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IMPORTANCE OF C-H...DONOR AND C-H...ANION CONTACT
INTERACTIONS FOR THE CRYSTAL PACKING, THE LATTICE SOFTNESS
AND THE SUPERCONDUCTING TRANSITION TEMPERATURES OF
ORGANIC CONDUCTING SALTS.

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INTRODUCTION

The organic donor molecule BEDT-TTF (1) and its analogs 2-4 have yielded a number of ambient-pressure superconducting salts. What structural and electronic factors govern the magnitudes of their superconducting transition temperature T_c has been a topic of intense studies.¹⁻⁴ Examination of the band electronic structures of closely related superconducting salts shows^{2,3} that the magnitudes of their T_c 's are primarily determined by the softness of their crystal lattices. The crystal packing and the lattice softness of organic donor salts are strongly influenced by the donor...donor and donor...anion contact interactions involving the donor-molecule C-H bonds.^{2,5,6} In the present work, we briefly

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review the electronic structures of some representative organic salt superconductors and discuss the softness of their crystal lattices on the basis of the interaction energies calculated for the C-H...donor and C-H...anion contact interactions.

LATTICE SOFTNESS AND SUPERCONDUCTIVITY

Figure 1 shows how the T_c values of β -(BEDT-TTF) $_2$ X ($X^- = I_3^-$, AuI_2^- , IBr_2^-) vary as a function of applied pressure P .⁷ For $X^- = AuI_2^-$ and IBr_2^- , the T_c of β -(BEDT-TTF) $_2$ X decreases gradually with increasing P . For $P < 0.5$ kbar, the T_c of β -(BEDT-TTF) $_2I_3$ decreases as well with increasing P . At $P \approx 0.5$ kbar, however, the T_c of β -(BEDT-TTF) $_2I_3$ jumps to 8K but decreases as P increases further. [β -(BEDT-TTF) $_2I_3$ with $T_c \approx 8$ K is commonly referred to as β^* -(BEDT-TTF) $_2I_3$.⁸] To understand what causes the T_c jump in β -(BEDT-TTF) $_2I_3$ under pressure, we first examine whether or not the electronic structure of β -(BEDT-TTF) $_2I_3$ undergoes any drastic change by applied pressure. Figures 2a and 2b respectively show the dispersion relations of the two highest-occupied (HO) bands and the Fermi surface calculated³⁴ for β -(BEDT-TTF) $_2I_3$ on the basis of its crystal structure⁹ determined at 9K under ambient pressure. The band dispersion relations and the Fermi surface of β^* -(BEDT-TTF) $_2I_3$, calculated on the basis of its crystal structure⁸ determined at 4.5K under 1.5 kbar, are shown in Figures 3a and 3b, respectively. Practically, the band electronic structures of the two salts are identical. Furthermore, the β -(BEDT-TTF) $_2$ X ($X^- = AuI_2^-$, IBr_2^-) salts have the band dispersion relations and the Fermi surfaces very similar to those in Figures 2 and 3. Consequently, the pressure- and anion-dependence of the T_c in β -(BEDT-TTF) $_2$ X do not originate from their electronic structures and therefore should be explained in terms of factors associated with their crystal structures.²

Figure 1. Pressure dependence of the superconducting transition temperatures T_c of β -(BEDT-TTF) $_2$ X ($X^- = I_3^-$, AuI_2^- , IBr_2^-)

With the BCS theory of superconductivity,^{10,11} Cooper pair formation is induced by electron-phonon interaction, and the extent of this interaction is measured by the electron-phonon coupling constant λ . Given a lattice with Debye temperature θ_D that has a phonon spectrum (i.e., phonon band) effective for electron-phonon coupling, the T_c is related to θ_D and λ as follows:¹¹

$$T_c = \frac{\theta_D}{1.45} \exp \left[- \frac{1.04 (1 + \lambda)}{\lambda - \mu^* \left(1 + \lambda \frac{\langle \omega \rangle}{\omega_0} \right)} \right] \quad (1)$$

where $\langle \omega \rangle$ and ω_0 are the average and the maximum frequency of the phonon band, respectively. The Coulomb pseudopotential μ^* and the frequency ratio $\langle \omega \rangle / \omega_0$ are on the

Figure 2. (a) Dispersion relations of the two highest occupied bands and (b) Fermi surface calculated for β -(BEDT-TTF)₂I₃ on the basis of its crystal structure determined at 9K. The dashed line in (a) refers to the Fermi level.

