J. Am. Chem. Soc. **1987**, *109*, 90-94

Importance of Intermolecular Hydrogen···Hydrogen and Hydrogen···Anion Contacts for the Lattice Softness, the Electron–Phonon Coupling, and the Superconducting Transition Temperatures, T_c, of Organic Conducting Salts β-(ET)$_2$X (X$^-$ = IBr$_2^-$, AuI$_2^-$, I$_3^-$)

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Abstract: On the basis of the crystal structures of β-(ET)$_2$X (X$^-$ = IBr$_2^-$, AuI$_2^-$, I$_3^-$) determined at low temperature under ambient and applied pressure, we examined the structural factors responsible for the occurrence of the structural modulation in β-(ET)$_2$I$_3$ under ambient pressure, its disappearance under pressure greater than ~0.5 kbar, and its effect on the superconducting transition temperature T_c and the dependence of T_c on anion X$^-$ in β-(ET)$_2$X. ET is an abbreviation for BEDT–TTF, i.e., bis(ethylenedithio)tetrathiafulvalene. The electron–phonon coupling constants, λ, calculated for β-(ET)$_2$X on the basis of the McMillan equation suggest that the lattice softness with respect to translational and/or librational modes of vibration increases in the order β-(ET)$_2$I$_3$ < β-(ET)$_2$IBr$_2$ < β-(ET)$_2$AuI$_2$ < β^*-(ET)$_2$I$_3$, where β^*-(ET)$_2$I$_3$ refers to the β-(ET)$_2$I$_3$ salt under an applied pressure greater than ~0.5 kbar with $T_c \simeq 8$ K. An explanation for this trend in the lattice softness is based on the observation that the principal forces providing the overall lattice cohesiveness of the β-(ET)$_2$X salts are attractive Coulombic interactions of oxidized ET molecule layers with anion X$^-$ layers and that each anion X$^-$ of β-(ET)$_2$X is enclosed in a hydrogen pocket made up of the ethylene groups of ET molecules, which leads to short intermolecular hydrogen···hydrogen (H···H) and hydrogen···anion (H···X$^-$) contacts. Thus, ET molecules are anchored around anions, X$^-$, through short H···X$^-$ contacts, so that the softness of the ET molecules with respect to translational and/or librational modes of vibration can be correlated with the lengths of their shortest H···H and H···X$^-$ contacts. Such short contacts, which depend sensitively upon the nature and size of the anion X$^-$, also govern whether the two ethylene groups of an ET are eclipsed or staggered in conformation, when viewed along the long molecular axis of an ET. For the ions X$^-$ = IBr$_2^-$ and AuI$_2^-$, both of which are smaller than I$_3^-$, all ETs of β-(ET)$_2$X have eclipsed conformations. In β-(ET)$_2$I$_3$ under ambient pressure, however, both eclipsed and staggered ET molecules are found in nearly equal proportions. Under an applied pressure greater than ~0.5 kbar, each eclipsed ET molecule of β-(ET)$_2$I$_3$ undergoes a conformational flipping at one of the two ethylene groups, so that all ETs of β^*-(ET)$_2$I$_3$ have staggered conformations. It is this conformational change that makes the lattice of β^*-(ET)$_2$I$_3$ softer than that of β-(ET)$_2$AuI$_2$ or β-(ET)$_2$I$_3$, resulting in an increase of T_c from ~1.4 to ~8 K. Finally, we discuss the importance of hydrogen···anion interactions in understanding the lower T_c values (1–1.5 K) of the other class of organic superconductors (TMTSF)$_2$X (X$^-$ = ClO$_4^-$, PF$_6^-$) compared to the β-(ET)$_2$X systems and the implications concerning the synthesis of new organic superconductors.

Two-dimensional metals β-(ET)$_2$X (X$^-$ = IBr$_2^-$, AuI$_2^-$, I$_3^-$),[1,2] where ET refers to bis(ethylenedithio)tetrathiafulvalene (BEDT–TTF, C$_{10}$H$_8$S$_8$), are all superconductors under ambient pressure (T_c = 2.8, 5.0, and 1.4 K for X$^-$ = IBr$_2^-$, AuI$_2^-$ and I$_3^-$ respectively).[3-6] For X$^-$ = IBr$_2^-$ and AuI$_2^-$, T_c of β-(ET)$_2$X decreases gradually with increasing applied pressure, P.[3,4,6] When $P \lesssim 0.5$ kbar, T_c of β-(ET)$_2$I$_3$ decreases gradually as well upon increasing applied pressure.[5,6] At $P \simeq 0.5$ kbar, however, T_c of β-(ET)$_2$I$_3$ jumps to ~8 K and decreases as P increases further.[6] We designate the high-T_c state as β^*-(ET)$_2$I$_3$ herein.[9] In the present work, the structural factors responsible for these apparently puzzling behaviors of T_c are examined on the basis of the crystal structures of β-(ET)$_2$X determined at low temperature by single-crystal X-ray and neutron diffraction studies.[7-9] These results show the importance of cation–anion interactions (C—H···X$^-$) and provide insight into new materials synthesis involving organic conductors and superconductors.

