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Electron-Transfer Boat-Vibration Mechanism for Superconductivity in Organic Molecules Based on BEDT-TTF

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Abstract: The highest T_c organic superconductors all involve the organic molecule bis(ethylenedithio)tetrathiafulvalene (denoted as BEDT-TTF or ET) coupled with an appropriate acceptor. This leads to ET, ET^+, or $(ET)_2^+$ species in the crystal. Using *ab initio* Hartree–Fock calculations (6-31G** basis set), we show that ET deforms to a boat structure with an energy 28 meV (0.65 kcal/mol) lower than that of planar ET (D_2 symmetry). On the other hand, ET^+ is planar. Thus, conduction in this system leads to a coupling between charge transfer and the boat deformation vibrational modes at 20 cm^{-1} (ET) and 28 cm^{-1} (ET^+). We suggest that this electron–phonon coupling is responsible for the superconductivity and predict the isotope shifts (δT_c) for experimental tests of the electron-transfer boat-vibration (ET-BV) mechanism. The low frequency of this boat mode and its coupling to various lattice modes could explain the sensitivity of T_c to defects, impurities, and pressure. We suggest that new higher temperature organic donors can be sought by finding modifications that change the frequency and stability of this boat distortion mode.

1. Introduction

Since the discovery of organic superconductors in 1980, the T_c of these materials has improved from 1.4 K[1] to 12.8 K.[2] The best organic superconductors all involve the donor molecule bis(ethylenedithio)tetrathiafulvalene (denoted as BEDT-TTF or ET), shown in Figure 1, packed into quasi-one-dimensional and two-dimensional arrays and complexed to appropriate electron acceptors. Although the T_c's for these materials have gradually increased, there is considerable uncertainty concerning the mechanism of superconductivity. The most popular mechanisms involve phonons and BCS (Bardeen–Cooper–Schriefer) theory. Yamaji[3] proposed that the mechanism of superconductivity in organic conductors involves coupling between the highest occupied molecular orbital (HOMO) and totally symmetric intramolecular vibrational modes. However, the pattern of isotope effects does not support this view.[9,11,18,19]

We report here *ab initio* quantum chemical calculations (Hartree–Fock with the 6-31G** basis set) for the structure, vibrational frequencies, and isotope shifts. On the basis of these calculations, we suggest a special role for the low-frequency boat modes (at 19.5 cm^{-1} for ET and 28.1 cm^{-1} for ET^+) in the superconductivity of these organic materials.

2. Results

2.1. Structures. The structure of ET is often discussed in terms of D_2 symmetry, which assumes a planar structure for the central TTF moiety. The crystal structures of the neutral ET crystal are consistent with planarity but show a distinct boatlike distortion.[4] Some deviations from planarity are also suggested in crystals containing electron acceptors, $(ET)_nX_m$.[25] Here the ET molecules often form dimers $(ET_2)^+$ sharing a single positive charge.

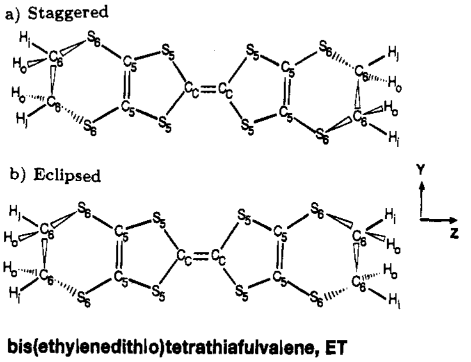

Figure 1. Structure of bis(ethylenedithio)tetrathiafulvalene (denoted as BEDT-TTF or ET): (a) staggered (C_2 symmetry), (b) eclipsed (C_s symmetry).

The terminal six-membered rings are nonplanar in order to avoid eclipsing of the CH_2–CH_2 groups at each end. This nonplanarity leads to two possible conformations:[25] (1) the *staggered* conformation indicated in Figure 1a in which the two C_6–C_6 bonds are pointing in opposite directions; assuming a planar TTF central region, this leads to D_2 symmetry; (2) the *eclipsed* conformation indicated in Figure 1b in which the two C_6–C_6 bonds are parallel; with planar TTF, this leads to C_{2h} symmetry. As discussed below these conformations are essentially degenerate, differing by only 0.000 005 2 hartree = 0.000 14 eV = 0.0032 kcal/mol, and we will consider the higher symmetry staggered case.