order of 0.1 and 0.5, respectively. Among the several factors affecting the magnitude of T_c in Eq. 1, the most important one is λ . In general, T_c increases with increasing λ . For a lattice with atoms of mass M , λ is expressed as¹¹

$$\lambda = \frac{n(e_f) \langle I^2 \rangle}{M \langle \omega^2 \rangle} \propto \frac{1}{M \langle \omega^2 \rangle} \quad (2)$$

where $n(e_f)$ is the electronic density of states at the Fermi level e_f , $\langle I^2 \rangle$ is the square of the electron-phonon matrix elements averaged over the Fermi surface, and the $\langle \omega^2 \rangle$ is the square of the phonon frequency averaged over the phonon band. As already discussed, the band electronic structures of β -(BEDT-TTF)₂X ($X^- = I_3^-$, AuI₂⁻, IBr₂⁻) are essentially identical and their $n(e_f)$ values are very similar (See Table 1). Thus the $n(e_f) \langle I^2 \rangle$ term should

Figure 3. (a) Dispersion relations of the two highest occupied bands and (b) Fermi surfaces calculated for β^* -(BEDT-TTF)₂I₃ on the basis of its crystal structure determined at 4.5K under 1.5 kbar.

Table 1. T_c , $n(e_f)$ and λ values of β -(BEDT-TTF) $_2$ X

Salt	T_c (K)	$n(e_f)$ (e ⁻ /eV)	λ
β -(BEDT-TTF) $_2$ IBr $_2$	2.8	3.69 ^a	0.43
β -(BEDT-TTF) $_2$ AuI $_2$	5.0	3.48 ^b	0.52
β^* -(BEDT-TTF) $_2$ I $_3$	8	3.53 ^c	0.62
β -(BEDT-TTF) $_2$ I $_3$	1.4	3.66 ^a	0.37

^a Based upon the crystal structure determined at 9 K under ambient pressure.

^b Based upon the crystal structure determined at 20 K under ambient pressure.

^c Based upon the crystal structure determined at 4.5 K under 1.5 kbar.

practically be constant^{2,11} for the β -(BEDT-TTF) $_2$ X salts, so that λ depends largely upon the denominator $M\langle\omega^2\rangle$, which has the dimension of a force constant. This means that a large λ value results when the lattice has soft phonons, which arise from vibrations with shallow potential wells.²

On the basis of the T_c values of β -(BEDT-TTF) $_2$ X ($X^- = I_3^-$, AuI $_2^-$, IBr $_2^-$), along with the parameters $\mu^* = 0.1$, $\langle\omega\rangle/\omega_0 = 0.3$,¹² and $\theta_D = 200$ K,¹³ we calculate the λ values of these salts by employing Eq. 1. As listed in Table 1, the T_c increases with λ , and the T_c jump in β -(BEDT-TTF) $_2$ I $_3$ under pressure correlates with a sudden increase of λ (i.e., a sudden increase in the lattice softness) under pressure.² Phonons important for superconductivity are expected to have frequencies of the order of $\sim 8k_B T_c$.¹⁴ Therefore, organic salt superconductors, phonons crucial for their superconductivity are translational and/or librational modes, which are strongly influenced by the C-H $\cdots$ donor and C-H $\cdots$ anion contact interactions.² Thus the lattice of an organic salt becomes softer for such phonon modes, when the C-H $\cdots$ donor and C-H $\cdots$ anion interactions possess shallow potential wells and also when the C-H $\cdots$ donor and C-H $\cdots$ anion contact distances become larger.

5a

5b

As shown in the perspective diagram 6 each anion X^- of β -(BEDT-TTF) $_2X$ ($X^- = I_3^-$, AuI_2^- , IBr_2^-) is enclosed in a hydrogen pocket made up of 12 BEDT-TTF molecules, and each terminal halogen atom of X^- is surrounded by six ethylene groups.² This packing of BEDT-TTF molecules around X^- gives rise to short intermolecular C-H...donor and C-H...anion contacts shorter in length than expected from the van der Waals (VDW) radii sum. When viewed along the central C = C bond of BEDT-TTF, the two ethylene groups of BEDT-TTF are either eclipsed (E) or staggered (S) as illustrated in 5a and 5b, respectively.²