Table I. Superconducting Transition Temperature (T_c), Unit Cell Volume (V), Electron–Phonon Coupling Constant (λ), and Conformation of ET in β-(ET)$_2$X

salt	T_c (K)	V (Å^3)	λ	conformation
β-(ET)$_2$IBr$_2$	2.8	798.4 (9)[a]	0.43	eclipsed
β-(ET)$_2$AuI$_2$	5.0	810.4 (5)[b]	0.52	eclipsed
β-(ET)$_2$I$_3$	1.4	819.7 (7)[b]	0.37	eclipsed and staggered
β^*-(ET)$_2$I$_3$	~8	799.1 (9)[c 11]	0.62	staggered

[a] X-ray diffraction at 9 K. Although high thermal motion is observed at one ethylene group at 298 K,[3a] low-temperature data at 125 and 9 K[8] show completely ordered ethylene positions with eclipsed conformations. [b] Neutron diffraction at 20 K carried out at Brookhaven National Laboratory. [c] Neutron diffraction at 4.5 K under pressure of 1.5 kbar carried out at Institute Laue-Langevin, Grenoble, France.

As shown in Table I, the unit cell volume of β-(ET)$_2$X decreases as the length of X$^-$ decreases (I$_3^-$ > AuI$_2^-$ > IBr$_2^-$). The electronic density of states at the Fermi level, $n(e_f)$, of β-(ET)$_2$X is calculated to increase slightly with increasing unit cell volume [$n(e_f)_{\mathrm{IBr}_2^-}$:$n(e_f)_{\mathrm{AuI}_2^-}$:$n(e_f)_{\mathrm{I}_3^-}$ = 1:1.05:1.11].[10] This small increase in $n(e_f)$ with increasing unit cell volume originates from the similarity of the electronic structures of the *isostructural* β-(ET)$_2$X salts[2] and the decrease in the degree of overlap between the ET molecules as the unit cell volume increases.[2a,10] Since the true unit cell volume of β^*-(ET)$_2$I$_3$ (i.e., the high-pressure structural phase of β-(ET)$_2$I$_3$)[9] is expected to be close to that of β-(ET)$_2$AuI$_2$,[11] $n(e_f)$ of β^*-(ET)$_2$I$_3$ is also expected to be close to that of β-(ET)$_2$AuI$_2$, i.e., smaller than that of ambient-pressure β-(ET)$_2$I$_3$. Conse-

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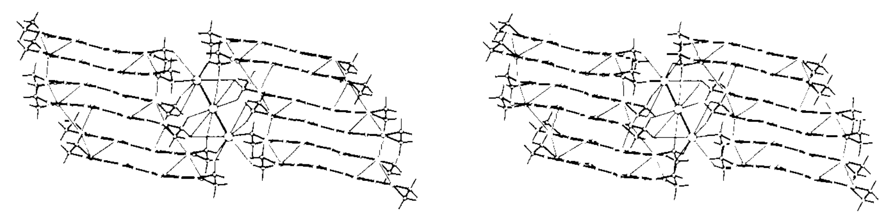
Chart I



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quently, the simple relationship $T_c \propto \exp[-1/n(e_f)]$[12] cannot explain the large difference in the T_c values of β-$(ET)_2X$ [$T_c(IBr_2^-)$:$T_c(AuI_2^-)$:$T_c(I_3^-$, 0.5 kbar) $\simeq$ 1:1.8:2.9] nor the fact that T_c of β-$(ET)_2I_3$ increases nearly sixfold to ~8 K under a pressure of ~0.5 kbar despite the expected decrease in $n(e_f)$. Therefore, we must probe more deeply the factors other than $n(e_f)$ affecting T_c.

Superconductivity and Electron–Phonon Coupling in β-$(ET)_2X$ Salts

What is essential for superconductivity is electron–phonon (i.e., electron–vibration) coupling arising from low-frequency lattice vibrations, which induces an effectively attractive interaction between a pair of electrons (i.e., Copper pair formation).[12a,d] The extent of electron–phonon coupling is measured by the dimensionless electron–phonon coupling constant λ.[13] Given a lattice with Debye temperature, θ_D, that has a phonon spectrum (i.e., phonon band) effective for electron–phonon coupling, T_c is related to λ as follows[13]

$$T_c = (\theta_D/1.45)\exp[-1.04(1+\lambda)/(\lambda - \mu^*(1+\lambda\langle\omega\rangle/\omega_0))] \qquad (1)$$

where $\langle\omega\rangle$ and ω_0 are the average and the maximum frequencies of the phonon band, respectively. In this McMillan equation, which makes the Bardeen–Cooper–Schrieffer theory[12d] of superconductivity applicable to strong-coupled superconductors, the Coulomb pseudopotential, μ^*, and the frequency ratio, $\langle\omega\rangle/\omega_0$, are on the order of 0.1 and 0.5, respectively.[13] By employing the observed T_c values of the β-$(ET)_2X$ salts in eq 1, along with the parameters $\mu^* = 0.1$,[14] $\langle\omega\rangle/\omega_0 = 0.3$,[14] and $\theta_D = 200$ K,[15] we obtain the coupling constants, λ, listed in Table I. Clearly, these λ values increase with T_c for all β-$(ET)_2X$ superconductors. Thus, in order to better understand the range of T_c's in the β-$(ET)_2X$ salts, we must investigate the structural factors affecting λ.

