The isotope effect for $^{13}$C substitution in the central double-bonded carbon atoms of TTF moiety of ET leads to an abnormally large isotope effect for ET-based organic superconductors than pressurized beta-(ET)$_2$I$_3$ because $T_c$ is easily reproducible from sample-to-sample at ambient pressure, whereas beta-(ET)$_2$I$_3$ can have a range of $T_c$ from 1.5 to 8.0 K depending on sample quality, thermal treatment, pressure, and a variety of mechanical stresses. 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 $\kappa$-(ET)$_2$Cu[N(CN)$_2$]Br and $\kappa$-(ET)$_2$Cu(NCS)$_2$. Although these findings apply specifically to the $\kappa$-phase salts of this study, we argue that these results apply generally to other ET phases ($\alpha$, $\beta$, $\delta$, and other phase types) as well.

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

![Diagram of isotope effect for ET in organic superconductors](image-url)
in two totally symmetric vibrational modes (a, species) at energies near 1500 cm⁻¹ and contribute about 90% of the total vibrational potential energy distribution in each mode. 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, and among the strongest coupled vibronic modes is the one a species of the C=C stretching motion. Because the central C=C atoms provide the largest carbon-atom contributions to the valence-level orbitals, a significant isotope effect upon ¹³C 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 \(^{13}\text{C} \) substitution is \( T_c^{(13}\text{C})/T_c^{(12}\text{C}) = (1.2)^{-1/2} \). This amounts to a decrease in \( T_c \) of \( \sim 4\% \) (\(-0.4 \) 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 isotope shifts \([^{13}\text{C}]/[^{12}\text{C}] \) in the 1550 (1521) cm⁻¹ and 1493 (1465) cm⁻¹ vibrational modes (see supplementary material). The 7.5% decrease in \( T_c \) reported for \( \beta\text-\text{(ET)}_2\text{J}_3 \) on \(^{13}\text{C} \) 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 homonuclear atomic 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 \(^{13}\text{C} \)-substituted (for the central C=C atoms) and unlabeled ET were synthesized according to the methods described by Larsen and Lenoir16 and Rae.17 In the \(^{13}\text{C} \)-substituted ET product, the ratio \( \text{ET}^{(13}\text{C}=-^{12}\text{C}, M = 386):\text{ET}^{(12}\text{C}=-^{12}\text{C}, M = 385):\text{ET}^{(13}\text{C}=-^{13}\text{C}, M = 384) \) to be found was 95:5:0 by the use of laser desorption Fourier transform mass spectrometry (see supplementary material). Raman and FTIR spectral measurements of the \(^{13}\text{C} \)-substituted and unlabeled ET materials showed the known frequencies for the vibronic modes, and the isotopic frequency shifts were in excellent agreement with the isotopic product rule (see supplementary material). Both \(^{13}\text{C} \)-labeled and unlabeled salts of \( \kappa(\text{ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br} \) and \( \kappa(\text{ET})_2\text{Cu}(\text{NCS})_2 \) were electrocrystallized in parallel experiments by methods previously described.8 The electrocrystallization H-cells were assembled in 0.2-0.8 mg) were harvested after ~3 weeks. The lattice constants for the vibronic modes, and the isotopic frequency shifts were in excellent agreement with the isotopic product rule (see supplementary material). Both \(^{13}\text{C} \)-labeled and unlabeled salts of \( \kappa(\text{ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br} \) and \( \kappa(\text{ET})_2\text{Cu}(\text{NCS})_2 \) 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 \( \chi \) 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 each of the two isotopic specimens was also studied with the use of a SQUID magnetometer and gave results in excellent agreement with the \( \chi \) determinations reported herein.

Figure 1 illustrates the superconducting transition curves for a normal and \(^{13}\text{C} \)-substituted crystal of \( \kappa(\text{ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br} \). 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 \( \kappa \)-phase salts. This table lists the diamagnetic onset temperatures \( T_{c0} \), the conventional mean-field definition of \( T_c \) which is the intercept of the line extrapolations of \( \chi(T) \) for \( T < T_c \) and \( T > T_c \), the transition midpoint \( T_{cm} \), and the maximum in the imaginary component of the total ac susceptibility \( (\chi'/\chi''_m) \), which is observed to be close to the transition midpoint, \( T_{cm} \).

The reproducibility of \( T_{cm} \) in Table I is within a precision of \( \pm 0.1 \) 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 \(^{13}\text{C} \)-labeled \( \kappa(\text{ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br} \) 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 \( \Delta T_c \), 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 \( \kappa(\text{ET})_2\text{Cu}[\text{N}(\text{CN})_2]\text{Br} \) and \( \kappa(\text{ET})_2\text{Cu}(\text{NCS})_2 \).
This leads to the expression

\[ T_c \propto \Theta_D \sim \sum \alpha_i \]

where \( \Theta_D \) is the Debye temperature and \( \sum \alpha_i = \alpha \approx 1/2 \) for the inclusion of a spectrum of both acoustic and optical phonons. This leads to the expression

\[ \ln \left( \frac{T_c}{T_{c0}} \right) = -\sum \alpha_i \ln \left( M_i' / M_i \right) \]

where \( M_i' \) and \( M_i \) are the shifted atomic masses and \( T_c \) values, respectively. For intramolecular electron–phonon pairing, the mass of each entire ET molecule vibrates together, so 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 \(^{13}\text{C}\) labels is 0.5%. Hence, with a conventional isotope shift (\( \alpha = 1/2 \)), the expected shift in \( T_{c0} \) \[ (1 - (388/383)^{1/2}) \], 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-photon-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, it seems to be an unlikely mechanism for any of the ET-based organic superconductors. Our interpretation of this mechanism 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\(^{7} \) 7.5% isotopic shift for the \( \beta^*-(\text{ET})_213 \) salt and our observation of a zero isotopic shift for the \( \beta^*-\text{(ET)}_213 \) salt is surprising. This discrepancy represents either a remarkable difference in pairing mechanisms between the \( \beta^* \)- and \( \alpha \)-phase salts or possibly some change, induced by the \(^{13}\text{C}\) substitution, in the modulated structure\(^{19} \) of ambient-pressure \( \beta^-(\text{ET})_213 \) that dramatically alters the isotopic shift in the \( \beta^*-(\text{ET})_213 \) phase. Otherwise, this discrepancy represents difficulties in establishing a reproducible \( T_c \) for \( \beta^*-(\text{ET})_213 \).\(^{20} \)

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


(20) The same principal authors of the study\(^{7} \) on \( \beta^*-(\text{ET})_213 \) have previously reported, as a preliminary result, a small inverse \(^{13}\text{C}\)-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.; Jérôme, D. Synth. Met. 1991, 41-43, 2137.