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# Electron Spin Resonance, Infrared Spectroscopic, and Molecular Packing Studies of the Thermally Induced Conversion of Semiconducting $\alpha$- to Superconducting $\alpha_t$-(BEDT-TTF)$_2$I$_3$

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The semiconducting $\alpha$- to superconducting $\alpha_t$-(ET)$_2$I$_3$ ($T_c \sim 7.2$ K) thermal conversion was studied by use of the temperature dependence of the ESR peak-to-peak line width and derived spin susceptibility. The term "ET" is an abbreviation for BEDT-TTF, i.e., bis(ethylenedithio)tetrathiafulvalene. The phase transition occurred above 340 K and was not fully complete during the time span of the ESR study. FT-IR reflectance measurements were also performed on $\alpha_t$-(ET)$_2$I$_3$, which was obtained by heating $\alpha$-(ET)$_2$I$_3$ at 343 K in an ethylene glycol bath for 4 days. The reflectance spectrum of the thermally converted non-single-crystalline $\alpha_t$-(ET)$_2$I$_3$ exhibits an absorption dip, which is due to the C–C–H···X interactions around the anion cavity, at ~1280 cm$^{-1}$, just as in the case of all superconducting $\beta$-(ET)$_2$X (X = I$_3^-$, IBr$_2^-$, AuI$_2^-$) salts, thereby suggesting that $\alpha_t$-(ET)$_2$I$_3$ has a $\beta$-like structure. Structural factors associated with the thermal conversion, $\alpha$- to $\alpha_t$-(ET)$_2$I$_3$, were also examined by analysis and comparison of the crystal structures of $\alpha$-(ET)$_2$I$_3$ and the unique superconducting phase, $\beta^*$-(ET)$_2$I$_3$ ($T_c \sim 8$ K).

## Introduction

Electrocrystallization of bis(ethylenedithio)tetrathiafulvalene[1,2] (BEDT-TTF or simply ET) with linear triatomic anions X$^-$ (e.g., I$_3^-$ or IBr$_2^-$) leads mainly to salts with differing $\alpha$- and $\beta$-(ET)$_2$X type structural motifs. In terms of electrical properties, $\beta$-(ET)$_2$I$_3$ is an ambient-pressure superconductor with a superconducting transition temperature $T_c \simeq 1.5$ K,[3-5] and it undergoes a transition[6] under pressures greater than 0.5 kbar to a unique structural phase,[7] $\beta^*$-(ET)$_2$I$_3$, that exhibits superconductivity at $T_c \simeq 8$ K. The crystal structures of $\beta^*$-(ET)$_2$I$_3$ and $\beta$-(ET)$_2$I$_3$ are essentially the same, except that the ethylene groups of low-$T_c$ $\beta$-(ET)$_2$I$_3$ are partially disordered whereas all the ethylene groups of high-$T_c$ $\beta^*$-(ET)$_2$I$_3$ are ordered.[7,8] Provided that the temperature is not raised above 125 K, $\beta^*$-(ET)$_2$I$_3$ is stable even after the conversion pressure is released. By comparison, $\alpha$-(ET)$_2$I$_3$ undergoes a metal–insulator transition at 135 K,[9] and thermal tempering at 70 °C for several days produces a new isomeric form, $\alpha_t$-(ET)$_2$I$_3$,[10] that is stable at room temperature and exhibits a superconducting transition near 8 K. The $\alpha_t$-phase is reported to have a $\beta$-like unit cell (either $\beta$- or $\beta^*$-) on the basis of Weissenberg photographs.[10a] A resonance Raman study performed at 2 K further indicates that the symmetrical stretching mode of the I$_3^-$ anions in the $\alpha_t$-phase does not split, which is identical with the case for the $\beta^*$-phase but not for the $\beta$-phase.[10d] However, no detailed x-ray or neutron diffraction crystal structure of $\alpha_t$-(ET)$_2$I$_3$ is available, because the thermal conversion does not yield single crystals of sufficiently high diffraction quality. Nevertheless, the similarity of the $T_c$'s (~8 K) of $\beta^*$- and $\alpha_t$-(ET)$_2$I$_3$ suggests that the two phases are probably very similar in structure. In the following, we present the ESR and FT-IR evidence indicating a $\beta$-like structure for $\alpha_t$-(ET)$_2$I$_3$ and discuss structural factors responsible for the conversion of $\alpha$-(ET)$_2$I$_3$ to $\alpha_t$-(ET)$_2$I$_3$ by use of relatively low temperature thermal tempering.