For a lattice with atoms of mass M, λ is expressed by[13]

$$\lambda = n(e_f)\langle I^2\rangle/M\langle\omega^2\rangle \propto 1/\langle\omega^2\rangle \qquad (2)$$

where $\langle I^2\rangle$ is the square of the electron–phonon matrix element averaged over the Fermi surface, and $\langle\omega^2\rangle$ is the square of the phonon frequencies averaged over the phonon band. For transition metals with the body centered cubic structure, the $n(e_f)\langle I^2\rangle$ term is constant within experimental uncertainty despite the fact that $n(e_f)$ and $\langle I^2\rangle$ individually vary by a factor of 10.[13,16] The band electronic structures of the β-$(ET)_2X$ ($X^- = I_3^-$, AuI_2^-, IBr_2^-) salts are identical in essential characteristics, and their $n(e_f)$ values vary only slightly.[2a,10] Therefore it is reasonable to assume that the $n(e_f)\langle I^2\rangle$ term is constant for the β-$(ET)_2X$ salts as well. Then λ depends primarily upon the phonon frequencies, and a large λ results when the lattice has a low-frequency phonon spectrum (i.e., soft phonons, which result from vibrations with shallow potential wells) and hence a small $\langle\omega^2\rangle$ value. Note also that the $M\langle\omega^2\rangle$ term has the dimension of a force constant.[29] For the β-$(ET)_2X$ salts, phonons important for their superconductivity are likely to be translational and/or librational modes.[14,17,27b] Therefore, when the lattice of β-$(ET)_2X$ is soft toward such phonon modes, it will lead to a large value for the electron–phonon coupling constant, λ, which is a measure of how soft the crystal lattice is toward translational and/or librational modes of vibration. The increase in the calculated λ values (from 0.37 to 0.62) of the β-$(ET)_2X$ salts must, therefore, be related to a corresponding increase in their lattice softness. In the following, we will examine the structural features of these salts which are related to the softness of their lattices. From this analysis we will gain considerable insight into some requirements for the synthesis of new conducting salts (vide infra).

Conformation of the ET Molecule and Hydrogen···Anion Interactions in β-$(ET)_2X$ Salts

Shown in **1** is a stereoview of the β-$(ET)_2AuI_2$ structure with the 12 ET molecules that surround one AuI_2^- anion, where the H···I and H···Au contacts less than 3.5 Å, as well as the S···S contacts less than 3.6 Å (the S···S van der Waals radius sum), are connected by thin lines. This H···X^- interaction motif is common to all β-$(ET)_2X$ salts. As illustrated in **1**, each anion X^- of β-$(ET)_2X$ is enclosed in a "hydrogen-pocket" made up of 12 ETs (and thus 12 ethylene groups),[18a] where each terminal

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(7) The crystal structures of β-$(ET)_2I_3$ and β-$(ET)_2IBr_2$ determined by X-ray diffraction at 9 K, and that of β-$(ET)_2I_3$ by neutron diffraction at 20 K, are given in the Supplementary Tables S3 and S4 of ref 8.

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(11) Under ambient pressure, V of β-$(ET)_2I_3$ determined by X-ray diffraction at 9 K is 819.7 (7) Å^3, which is practically the same as that determined by neutron diffraction at 20 K under ambient pressure at Brookhaven National Laboratory.[7] Since V of β-$(ET)_2I_3$ determined at 4.5 K under ambient pressure at Institute Laue-Langevin is 807.6 (16) Å^3, the true V value of β*-$(ET)_2I_3$ is likely to be 810.5 Å^3 (i.e., 799.1 × 819.1/807.6), which is close to that of β-$(ET)_2AuI_2$ under ambient pressure.