To determine the structure and vibrational modes of ET, we carried out *ab initio* Hartree–Fock calculations using the 6-31G** basis set.[5,6] Restricting the symmetry to D_2 leads to an optimized structure with two imaginary frequency vibrational modes (Table 2). We optimized the structure by relaxing the

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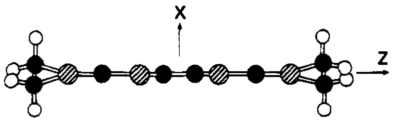
(a) PLANAR ET (D_2 SYMMETRY)



(b) BOAT ET (C_2 SYMMETRY)

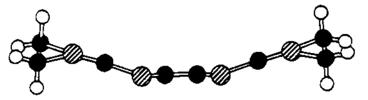


Figure 2. Side view of the optimized structure for ET: (a) D_2 symmetry (planar), (b) C_2 symmetry (boat). Carbons are the solid circles, hydrogens are the open circles, and sulfurs are the hatched circles.

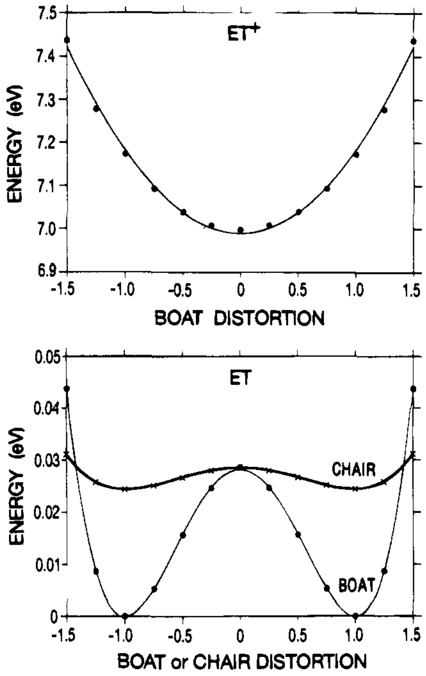


Figure 3. (a, bottom) Energy of the boat structure of ET as a function of the boat distortion. The pathway for the boat is obtained from a three-point fit to the planar, + boat, and − boat structures. Also included is the chair distortion. This does not lead to an absolute minimum (symmetry constraints were used). (b, top) Energy for ET^+ using the boat structures of ET (based on the Koopmans theorem).

symmetry, leading to the boat structure with C_2 symmetry. In this case, all vibration frequencies are positive, indicating a stable (boat) structure. Figure 2 shows the side view of the planar and boat structures.

Figure 3 shows the double well potentials along the reaction coordinate of the boat deformation. The boat structure is calculated to be 28 meV (0.65 kcal/mol) lower than planar ET. In contrast, we find that ET^+ leads to a stable planar D_2 structure (see Figure 3).

Using the HF/6-31G** wave function, we calculated all $3N - 6 = 72$ molecular vibrations for the boat and planar ET structures and for ET^+. Table 2 compares the lowest four vibrational modes, and Figure 4 shows the boat vibrational mode. This mode is the lowest frequency (19.5 cm^{-1} [ET], 28.1 cm^{-1} [ET^+]) mode and also is the mode converting the ET structure to ET^+. As the structure distorts from the boat to planar, the boat and chair deformation modes become imaginary while the other 70 modes ($3N - 8$) of neutral ET change slightly. The biggest change is 7% (21 cm^{-1}) for the 294 cm^{-1} mode (and symmetry D_2). These calculations were used to obtain the vibrationally adiabatic potential curves.

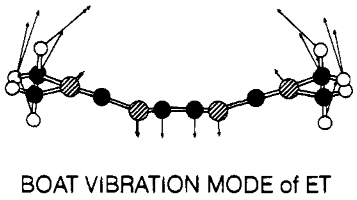


Figure 4. Boat deformation mode of the boat structure ($\omega_b = 19.5$ cm^{-1}).