## Experimental Section

Crystals of $\alpha$-(ET)$_2$I$_3$ were prepared by use of standard electrocrystallization techniques from ET and (NBu$_4$)I$_3$ in 1,1,2-trichloroethane solvent.[4a] The $\alpha$-phase crystals were selected individually on the basis of their room-temperature ESR line width ($\Delta H_{pp}$ = 70–110 G).[11] The $\alpha_t$-(ET)$_2$I$_3$ crystals were obtained by heating $\alpha$-(ET)$_2$I$_3$ specimens in a test tube immersed in an ethylene glycol bath at 70 °C for 4 days. The ESR experiments employed an IBM ER-200 spectrometer with a TE$_{102}$ rectangular cavity and an IBM ER-4111 VT liquid-nitrogen variable-temperature controller. Each analyzed spectrum was digitized (~300

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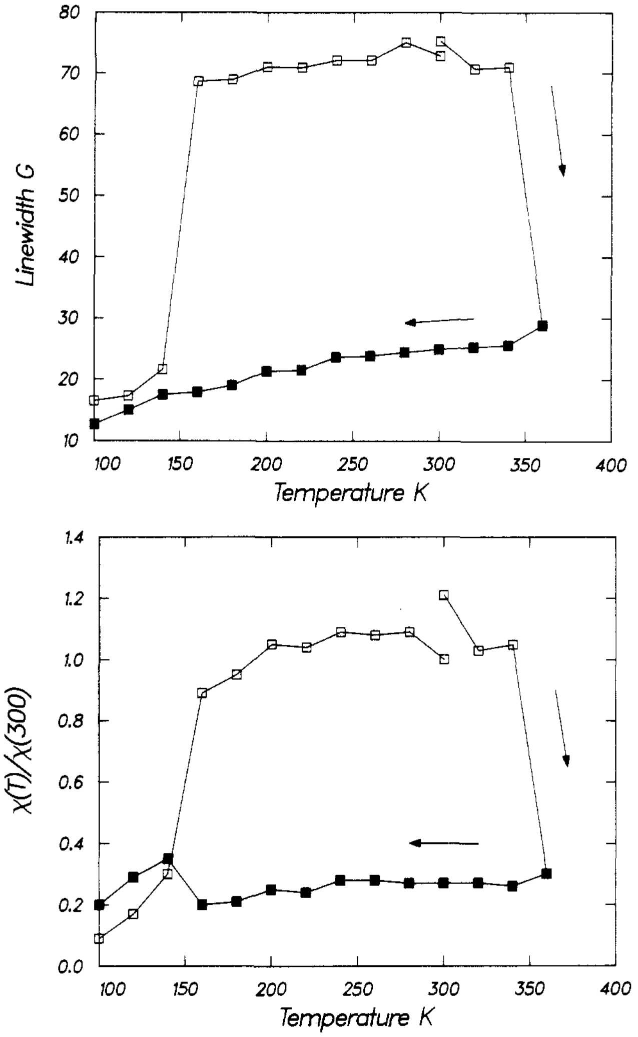

**Figure 1.** α- to $\alpha_t$-$(ET)_2I_3$ thermal conversion as monitored by (top) ESR peak-to-peak line width and (bottom) relative spin susceptibility. The hollow squares are the α-phase sample, and the solid squares are the converted $\alpha_t$-phase sample.

points) on a Lundy 5688 graphics terminal with a bit pad. A computer program was developed to fit the first derivatives of the ESR spectra to a linear combination of Lorentzian derivatives.[11] Room-temperature FT-IR reflectance measurements on $\alpha_t$-$(ET)_2I_3$ were made by use of a Digilab FTS-40 purged spectrometer interfaced with a UMA 300-A microscope. A cadmium-mercury-telluride detector was used at a resolution of 4 $cm^{-1}$, and a typical spectrum was acquired with 256 scans. A Kramers-Kronig dispersion relationship was used for all reflectance spectra, and the results are plotted in absorbance units.