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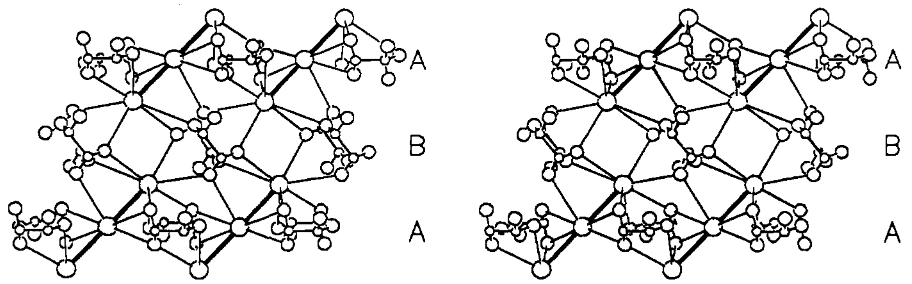
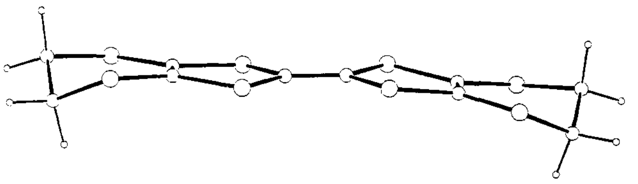
Chart II

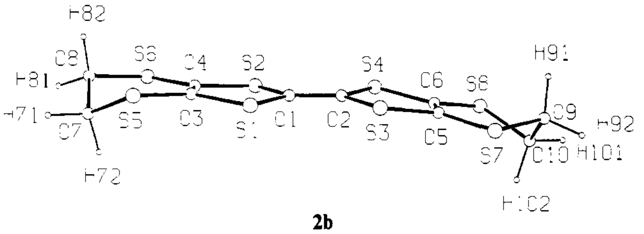


3

halogen of X$^-$ is surrounded by six ethylene groups. This packing of ETs around X$^-$, strongly affected by the length of X$^-$, is crucial for determining whether the resulting ET molecule network becomes one- or two-dimensional in its electronic properties.[18] When viewed along the *long* molecular axis, the two ethylene groups of an ET molecule are either "eclipsed" or "staggered" with respect to each other, as shown in **2a** and and **2b**, respectively. Although the two conformations would be nearly equivalent energetically for an isolated ET molecule, one or the other is favored under the influence of crystal packing forces. In the β-(ET)$_2$IBr$_2$ and β-(ET)$_2$AuI$_2$ salts, all ET molecules are found to have eclipsed conformations.[7,8] In the β-(ET)$_2$I$_3$ salt, however, both eclipsed and staggered ET molecules are found in nearly equal proportions.[8,19] As observed for β^*-(ET)$_2$I$_3$,[9] the most striking structural change that occurs in β-(ET)$_2$I$_3$ under pressure greater than 0.5 kbar is that all ET molecules adopt staggered conformations thereby removing the structural modulation that appears in β-(ET)$_2$I$_3$ below ~200 K under ambient pressure.[19]



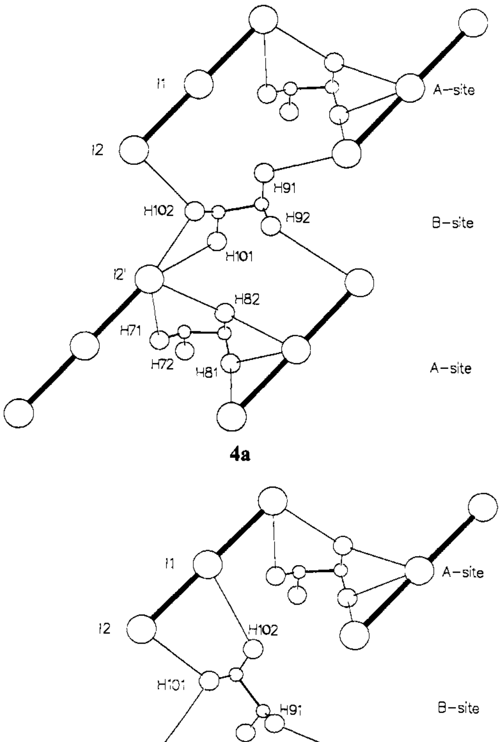
2a



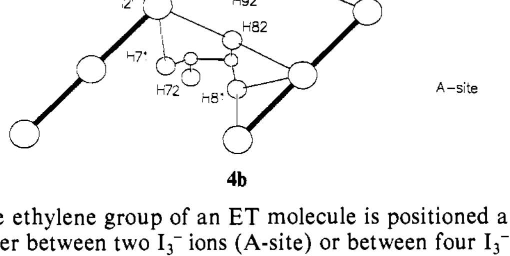
2b

One can evaluate the structural changes in the ET networks of β-(ET)$_2$I$_3$ caused by the applied pressure by examining the intermolecular S···S contact distances and also by comparing the three geometrical parameters R_{ij}, ΔY_{ij}, and φ_{ij} that define the relative arrangement for each pair of nearest-neighbor ET molecules *i* and *j*.[20] Comparison of those structural parameters for β-(ET)$_2$I$_3$ and β^*-(ET)$_2$I$_3$ shows that the relative arrangements of the ET molecules in the ET *network* change very little under pressure.[30] However, unusual changes do occur in the relative conformation of two ethylene groups within each ET, and consequently in the extent of the hydrogen···anion interactions as discussed below.

