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$^{13}C{=}^{13}C$ Isotope Effect for T_c and Consequences Regarding the Superconducting Pairing Mechanism in κ-$(ET)_2X$ Superconductors

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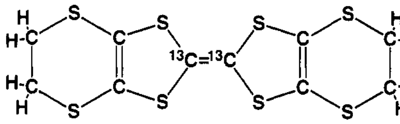
Remarkable advances have been achieved recently in the rational design, synthesis, and physical characterization of layered organic superconductors composed of organic electron-donor molecules and inorganic anions.[1] However, the question of the superconducting electron-pairing mechanism remains unresolved. In ordinary superconductors, electrons or holes are paired via phonon exchange, and this mechanism can be probed by use of the isotope effect, i.e., the shift in T_c on isotopic substitution, the magnitude of which is predicted by the BCS theory.[2] Studies of the isotope effect for ET-based organic superconductors [ET is bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF)] have focused primarily on deuterium or ^{13}C substitutions in the terminal $-CH_2$ groups with largely inconsistent results.[3,4] However, a recent study by Merzhanov et al.[5] concluded that ^{13}C substitution in the electronically active *central* double-bonded carbon atoms (C=C) of the TTF moiety of ET leads to an abnormally large isotope effect (~7.5%) in β^*-$(ET)_2I_3$ [also denoted as β_H-$(ET)_2I_3$], which has $T_c \approx 8$ K and is a crystallographically ordered form of β-$(ET)_2I_3$ achieved by application of pressure.[1] This result would imply that holes (layered organic superconductors are predominantly hole conductors) are paired through exchange of relatively high-energy phonons associated with *intra*molecular vibrational modes,[6,7] that conventional BCS theory does not apply to this or similar systems, and that new theoretical developments are required to explain the pairing mechanism.[5-7]

In this communication, we report the *first* determination of the isotope effect for ^{13}C substitution in the central C=C atoms of ET in the organic superconductors κ-$(ET)_2Cu[N(CN)_2]Br$[8] ($T_c = 11.6 \pm 0.05$ K, diamagnetic onset) and κ-$(ET)_2Cu(NCS)_2$[9] ($T_c = 9.8 \pm 0.3$ K,[10] diamagnetic onset). These materials, presently the highest-T_c electron-donor-based, ambient-pressure organic superconductors, are much better materials for tests of the isotope effect for ET-based superconductors than pressurized β-$(ET)_2I_3$ because T_c is easily reproducible from sample-to-sample at *ambient pressure*, whereas β-$(ET)_2I_3$ can have a range of T_c's from 1.5 to 8.0 K depending on sample quality, thermal treatment, pressure, and a variety of mechanical stresses.[1,11] Our results show that the central C=C stretching motion is *not a dominant exchange mechanism* over conventional BCS-type phonon exchange for superconducting pairing in κ-$(ET)_2Cu[N(CN)_2]Br$ and κ-$(ET)_2Cu(NCS)_2$. Although these findings apply specifically to the κ-phase salts[12] of this study, we argue that these results apply generally to other ET phases (α, β, θ, and other phase types[1]) as well.

The ^{13}C substitution in the central C=C atoms of ET is illustrated in the following diagram:



The stretching motion of the central C=C atoms and the outer C=C atoms of the TTF moiety of ET participate about equally

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in two totally symmetric vibrational modes (a_g species) at energies near 1500 cm^{-1} and contribute about 90% of the total vibrational potential energy distribution in each mode.[13] The importance of these molecular vibrations is that the a modes couple with the valence-level holes constituting the conduction band of the organic charge-transfer salts,[14] and among the strongest coupled vibronic modes is one of the two a species of the C=C stretching motion.[13] Because the central C=C atoms provide the largest carbon-atom contributions to the valence-level orbitals,[15] a significant isotope effect upon ^{13}C substitution in the central C=C atoms implies that hole pairing involves exchange of an optical phonon associated with the vibration of the C=C atoms rather than exchange of lower-energy acoustic phonons common to BCS theory.