## ESR Study

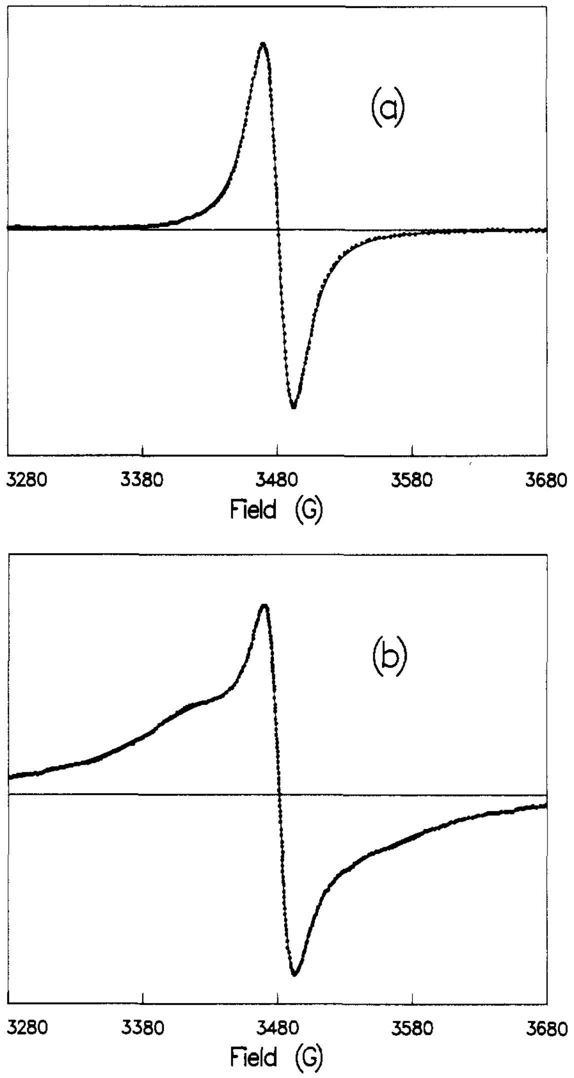

**Figure 2.** (a, Top) ESR spectrum of the thermally converted $\alpha_t$-$(ET)_2I_3$ (crystal A) showing a good fit[11] with one absorption line. The circles are the digitized spectrum, and the solid line is the computer fit. (b, Bottom) ESR spectrum of heated crystal B showing a good fit with two absorption lines.

The use of the single-crystal ESR line width has proven to be a very effective way of searching for structural phase transformations in organic conducting salts. The technique has been applied to the study of the conversions of α- to β-$(ET)_2IBr_2$[12] and δ- to α′-$(ET)_2AuBr_2$.[13] In the present study, a platelet-shaped crystal of α-$(ET)_2I_3$ was oriented with the long crystal axis vertical in an ESR cavity, which resulted in the $c^*$ axis being perpendicular to the static magnetic field. The room-temperature peak-to-peak ESR line width was around 70 G by use of this orientation of the crystals. The low-temperature (300-100 K) behavior was measured at 20 K intervals in order to contrast with the $\alpha_t$-modification. As shown in Figure 1, the peak-to-peak line width ($\Delta H_{pp}$) and derived spin susceptibility (χ) are both constant from 300 to 160 K. The behavior is consistent with that of a metal, as reported in the literature.[9] A large drop in $\Delta H_{pp}$ and χ is clearly observed near 140 K, which is consistent with the known metal-insulator (MI) transition in α-$(ET)_2I_3$.[9] Below 140 K, χ continued to drop rapidly. The MI transition in this compound was completely reversible, and the crystal was quickly warmed to 300 K and then increasingly heated (20 K intervals). Above 340 K, a similar drop in the line width and spin susceptibility was observed that was assigned to an α- to $\alpha_t$-$(ET)_2I_3$ structural phase transformation. The line width of the $\alpha_t$-phase at 360 K was around 29 G, which is similar to that of β-$(ET)_2I_3$. The spin susceptibility of the $\alpha_t$-phase was around 30% of the α-phase value. This percentage was lower than expected[14] and suggested in-