The stereoview **3** shows the interactions between the terminal ethylene groups of the ET molecules and the I$_3^-$ anions in β^*-(ET)$_2$I$_3$ at 4.5 K and 1.5 kbar (i.e., the high T_c superconducting phase). Note that there are two different ethylene sites. The ethylene groups in the A-sites have short H···I contacts with two I$_3^-$ anions, while those in the B-sites interact with four I$_3^-$ anions through short H···I contacts. A similar arrangement of anions and terminal ethylene groups of ET molecules is found for the other β-(ET)$_2$X (X$^-$ = I$_3^-$, AuI$_2^-$, IBr$_2^-$) salts as well. Shown in **4a** and **4b** are perspective views of the ethylene groups of ET molecules located below a layer of I$_3^-$ anions in the ambient-pressure β-(ET)$_2$I$_3$ structure for the cases when ET molecules have eclipsed and staggered conformations, respectively. In **4a** and **4b**, the H···I contacts less than 3.5 Å are joined by thin lines. Note that one ethylene group of an ET molecule is positioned at the site either between two I$_3^-$ ions (A-site) or between four I$_3^-$ ions (B-site).[19b] It is at the B-sites where the nature of the H···I contacts varies depending upon whether an ET molecule has an eclipsed or staggered conformation. As shown in **4a** for the case of eclipsed ETs, one ethylene group at a B-site makes five H···terminal I



4a



4b

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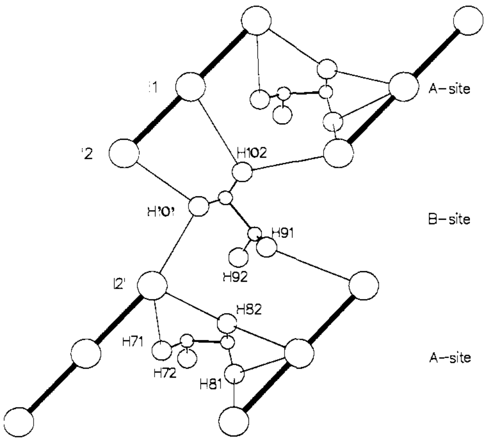
contacts less than 3.5 Å, one of which is extremely short (i.e., 2.84 Å for H102···I2). This short H···I contact is removed when the ethylene group of the B-site undergoes conformational flipping as shown in **4b**, where the ethylene group at the B-site has two fewer H···terminal I contacts less than 3.5 Å, with the shortest one now being 2.99 Å (H101···I2). In **4b**, however, there arises one fairly short H···H contact (i.e., 2.15 Å for H82···H92), which is absent in **4a**. Therefore, an extremely short (energetically unfavorable)[21,22] intermolecular contact (H···I or H···H) exists in β-$(ET)_2I_3$ for either the eclipsed or the staggered conformation. The structural modulation of β-$(ET)_2I_3$ which occurs below ~200 K is an effective way to reduce the extent of such unfavorable intermolecular contacts. In β^*-$(ET)_2I_3$[9] the arrangement of ethylene groups around I_3^- ions is similar to that shown in **4b**, except that the ethylene group at the B-site *slips* slightly under the applied pressure so as to make the shortest H···H contact longer (i.e., 2.26 Å for H82···H92). As a consequence, the ethylene group of the B-site makes four H···terminal I contacts less than 3.5 Å as shown in **4c**, the shortest being 3.01 Å (H101···I2).[9] When β-$(ET)_2I_3$ transforms to become the high-temperature superconducting phase (i.e., β^*-$(ET)_2I_3$, $T_c \simeq 8$ K), the ethylene group of an eclipsed ET molecule at each B-site must undergo conformational flipping. For this conformational flipping to occur, the forces exerted on the ethylene group via the H···I contacts should be anisotropic, which may be related to the observation that β^*-$(ET)_2I_3$ cannot be obtained by purely hydrostatic pressure but only by pressure with a substantial shear component.[6,9]



4c

For β-$(ET)_2IBr_2$ and β-$(ET)_2AuI_2$ as well,[7,8] the arrangements of the ethylene groups of eclipsed and staggered (hypothetical) ETs around each anion X^- are similar to those shown in **4a** and **4b**, respectively, for β-$(ET)_2I_3$. Summarized in Table II are the shortest H···H and hydrogen···terminal halogen (H···Y) distances of β-$(ET)_2X$ when ET molecules assume eclipsed and staggered conformations. For $X^- = IBr_2^-$ and AuI_2^-, unfavorably short H···H and H···Y distances would occur if the ET molecules adopted staggered conformations, in agreement with the fact that both β-$(ET)_2IBr_2$ and β-$(ET)_2AuI_2$ have eclipsed ET molecules. What makes β-$(ET)_2I_3$ different from these two salts is that, in contrast to IBr_2^- and AuI_2^-, the I_3^- anion is a bit too large to be comfortably accommodated in the hydrogen pocket comprising 12 ET molecules (see **1**) thereby leading to the structural modulation in β-$(ET)_2I_3$.