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For $X^- = AuI_2^-$ and IBr_2^- , the donor molecules of β -(BEDT-TTF) $_2X$ have an eclipsed arrangement of ethylene groups. In β -(BEDT-TTF) $_2I_3$ both eclipsed and staggered donor molecules are present in nearly equal proportions. The most important structural change β -(BEDT-TTF) $_2I_3$ undergoes under pressure greater than 0.5 kbar is that all BEDT-TTF molecules adopt a staggered arrangement of ethylene groups, thereby altering the intermolecular contact distances associated with the C-H bonds.² Table 2 lists the shortest C-H...H and C-H...anion (with the terminal halogen atom) contact distances found for β -(BEDT-TTF) $_2X$ ($X^- = I_3^-$, AuI_2^- , IBr_2^-) in their crystal structures below 20K.² These C-H...H and C-H...anion distances increase in the order β -(BEDT-TTF) $_2IBr_2 < \beta$ -(BEDT-TTF) $_2AuI_2 < \beta^*$ -(BEDT-TTF) $_2I_3$. Thus the lattice softness of these salts increases in the same order, which is consistent with the increase in λ in the same order. Under ambient pressure, β -(BEDT-TTF) $_2I_3$ has unfavorably short C-H...H and C-H...I contacts. The structural modulation of β -(BEDT-TTF) $_2I_3$, which occurs below 200K,¹⁵ reflects the presence of structural strain that leads to the λ value smaller than that of β -(BEDT-TTF) $_2IBr_2$. Adoption of a staggered ethylene group arrangement by BEDT-TTF, under $P > 0.5$ kbar, makes the lattice of β^* -(BEDT-TTF) $_2I_3$ particularly soft (for the translational and/or the librational modes of vibration) because it makes the C-H...H and C-H...anion contacts longer.² A further increase in pressure beyond 0.5 kbar in β^* -(BEDT-TTF) $_2I_3$ makes the lattice stiffer and lowers the T_c , just as in the case of β -(BEDT-TTF) $_2X$ ($X^- = AuI_2^-$, IBr_2^-).

ISOTOPE EFFECT ON T_c

To discuss how an isotope substitution affects the magnitude of T_c , it is convenient to simplify Eq. 1 as

Table 2. Ethylene group arrangements and the shortest C-H...H and C-H...anion (with the terminal halogen) contact distances in β -(BEDT-TTF)₂X

Salts	Ethylene group arrangement	Shortest intermolecular distance (Å)	
		C-H...H	C-H...anion
β -(BEDT-TTF) ₂ IBr ₂	E	2.169	2.887
β -(BEDT-TTF) ₂ AuI ₂	E	2.224	2.966
β^* -(BEDT-TTF) ₂ I ₃	S	2.261	3.014
β -(BEDT-TTF) ₂ I ₃	E & S	2.152	2.842

$$T_c \propto \theta_D \exp \left(- \frac{1}{\lambda} \right) \quad (3)$$

When the hydrogen atoms of BEDT-TTF are replaced with deuterium atoms, the resulting BEDT-TTF-dg has a higher mass than BEDT-TTF. According to the preexponential term θ_D of Eq. 3, the isotope substitution $H \rightarrow D$ should lower the T_c , because the lowering of the vibrational frequencies associated with the isotope substitution will lower the Debye temperature θ_D . The T_c of an organic salt superconductor should decrease by the $H \rightarrow D$ substitution if the electron-phonon coupling constant λ is not affected by the isotope substitution. However, this assumption is not necessarily valid. The C-D bond has a lower 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 expected for the H atom displacement. Thus, 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. Therefore, the $H \rightarrow D$ substitution may provide a softer lattice and hence lead to a larger λ value thereby raising the T_c according to the exponential term $\exp(-1/\lambda)$ of Eq. 3. That is, Eq. 3 shows that an isotope substitution such as $H \rightarrow D$ should lower the T_c according to the pre-exponential term θ_D but raise the T_c according to the exponential term $\exp(-1/\lambda)$. When the latter effect dominates, the isotope substitution $H \rightarrow D$ raises the T_c as observed for κ -(BEDT-TTF)₂Cu(NCS)₂ (i.e., 10.4 $\rightarrow$ 10.8 K).¹⁶

DONOR...DONOR AND DONOR...ANION INTERACTION

As discussed earlier, the lattice softness as measured by the shortest C-H...H and C-H...anion contact distances allows us to rationalize the pressure- and anion-dependence of the T_c in β -(BEDT-TTF)₂X ($X^- = I_3^-$, AuI₂⁻, IBr₂⁻). For general organic donor salts with monovalent anions, donor...donor contacts shorter than the VDW distances (r_{vdw}) consist of

Table 3. Interaction energies ΔE_{vdw} and ΔE_{opt} of the chalcogen...chalcogen contacts calculated at their r_{vdw} and r_{opt} values

Contact	r_{vdw} (Å)	ΔE_{vdw} (kcal/mol)	r_{opt} (Å)	ΔE_{opt} (kcal/mol)
O...O	3.00	1.85	∞	0.00
S...S	3.60	-0.10	4.05	-0.41
Se...Se	3.80	-0.19	---	---
Te...Te	4.20	-1.02	---	---

Table 4. Interaction energies ΔE_{vdw} and ΔE_{opt} of the C-H...donor contacts calculated at their r_{vdw} and r_{opt} values