For the lowest energy boat structure of ET, we optimized the neutral molecules for both the eclipsed and staggered conformations of the terminal $-CH_2-CH_2-$ groups. We found that the eclipsed and staggered conformations have essentially the same energy (with the eclipsed conformation lower by 0.0032 kcal/mol; see Table 1), leading to the same bonds and angles. Hence, even at 10 K both forms of the monomers would be nearly equally populated. In the crystals, packing interactions (donor−donor and donor−anion) may lead to preferences for either conformation. For the detailed structural and vibrational calculations of ET and ET^+ performed herein, we focus on the staggered conformation which leads to C_2 symmetry (the results for the eclipsed conformation should be essentially the same).

2.2. Electron Transfer. The fact that ET is nonplanar whereas ET^+ is planar leads to electron−phonon coupling that we believe is critical to the superconductivity. After the boat ET loses the electron, ET^+ relaxes toward the planar geometry. Simultaneously the planar ET^+ upon accepting the electron distorts to the boat ET conformation. Denoting the adiabatic ionization energy as I_o, the vertical (fixed geometry) ionization from the boat distorted ground state of neutral ET costs an energy of $I_o + 0.177$ eV, while the electron affinity of ET^+ (at its optimum planar geometry) is $I_o - 0.028$ eV. Thus, isolated ET and ET^+ molecules with their optimum structures lead to a hopping barrier of 0.205 eV (ignoring polarization of the environment which might increase the barrier). Figure 5 shows the corresponding Marcus-type electron-transfer diagram, using as the abscissa the simultaneous boat distortion in which the structure of the boat ET changes to planar simultaneously with the structure of planar ET^+ changing to the stable boat structure of ET. This leads to a net barrier of $\sim 0.205/4 = 0.05$ eV and a curvature corresponding to a frequency of $\omega = \{(1/2)[\omega_b^2 + (\omega_b^+)^2]\}^{1/2} = 24.2$ cm^{-1}.

2.3. ET Dimer. In the organic superconductors $(ET)_nX_m$, ET molecules donate electrons to the anion layer. Thus, in ET_2I_3, each I_3 accepts one electron from a pair of ET molecules, forming $(ET)_2^+$ and I_3^-. Ignoring electronic interactions (orbital overlap) and steric interactions, Figure 5 describes the charge transfer between the two ET and ET^+ molecules of the dimer. If the overlap of the HOMOs of these two ET molecules is sufficiently large, the system will lead to a structure (denoted as $ET^{1/2}$) intermediate between ET and ET^+. This requires interaction energies greater than the barrier of 0.05 eV.

The crystals of ET molecules exhibit a wide variety of phases and stackings. Some lead to columnar stacking while others do not. Some lead to quasi-one-dimensional conductors; others lead to two-dimensional conductors. The best superconductors are generally two-dimensional. The S···S networks generally increase the intercolumn interactions. The relative orientation of monomers in these dimers and the dimers with respect to the other dimers will change the magnitude of transfer integrals and determine the rate of the electron transfer. In addition, all

Table 1. Total Energy of the Conformations of ET and ET^+ (hartrees)

conformation[a]	staggered	staggered	staggered	eclipsed
species	boat ET	planar ET	planar ET^+	boat ET
symmetry	C_2	D_2	D_2	C_s
	−3563.360 692	−3563.359 652	−3563.147 578	−3563.360 697

[a] Orientation of C_6-C_6 bonds of ET; see Figure 1.

Table 2. Lowest Four Vibrational Modes (cm^{-1}) of ET and ET^+

mode	boat ET C_2	planar ET D_2	planar ET^+ D_2
first boat	19.5	23.1 i	28.1
first chair	37.8	24.2 i	36.4
second boat	42.6	36.7	42.6
second chair	43.8	41.3	49.0

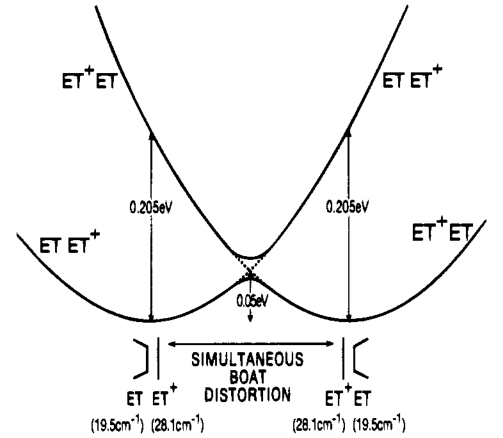


Figure 5. Marcus-type electron-transfer diagram for $(ET)(ET^+) \rightarrow (ET^+)(ET)$. Electron transfer from $(ET)(ET^+)$ to $(ET^+)(ET)$ is coupled to simultaneous boat distorsions for both molecules, $\omega = [(1/2)[\omega_b^2 + (\omega_b^+)^2]]^{1/2} = 24.2\ cm^{-1} = 0.0030$ eV. This strong coupling between conduction electrons and vibration is the basis of the electron-transfer boat-vibration mechanism for superconductivity.