Table II. Shortest Intermolecular Hydrogen···Hydrogen (H···H) and Hydrogen···Terminal Halogen (H···Y) Contact Distances (Å) in β-$(ET)_2X$ Which Occur When Each ET Molecule Adopts an Eclipsed or a Staggered Conformation[a,b]

	eclipsed		staggered	
salt	H82···H101	H102···Y	H82···H92	H101···Y
β-$(ET)_2IBr_2$[d]	2.169	2.887	2.067[c]	2.662[c]
β-$(ET)_2AuI_2$[e]	2.224	2.966	2.006[c]	2.819[c]
β-$(ET)_2I_3$[e]	2.477	2.842	2.152	2.988
β^*-$(ET)_2I_3$[f]			2.261	3.014

[a] The atom numbers refer to those shown in **4** for $X^- = I_3^-$. For $X^- = AuI_2^-$ or IBr_2^-, the positions of the terminal halogen atom (i.e., I in AuI_2^-, Br in IBr_2^-) and the central atom (i.e., Au in AuI_2^-, I in IBr_2^-) correspond respectively to those of I2 and I1 in **4**. [b] The standard deviations of the H···H and H···Y distances determined for β-$(ET)_2AuI_2$ (20 K), β-$(ET)_2I_3$ (20 K), and β^*-$(ET)_2I_3$ (4.5 K, 1.5 kbar) by single-crystal neutron diffraction are all less than 0.01 Å.[8,9a] The same accuracy is expected for the calculated H···H and H···Y distances from the 9 K X-ray diffraction study[7,8] of β-$(ET)_2IBr_2$ according to the standard deviations of the carbon and sulfur atom positions. [c] For β-$(ET)_2IBr_2$ and β-$(ET)_2AuI_2$, the hypothetical staggered conformation of ET was obtained by simply flipping the ethylene group of ET at each B-site. [d] X-ray diffraction at 9 K. The hydrogen positions were calculated with the C–H bond length of 1.09 Å. [e] Neutron diffraction[8] at 20 K carried out at Brookhaven National Laboratory. [f] Neutron diffraction at 4.5 K under 1.5 kbar pressure carried out at Institute Laue-Langevin, Grenoble, France.

The Relationship between Structures and Lattice Softness in β-$(ET)_2X$

Let us now discuss how the structural features associated with the H···H and H···Y contacts of the β-$(ET)_2X$ salts are related to the softness of their lattices and, therefore, to their electron–phonon coupling constants, λ, and the occurrence of superconductivity. There are many short intermolecular S···S contacts less than the van der Waals radii sum of 3.6 Å in β-$(ET)_2X$, but all these S···S interactions are weakly antibonding (essentially nonbonding) since the overlap populations calculated for those S···S contacts are all slightly negative numbers in the second decimal place.[23,24] From the viewpoint of covalent bonding, therefore, ET molecules in the ET networks are not strongly bound at all. Therefore, the principal forces providing overall lattice cohesiveness must be attractive Coulombic interactions of oxidized ET-molecule layers with anion X^- layers. This leads to a number of short hydrogen···anion (C—H···X^-) contacts so that ET molecules are *anchored around* anions X^- as if effectively weak "hydrogen

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(21) The H···H contact of 2.15 Å and the H···I contact of 2.84 Å are repulsive according to the empirical potential functions[22] for H···H and H···O contacts.

(22) Coppens, P. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York, 1983; Vol. 1, p 333.

(23) Given $p(e)$ as the crystal orbital overlap population[24] of an S···S contact at a given energy, e, the overall overlap population, $\langle p \rangle$, of that contact is given by $\langle p \rangle = \int_{-\infty}^{e_f} p(e)\, de$, where e_f is the Fermi level. The $\langle p \rangle$ values calculated for the short S···S contacts less than 3.6 Å are all slightly negative as listed in Table S3. Therefore, it would be incorrect to suppose covalent bonding character in such S···S contacts and hence electron density accumulation in the regions between the sulfur atoms that define such contacts. Superconductivity is largely governed by those electrons at the Fermi level.[12a] Thus we also calculated the crystal orbital overlap populations at the Fermi level, $p(e_f)$, for the short S···S contacts, all of which are found to be very slightly negative or zero as listed in Table S3. Small values of the overlap populations $\langle p \rangle$ for the short intermolecular S···S contacts should not be considered to mean that such interactions are not important, nor that the HOMO interaction energies $\beta_{ij} = \langle \psi_i | H^{\text{eff}} | \psi_j \rangle$, where ψ_i and ψ_j are respectively the HOMOs of nearest-neighbor ET molecules i and j,[20] are negligible. The HOMO interaction energies β_{ij} indicate how strongly the HOMOs ψ_i and ψ_j overlap. The characteristics of the highest occupied bands of the β-$(ET)_2X$ salts, and hence their electrical properties, are well explained in terms of β_{ij} values.[20]. On the other hand, the overlap population $\langle p \rangle$ of a short intermolecular S···S contact describes the net result of summing all the bonding and antibonding interactions (associated with the contact) present in all the occupied band levels.