Contact	r_{vdw} (Å)	ΔE_{vdw} (kcal/mol)	r_{opt} (Å)	ΔE_{opt} (kcal/mol)
C-H...O	2.70	-2.35	2.61	-2.43
C-H...S	3.00	-0.24	3.43	-0.45
C-H...Se	3.10	-0.43	3.44	-0.67
C-H...Te	3.30	-0.31	3.72	-0.54
C-H...C(sp ²)	2.85	-0.55	3.21	-0.69
C-H...H	2.40	-0.11	2.69	-0.15

Table 5. Interaction energies ΔE_{vdw} and ΔE_{opt} of the C-H...anion contacts C-H...Y-I-Y⁻ calculated at their r_{vdw} and r_{opt} values

Contact	r_{vdw} (Å)	ΔE_{vdw} (kcal/mol)	r_{opt} (Å)	ΔE_{opt} (kcal/mol)
C-H...I	3.15	-0.98	3.50	-1.13
C-H...Br	3.00	-1.19	3.14	-1.27
C-H...Cl	2.90	-1.48	2.85	-1.58

chalcogen...chalcogen, C-H...chalcogen, C-H...C and C-H...H contacts, while donor...anion contacts shorter than r_{vdw} include only the C-H...anion contacts in most cases. Recently, the nature of such short intermolecular interactions has been examined^{5,17-19} by performing ab initio MP2 calculations²⁰ on model molecular systems, essential results of which are summarized in this section.

Chalcogen...chalcogen (X...X) contact interaction energies, obtained by ab initio MP2 calculations¹⁸ on $H_2X...XH_2$ (X = O, S, Se, Te) with the 6-311G(3df, 3pd) basis sets at the VDW and optimum X...X distances (r_{vdw} and r_{opt} , respectively), are listed in Table 3. The O...O contact interaction is repulsive at all O...O distances, but other X...X (X = S, Se, Te) interactions are attractive at r_{vdw} . In the vicinity of r_{vdw} , the magnitudes of the attractive X...X interactions increase in the order: S...S, Se...Se < Te...Te. We note that $r_{opt} > r_{vdw}$ for the S...S interaction. The same trend is expected for the Se...Se and Te...Te interactions.

To evaluate the energies of the C-H...X (X = O, S, Se, Te), C-H...C(sp²) and C-H...H contact interactions, ab initio MP2 calculations^{5b,19} with the 6-311G(d, p) basis set are carried out for $H_3C-H...XH_2$ (X = O, S, Se, Te) with a C_s-symmetry arrangement and the methane C-H bond aligned along the p_π-orbital or XH_2 , $H_3C-H...CH_2 = CH_2$ with a C_s-arrangement and the methane C-H bond aligned along one p_π-orbital of CH₂=CH₂, and $H_3C-H...H-CH_3$ with a D_{3h}-symmetry arrangement. The interaction energies of these contacts calculated at their r_{opt} and r_{vdw} distances are summarized in Table 4. At r_{vdw} all these C-H...donor interactions are attractive, and their magnitudes increase in the following order: C-H...H < C-H...X (X=S, Se, Te), C-H...C(sp²) << C-H...O.

Ab initio MP2 calculations with the 3-21+G(d, p) basis set are performed^{5b,17} on $H_3C-H...Y-I-Y^-$ (Y = I, Br, Cl) to estimate the interaction energies of the C-H...anion contacts C-H...Y (Y = I, Br, Cl). The interaction energies calculated at r_{opt} and r_{vdw} are summarized in Table 5. At r_{vdw} these C-H...anion interactions are attractive and their magnitudes increase in the order: C-H...I < C-H...Br < C-H...Cl.

From Tables 3-5 the magnitudes of the attractive donor...donor and donor...anion contact interactions at their r_{vdw} are found to increase in the following order:

Except for the C-H...O and Te...Te interactions, the C-H...anion interactions C-H...Y-I-Y⁻ are more attractive than all the C-H...donor interactions. The C-H...O interaction is more attractive than the C-H...Y-I-Y⁻ interactions, while the Te...Te interaction is comparable to the C-H...anion interactions C-H...Y-I-Y⁻. The C-H...donor interactions C-H...X (X = S, Se, Te, C(sp²)) are more attractive than the C-H...H, S...S, and Se...Se interactions. In the following two sections we show that the thermal phase transitions of some organic salt and the unique donor-layer packing of the BEDO-TTF salts are easily explained on the basis of the intermolecular contact interaction energies discussed above.

