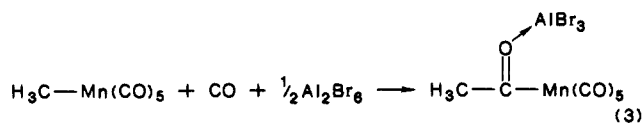


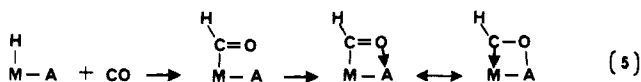
at 25 °C. This reaction involves carbonyl insertion, formation of the carbonyl oxygen-aluminum bond, and also creation of a dative bond between one of the bromine atoms and manganese. In the second step of this arm of the cycle (reaction B') the Br-Mn bond is cleaved by CO. The enthalpy of this reaction in CH<sub>2</sub>Cl<sub>2</sub> solution,  $-16.2 \pm 1.5$  kcal/mol, can be used to estimate the Mn-Br bond strength. A recent estimate of the Mn-CO bond strength is  $36 \pm 2$  kcal/mol,<sup>7</sup> which implies that the Mn-Br bond strength (for the Mn-Br dative bond<sup>8</sup>) is on the order of 20 kcal/mol. The diagonal reaction in Scheme I, carbonyl insertion coupled with formation of the Lewis adduct, is calculated to be exothermic by  $41.8 \pm 2.7$  kcal/mol by summing the enthalpies of reactions A + B and  $38.4 \pm 2.1$  kcal/mol by summing the reactions of A' + B'. Considering the extremely air-sensitive nature of the reactants, this agreement is good and we believe the average value of  $-40 \pm 3$  kcal/mol adequately defines the enthalpy of reaction 3.



It has long been held that failure to observe carbonyl insertion into metal-hydrogen bonds is due to thermodynamic factors.<sup>9</sup> Recently, it has been shown that for gas-phase formyl insertion shown in reaction 4,  $\Delta H = +10.3 \pm 7.4$  kcal/mol.<sup>9</sup> It is clear



that, in the absence of competing side reactions,<sup>10</sup> the presence of a strong Lewis acid such as aluminum bromide would be sufficient to overcome such a barrier. This is of interest since interaction with Lewis acidic supports may enhance the insertion of carbon monoxide into transition-metal hydrogen bonds either through formation of Lewis acid adducts or possibly through hydroxy carbene complexes<sup>11</sup> as shown in reaction 5. Oxophilic



metals such as thorium have been shown to undergo carbonyl insertion forming  $\eta^2$ -formyls. Complete kinetic and thermodynamic data for this reaction are known, and the thorium-oxygen interaction is estimated to be on the order of 5 kcal/mol.<sup>12</sup> This is clearly lower than the interaction with the external Lewis acid, Al<sub>2</sub>Br<sub>6</sub>.

In summary, the thermodynamic cycle in Scheme I illustrates the range of thermodynamic effects that can be expected when carbonyl insertion is coupled to formation of Lewis acid adducts. The role of the transition metal in determining the strengths of these bonds appears minor. The approximation that stabilization of other insertion products can be modeled by known thermochemical data for organic substrates appears to be justified. Additional experimental work is in progress to test this hypothesis.

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## Effect of Structural Disorder on Organic Superconductors: A Neutron Diffraction Study of "High-T<sub>c</sub>" β<sup>\*</sup>-(BEDT-TTF)<sub>2</sub>I<sub>3</sub> at 4.5 K and 1.5 kbar

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Synthetic organic metals based on bis(ethylenedithio)tetra-thiafulvalene (BEDT-TTF, C<sub>10</sub>S<sub>8</sub>H<sub>8</sub>, or abbreviated ET) offer a unique opportunity to systematically study structure-property relationships.<sup>1</sup> Salts of ET typically contain two-dimensional networks of intermolecular intra- and interstack S··S contacts of  $3.60 \pm 0.1$  Å (the van der Waal radii sum) which provide the electron conduction pathways. Within the nearly isostructural (triclinic space group P $\bar{1}$ , Z = 2) series β-(ET)<sub>2</sub>X, X = I<sub>3</sub><sup>-</sup>, I<sub>2</sub>Br<sup>-</sup>, AuI<sub>2</sub><sup>-</sup>, and IBr<sub>2</sub><sup>-</sup>, all are ambient-pressure superconductors at low temperatures except for the I<sub>2</sub>Br<sup>-</sup> salt, which remains metallic down to at least 0.45 K.<sup>2</sup> Since the central atoms of the anions are located on crystallographic inversion centers, the I<sub>2</sub>Br<sup>-</sup> salt is randomly disordered (I-I-Br<sup>-</sup> and Br-I-I<sup>-</sup>), and it has been proposed that the resulting variation of local potentials in the ET network prevents the onset of superconductivity.<sup>2a</sup>