(24) For applications of overlap populations in describing the electronic structures of solids, see: (a) Hughbanks, T.; Hoffmann, R. *J. Am. Chem. Soc.* **1983**, *105*, 3528. (b) Kertesz, M.; Hoffmann, R. *J. Am. Chem. Soc.* **1984**, *106*, 3453.

(25) (a) Bechgard, K. *Mol. Cryst. Liq. Cryst.* **1982**, *79*, 1. (b) Jērome, D.; Schultz, H. J. *Adv. Phys.* **1982**, *31*, 299. (c) Williams, J. M.; Beno, M. A.; Wang, H. H.; Leung, P. C. W.; Emge, T. J.; Geiser, U.; Carlson, K. D. *Acc. Chem. Res.* **1985**, *18*, 261. (d) Whangbo, M.-H.; Williams, J. M.; Dorfman, J. R. *J. Am. Chem. Soc.* **1983**, *105*, 645.

(26) Weger, M.; Kaveh, M.; Gutfreund, H. *Solid State Commun.* **1981**, *37*, 421.

(27) (a) Mitrovic, B.; Leavens, C. B.; Carbotte, J. P. *Phys. Rev. B: Condens. Matter* **1980**, *21*, 5048. (b) Hawley, M. E.; Gray, K. E.; Terris, B. D.; Wang, H. H.; Carlson, K. D.; Williams, J. M. *Phys. Rev. Lett.* **1986**, *57*, 629.

(28) Ashcroft, N. W.; Mermin, N. D. *Solid State Physics*; Holt, Rinehart and Winston: Saunders College, 1976; p 458.

bonding" exists in the C—H$\cdots$X$^-$ contacts. Thus, how "soft" ET molecules are with respect to translational and/or librational modes of vibration depends on, and may be correlated with, the lengths of their shortest H$\cdots$H and H$\cdots$Y contacts, which indirectly represent the strengths of their interactions.

Table II shows that, for the experimentally observed structures of β-(ET)$_2$X, the H$\cdots$H and H$\cdots$Y distances increase in the order β-(ET)$_2$IBr$_2$ < β-(ET)$_2$AuI$_2$ < β^*-(ET)$_2$I$_3$. Thus the lattice of β-(ET)$_2$IBr$_2$ would be stiffer than that of β-(ET)$_2$AuI$_2$ or β^*-(ET)$_2$I$_3$, which is consistent with the fact that λ of β-(ET)$_2$IBr$_2$ is smaller than that of either β-(ET)$_2$AuI$_2$ or β^*-(ET)$_2$I$_3$. Under ambient pressure, β-(ET)$_2$I$_3$ has unfavorably short H$\cdots$H and H$\cdots$I contacts, the extent of which is somewhat reduced upon introducing structural modulation.[19] In other words, the structural modulation in β-(ET)$_2$I$_3$ reflects the presence of structural strain, i.e., lattice stiffness, which would be primarily responsible for its λ value smaller than that of β-(ET)$_2$IBr$_2$. The shortest H$\cdots$H and H$\cdots$I contacts are longer in β^*-(ET)$_2$I$_3$ than in β-(ET)$_2$AuI$_2$. This difference would be greater if the systematic errors in measuring unit cell volumes on three different instruments could be eliminated, in which case the true unit cell volume of β^*-(ET)$_2$I$_3$ would not be smaller but almost equal to that of β-(ET)$_2$AuI$_2$.[11] Thus, the lattice of β^*-(ET)$_2$I$_3$ is softer than that of β-(ET)$_2$AuI$_2$, which explains why the former has a greater λ and a higher T_c. Surprisingly, it is the adoption of a staggered conformation by each ET molecule under a pressure greater than 0.5 kbar that makes the lattice of β^*-(ET)$_2$I$_3$ particularly soft. A further increase in applied pressure beyond ~0.5 kbar in β^*-(ET)$_2$I$_3$ would make its lattice stiffer, which makes its T_c lower than 8 K as experimentally observed.[6]

