript{2}−, should lead to even higher transition temperatures.

Superconducting (ET)\textsubscript{2}Cu(NCS)\textsubscript{2} indeed was synthesized [24] and held the \( T_c \) record (10.4 K) for a few years. However, its crystal structure contained a completely different way of packing the ET molecules (κ-type, see below), and the anion was not discrete-linear, but it polymerized into chains that contained three-coordinate copper(I) centers, with both a bridging and a terminal thiocyanate group. This discovery led to the search for ET salts with other cuprous complex anions.

In 1990, our group discovered the two isostructural superconducting salts K-(ET)\textsubscript{2}Cu[N(CN)\textsubscript{2}]Br [9] and K-(ET)\textsubscript{2}Cu[N(CN)\textsubscript{2}]Cl [10], which to this day hold the record for highest transition temperatures for organic cation radical salts (\( T_c = 11.6 \) K at ambient pressure for the Br salt, \( T_c = 12.5 \) K at 0.3 kbar applied pressure in the Cl salts). K-(ET)\textsubscript{2}Cu[N(CN)\textsubscript{2}]Cl was also found to possess a canted antiferromagnetic ground state [25] at ambient pressure with a rich phase diagram in applied magnetic fields [26]. In contrast, K-(ET)\textsubscript{2}Cu[N(CN)\textsubscript{2}]I was not found to become superconducting, even under pressure. The reason is probably the presence of a disordered ethylene end group which persists to low temperature. K-(ET)\textsubscript{2}Cu(NCS)\textsubscript{2} and K-(ET)\textsubscript{2}Cu[N(CN)\textsubscript{2}]Br are among the most studied organic salts in the literature, with at least 300 papers on their physical properties in print.

At the time of this writing, well over 50 organic superconductors based on electron donor cations are known, too many to mention all in this space. Noteworthy are a family of superconducting ET salts with organometallic M(CF\textsubscript{3})\textsubscript{2}− (M = Cu, Ag, Au) anions that also incorporate 1,1,2-trihaloethane (with Cl and Br substituents) solvent
molecules in the crystal structure, reviewed by Schlueter [27]. In contrast to earlier experience, the presence of crystallographic disorder in these salts does not inhibit superconductivity. Furthermore, these salts are synthesized in two “flavors”, a plate-like phase with well defined crystal structures and $T_c$s of 2–5 K and a needle-like phase that has not yet yielded crystals suitable for structural analysis, and $T_c$s up to 11 K [28]! It is tempting to speculate that the higher superconducting transition temperatures are due the absence of crystallographic disorder (compared to the low-$T_c$ phases), but better samples are clearly needed for thorough characterization.

A common misconception for many years was that the presence of magnetic ions was incompatible with superconductivity. This was proven wrong by the discovery of a superconducting ground state in the salt $\beta''$-(ET)$_4$(H$_2$O)[Fe(C$_2$O$_4$)$_3$](C$_6$H$_5$CN) [29] and the corresponding chromium complex salt. Paramagnetism in the anion and superconductivity in the organic layers appear to coexist quite independently. It remains to be seen whether superconductivity can coexist with long-range magnetically ordered anions.

While most of the anions utilized in the synthesis of cation radical salts have been inorganic in nature, we have recently emphasized the search for new superconductors with organic anions such as carboxylates and sulfonates. We recently succeeded in observing superconductivity at 5 K in an all-organic salt, $\beta''$-(ET)$_4$(SF$_3$CH$_2$CF$_2$SO$_3$) [30]. We feel that ultimately, organic anions will be more versatile to obtain homologous series of salts because of the multitude of possible substitution patterns. However, as will be shown below, not all substitutions, not even seemingly minor ones, lead to isostructural salts, much less superconductivity.

![Figure 3. Schematic view of the main packing types of ET and related cation radical salts. The heavy bars represent the projection of the donor molecule along central C=C bond (which is usually inclined with respect to the layer normal, see Figure 2), and dashed lines short intermolecular contacts.](image-url)
4. Crystal Structures of Cation Radical Salts

Over 200 crystal structures of ET salts are known to date (see the book by Williams et al. [11] for a list up to 1991), and a similar number of derivative salts have been determined. While there is great variety in packing motifs of the electron donor layers, a few principal prototypes have emerged. Mori, in a series of two articles, has recently reviewed the main packing types in great detail [31, 32]. A schematic representation is given in Figure 3.