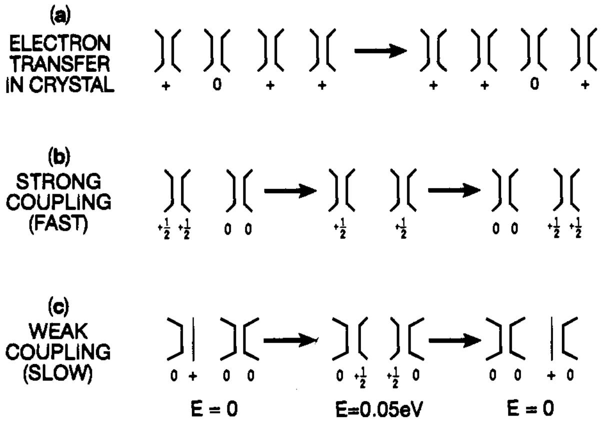


Figure 6. Illustration of electron transfer in $(ET)_2^+$ superconductors: (a) one extra electron, (b) structural changes for fast transfer, (c) structural changes for slow transfer.

Table 3. Frequency Shifts (%) in the Boat Vibrational Mode of Isolated ET and ET^+ Molecules[a]

substitution	ET (19.5 cm^{-1})	ET^+ (28.1 cm^{-1})	ω (24.2 cm^{-1})
D	−4.10	−6.05	−5.41
$^{13}C_6$	−1.03	−1.07	−1.06
$^{13}C_c$	0.00	−0.36	−0.24
$^{13}C_c + {}^{13}C_5$	0.00	−1.42	−0.96
^{34}S	−1.03	−1.07	−1.06
$D + {}^{13}C_6$	−5.64	−6.76	−6.39
$D + {}^{13}C_6 + {}^{34}S$	−6.67	−7.47	−7.20

[a] Also listed are the frequency shifts for the coupled vibrational frequency, $\omega = [(1/2)[\omega_b^2 + (\omega_b^+)^2]]^{1/2} = 24.2\ cm^{-1}$ (see Figure 1 for nomenclature) for various isotopic substitutions.

these structural effects can modify both vibrational and electronic modes which, in turn, may change T_c.

2.4. Electron-Transfer Boat-Vibration Mechanism For Electron−Phonon Coupling. Figure 6a illustrates the electron transfer for a case in which one extra electron is on one of the $(ET)_2$ dimers (making it neutral). In the limit of slow electron transfer, the system might go through the structures in Figure 6b (for strong coupling within a dimer) or Figure 6c (weak coupling within a dimer). Thus, *there is a strong coupling between the boat vibrational distortion and electron transfer.* For a good conductor with rapid electron transfer, the molecules would all remain in conformations close to that for $ET^{1/2}$, but there would be a tendency toward a larger boat distortion as the electron hops onto ET and then a smaller distortion as it hops off. [This discussion implies that the hopping of electrons is directly between the ET dimers; however, electron transfer between the $(ET_2)^+$ and the acceptor (to neutralize each) can also play a role in the conduction.] Thus, we believe that it is this coupling of the conduction electrons to the boat vibrational mode that is involved in the BCS mechanism for these systems. We refer to this as the electron-transfer boat-vibrational (ET-BV) mechanism for superconductivity.

We should emphasize that all vibrational energies are obtained from Hessians involving self-consistent wave functions. Thus, the frequencies include the effect of changing the wave function upon distortion.

Some analyses of the superconductivity of ET molecules have assumed that the molecule is planar and have used a formalism on which the MOs of the equilibrium molecule (assumed planar) are mixed by various vibrations.[3] The origins of the electron−phonon coupling responsible for superconductivity have been sought in terms of how the various vibrations might couple with the MOs.