If one *assumes* that the conventional BCS isotope shift is applicable to coupling involving optical phonons and that these phonons are dominated by the C=C stretching motion, then $T_c \propto M^{-\alpha}$, where M is the mass of the atoms involved and $\alpha \approx {}^1/_2$, so that the change in T_c on ^{13}C substitution is $T_c(^{13}C)/T_c(^{12}C) = (^{13}/_{12})^{-1/2}$. This amounts to a decrease in T_c of ~4% (~0.4 K). Alternatively, because T_c is proportional to an average vibrational frequency in the conventional BCS isotope effect, we calculate a shift of 1.9% (0.2 K) in T_c from the ratio of the observed isotopic shifts [^{12}C (^{13}C)] in the 1550 (1521) cm^{-1} and 1493 (1465) cm^{-1} vibrational modes (see supplementary material). The 7.5% decrease in T_c reported[5] for β^*-$(ET)_2I_3$ on ^{13}C substitution in the central C=C atoms clearly suggests the involvement of the C=C stretching motion, but it also demonstrates the inapplicability of formulas for the conventional BCS isotope effect. Such simple prescriptions *only* apply for homoatomic systems with weak coupling due to acoustic phonons. They must be modified for strong electron-phonon coupling, for specific optical phonons, and for strong Coulomb interactions.

Both ^{13}C-substituted (for the central C=C atoms) and unlabeled ET were synthesized according to the methods described by Larsen and Lenoir[16] and Rae.[17] In the ^{13}C-labeled ET product, the ratio ET(^{13}C=^{13}C, M = 386):ET(^{13}C=^{12}C, M = 385):ET(^{12}C=^{12}C, M = 384) was found to be 95:5:0 by the use of laser desorption Fourier transform mass spectrometry (see supplementary material). Raman and FTIR spectral measurements of the ^{13}C-substituted and unlabeled ET materials showed the known frequencies for the vibronic modes,[13] and the isotopic frequency shifts were in excellent agreement with the isotopic product rule (see supplementary material). Both ^{13}C-labeled and unlabeled salts of κ-$(ET)_2Cu[N(CN)_2]Br$ and κ-$(ET)_2Cu(NCS)_2$ were electrocrystallized in parallel experiments by methods previously described.[8] The electrocrystallization H-cells were assembled in an argon-filled drybox.[8c] Constant currents of 0.2 μA/cm^2 were applied, and the crystals (platelike specimens typically weighing 0.2–0.8 mg) were harvested after ~3 weeks. The lattice constants determined by X-ray diffraction of labeled and unlabeled κ-$(ET)_2Cu[N(CN)_2]Br$ and κ-$(ET)_2Cu(NCS)_2$ exhibited no significant differences between sets (see supplementary material).

Superconducting transitions were determined with the use of a commercial ac susceptometer (Lake Shore Cryotronics, Inc.) operated with a modulation field and frequency of 1 Oe and 111.1 Hz, respectively. The crystals were slowly cooled from room temperature to 4 K in a period of 30 min or more to avoid the disorder-induced suppression of T_c, as previously reported.[18] Susceptibilities χ for each crystal were recorded at temperature intervals of 0.1 K on warming from 5 to 20 K and, in one experiment, at temperature intervals of 0.01 K. One crystal of each of the two isotopic specimens was also studied with the use of a SQUID magnetometer and gave results in excellent agreement with the χ determinations reported herein.

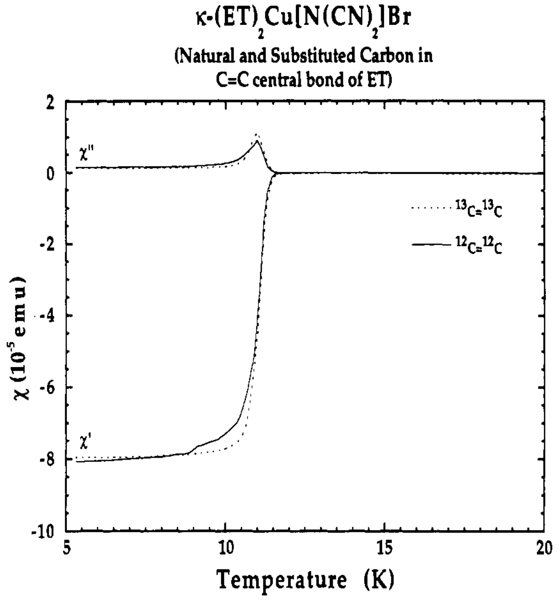

Figure 1. Superconducting transition, as determined by ac susceptibility measurements, of κ-$(ET)_2Cu[N(CN)_2]Br$ with normal ^{12}C=^{12}C and with ^{13}C=^{13}C labeling in the central double-bonded carbon atoms of ET. The symbols χ' and χ'' refer to the real (in-phase) and imaginary components, respectively, of the total susceptibility. The mean-field superconducting transition temperatures (T_{c1}) are 11.42 ± 0.05 K for the ^{12}C=^{12}C crystal and 11.43 ± 0.04 K for the ^{13}C=^{13}C crystal.