β-(ET)<sub>2</sub>I<sub>3</sub> is also structurally disordered, but in this case the disorder involves only one ethylene group on one end of the ET molecule. The terminal -C<sub>2</sub>H<sub>4</sub> group has two conformations, labeled A and B in Figure 1b, in the crystal above 200 K.<sup>3</sup> Below 200 K satellite reflections appear in the neutron<sup>4a</sup> and X-ray<sup>4b</sup> diffraction patterns which have been analyzed in terms of rigid-body sinusoidal displacive modulations of the ET molecules and the I<sub>3</sub><sup>-</sup> anions about their average positions in the unit cell.<sup>4b,c</sup> Because this results in fluctuations in intermolecular distances from one unit cell to another, it was proposed<sup>4c</sup> that, in order to avoid unfavorable H··I contacts, the site occupancies corresponding to the A and B conformations of the ET molecules would become ordered with the same periodicity of the modulation. Recent structure-property correlations and calculations indicate<sup>1a</sup> that the superconducting transition temperature at ambient pressure for β-(ET)<sub>2</sub>I<sub>3</sub> (T<sub>c</sub> = 1.4 K) is anomalously low with respect to β-(ET)<sub>2</sub>I<sub>2</sub>Br<sub>2</sub> (T<sub>c</sub> = 2.8 K) and β-(ET)<sub>2</sub>AuI<sub>2</sub> (T<sub>c</sub> = 5 K), so that, even though the low-temperature structure is ordered, the incommensurate periodic variations in the local potentials may increase electron-pair scattering and prevent the onset of superconductivity in β-(ET)<sub>2</sub>I<sub>3</sub> above 1.4 K.

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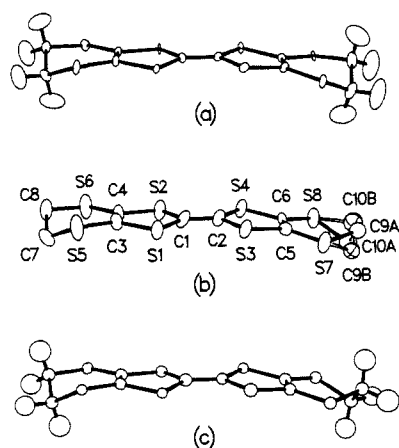
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**Table I.** Unit Cell Parameters for  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub>

T, K	P, kbar	a	b	c	$\alpha$	$\beta$	$\gamma$	V	ref
298	0	6.615 (1)	9.100 (1)	15.286 (2)	94.38 (1)	95.59 (1)	109.78 (1)	855.9 (2)	1e
120	0	6.561 (1)	9.013 (2)	15.173 (3)	95.07 (2)	95.93 (2)	110.28 (2)	829.2 (3)	1e
20	0	6.543 (2)	8.968 (3)	15.114 (77)	95.34 (3)	96.05 (3)	110.30 (3)	819.1 (8)	a
4.5	0	6.519 (2)	8.920 (6)	15.052 (15)	95.32 (8)	96.09 (6)	110.44 (4)	807.6 (16)	this work
4.5	1.5	6.449 (3)	8.986 (4)	15.034 (12)	94.79 (4)	96.57 (3)	111.29 (3)	799.1 (9)	this work
6.1	4.6	6.433 (4)	8.947 (7)	14.927 (19)	95.15 (9)	96.77 (7)	111.40 (5)	786.1 (13)	this work

<sup>a</sup>Emge, T. J.; Wang, H. H.; Williams, J. M., unpublished results.



**Figure 1.** (a) B conformation of the ET molecule in  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub>Br at 20 K from neutron diffraction data.<sup>11</sup> The B conformation is also found in the  $\beta$ -(ET)<sub>2</sub>X, X = AuI<sub>2</sub><sup>-</sup> and IBr<sub>2</sub><sup>-</sup>, salts. (b) The disordered ET molecule in  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> under ambient pressure above 200 K. One ethylene group has two conformations (hydrogen atoms not shown). (c) The ET molecule in  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub> at 4.5 K and 1.5 kbar from neutron diffraction data. The ET molecule is ordered and has the A conformation, whereas all the other  $\beta$ -(ET)<sub>2</sub>X salts have the B conformation.