THERMAL PHASE TRANSITIONS

Under thermal tempering, α -(BEDT-TTF) $_2$ I $_3$ undergoes a phase transition to α' -(BEDT-TTF) $_2$ I $_3$,^{6a,21-22} which exhibits a superconducting transition near 8K. Several experimental studies strongly suggest that α' -(BEDT-TTF) $_2$ I $_3$ is structurally very similar to β^* -(BEDT-TTF) $_2$ I $_3$. Conversion of α -(BEDT-TTF) $_2$ I $_3$ to a β -like structure by thermal

Figure 4. Stereodiagrams of how the donor molecules make C-H...anion and C-H...donor contacts in (a) β^* -(BEDT-TTF) $_2$ I $_3$ and (b) α -(BEDT-TTF) $_2$ I $_3$.

tempering means that α -(BEDT-TTF) $_2$ I $_3$ is thermodynamically less stable than β^* -(BEDT-TTF) $_2$ I $_3$. Figures 4a and 4b show the stereodiagrams of how the C-H bonds of one BEDT-TTF interact with the surrounding donor molecules and I $_3^-$ anions in β^* -(BEDT-TTF) $_2$ I $_3$ and α -(BEDT-TTF) $_2$ I $_3$, respectively.^{6a} Each ethylene group uses three C-H Bonds to make C-H...anion contacts in β^* -(BEDT-TTF) $_2$ I $_3$ but only two C-H bonds in α -(BEDT-TTF) $_2$ I $_3$. Therefore, every BEDT-TTF makes more C-H...anion contacts in β^* -(BEDT-TTF) $_2$ I $_3$ than α -(BEDT-TTF) $_2$ I $_3$. Since the C-H...anion interaction C-H...I is more attractive than the C-H...donor interactions such as C-H...S, C-H...C(sp 2) and C-H...H, β^* -(BEDT-TTF) $_2$ I $_3$ is expected to be thermodynamically more stable than α -(BEDT-TTF) $_2$ I $_3$, in agreement with experiment.

δ -(BEDT-TTF) $_2$ AuBr $_2$ is converted to α' -(BEDT-TTF) $_2$ AuBr $_2$ at 420K thereby indicating that the latter is thermodynamically more stable.^{6b} Figures 5 and 6 show the C-H...anion contacts of δ -(BEDT-TTF) $_2$ AuBr $_2$ and α' -(BEDT-TTF) $_2$ AuBr $_2$, respectively. Clearly, the donor molecules have more C-H...anion contacts in α' -(BEDT-TTF) $_2$ AuBr $_2$ than in δ -(BEDT-TTF) $_2$ AuBr $_2$.^{6b} Since the C-H...anion interaction C-H...Br is more attractive than the C-H...donor interactions such as C-H...S, C-H...(sp 2) and C-H...H, α' -(BEDT-TTF) $_2$ AuBr $_2$ is expected to be thermodynamically more stable than δ -(BEDT-TTF) $_2$ AuBr $_2$. This is consistent with the phase transition δ -(BEDT-TTF) $_2$ AuBr $_2 \rightarrow \alpha'$ -(BEDT-TTF) $_2$ AuBr $_2$ under thermal tempering.

Figure 5. Short C-H...anion contacts in δ -(BEDT-TTF) $_2$ AuBr $_2$.

Figure 6. Short C-H...anion contacts in α' -(BEDT-TTF)₂AuBr₂.

UNIQUE DONOR-LAYER PACKING OF BEDO-TTF SALTS

In a donor stack of (BEDO-TTF)₂AuBr₂ the donor molecules BEDO-TTF (2) slip along the direction perpendicular to the donor molecule central C=C bond, as depicted in 7.5. ²³ This slipping allows the BEDO-TTF molecules of (BEDO-TTF)₂AuBr₂ make short C-H...O contacts within each donor stack as well as between adjacent donor stacks as shown in Figures 7. This pattern of donor-molecule packing is common to all known BEDO-TTF salts with different anions including the superconducting phase ²⁴ β_m -(BEDO-TTF)₂Cu₂(NCS)₃. This reflects the fact that the C-H...donor interaction C-H...O is strongly

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attractive, even more attractive than the C-H...anion interactions such as C-H...Y-I-Y⁻ (Y = I, Br, Cl) as discussed in the earlier section. For many BEDO-TTF salts it is difficult to resolve the structures of their anion layers due to their disorder. It appears that the particular donor

Figure 7. Short C-H...O contacts in the donor layers of (BEDO-TTF)₂X (a) within a donor stack and (b) between adjacent donor stacks.

layer packing of the BEDO-TTF salts does not provide good C-H...anion contacts to stabilize their anion layer structures.