A number of compositions exist in more than one crystallographic phase, sometimes even growing simultaneously. The “chameleon” with the most phases is probably the system ET:polyiodide. Not only are there at least five (ET)$_n$I$_3$ phases (α, β, θ, κ, and λ) under ambient conditions (not counting high pressure and low temperature phases!), but several other cation:anion ratios as well as solvated phases and compositions with larger polyiodide anions (I$_5^-$, I$_6^{2-}$) exist. The specific Greek lettering reflects traditional terminology rather than thermodynamic stability. The α- and various β-like phases all contain discernible stacks (running approximately vertically in Fig. 3). In the α-type packing, adjacent stacks contain donor molecules that are inclined in opposite directions with respect to the stack axis. The β-types all contain donor molecules that are in parallel orientation to each other. β' and β" structures may be thought as two different distortions of the basic honeycomb-like standard β-type. The β'-packing is strongly dimerized (leading to nonmetallic properties), whereas the β"-type is a tilted variant of the β-type. Finally, the basic motif of the κ-type packing is a face-to-face dimer. Adjacent dimers are rotated by approximately 90° with respect to each other. The organic superconductors with the highest transition temperatures all contain the κ-packing type.

The vast majority of α- and β-like phases is triclinic, although not all are isomorphous. Depending on the size of the anion, structures with 2, 3, 4, or even more donor molecules per unit cell are found. On the other hand, most κ-phases possess higher crystallographic symmetry, with at least a 2, screw rotation axis within the donor plane connecting dimers of opposite tilt.

From the plethora of donor molecule packing types, even in salts of the same composition, it is clear that the specific crystal packing adopted is not intrinsic to the donor molecule, especially not for ET. Rather, it is the anion that determines the donor layer packing. The main interaction area between the anions and the donor radical cations is the ethylene end group (see Fig. 2). These interactions are discussed in the following section.
5. Design Principles: Donor–Anion Interactions

As is illustrated in numerous examples in this volume, the principal intermolecular interactions in organic solids are van der Waals dispersive forces (always present) and specific hydrogen bonding when suitable functional groups are present. \( X-H \cdots Y \) \((X, Y = O, N, \text{etc.})\) hydrogen bonding interactions, where present, are the strongest interactions possible in organic solids. Crystal engineering, i.e., the design and synthesis of crystal structures with predefined topology and functionality, makes heavy use of these hydrogen bonding interactions, as is evident from many contributions to this volume.

Organic conducting cation radical salts are by design composed of at least two different components: cations and counter-anions. One therefore has to consider at least three types of interactions: cation–cation, anion–anion, and cation–anion. Furthermore, at least two more bonding interactions must be considered in addition to van der Waals and hydrogen interactions, i.e., ionic (electrostatic) interaction, and metallic bonding due to the electron delocalization in the conducting cation layers. Let us consider each interaction in turn:

Van der Waals interactions are strongest between large, polarizable atoms, such as the sulfur or selenium atoms of the TTF derivative electron donor molecules. The packing of the ET cations into layers generally maximizes the number of intermolecular S\cdots S contacts, which may be as short as 3.4 Å compared to the sum of the van der Waals radii of 3.6 Å [33]. The topology of the short S\cdots S contacts is frequently indicative of significant electron overlap (leading to electron delocalization and ultimately electronic conduction), however, band electronic structure calculations are usually required in order to unambiguously determine the exact conduction pathways.

Hydrogen bonding interactions involving the electron donor molecules are usually restricted to the weak attraction of the aliphatic ethylene end group hydrogen atoms to electronegative atoms of the anion layer. While these hydrogen bonds are weak, they nevertheless provide the "glue" that binds the cation and anion layers together. The effect of deuterium substitution on the superconducting properties has been studied extensively, and the surprising result that at least in the \( \kappa \)-phase materials the deuterated salts have increased superconducting transition temperatures (first noted by Oshima et al. [34]) implicates the hydrogen–anion interactions in the electronic coupling between adjacent conducting layers. Stronger, more specific hydrogen bonding is sometimes found among anions or between anions and co-crystallized solvent molecules. Impurity water in the solvent used for crystallization has occasionally been found incorporated in the crystal structures of cation radical salts where it is invariably involved in a hydrogen bonding network with the anions (see the following section for an example).