Thus, the discovery of a "high- $T_c$ " state for  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> was obviously of great interest. It was reported<sup>5-8</sup> that  $T_c$  for  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> decreases with the application of increasing pressure up to about 1.2–1.3 kbar, where  $T_c$  jumps to  $\sim 8$  K and then continues to decrease with further increases in pressure. We recently observed<sup>9</sup> that if a pressure  $>0.5$  kbar was applied at room temperature prior to cooling to 20 K, the satellite reflections due to the modulated structure do not appear in the neutron diffraction pattern. The absence of the modulated structure could either mean the high- $T_c$

**Table II** Selected Intermolecular Distances (Å) in  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub> at 4.5 K and 1.5 kbar

atoms <sup>a</sup>	distance	atoms	distance
I(2)···I(2) <sup>1</sup>	4.279 (7)	S(1)···S(4) <sup>8</sup>	3.643 (11)
I(1)···H(8b)	3.149 (13)	S(1)···S(4) <sup>9</sup>	3.671 (15)
I(1)···H(10b) <sup>2</sup>	3.363 (9)	S(2)···S(3) <sup>8</sup>	3.640 (12)
I(1)···H(8a)	3.368 (15)	S(2)···S(5) <sup>10</sup>	3.538 (17)
I(2)···H(10a) <sup>3</sup>	3.014 (7)	S(3)···S(4) <sup>8</sup>	3.646 (22)
I(2)···H(8a)	3.090 (15)	S(3)···S(8) <sup>9</sup>	3.526 (19)
I(2)···H(10a) <sup>4</sup>	3.107 (9)	S(4)···S(6) <sup>4</sup>	3.610 (13)
I(2)···H(8b) <sup>5</sup>	3.154 (11)	S(5)···S(6) <sup>9</sup>	3.451 (8)
I(2)···H(9b) <sup>6</sup>	3.310 (9)	S(5)···S(7) <sup>11</sup>	3.480 (10)
I(2)···H(7a) <sup>5</sup>	3.404 (15)	S(6)···S(8) <sup>4</sup>	3.548 (8)
I(2)···H(10b) <sup>7</sup>	3.414 (13)	S(7)···S(8) <sup>9</sup>	3.420 (9)

<sup>a</sup>Superscripts refer to symmetry operations: (1)  $1-x, 1-y, -z$ ; (2)  $x, y, -1+z$ ; (3)  $1+x, 1+y, -1+z$ ; (4)  $-x, -y, 1-z$ ; (5)  $1-x, -y, -z$ ; (6)  $x, 1+y, -1+z$ ; (7)  $1-x, -y, 1-z$ ; (8)  $-x, -1-y, 1-z$ ; (9)  $1+x, y, z$ ; (10)  $-1+x, y, z$ ; (11)  $1-x, -1-y, 1-z$ .

state is completely ordered or it is randomly disordered as in the room temperature  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> structure. Very recent measurements of superconductivity by the low-field ESR technique have also shown a critical pressure of 0.5 kbar for producing the high- $T_c$  state.<sup>13</sup> In this paper we report the existence of a new ordered structural phase, denoted as  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub>, at  $T = 4.5$  K and  $P = 1.5$  kbar. To our knowledge, this is the first structural study of an organic superconductor with the sample at a temperature below the onset temperature for superconductivity.

Neutron diffraction data were obtained at the Institut Laue-Langevin reactor (Grenoble, France) using the "D15" normal-beam geometry diffractometer (lifting counter technique) equipped with a liquid helium cryostat and a helium pressure cell.<sup>10</sup> Initially, at zero applied pressure and  $T = 4.5$  K, satellite reflections were observed at  $(hkl) \pm \mathbf{q}$ , where  $\mathbf{q} = 0.074 (1)\mathbf{a}^* + 0.284 (9)\mathbf{b}^* + 0.212 (7)\mathbf{c}^*$ . After warming to 235 K, pressurizing to 1.5 kbar, and cooling to 4.5 K, the satellites were absent in agreement with our very recent findings.<sup>9</sup> Unit cell parameters for various temperature and pressure conditions are presented in Table I.