Figure 1 illustrates the superconducting transition curves for a normal and ^{13}C-substituted crystal of κ-$(ET)_2Cu[N(CN)_2]Br$. This figure shows the *absence* of an isotope effect, typical of all of our measurements as summarized in Table I for four crystal specimens each for the different isotopic compositions of the two κ-phase salts. This table lists the diamagnetic onset temperature (T_{co}), the conventional mean-field definition of T_c, which is the intercept of the linear extrapolations of $\chi(T)$ for $T < T_c$ and $T > T_c$ (T_{c1}), the transition midpoint (T_{cm}), and the maximum in the imaginary component of the total ac susceptibility (χ''_{max}), which is observed to be close to the transition midpoint, T_{cm}.

The reproducibility of T_c's in Table I is within a precision of ±0.1 K or better, depending on the choice of T_c. To check the reproducibility of the synthetic procedures, we determined the T_c's of two crystal specimens each taken from three independent syntheses of the ^{13}C-labeled κ-$(ET)_2Cu[N(CN)_2]Br$ salt and found no differences outside of our precision of 0.1 K. An examination of the data of Table I shows that there is no discernible isotope effect within a standard deviation of 0.1 K in ΔT_c, or ~1% of T_c, compared to the ~4% shift calculated above for the C=C isotope mass effect or the 1.9% derived from the observed phonon frequency shift. We thus conclude that the central C=C stretching motion is *not a dominant exchange mechanism* for superconducting pairing in κ-$(ET)_2Cu[N(CN)_2]Br$ and κ-$(ET)_2Cu(NCS)_2$.

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(12) The designations β and κ denote differences in the donor-molecule layer packing motifs (see ref 1).

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Table I. Superconducting Transition Temperatures[a] (T_c's) at Ambient Pressure for Natural ^{12}C and ^{13}C-Substituted κ-(ET)$_2$Cu[N(CN)$_2$]Br and κ-(ET)$_2$Cu(NCS)$_2$, Where the ^{13}C-Labeling Involves the Central C═C Atoms of ET

κ-(ET)$_2$Cu[N(CN)$_2$]Br					
^{12}C crystals	No. 1	No. 2	No. 3	No. 4	Average
T_{co} (K)	11.9	11.8	11.7	11.5	11.72±0.10
T_{cl} (K)	11.5	11.4	11.4	11.3	11.40±0.05
T_{cm} (K)	10.9	11.0	10.9	11.0	10.95±0.03
χ'' max (K)	10.9	11.0	11.0	11.0	10.98±0.03
^{13}C crystals					
T_{co} (K)	11.7	11.9	11.6	11.7	11.72±0.07
T_{cl} (K)	11.6	11.4	11.4	11.4	11.45±0.06
T_{cm} (K)	11.1	11.0	11.1	11.0	11.05±0.03
χ'' max (K)	11.0	11.0	11.1	11.0	11.02±0.03
				$\Delta T_c = T_c(^{13}C) - T_c(^{12}C)$	
		T_{co} (K)		+0.00±0.12	
		T_{cl} (K)		+0.05±0.08	
		T_{cm} (K)		+0.10±0.04	
		χ''max (K)		+0.04±0.04	
κ-(ET)$_2$Cu(NCS)$_2$					
^{12}C crystals	No. 1	No. 2	No. 3	No. 4	Average
T_{co} (K)	9.4	9.6	9.5	9.9	9.60±0.12
T_{cl} (K)	9.4	9.2	9.3	9.3	9.30±0.05
T_{cm} (K)	9.1	8.9	9.0	9.0	9.00±0.05
χ'' max (K)	9.1	8.8	9.0	9.0	8.98±0.07
^{13}C crystals					
T_{co} (K)	9.6	9.7	9.3	9.6	9.55±0.10
T_{cl} (K)	9.3	9.4	9.2	9.4	9.32±0.06
T_{cm} (K)	9.0	9.1	8.9	9.0	9.00±0.05
χ'' max (K)	9.1	9.0	8.9	8.7	8.92±0.10
				$\Delta T_c = T_c(^{13}C) - T_c(^{12}C)$	
		T_{co} (K)		–0.05±0.16	
		T_{cl} (K)		+0.02±0.08	
		T_{cm} (K)		+0.00±0.07	
		χ''max (K)		–0.06±0.12	