The ionic interactions leading to lattice stabilization via the Madelung energy are difficult to quantify in these salts since the ionic charge is diffuse, and nowhere in the lattice does the latter attain large values. The layered packing found in most cation radical salts is not the minimum configuration based on the ionic forces alone. If ionic
interactions were the only ones operative, the cations and anions would be much more intimately interspersed. The observation of self-organized cation and anion layers indicates that the ionic interactions are less than dominant in the stabilization of the crystal structures, but clearly they cannot be neglected completely.

The role of metallic bonding in lattice stabilization is likely to be small, based on the small carrier densities (less than one electron/hole per donor molecule containing 20–30 atoms), and it is only operative within the donor cation layer. Furthermore, topologically similar packing patterns are observed in metallic as well as semiconducting salts, thus further indicating that metallic bonding has a minor effect on the crystal structures.

In summary, it appears that van der Waals, C–H-anion hydrogen bonding, and ionic interactions are all weak but of similar magnitude in organic conductors and superconductors. Any attempt at a priori design or crystal structure prediction must take into account all of these interactions simultaneously. A detailed knowledge of the charge distribution over the atoms of the component molecules (made even more difficult due to the partial molecular charges and open electronic shells) is required for proper treatment, and it is no wonder that no calculations have been published yet. Any discussion of crystal engineering in these systems is currently limited to the crystallographic study of typical examples that illustrate the relative role of various intermolecular interactions.

6. Case Studies

6.1 ET SALTS WITH SF₅R-SO₃⁻ ANIONS

As indicated above, β"-(ET)₂SF₅CH₂CF₂SO₃ was the first all-organic superconductor discovered. The anion offers a number of substitutions that might lead to isostructural salts and expected new superconductors: (1) The SF₅ head group may be replaced by CF₃, SiF₃, or similar. (2) The SO₃⁻ anionic end group may be replaced by carboxylate or similar. (3) The hydrogen and fluorine substitution pattern may be changed on the carbon backbone. (4) The number of carbon atoms on the backbone may be varied. We have obtained results on (3) and (4) so far, unfortunately with the result that none of the new anions led to an isostructural, superconducting salt.
Figure 4. Anion and surrounding ET-ethylene groups in β"-(ET)₂SF₅CHRCF₂SO₃, R = H (left), F (right). Short H–F and H–O contacts are indicated by thin lines. In the right-hand structure, the anion is crystallographically disordered, with a superposition of the two possible enantiomers in an approximately 2:1 population ratio (the majority isomer is drawn darker).

The results of the simple replacement of one anion hydrogen atom by fluorine [35] are shown in Figure 4. While the unit cell metric of the two salts is quite similar (a=9.154 Å, b=11.440 Å, c=17.490 Å, α=94.32°, β=91.13°, γ=102.76° for the CH₂ derivative vs. a=9.246 Å, b=11.361 Å, c=17.714 Å, α=94.12°, β=94.91°, γ=103.14° for the CHF derivative), and the space group remains the same, P1, the anion adjusts its conformation due to the involvement of the extra fluorine atom in weak hydrogen bonding with donor cation ethylene groups. This change in turn leads to a small distortion of the ET donor molecule network (note the change of the β-angle by 3.8° although the overall β"-type packing remains intact) which is sufficient to change the electronic properties. Not only is superconductivity suppressed (which by itself could be rationalized by the presence of anion crystallographic disorder), but the salt undergoes a gradual transition to a non-metallic ground state below 150 K which must have its origin in the subtle changes of the band electronic structure due to the small distortion. The anion site is a general position in the crystal structure, and the two enantiomers of the anions could occupy inversion-equivalent sites (a racemic mixture was employed in the synthesis). However, a superposition of the two enantiomers is found (in a ~2:1 ratio, opposite on the inversion-symmetric site) as the anion pocket is large enough to accommodate both with a similar number of C–H–F and C–H–O contacts, see Figure 4.

We have also studied the crystal structures of the ET salts with the corresponding anions containing only one carbon atom in the backbone (CH₂, CHF, and CF₂ derivatives) [36]. Of these, the former two also crystallize in β"-type structures, while the latter adopts the strongly dimerized β'-structure. Again, the β"-structures are distorted from that found in β"-(ET)₂SF₅CH₂CF₂SO₃, and no superconductors are found. In this case, the distortion derives from weak hydrogen bonding between pairs of anions, as shown in Figure 5 for (ET)₂SF₅CH₂SO₃. Note that this particular hydrogen
bonding pattern is not possible for the two-carbon analogues described above, since they contain CF₂ moieties (lacking hydrogen) adjacent to the sulfonate groups.