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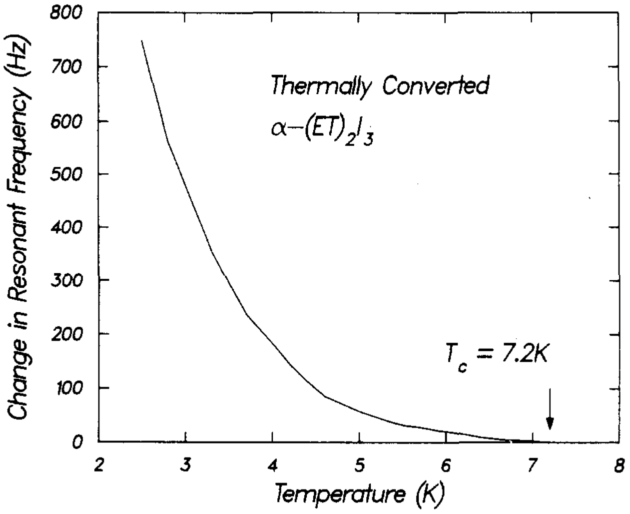

**Figure 3.** Rf penetration depth measurements of $\alpha_t$-$(ET)_2I_3$, showing a superconductivity onset near 7.2 K and a broad transition curve.

complete phase conversion during the ESR experiments. In contrast to the MI transition near 140 K (vide supra), the $\alpha$- to $\alpha_t$-$(ET)_2I_3$ transformation was irreversible, and the spin susceptibility of the $\alpha_t$-phase remained approximately constant from 360 to 100 K (Figure 1). The constant spin susceptibility is consistent with the Pauli paramagnetism of a metal. A small jump in the spin susceptibility of $\alpha_t$-$(ET)_2I_3$ near 140 K indicated the presence of some unconverted $\alpha$-$(ET)_2I_3$, due to the short heating time in the ESR experiment.

In an attempt to further understand the thermal conversion process of the $\alpha$- to $\alpha_t$-$(ET)_2I_3$ phases, crystals labeled A and B from different preparative batches, but of similar size (1.16 × 1.50 × 0.05 mm$^3$ and 1.50 × 1.73 × 0.035 mm$^3$, respectively), were heated at 65 °C, which is slightly lower than the reported conversion temperature, for 18 h. As shown in Figure 2, on the basis of ESR line shape analysis,[11] crystal A reaches 100% conversion, while crystal B only reaches 28%. During demounting, crystal B broke into several pieces. Among those pieces, a pure unreacted $\alpha$-phase crystal was identified by use of ESR line shape analysis. These observations indicate that the extent of the structral phase transformation during thermal cycling varies from sample to sample. The reason is not clearly understood, but it may be associated with different degrees of crystal imperfection. This results in a noteworthy observation: i.e., in the partially converted crystal, there are domains of pure (semiconducting) $\alpha$- and (superconducting) $\alpha_t$-phases.

### Superconductivity in $\alpha_t$-$(ET)_2I_3$

Bulk superconductivity in thermally converted crystals of $\alpha_t$-$(ET)_2I_3$ was studied by rf penetration depth measurements with the use of equipment and procedures described previously.[16] For these measurements, superconductivity is detected by an increase in the resonant frequency (~500 kHz) of an rf coil in an LC circuit caused by the exclusion of the rf field from the sample due to the presence of persistent shielding currents that arise below $T_c$. The crystal specimens were prepared by heating an $\alpha$-phase single crystal (~870 $\mu$g) for 4 days at 70 °C.