The structure of  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub> derived from the data set obtained with the sample below the superconducting transition temperature, at 4.5 K and 1.5 kbar, is completely ordered but is *not* isostructural with the  $\beta$ -phase structures of the I<sub>2</sub>Br<sup>-</sup>, AuI<sub>2</sub><sup>-</sup>, and IBr<sub>2</sub><sup>-</sup> salts, as shown in Figure 1. Important distances and angles are provided in Table II. The structure derived from a second neutron diffraction data set obtained in the metallic region of the  $P$ - $T$  phase diagram at 6.1 K and 4.5 kbar is also of the  $\beta^*$ -type.<sup>12</sup>

The shortest H···I contact in  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub> at 4.5 K and 1.5 kbar, with the ET molecule in its A conformation, is 3.014 (7) Å. We calculate that if the ET molecule in  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub> adopted the B conformation, the shortest H···I contact would be  $\sim 2.85$  Å, which appears to be very unfavorable since the sum of the hydrogen and iodine van der Waal radii is 3.35 Å. Therefore, the large van der Waal length of the I<sub>3</sub><sup>-</sup> anion ( $\sim 10.1$  Å) relative to the other  $\beta$ -(ET)<sub>2</sub>X anion salts (I<sub>2</sub>Br<sup>-</sup>,  $\sim 9.7$  Å; AuI<sub>2</sub><sup>-</sup>,  $\sim 9.4$  Å; IBr<sub>2</sub><sup>-</sup>,  $\sim 9.3$  Å) apparently forces the ET molecule in  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub> to adopt the A conformation. Thus,  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub> is structurally unique among the so-called  $\beta$ -phases.

The intermolecular S···S contacts at 4.5 K and 1.5 kbar are provided in Table II. In general, the S···S network in  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub>

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(10) Although the detector can rotate 30° above and 8° below the conventional diffraction plane, it was not possible to obtain all data within a shell since, in order to accommodate the cryostat and pressure cell, the crystal only rotates about the  $\omega$  axis. Data were obtained from a 2.6-mg crystal,  $2\theta_{\max} = 160^\circ$ , neutron  $\lambda = 1.1744$  Å. Total of 1032 independent reflections were corrected for cryostat and pressure cell absorption. The final least-squares refinements with isotropic thermal parameters and an isotropic extinction parameter were based on 687 reflections with  $F^2 \geq 3\sigma(F^2)$  and converged with  $R(F) = 0.042$  and  $R_w(F^2) = 0.088$ . "Neutron Beam Facilities at the HFR Available for Users", Institut Laue-Langevin, internal report, 1983.

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(12) The crystal had to be remounted before collecting data at 6.1 K and 4.5 kbar. In the new orientation, only 696 independent data were obtained of which 397 have  $F^2 > 3\sigma(F^2)$ . The variables were blocked with the scale factor, extinction parameter, and isotropic thermal parameters in one block and the scale factor and positional parameters in a second block. In the final least-squares cycles 15 outliers with  $F_o^2 - F_c^2 > 6\sigma(F_o^2)$  were excluded, possibly because of aluminum powder lines from the cryostat and pressure cell. The final refinement converged with  $R(F) = 0.068$  and  $R_w(F^2) = 0.136$ .

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remains similar to those in the other  $\beta$ -(ET)<sub>2</sub>X salts.

In conclusion, the high- $T_c$  superconducting phase,  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub>, is completely ordered although it is not isostructural with other known  $\beta$ -(ET)<sub>2</sub>X materials. Furthermore, there appears to be a correlation between the degree of structural ordering and  $T_c$  in these compounds. That is,  $\beta$ -(ET)<sub>2</sub>I<sub>2</sub>Br does not become superconducting apparently because of the random I/Br occupancy of the terminal anion position. The ambient-pressure modulated  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> structure is ordered, but the periodicity of the modulation is incommensurate with the average lattice. This may result in suppression of  $T_c$  to 1.4 K. Finally, the pressure-induced structural phase transition from the modulated  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> to the completely ordered  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub> produces a dramatic rise in  $T_c$  to 8 K. This value is now in agreement with band calculation predictions of increasing  $T_c$ 's for the IBr<sub>2</sub><sup>-</sup>, AuI<sub>2</sub><sup>-</sup>, and I<sub>3</sub><sup>-</sup> salts, in that order,<sup>1a</sup> which is also the order of increasing anion size.

**Note Added in Proof.** In a very recent report<sup>14</sup> (in Russian), an X-ray diffraction study of  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> at room temperature and  $P = 9.5$  kbar is described. Although hydrogen atoms were not located, the reported crystal structure is isostructural with the  $\beta^*$ -phase presented here. Thus, the  $\beta^*$  structural phase, characterized with the sample in its high- $T_c$  superconducting state, exists at room temperature if sufficient pressure is applied.