Conclusions

The packing of ET molecules, and thus the formation of hydrogen-pockets around anions X$^-$, plays a crucial role in determining the physical properties of the β-(ET)$_2$X (X$^-$ = IBr$_2^-$, AuI$_2^-$, I$_3^-$) salts. Whether the ET molecules adopt eclipsed or staggered conformations is determined by the hydrogen$\cdots$hydrogen and hydrogen$\cdots$anion interactions associated with these hydrogen-pockets. These interactions also determine the softeness of the β-(ET)$_2$X lattice with respect to *the translational and/or librational modes of vibration.* [It should be emphasized that the softness (or stiffness) of the lattice we refer to in connection with the electron–phonon coupling constant, λ, is *totally different* from the "mechanical" softness (or stiffness) of the lattice often measured by its Debye temperature θ_D.[28] According to eq 1,[13] a mechanically stiff lattice (i.e., a lattice with a large θ_D value) will lead to a high T_c value, as has been experimentally observed.[12b]] The occurrence of the structural modulation[19] in β-(ET)$_2$I$_3$ under ambient pressure, its disappearance under $P \gtrsim 0.5$ kbar[9b] and its effect on T_c, and the dependence of T_c on anion X$^-$ in β-(ET)$_2$X are all explicable in terms of the hydrogen$\cdots$hydrogen and hydrogen$\cdots$anion interactions associated with the hydrogen-pockets created by the ET molecule ethylene groups.

Such H$\cdots$anion interactions[31] are also important for the other class of organic superconductors, (TMTSF)$_2$X (X$^-$ = ClO$_4^-$, PF$_6^-$),[25] which are estimated to have smaller λ values ($\lambda \simeq$ 0.15–0.20)[14,26] than do β-(ET)$_2$X (X$^-$ = IBr$_2^-$, AuI$_2^-$, I$_3^-$). A potential energy well describing an intermolecular contact A$\cdots$B would be shallow (i.e., the A$\cdots$B interaction is soft), when the polarizabilities of A and B are large. Thus, the Se$\cdots$Se interactions of (TMTSF)$_2$X would be softer than the S$\cdots$S interactions of β-(ET)$_2$X, while the H$\cdots$O and H$\cdots$F interactions found in the former would be harder than the H$\cdots$I and H$\cdots$Br interactions found in β-(ET)$_2$X (X$^-$ = halogen containing anion). Consequently, the hydrogen$\cdots$anion interactions are largely responsible for making the lattice of (TMTSF)$_2$X harder than that of β-(ET)$_2$X. This "hardness" may partially explain the lower T_c's (~1–1.5 K) of the (TMTSF)$_2$X materials compared to the T_c's (~1.5–8 K) of the β-(ET)$_2$X salts. In general, the softness of hydrogen$\cdots$anion interactions, and hence that of a lattice associated with such interactions, is expected to increase in the following order: H$\cdots$F, H$\cdots$O, < H$\cdots$Cl < H$\cdots$Br < H$\cdots$I. Consequently, weakly hydrogen bonding anions containing I and Br may be anions of choice in the future synthesis of new organic superconductors based on donor molecule and anion combinations.

Finally, a soft phonon spectrum results from a soft lattice. The transition temperature, T_c, and the energy gap, Δ,[12b] of a superconductor are most sensitively affected by phonon frequencies on the order of $8k_BT_c$ and $4k_BT_c$, respectively,[27] where k_B is the Boltzmann constant. Thus, it would be valuable to search for and characterize those phonon modes of β-(ET)$_2$X having frequencies less than 50 cm^{-1}.

Acknowledgment. Work at Argonne National Laboratory is performed under the auspices of the Office of Basic Energy Sciences, Division of Materials Sciences, of the U.S. Department of Energy under Contract W-31-109-ENG-38. Research at North Carolina State University was supported in part by DOE, Office of Basic Sciences, Division of Materials Sciences, under Grant DE-FG05-86-ER45259. M.-H.W. is a participant in the Faculty Research Program, sponsored by Argonne Division of Education Programs with funding provided by DOE.

Supplementary Material Available: Table S1 listing R_{ij}, ΔY_{ij}, and ϕ_{ij} values calculated for the six nearest-neighbor ET pairs (i–j) in the ET molecule layers of β-(ET)$_2$AuI$_2$ (20 K, neutron data), β-(ET)$_2$I$_3$ (20 K, neutron data), and β^*-(ET)$_2$I$_3$ (4.5 K, 1.5 kbar, neutron data); Table S2 listing short intermolecular S$\cdots$S contact distances in β-(ET)$_2$IBr$_2$ (9 K, X-ray data), β-(ET)$_2$AuI$_2$ (20 K, neutron data), β-(ET)$_2$I$_3$ (20 K, neutron data), and β^*-(ET)$_2$I$_3$ (4.5 K, 1.5 kbar, neutron data); Table S3 listing $p(e_f)$ and $\langle p \rangle$ values calculated for the short S$\cdots$S contacts less than 3.6 Å of β-(ET)$_2$IBr$_2$ (9 K, X-ray data) (3 pages). Ordering information is given on any current masthead page.

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(30) The R_{ij}, ΔY_{ij}, and ϕ_{ij} valus as well as the S$\cdots$S contact distances of β-(ET)$_2$X are listed in the Supplementary Tables S1 and S2.

(31) Beno, M. A.; Blackman, G. S.; Leung, P. C. W.; Williams, J. M. *Solid State Commun.* **1983**, *48*, 99.