The superconducting transition curve determined by the rf measurements is shown in Figure 3. The onset of superconductivity was 7.2 K, and the transition extended to well below 2.5 K before the volume superconductivity was fully developed. Although organic superconductors typically exhibit superconducting transitions extending over several degrees, the present transition is unusually broad (>5 K width). The onset temperature and shape of the transition curve were unchanged after aging of the crystal in an ambient environment for 3 months.

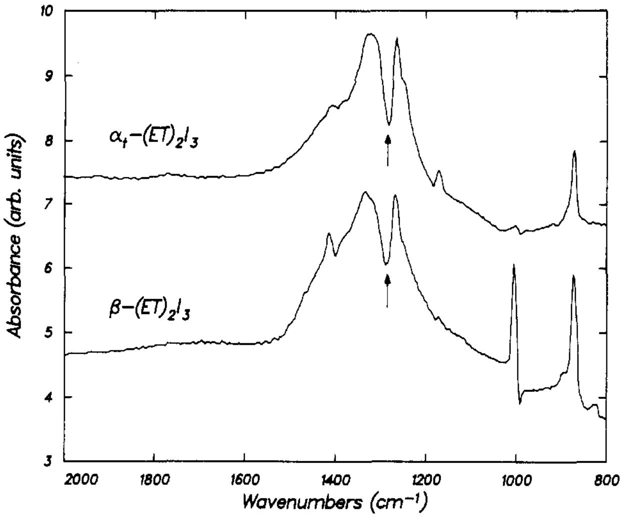

**Figure 4.** FT-IR reflectance spectra of $\alpha_t$-$(ET)_2I_3$ and $\beta$-$(ET)_2I_3$, showing the absorption dip at ~1280 cm$^{-1}$, which originates[18] from the C–C–H···I bending mode in ET:anion conductors.

It is instructive to compare the present superconducting transition curve for $\alpha_t$-$(ET)_2I_3$ to that of a different anion salt of ET, i.e., thermally converted $\alpha$-$(ET)_2IBr_2$. At ambient pressure, $\beta$-$(ET)_2IBr_2$ has a superconducting $T_c \sim 2.8$ K.[17] For the latter, the transition was relatively sharp, with 90% completion of the transition occurring only 1 K lower than the onset temperature (2.66 K).[12] The very much broader transition for $\alpha_t$-$(ET)_2I_3$ suggests a distribution of superconducting regions with different $T_c$'s. There is only one known superconducting modification for the $IBr_2^-$ salt of ET, namely $\beta$-$(ET)_2IBr_2$, but there are at least two $\beta$-like structures for the $I_3^-$ salt, $\beta$-$(ET)_2I_3$ ($T_c \simeq 1.5$ K) with a partially disordered (ethylene group) structure and $\beta^*$-$(ET)_2I_3$ ($T_c \simeq 8$ K) with an ordered (ethylene group) structure. Therefore, it is possible that there exists a differing range of structural order from the $\beta$- to the $\beta^*$-modification.

### FT-IR Study

The reflectance spectra of $\alpha_t$- and $\beta$-$(ET)_2I_3$ are shown in Figure 4. The spectrum of $\alpha_t$-$(ET)_2I_3$ shows a pronounced absorption dip at 1280 cm$^{-1}$ in the 1200–1400-cm$^{-1}$ region, just as in the case of $\beta$-$(ET)_2I_3$.[18] Differences in peak intensities are observed for $\alpha_t$-$(ET)_2I_3$ and $\beta$-$(ET)_2I_3$, which may be due to differences in the conformations of the terminal $-C_2H_4-$ groups in the hydrogen anion cavities in the two compounds. Polarized reflectance spectra were also obtained, and only slight differences in intensities were observed. The absorption dip at ~1280 cm$^{-1}$ in the reflectance spectrum of $\beta$-$(ET)_2I_3$ originates[18] from the bending mode associated with the C–C–H···I interactions in the hydrogen pockets[19] of ET donor molecules surrounding the $I_3^-$ anions. As reported elsewhere,[18] $\alpha$-$(ET)_2I_3$ does not show a similar absorption dip in the 1200–1400-cm$^{-1}$ region of its reflectance spectrum. Therefore, the occurrence of the absorption dip at ~1280 cm$^{-1}$ in the re-