Our view is quite different. We find that the ET molecule is distorted and that electron−phonon coupling arises from electron transfer between molecules. The phonons that must couple strongly with electron transfer involve boat vibrations. For the distorted (boat) geometry, the boat vibrational mode, the HOMO, and the LUMO are all of A symmetry (for C_2). However, for the full planar geometry (neglecting also the nonplanarity of six-membered rings) these will have B_{1u}, B_{1u}, and A_g symmetry (of D_{2h}), respectively.

3. Isotope Effects

3.1. Shifts in the Boat Frequency. The most direct test of the role of the ET-BV mechanism in superconductivity is the effect of isotope substitutions on the superconducting properties, T_c. Crystal effects such as donor−anion and donor−donor interactions can influence the strength of the electron−phonon coupling, leading to substantial changes in T_c for different ET salts. For an accurate estimate of T_c, one should consider all such effects and carry out calculations for the molecular crystals. However, to provide a means for rapid testing of the ET-BV model, we present estimates of isotopic shifts on T_c. We find cases where the isotopic shifts should be quite large, allowing a direct experimental test of the ET-BV model.

Using the Hessian (second-derivative matrix) of the Hartree−Fock wave functions [6-31G** basis set], we calculated the

Table 4. Predicted Isotopic Shifts (δT_c) Based on the Coupled Boat Phonon Model for Organic Superconductors[i]

	T_c	D	$^{13}C_6$	$^{13}C_c$	$^{13}C_c + ^{13}C_5$	^{34}S	D + $^{13}C_6$	D + $^{13}C_6$ + ^{34}S
$\kappa - (ET)_2Cu[N(CN)_2]Br$	11.8[a]	−0.90	−0.18 (−0.13)	−0.04 (−0.03)[h]	−0.16 (−0.12)	−0.18 (−0.13)[i]	−1.06 (−1.12)	−1.20 (−1.31)
$\kappa - (ET)_2Cu(NCS)_2$	10.4[b]	+0.70	+0.14 (−0.06)[g]	+0.03 (−0.02)[h]	+0.12 (−0.06)	+0.14 (−0.06)[j]	+0.83 (+1.10)	+0.93 (+1.49)
$\kappa - (ET)_2Cu(CN)[N(CN)_2]$	11.2[c]	+1.10	+0.21 (−0.05)	+0.05 (−0.02)	+0.19 (−0.05)	+0.21 (−0.05)	+1.30 (+1.66)	+1.46 (+2.22)
$\kappa - (ET)_2Ag(CN)_2H_2O$	5.0[d]	+1.00	+0.20 (+0.00)	+0.04 (−0.01)	+0.18 (−0.01)	+0.20 (+0.00)	+1.18 (+1.45)	+1.33 (+1.89)
$\beta - (ET)_2I_3$	1.15[e]	+0.28	+0.05 (+0.00)	+0.01 (+0.00)	+0.05 (0.00)	+0.05 (+0.00)	+0.33 (+0.40)	+0.37 (+0.52)
$\kappa - (ET)_2Cu[N(CN)_2]Cl$	12.8[f]	1.0[f]	+0.20 (−0.07)	+0.04 (−0.03)	+0.18 (−0.07)	+0.20 (−0.07)	+1.18 (+1.54)	+1.33 (+2.08)

[a] Reference 7. [b] Reference 8. [c] Reference 23. [d] Reference 15. [e] Reference 16. [f] Reference 14. The isotopic shifts were observed in the range 0.5−1.5 K for different samples. We used 1.0 K. [g] For substitutions of $^{12}C_6$ with $^{13}C_6$ in $\kappa - (ET)_2Cu(NCS)_2$, T_c was found "just between those of H and D salts". See ref 17. [i] $\delta T_c = -0.08 \pm 0.07$ K was observed with ^{34}S substitutions (see ref 12). [j] No isotope effect (within standard deviations) was observed with ^{34}S substitutions (see ref 12). [h] No isotope effect (within standard deviations $\delta T_c = 0.1$ K) was observed with $^{13}C_c$ substitutions (see refs 9 and 11). [i] See Figure 1 for nomenclature. All results are in kelvin. The experimental deuterium isotopic shift (δT_D) was used with $\delta\omega_D$ in eq 5a to obtain the values listed while eq 5b was used for the values in parentheses.

isotopic shifts for the boat modes of ET and ET$^+$. Table 3 shows the frequency shifts for a number of isotope substitutions. These results will be used to test of the role of the ET-BV mechanism in the superconductivity.