ELECTRONIC STRUCTURES OF κ -PHASE

Ambient pressure κ -phase superconductors include κ -(BEDT-TTF)₂X (X^- = Cu[N(CN)₂]Br⁻,²⁵ Cu(NCS)₂⁻,²⁶ I₃⁻,²⁷), κ -(MDT-TTF)₂AuI₂,²⁸ and κ -(DMET)₂AuBr₂.²⁹ The band dispersion relations of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br and κ -(BEDT-TTF)₂Cu(NCS)₂ calculated on the basis of their ~120K structures³⁰ are shown in Figures 8a and 8b, respectively. In both salts, the lowest-unoccupied (LU) bands derived from the anion chains overlap with the HO, half-filled, bands derived from the donor-molecule layers. This is in contrast to the case of β -(BEDT-TTF)₂I₃ in which the LU band derived from the I₃⁻ anions does not overlap with the HO band of the donor molecules as shown in Figure 9.³¹ The LU bands of β -(BEDT-TTF)₂Cu[N(CN)₂]Br and β -(BEDT-TTF)₂Cu(NCS)₂ have primarily the π^* orbital character of the N≡C-N-C≡N⁻ and N≡C-S⁻ units, respectively.

The Fermi surfaces associated with the HO bands of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br and κ -(BEDT-TTF)₂Cu(NCS)₂ are shown in Figures 10a and 10b,

respectively. Essentially, these Fermi surfaces have a shape of overlapping circles. In $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$, the degeneracy of the intended crossing points of overlapping circles is lifted due to the presence of two nonequivalent donor molecules. Therefore its Fermi surface is split into one-dimensional wavy lines and two-dimensional ellipses. More explicitly, the Fermi surface of $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$ contains the hole surface (Figure 11a) and the electron surface (Figure 11b), which are respectively associated with the lower and upper subbands of the HO band in Figure 8b. This explains why the nature of the

Figure 8. Dispersion relations of the occupied and unoccupied bands around the Fermi level in (a) $\kappa\text{-(BEDT-TTF)}_2\text{Cu[N(CN)}_2\text{]Br}$ and (b) $\kappa\text{-(BEDT-TTF)}_2\text{Cu(NCS)}_2$.

Figure 9. Dispersion relations of the occupied and unoccupied bands around the Fermi level in β -(BEDT-TTF) $_2$ I $_3$.

Figure 10. Fermi surface of (a) κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br and κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$.

carriers, as determined by the thermoelectric power measurements, is hole-like along the $\Gamma \rightarrow Z$ direction (i.e., the crystallographic c-direction) but electron-like along the $\Gamma \rightarrow Y$ direction (i.e., the crystallographic b-direction.)³² In the Fermi surface of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br, the degeneracy of the crossing points of the overlapping circles is not lifted. Even in this case, the Fermi surface can be separated into the hole surface (Figure 12a) and the electron surface (Figure 12b), which are respectively associated with the lower and upper subbands of the HO band in Figure 8a. Consequently, the nature of the carriers in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br, as determined by thermoelectric power measurements, should be hole-like along the $\Gamma \rightarrow X$ direction (i.e., the crystallographic a-direction) but electron-like along the $\Gamma \rightarrow Z$ direction (i.e., the crystallographic c-direction).³³ All known κ -phase superconductors should exhibit similar thermoelectric characteristics since their Fermi surface, having the shape of overlapping circles³, can be separated into hole and electron surfaces. As reported elsewhere,³ the electronic structures of κ -phase salts are quite similar.

Figure 11. (a) Hole and (b) electron Fermi surfaces of κ -(BEDT-TTF)₂Cu(NCS)₂, where the occupied wave vectors are indicated by shading.

Table 6. T_c and $n(e_f)$ values of κ -phase superconducting salts

Salt	T_c (K)	$n(e_f)$ (e ⁻ /eV)
κ -(DMET) ₂ AuBr ₂	1.8	8.92 ^a
κ -(BEDT-TTF) ₂ I ₃	3.6	7.09 ^a
κ -(MDT-TTF) ₂ AuI ₂	4.5	7.98 ^a
κ -(BEDT-TTF) ₂ Cu(NCS) ₂	10.4	7.39 ^b
κ -(BEDT-TTF) ₂ Cu[N(CN) ₂]Br	11.6	7.27 ^b

^a Based upon the crystal structure determined at room temperature.

^b Based upon the crystal structure determined at ~ 120 K.

The T_c and calculated $n(e_f)$ values of the superconducting κ -phase salts are listed in Table 6. As in the case of the β -phase superconductors, there exists no apparent correlation between the T_c and $n(e_f)$ values.³ In the κ -phase superconductors as well, the magnitude of the T_c appears to be largely governed by factors associated with their crystal structures.

Figure 12. (a) Hole and (b) electron Fermi surfaces of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br.