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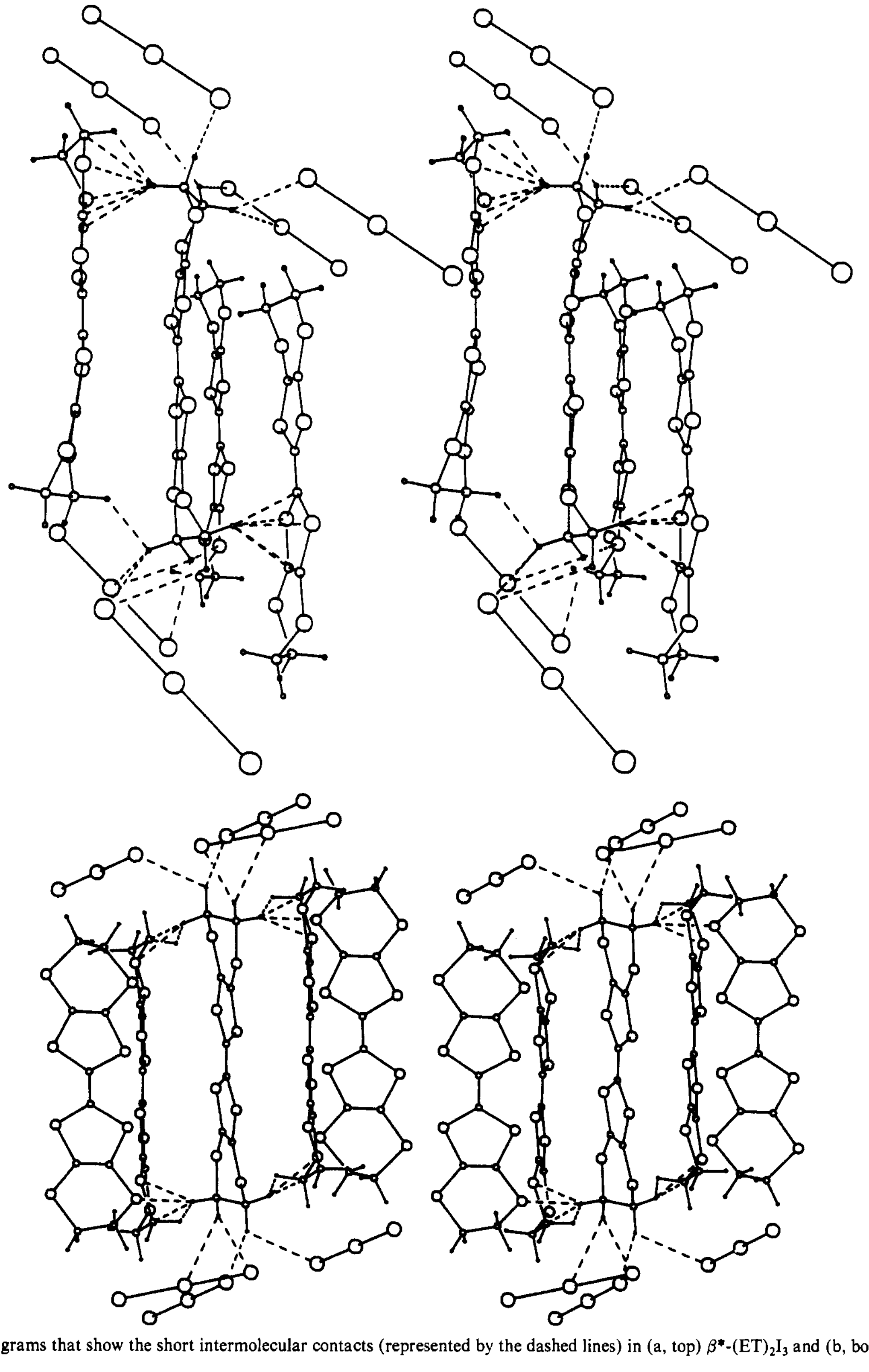

**Figure 5.** Stereodiagrams that show the short intermolecular contacts (represented by the dashed lines) in (a, top) $\beta^*$-$(ET)_2I_3$ and (b, bottom) $\alpha$-$(ET)_2I_3$.

flectance spectrum of $\alpha_t$-$(ET)_2I_3$, together with the ESR results and the fact that the $T_c$'s of $\alpha_t$-$(ET)_2I_3$ and $\beta^*$-$(ET)_2I_3$ are similar, strongly indicates that $\alpha_t$-$(ET)_2I_3$ has a $\beta$-like crystal structure.