In all cases, we find that an increase in the isotopic mass decreases the frequency of the boat mode. We obtain the largest frequency shifts for H to D substitutions $\{(\delta\omega_b/\omega_b) = -0.041[-0.060]\}$ for ET [ET$^+$], smaller shifts for $^{12}C_6$ to $^{13}C_6$ $\{(\delta\omega_b/\omega_b) = 0.010[-0.011]\}$ and ^{32}S to ^{34}S $\{(\delta\omega_b/\omega_b) = -0.010[-0.011]\}$, and very small shifts for $^{12}C_c$ to $^{13}C_c$ $\{(\delta\omega_b/\omega_b) = -0.000[-0.004]\}$ and $^{12}C_5$ to $^{13}C_5$ $\{(\delta\omega_b/\omega_b) = -0.000[-0.014]\}$. Table 4 shows that multiple isotopic substitutions give almost additive frequency shifts for the "boat mode". These trends that H, C_6, and S_6 atoms on the outer rings of ET provide the biggest shifts in ω_b are consistent with the character of the boat mode in Figure 4.

3.2. Effect of $\delta\omega$ on δT_c. Assuming that the electron−phonon matrix elements are dominated by the boat phonon mode and using the weak coupling formulation of BCS theory leads to[24] eq 1for T_c, where ω is the frequency for the coupled boat

$$kT_c = 1.14\hbar\omega \exp\left[-\frac{1}{(N_0V)}\right] = 1.14\hbar\omega \exp\left[-\frac{1}{\lambda}\right] \quad (1)$$

phonon mode ($\omega = 24.2$ cm^{-1}), N_0 is the density of states of the electrons at the Fermi surface, and V is the attractive interaction between electrons. However, using $\omega = 24.2$ cm^{-1} and $T_c = 10$ K in eq 1 gives $\lambda = 0.73$. Thus, we use the Kresin strong-coupling formulation[22] shown in eq 2.

$$T_c = 0.25\langle\omega^2\rangle^{1/2}[\exp(2/\lambda) - 1.0]^{-1/2} \quad (2)$$

Assuming that an isotope substitution which changes ω by $\delta\omega$ also changes λ by $\delta\lambda$, eq 2 leads to

$$\frac{\delta T_c}{T_c} = \frac{\delta\omega}{\omega} + \frac{\delta\lambda}{\lambda^2}\left(1 + 16\frac{T_c^2}{\omega^2}\right) \quad (3)$$

The magnitude of λ should be related to the boat frequency ω and to the energy barrier (0.05 eV) which in turn depends on ω. In the crystal these quantities also depend on the packing of the other molecules (particularly the dimer pairing) and on the pressure.

In order to estimate the effect of the isotope substitutions on λ, we write

$$\lambda(\omega) = \lambda_0 + \lambda_1\delta\omega + \lambda_2(\delta\omega)^2 + \ldots$$

This will likely lead to a linear dependence

$$\delta\lambda = \lambda_1\delta\omega \quad (4a)$$

but because of the double well nature of the boat mode, the net dependence might be

$$\delta\lambda = \lambda_2(\delta\omega)^2 \quad (4b)$$

We will estimate λ_1 or λ_2 by using the experimental δT_c for H to D substitutions. Using λ_1 or λ_2 with the predicted ω allows the prediction of δT_c for other isotopic substitutions.

Combining terms leads to

$$\delta T_c = (\delta T_D/\delta\omega_D)\delta\omega \quad (5a)$$

and

$$\delta T_c = \frac{T_c}{\omega}\delta\omega + \left\{-\frac{T_c}{\omega(\delta\omega_D)} + \frac{\delta T_D}{(\delta\omega_D)^2}\right\}(\delta\omega)^2 \quad (5b)$$

for approximations 4a and 4b, respectively. Here δT_D and $\delta\omega_D$ are the shifts for H to D substitution.