[a] T_{co} = diamagnetic onset, T_{cl} = linearly extrapolated mean-field T_c (see text), T_{cm} = transition midpoint, and χ''_{max} = maximum in the imaginary component of the ac susceptibility.

Our results are consistent with BCS-type *inter*molecular phonon–electron pairing. In superconductors with many atoms per unit cell

$$T_c \propto \Theta_D \sim \prod_i M_i^{-\alpha_i} \tag{1}$$

where Θ_D is the Debye temperature and $\sum_i \alpha_i = \alpha \approx {}^1/_2$ for the inclusion of a spectrum of both acoustic and optical phonons. This leads to the expression

$$\ln (T_c'/T_c) = -\sum_i \alpha_i \ln (M_i'/M_i) \tag{2}$$

where M_i' and T_c' are the shifted atomic masses and T_c values, respectively. For *inter*molecular electron–phonon pairing, the mass of each entire ET molecule vibrates together, so that the relevant masses in eq 2 are those of the two ET molecules and the anions. If the anions are not involved in the pairing, the percentage mass change of the ET molecules with two ^{13}C labels is 0.5%. Hence, with a conventional isotope shift ($\alpha = {}^1/_2$), the expected shift in T_c, $[1 - (^{386}/_{384})^{-1/2}]$, is on the order of 0.25%, or 0.03 K. This shift is too small compared to the precision of our measurements to be detectable. Our results, of course, are also consistent with some non-phonon-dominated form of pairing, such as one of electronic origin.

While pairing by exchange of optical phonons of the C═C stretching motion is an interesting proposal,[6] it seems to be an unlikely mechanism for any of the ET-based organic superconductors. Our interpretation of this mechanism[7] is that it might apply most appropriately for pairing of holes on the *same* ET molecule. However, for these systems with a one-half-filled band, there is one conduction hole for every two ET molecules, so that the likelihood of two free charges of the same sign residing on the same ET molecule simultaneously is rather remote, especially in view of the increased Coulomb interactions. Our results, therefore, are reasonable, but the difference between the reported[5] 7.5% isotopic shift for the β^*-(ET)$_2$I$_3$ salt and our observation of a zero isotopic shift for the κ-phase salts with higher T_c's is surprising. This discrepancy represents either a remarkable difference in pairing mechanisms between the β^*- and κ-phase salts or possibly some change, induced by the ^{13}C substitution, in the modulated structure[19] of ambient-pressure β-(ET)$_2$I$_3$ that drastically alters the isotopic shift in the β^*-(ET)$_2$I$_3$ phase. Otherwise, this discrepancy represents difficulties in establishing a reproducible T_c for β^*-(ET)$_2$I$_3$.[20]

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Supplementary Material Available: Figures showing the mass spectrum of ET with ^{13}C═^{13}C in the double-bonded carbon atoms (Figure S1), Raman spectra of ^{13}C═^{13}C-labeled and unlabeled ET (Figure S2), and FTIR spectra of ^{13}C═^{13}C-labeled and unlabeled ET (Figure S3) and a table (Table S1) of the crystallographic lattice constants for ^{12}C- and ^{13}C-substituted κ-(ET)$_2$Cu[N(CN)$_2$]Br and κ-(ET)$_2$Cu(NCS)$_2$ (4 pages). Ordering information is given on any current masthead page.

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(20) The same principal authors of the study[5] on β^*-(ET)$_2$I$_3$ have previously reported, as a preliminary result, a *small inverse* ^{13}C-isotope effect (T_c = 8.2 K) for the same material, which suggests possible problems with accurate T_c determinations: Leising, G.; Lefrant, S.; Buisson, J. P.; Kang, W.; Lenoir, C.; Batail, P.; Jérome, D. *Synth. Met.* **1991**, *41–43*, 2137.