There is final point regarding the thermal conversion reaction: i.e., some evidence for slight decomposition during the thermal-tempering reaction of $\alpha$-$(ET)_2I_3$ was found. A red spot in the $\alpha_t$-$(ET)_2I_3$ sample was identified by FT-IR spectroscopy to have absorptions that could be assigned to neutral ET (red-orange color).[20]

## Molecular Packing Study

On the basis of the aforementioned studies, $\alpha_t$-$(ET)_2I_3$ appears to be very similar structurally to $\beta^*$-$(ET)_2I_3$. Conversion of $\alpha$-$(ET)_2I_3$ to a "$\beta$-like" structure by thermal tempering suggests that $\alpha$-$(ET)_2I_3$ is thermodynamically less stable than either $\beta$-$(ET)_2I_3$ or $\beta^*$-$(ET)_2I_3$. Although the $\alpha$- to $\alpha_t$-phase transformation involves a *dramatic donor-packing rearrangement* and the breaking and forming of many types of close intermolecular contacts, one of the major structural differences between the low-$T_c$ phase ($\beta$) and the high-$T_c$ phase ($\beta^*$) lies in the ordering of the terminal ethylene groups.

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We now examine the hydrogen atom cavities formed by the $-C_2H_4-$ groups around the $I_3^-$ anion in the $\beta^*$- and $\alpha$-phases. The stereodiagrams of Figure 5 depict how the ethylene group hydrogen atoms of one ET molecule in $\beta^*$-(ET)$_2$I$_3$ and $\alpha$-(ET)$_2$I$_3$ interact with the surrounding ET molecules and anions, respectively.[21] In $\beta^*$-(ET)$_2$I$_3$, three hydrogen atoms of each ethylene group have short contacts with the $I_3^-$ anions (i.e., C–H···I interactions),[7a] while the remaining hydrogen atom sits on top of either a five- or six-membered ring of the adjacent ET molecule (i.e., C–H···S interactions). In $\alpha$-(ET)$_2$I$_3$, two hydrogen atoms of each ethylene group have short contacts with the $I_3^-$ anions, and the other two hydrogen atoms have short contacts with sulfur and/or hydrogen atoms of the adjacent ET molecules. For every ethylene group, therefore, $\beta^*$-(ET)$_2$I$_3$ always has more C–H···$I_3^-$ interactions than does $\alpha$-(ET)$_2$I$_3$. According to ab initio SCF–MO/MP2 calculations[22] on $H_3C–H···I_3^-$ and $H_3C–H···SH_2$ with the 6-311G** quality basis set, the H···I and H···S contacts, respectively, have attractive interaction energies of 1.13 and 0.47 kcal/mol at their minimum-energy distances. Since $\beta^*$-(ET)$_2$I$_3$ has more C–H···$I_3^-$ contacts than does $\alpha$-(ET)$_2$I$_3$, it may be speculated that $\beta^*$-(ET)$_2$I$_3$ is thermodynamically more stable. This expectation is consistent with the conversion of $\alpha$-(ET)$_2$I$_3$ to a $\beta$-like structure by thermal tempering.