STRAIN INDEX AND LATTICE SOFTNESS

The κ -phase superconductors are made from different types of donor molecules and different types of anions. Therefore, it is difficult to single out a geometrical parameter that reflects their lattice softness. Nevertheless, the T_c 's of the three κ -phases κ -(DMET) $_2$ AuBr $_2$, κ -(BEDT-TTF) $_2$ I $_3$ and κ -(MDT-TTF) $_2$ AuI $_2$ may be rationalized on the basis of their C-H...donor and C-H...anion interactions: Since iodine is more polarizable than bromine the C-H...anion contact C-H...I should lead to a softer lattice than does the C-H...anion contact C-H...Br. The latter is consistent with the observation that κ -(BEDT-TTF) $_2$ I $_3$ and κ -(MDT-TTF) $_2$ AuI $_2$ have a higher T_c than does κ -(DMET) $_2$ AuBr $_2$. κ -(BEDT-TTF) $_2$ I $_3$ has short C-H...donor contacts such as C-H...S and C-H...C(sp 2) while such C-H...donor contacts are absent in κ -(MDT-TTF) $_2$ AuI $_2$. Thus κ -(MDT-TTF) $_2$ AuI $_2$ would have a softer lattice and hence a higher T_c than does κ -(BEDT-TTF) $_2$ I $_3$, as observed.

The Cu[N(CN) $_2$]Br anions of κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br and the Cu(NCS) $_2$ anions of κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ are ribbon-like chains. In κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br one ethylene group of each donor primarily has the C-H...anion contacts (C-H...C(sp) and C-H...N while the other ethylene group primarily has the C-H...anion contact C-H...Br (See Figure 13). In κ -(BEDT-TTF) $_2$ Cu(NCS) $_2$ one of the two nonequivalent donors makes primarily the C-H...anion contacts C-H...C(sp) and C-H...N

Figure 13. Schematic diagram of how the ethylene groups make short C-H...anion and C-H...H contacts in κ -(BEDT-TTF) $_2$ Cu[N(CN) $_2$]Br.

while the other donor primarily has the C-H...anion contact C-H...S (See Figure 14). All these C-H...anion contact interactions cannot be softer than the C-H...anion interaction C-H...I present in κ -(BEDT-TTF)₂I₃ and κ -(MDT-TTF)₂AuI₂, but κ -(BEDT-TTF)₂X (X⁻ = Cu[N(CN)₂]Br⁻, Cu(NCS)₂⁻) has a much higher T_c. Therefore the ribbon-like chain anions must provide a phonon spectrum conducive for high-T_c superconductivity.

Table 7 summarizes some important structural properties of the κ -(BEDT-TTF)₂X (X⁻ = Cu[N(CN)₂]Br⁻, Cu(NCS)₂⁻) salts obtained from their crystal structures at ~120K. The number of all donor...donor and donor...anion contacts shorter than r_{vdw} is greater in κ -(BEDT-TTF)₂Cu(NCS)₂ than in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br. This suggests that κ -(BEDT-TTF)₂Cu[N(CN)₂]Br has a softer lattice than does κ -(BEDT-TTF)₂Cu(NCS)₂, in agreement with the observation that κ -(BEDT-TTF)₂Cu[N(CN)₂]Br has a higher T_c. It is desirable to devise an index by which to measure a lattice softness. For an intermolecular contact with the actual and VDW distances r and r_{vdw}, respectively, we define the strain index (SI) as follows:

$$SI = \frac{r_{vdw} - r}{r_{vdw}} \times 100 \quad (5)$$

Among the numerous intermolecular contacts or organic donor salts, the most important contacts associated with the lattice strain and hence the lattice hardness are the shortest ones in various categories of the donor...donor and the donor...anion interactions. For such contacts, $r < r_{vdw}$ and the strain indices are positive. Since a contact with a greater amount of strain should have a larger strain index, a softer crystal lattice would have more

Figure 14. Schematic diagram of how the ethylene groups make short C-H...anion and C-H...H contacts in κ -(BEDT-TTF)₂Cu(NCS)₂.

Table 7. Structural properties of κ -(BEDT-TTF)₂X

Property	X ⁻ = Cu[N(CN) ₂]Br ⁻	X ⁻ = Cu(NCS) ₂ ⁻
Anion shape	Ribbon-like chain	Ribbon-like chain
Intradimer spacing	3.30 Å	3.32 Å
Ethylene group arrangement	Eclipsed	Staggered
Donor leaning direction	Parallel to the anion chain	Perpendicular to the anion chain
Number of intermolecular contacts shorter than r _{vdw}	Fewer	More

Table 8. Strain indices (SI) calculated for the shortest donor...donor and donor...anion contacts of κ -(BEDT-TTF)₂X