![Figure 5: Hydrogen bonded anion dimer in (ET)₂SF₆CH₂SO₃](image)

### 6.2. TWO DIFFERENT PACKING PATTERNS IN (ET)₂(C₆H₅CH₂SO₃)(H₂O)

In our search for ET-based superconductors with all-organic anions, we also explored salts with the benzylsulfonate anion (C₆H₅CH₂SO₃⁻) [37]. We found that ET crystallized with this anion simultaneously in two distinct crystallographic phases (β and κ-4×4) of the same 2:1 stoichiometry, each incorporating a molecule of solvent water per anion. Unfortunately, neither salt is superconducting, and the one whose crystals are large enough to be examined by standard physical methods is not even metallic but a semiconductor. Nevertheless, their crystal structures are illustrative in the context of crystal engineering.

The packing of the ET donor molecules in the κ4×4 salt is shown in Figure 6. Compared to the standard κ-type packing, the basic unit is a tetramer (instead of a dimer). Neighboring tetramers in the c-direction are parallel, but in the β-direction, they are tilted in the opposite direction (by ca. 90°). On the other hand, in the β-salt, all ET molecules are parallel to each other, similar to the schematic diagram in Figure 4. However, compared to the standard β-phase salts, the unit cell is twice as large, and some tetramerization along the stack direction (a+b) is noted.

The differences between these packing types are related to the anion packing, see Figure 7. The strongest intermolecular interaction is the hydrogen bonding between the sulfonate oxygen atoms and the water protons. This interaction is so strong that even minute amounts of water present in the form as solvent and glass surface contamination is incorporated into the crystal structure. Thus, dimers of anion with two water bridges are formed, similar to those found in the monohydrates of carboxylate salts, involving O–H–O hydrogen bonds. Adjacent dimers line up in a tilted way into ribbons by the formation of much weaker hydrogen bonds involving C–H–O interactions with the benzylic and aromatic hydrogen atoms. This leaves the hydrophobic benzene rings...
Figure 6. \( \kappa 4\times 4 \)-type ET molecular layer packing in \( \kappa 4\times 4-(\text{ET})_2(\text{C}_6\text{H}_4\text{CH}_2\text{SO}_3)\)(\text{H}_2\text{O}) \). The layer plane is parallel to \( bc \), but this perspective view is oblique and approximately along the long molecular axis. Compare with Figure 4 for a schematic diagram of standard \( \kappa \)-packing. Most of the ethylene groups are conformationally disordered at room temperature.

sticking out of the side of the ribbons on alternating sides. Now there are two ways of interlocking the ribbons: one in parallel and the other with flipped neighbors. These two patterns are observed in the \( \beta \)- and \( \kappa \)-phases, respectively.

Figure 7. Anion network in \( \beta \)- and \( \kappa 4\times 4-(\text{ET})_2(\text{C}_6\text{H}_4\text{CH}_2\text{SO}_3)\)(\text{H}_2\text{O}) \). The water-bridged anion dimer is highlighted with shading in each case. Hydrogen bonds are indicated by dashed lines.

Coincidentally, the dimensions of the anion dimer, ca. 11.5 \( \text{Å} \times 5.4 \text{Å} \) match the footprint of the ET tetramer. In each case, there is a center of inversion in the middle of the tetramer, thus the inner ET molecules are equivalent to each other, and the outer ones correspondingly. The ET-hydrogen-to-anion interactions of the inner ET molecules are primarily to the sulfonate and water oxygen atoms, whereas those of the outer ET molecules are with the benzene rings of the anion. This example shows that
hydrogen bond building principles may be utilized to form the anion layer, which then in turn dictates the packing of the ET molecule conducting layer.

7. Conclusions

We have seen that many different types of intermolecular interactions in organic conducting cation radical salts. Hydrogen bonding between the donor molecules and the anions is weak but not negligible. The ionic Madelung energy is insufficient to completely intersperse anions and cations, thus the layers favored by the van der Waals interactions remain intact. The search for new conducting and superconducting salts has been mainly by trial-and-error methods, even though simple substitutions have been employed in order to obtain isostructural analogs of successful (e.g., superconducting) salts. However, even seemingly minor substitutions sometimes destroy the packing type, and different crystal structures result. Simulations with the aim at predicting crystal structures have not succeeded, mainly because the different interaction types are of comparable energy, and the delocalized and partial charges render the calculations of the ionic terms extremely unreliable. Clearly, the development of suitable crystal modeling techniques with predictive capabilities is one of the great needs of the field.

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