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**Supplementary Material Available:** Tables of positional and thermal parameters for  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub> at 4.5 K and 1.5 kbar and at 6.1 K and 4.6 kbar (2 pages); table of structure factors for  $\beta^*$ -(ET)<sub>2</sub>I<sub>3</sub> (5 pages). Ordering information is given on any current masthead page.

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## Biosynthetic Origins and Assignments of <sup>13</sup>C NMR Peaks of Brevetoxin B

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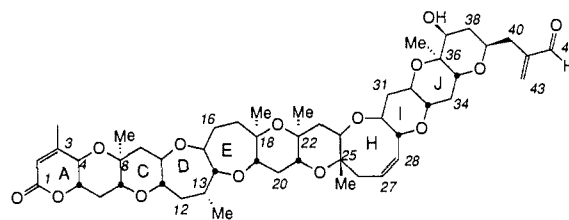
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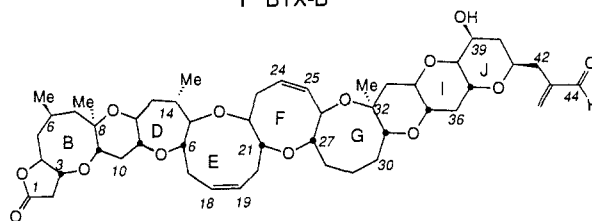
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The explosive growth of dinoflagellates, *Gymnodinium breve* Davis (*Ptychodiscus brevis* Davis), the "red tide", has led to massive fish kills, mollusk poisoning, and human food poisoning along the Florida coast and the Gulf of Mexico.<sup>1</sup> The potent neurotoxins responsible for this are the brevetoxins (BTX) with linear polycyclic ether structures represented by brevetoxin B (BTX-B) (1) C<sub>50</sub>H<sub>70</sub>O<sub>14</sub> and congeners;<sup>2</sup> recently, the structure

of BTX-A (2) having a different carbon skeleton has been elu-



1 BTX-B



2 BTX-A

cidated.<sup>3</sup> Here we report the assignment of <sup>13</sup>C NMR peaks and biosynthetic origins of carbon atoms in BTX-B by applying the 2D NMR INADEQUATE sequence<sup>4</sup> to BTX-B biosynthesized from sodium [1,2-<sup>13</sup>C<sub>2</sub>]acetate. This led to clarification of C-C connectivities of 14 acetate units by using 1.5 mg of sample (Figure 1).

The NMR assignment of hydrogens and carbons in nonlabeled BTX presents a challenge, due to limited sample amount and repetition of similar moieties, i.e., 10 cyclic ethers or 17 -O-CH- groups, 12 methylenes, and 6 angular methyls. The methyl, methylene, and methine carbons were identified by the DEPT technique,<sup>5</sup> while quaternary carbons were identified by a quaternary-only sequence<sup>6</sup> under conditions of suppressed nuclear Overhauser enhancement. A combination of <sup>1</sup>H-<sup>1</sup>H COSY<sup>7</sup> and <sup>1</sup>H-<sup>13</sup>C COSY (HETCOR)<sup>8</sup> via one-bond coupling allowed assignment of most protonated carbons and many protons, especially the severely overlapping methylene protons. These experiments resulted in assignments of 35 carbons. Of the remaining 15 carbons, eight were quaternary, all of which could be assigned by the COLOC sequence<sup>9</sup> designed to detect <sup>1</sup>H-<sup>13</sup>C two- and three-bond coupling; namely, it allowed one to correlate all methyl protons to quaternary carbons (<sup>2</sup>J<sub>CH</sub>) and methylene carbons (<sup>3</sup>J<sub>CH</sub>).

The biogenesis and NMR assignments of carbon atoms were next carried out by measurements of samples enriched with [1-<sup>13</sup>C]-, [2-<sup>13</sup>C]-, [1,2-<sup>13</sup>C<sub>2</sub>]acetates and methyl-<sup>13</sup>C-methionine. In a typical labeling experiment, artificial saltwater medium (NH-15)<sup>10</sup> is inoculated with *G. Breve* culture and 10 days later treated with penicillin G and streptomycin sulfate. On day 11 the culture medium is treated with 0.68 mM labeled sodium acetate, the culture is grown for a further 7 days at 20 °C under constant illumination, and the BTX's are isolated. Namely, *G. breve* is extracted with ether and the crude extract is purified by preparative TLC, 5:1 hexane/isopropyl alcohol. The BTX's are further purified by normal-phase HPLC by using 6:1 iso-octane/isopropyl alcohol; 18 L of *G. breve* culture usually yielded 1-2 mg of BTX-B and 0.5-0.8 mg of BTX-A. However, in some

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