Class	Contacts	r _{vdw} (Å)	X ⁻ = Cu[N(CN) ₂]Br ⁻		X ⁻ = Cu(NCS) ₂ ⁻	
			r(Å)	SI	r(Å)	SI
Donor...donor	S...S	3.60	3.45	4.2	3.51	2.5
	C-H...H	2.40	2.15	10	2.18	9.2
	C-H...S	3.00	2.77	7.7	2.64	12
Donor...anion	C-H...Br	3.00	2.98	0.7	-----	-----
	C-H...S	3.00	-----	-----	2.71	9.7
	C-H...C	2.85	2.74	3.9	2.71	4.8
	C-H...N	2.75	2.69	2.2	2.56	7.4

intermolecular contacts with smaller strain indices. Table 8 summarizes the strain indices calculated for κ -(BEDT-TTF)₂X (X⁻ = Cu[N(CN)₂]Br⁻, Cu(NCS)₂⁻) on the basis of their ~120K crystal structures. Except for the donor...donor contacts S...S and C-H...H, all the shortest contacts have smaller strain indices in κ -(BEDT-TTF)₂Cu[N(CN)₂]Br thereby suggesting that the crystal lattice of κ -(BEDT-TTF)₂Cu[N(CN)₂]Br is softer than that of κ -(BEDT-TTF)₂Cu(NCS)₂. This is consistent with the finding that κ -(BEDT-TTF)₂Cu[N(CN)₂]Br has a higher T_c.²⁵

CONCLUDING REMARKS

The electronic properties of the β -phase superconducting salts are very similar, and so are those of the κ -phase superconductors. Therefore, the anion- or pressure-dependence of the T_c 's of these salts is not controlled by their electronic structures but by the softness of their lattices toward the translational and/or librational modes of vibrations (with frequencies of the order of $\sim 8k_B T_c$). Such vibrations are strongly governed by the intermolecular C-H $\cdots$ donor and C-H $\cdots$ anion contact interactions. In general, a softer lattice has a larger electron-phonon coupling constant λ and thus a higher superconducting transition temperature T_c .

As a semi-quantitative measure of the lattice softness, we defined the strain indices of short intermolecular contacts and examined the softness of the κ -phase salts κ -(BEDT-TTF) $_2$ X ($X^- = \text{Cu}[\text{N}(\text{CN})_2]\text{Br}^-$ and $\text{Cu}(\text{NCS})_2^-$ in terms of their softness indices. In general, a softer lattice is expected to possess more short contacts with smaller strain indices.

An isotope substitution such as $\text{H} \rightarrow \text{D}$ in a donor molecule induces two opposing effects on the T_c of its salt, i.e., a T_c -lowering due to a decrease in the Debye temperature and a T_c -raising due to an increase in the lattice softness. When the latter dominates, the T_c increases by an isotope substitution such as $\text{H} \rightarrow \text{D}$.

The C-H $\cdots$ donor and C-H $\cdots$ anion contact interactions are also crucial for the packing of the organic salts and hence for their electronic structures. At the VDW distances, the donor $\cdots$ donor contacts $\text{X}\cdots\text{X}$ ($\text{X} = \text{S}, \text{Se}, \text{Te}$), C-H $\cdots\text{X}$ ($\text{X} = \text{O}, \text{S}, \text{Se}, \text{Te}, \text{C}(\text{sp}^2)$) and C-H $\cdots\text{H}$ as well as the donor $\cdots$ anion contacts C-H $\cdots\text{Y-I-Y}^-$ ($\text{Y} = \text{I}, \text{Br}, \text{Cl}$) are all attractive. The magnitude of these interactions at the VDW distances increase in the order: C-H $\cdots\text{H}$, $\text{S}\cdots\text{S}, \text{Se}\cdots\text{Se} < \text{C-H}\cdots\text{X}$ ($\text{X} = \text{S}, \text{Se}, \text{Te}, \text{C}(\text{sp}^2)$) $< \text{Te}\cdots\text{Te}$, C-H $\cdots\text{Y-I-Y}^-$ ($\text{Y} = \text{I}, \text{Br}, \text{Cl}$) $< \text{C-H}\cdots\text{O}$. The thermal transformations α - to α' -(BEDT-TTF) $_2\text{I}_3$ and δ - to α' -(BEDT-TTF) $_2\text{AuBr}_2$ are both found to be a phase transition which increases the number of the C-H $\cdots$ anion contacts per molecule in the lattice thereby leading to a thermodynamically more stable crystal packing. The BEDO-TTF salts have a unique packing in which the donor molecules make short C-H $\cdots\text{O}$ contacts within each donor stack as well as between adjacent donor stacks. This packing is a consequence of the fact that the C-H $\cdots$ donor interaction C-H $\cdots\text{O}$ is strong compared with the C-H $\cdots$ anion interactions present in the salts.

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