## Concluding Remarks

The unusual $\alpha$- to $\alpha_t$-(ET)$_2$I$_3$ (semiconductor to superconductor) thermal conversion has been monitored by use of a high-temperature ESR line width analysis technique. The ESR and FT-IR studies indicate that the $\alpha_t$-phase has a $\beta$-like structure. The superconducting $T_c$ measurements, as well as Raman results,[10d] further suggest that the $\alpha_t$-phase is similar to structurally unique[7,8] $\beta^*$-(ET)$_2$I$_3$. The thermal conversion of $\alpha$- to $\alpha_t$-(ET)$_2$I$_3$ implies that the $\beta$-like structure is thermodynamically more stable than the $\alpha$-structure. This appears to originate from the fact that the $\beta$-like structure allows more short contacts between donor-molecule hydrogen atoms and anions (i.e. C–H···$I_3^-$ contacts) than does the $\alpha$-structure. Thus, the thermal-tempering technique provides a convenient procedure for obtaining a large quantity of a $\beta$-like salt from a mixture of $\alpha$- and $\beta$-salts, which typically occurs during the electrocrystallization synthesis reaction.

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[21] $\beta^*$-(ET)$_2$I$_3$ has one unique ET molecule,[7] but $\alpha$-(ET)$_2$I$_3$ has three unique ET molecules (i.e., A, B, and C).[9b] Figure 5b shows the environment around molecule B. Molecules A and C have environments similar to that around molecule B.

[22] Novoa, J. J.; Whangbo, M.-H.; Williams, J. M. To be submitted for publication.

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# Effects of Conformational Change in the Acceptor on Intramolecular Electron Transfer

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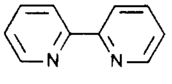
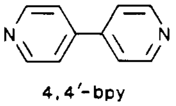
The structure of $[(bpy)Re(CO)_3(MQ^+)](PF_6)_2$ (bpy is 2,2′-bipyridine; MQ$^+$ is *N*-methyl-4,4′-bipyridinium cation) determined by X-ray diffraction shows that the complex is the *facial* isomer and is of distorted-octahedral geometry. The dihedral angle between the two pyridyl rings of the MQ$^+$ ligand is 47° in the crystal. The similarities in $d\pi \rightarrow \pi^*(MQ^+)$ transition energies in solution, in an organic glass, and in KBr pellets suggest that the dihedral angle between the two rings of the MQ$^+$ ligand may be nearly medium-independent. The results of spectral and electrochemical studies on a series of complexes show the following: (1) the dihedral angle has a significant effect on the energies and intensities of the MQ$^+$-based metal to ligand charge-transfer (MLCT) transitions, (2) the relative ordering of the bpy- and MQ$^+$-based MLCT excited states in $[(bpy)Re(CO)_3(MQ^+)]^{2+}$ depends upon the dihedral angle, and (3) changes in the dihedral angle and in solvent dipole reorientation play important roles in light-induced $\pi^*(bpy) \rightarrow \pi^*(MQ^+)$ intramolecular electron transfer, $[(bpy^{\bullet-})Re^{II}(CO)_3(MQ^+)]^{2+*} \rightarrow [(bpy)Re^{II}(CO)_3(MQ^{\bullet})]^{2+*}$.

## Introduction

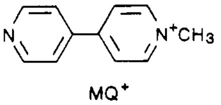
In chromophore–quencher (CQ) complexes where there is a metal to ligand charge-transfer (MLCT) excited state and a pyridinium electron-transfer acceptor, e.g., $[(bpy)_2Os(CO)(MQ^+)]^{3+}$ (bpy is 2,2′-bipyridine, MQ$^+$ is the *N*-methyl-4,4′-bipyridinium dication), a bpy-based MLCT emission is observed



bpy



4,4′-bpy



MQ$^+$

at low temperatures in glasses, e.g., eq 1. The emissions are

$$[(bpy)(bpy^{\bullet-})Os^{III}(CO)(MQ^+)]^{3+*} \rightarrow [(bpy)_2Os^{II}(CO)(MQ^+)]^{3+} + h\nu \quad (1)$$

comparable in energy and lifetime to the MLCT-based emission from related complexes such as $[(bpy)_2Os(CO)(4,4'\text{-}bpy)]^{2+}$.[1,2] However, in fluid solution, rapid intramolecular electron transfer occurs in the CQ complex to give a lower energy MQ$^+$-based excited state. The lower excited state is short-lived and emits weakly at room temperature.[2]

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