3.3. Observed δT_c for H to D Substitutions. Recent isotopic shift experiments show the following results for replacing the hydrogen atoms of ET with deuterium: (i) $\kappa - (ET)_2Cu[N(CN)_2]Br$ ($T_c = 11.8$ K) leads to a normal isotope effect of $\delta T_c = -0.09$ K.[7] In addition, Andres et al.[13] found a "normal" isotope shift for the "high T_c" phase of $\beta^* - (ET)_2I_3$- ($T_c = 8$ K); however, they considered the significance uncertain because of the sensitivity of T_c to pressure. (ii) On the other hand the systems (1) $\kappa - (ET)_2Cu(NCS)_2$ ($T_c = 10.4$ K), (2) $\kappa - (ET)_2Cu[N(CN)_2]Cl$ ($T_c = 12.8$ K), (3) $\kappa - (ET)_2Cu(CN)[N(CN)_2]$ ($T_c = 11.2$ K), (4) $\kappa - (ET)_2Ag(CN)_2H_2O$ ($T_c = 5.0$ K), and (5) $\beta - (ET)_2I_3$ ($T_c = 1.15$ K) all showed inverse isotope effects, with $\delta T_c \approx 0.7$, 0.5−1.5, 1.1, 1.0, and 0.28 K, respectively.[8,14−16,23]

3.4. Predicted δT_c for Other Isotopic Substitutions. Using the experimental δT_c (denoted δT_D) and the calculated $\delta\omega$ (denoted $\delta\omega_D$) from Table 3, we estimated the parameters in eq 5. This leads to the predicted isotopic effects in Table 4. These results are generally in agreement with experiment. (i) In $\kappa - (ET)_2Cu(NCS)_2$, the substitution $^{12}C_6$ to $^{13}C_6$ leads to a T_c "just between those of H and D salts".[17] This inverse effect is expected from eq 5 (see Table 4). (ii) Carlson et al.[9] checked the controversial "giant isotope effect" results of Merzhanov et

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al.[10] and found no isotopic shifts (within the standard deviations $\delta T_c = 0.1$ K) for the substitutions of (1) $^{12}C_c$ with $^{13}C_c$ in $\beta^* - (ET)_2I_3$, $\kappa - (ET)_2Cu(NCS)_2$, and $\kappa - (ET)_2Cu[N(CN)_2]Br$[9,11] and (2) all $^{12}C_c$ and $^{12}C_5$ with ^{13}C in $\beta^* - (ET)_2I_3$.[18,19] Indeed as shown in Table 4, we find very small shifts (δT_c less than 0.06 K) for all C_c substitutions with ^{13}C. In addition, we find δT_c less than 0.20 K for simultaneous $^{12}C_c$ and $^{12}C_5$ substitutions with ^{13}C. (iii) Carlson et al.[9] found a very small isotopic shift, $\delta T_c = -0.08 \pm 0.07$ K, upon substituting all ^{32}S with ^{34}S in $\kappa - (ET)_2Cu[N(CN)_2]Br$. As shown in Table 4 we estimate that $\delta T_c = -0.18$ to -0.13 K in reasonable agreement. In $\kappa - (ET)_2Cu(NCS)_2$ "less detailed" studies[12] indicate no isotope effect whereas we find +0.14 to −0.06 K.

From Table 4 we see that the largest isotope shifts are for H, C_6, and S_6. Indeed (a) simultaneously substituting for both H and C_6 should increase δT_c by ~18−57% over that for H alone, while (b) simultaneously substituting H, C, and S_6 leads to an increase in δT_c of ~33−113% over that for H only. Thus, multiple isotope substitution experiments should provide a clear-cut test of the ET-BV mechanism.

4. Summary

The stable structure of ET is boatlike whereas ET^+ is planar. The energy of boat distortion is 28 meV (for ET) and the boat frequency is 19.5 cm^{-1}. We propose that the mechanism for superconductivity of these materials involves the coupling of charge transfer to the boat deformation mode. This boat mechanism can be tested by measuring the isotopic shifts for specific simultaneous isotopic substitutions.

This ET-BV mechanism provides some guidance for modifying ET to obtain new higher T_c materials. Thus, we require donor molecules that distort into the boat form for the neutral form, but change significantly (becoming planar) upon ionization. We expect T_c to be sensitive to the boat frequency ω, and to the magnitude of the distortion energy. On the basis of these ideas, one can postulate various modifications of ET that would increase T_c. Consequently, we are carrying out quantum mechanical calculations for some such cases.

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