

and  $R_m$  values<sup>22</sup> of the trimer were almost consistent with those of the corresponding linear structure, ApGpC, reported by Khorana.<sup>23</sup> The trimer was resistant to nuclease P<sub>1</sub> and ribonuclease T<sub>2</sub>. The trimer was resistant to nuclease P<sub>1</sub> but digested with snake venom phosphodiesterase to give pC, pG, and A in the ratio of 1.00:0.96:1.10. These results were consistent with those reported by Ruskin<sup>3a</sup> and Wallace.<sup>1</sup> Furthermore, structural proof of the trimer was also obtained at the level of the dimer. The main product **12**<sup>22,24</sup> isolated in 79% yield by a similar deprotection procedure from **10** was incubated with alkaline phosphatase. This enzyme reaction gave quantitatively 2'-5'-linked ApG, which was found to be resistant to nuclease P<sub>1</sub> but yet digestible to A and pG upon treatment with snake venom phosphodiesterase. These properties were in agreement with those of 2'-5' RNAs.

Biological properties of **1** and **12** will be reported shortly in detail elsewhere.

(22) **1**:  $R_f$  0.74 (relative to pU) (*n*-PrOH/concentrated ammonia/H<sub>2</sub>O, 55:10:35, v/v/v);  $R_m$  0.47 (relative to pU) (0.03 M phosphate buffer, pH 7.1), **12**:  $R_f$  0.66;  $R_m$  0.85.

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## Band Electronic Structures of the Ambient Pressure Organic Superconductors $\beta$ -(ET)<sub>2</sub>X (X = I<sub>3</sub><sup>-</sup>, IBr<sub>2</sub><sup>-</sup>)

Myung-Hwan Whangbo\*

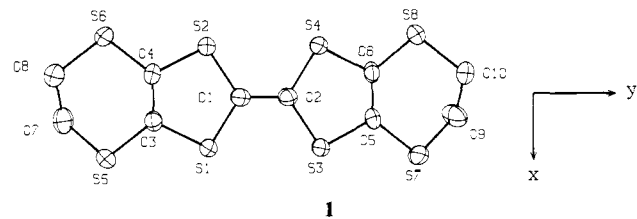
Department of Chemistry  
North Carolina State University  
Raleigh, North Carolina 27650

Jack M. Williams,\* Peter C. W. Leung, Mark A. Beno,  
Thomas J. Emge, Hau H. Wang, K. Douglas Carlson, and  
G. W. Crabtree

Chemistry and Materials Science and  
Technology Divisions, Argonne, Illinois 60439

Received March 18, 1985

Recently, bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or simply ET, C<sub>10</sub>S<sub>8</sub>H<sub>8</sub>) (**1**) has been found to yield two ambient



pressure organic superconductors  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> ( $T_c = 1.2$ – $1.6$  K)<sup>1-6</sup>

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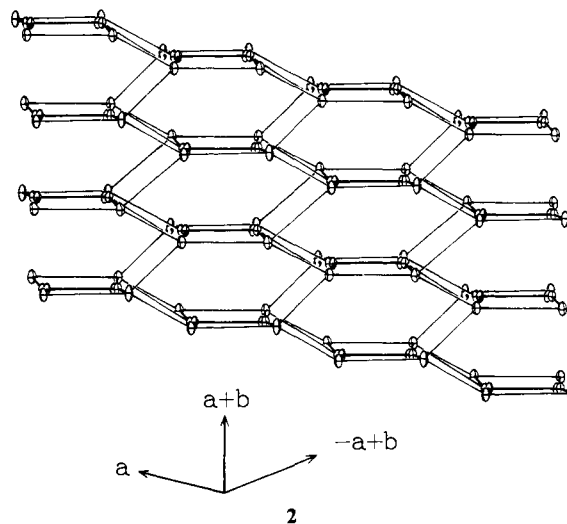
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and  $\beta$ -(ET)<sub>2</sub>IBr<sub>2</sub> ( $T_c = 2.3$ – $2.8$  K).<sup>7,8</sup> Crystal structures determined at two temperatures (298, 125 K) reveal<sup>3,7,9</sup> that the ET stacks have a number of short interstack S...S contact distances less than the van der Waals radius sum of sulfur (3.60 Å) along the *a* and *a* + *b* directions, as shown by a schematic illustration **2** of a sheet of ET stacks projected along the local *y* axis of ET



defined in **1** (only the sulfur atoms of ET are shown in **2**, where the thin lines joining adjacent ET molecules indicate short interstack S...S contacts less than 3.6 Å). Thus the  $\beta$ -(ET)<sub>2</sub>X (X = I<sub>3</sub><sup>-</sup>, IBr<sub>2</sub><sup>-</sup>) synthetic metals appear much more two dimensional (2D) in terms of crystal packing than any other known organic conductors. In the above  $\beta$ -(ET)<sub>2</sub>X salts the corrugated sheets of ET stacks are separated by sheets containing anions X<sup>-</sup>,<sup>3,7</sup> thereby leading to alternating layers of cations and anions perpendicular to *c* (*y* axis in the Cartesian system). In agreement with these structural characteristics, electrical<sup>1-3</sup> and optical<sup>10</sup> conductivity measurements and critical magnetic field studies<sup>4,11</sup> have shown that  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub> is a 2D metal. The band electronic structure<sup>12</sup> of  $\beta$ -(ET)<sub>2</sub>I<sub>3</sub>, estimated for the room temperature structure by calculating the overlap integrals between the HOMO's of nearest-neighbor ET molecules, indicated that the Fermi surface is closed and nearly isotropic in two dimensions. The crystal structures of  $\beta$ -(ET)<sub>2</sub>X vary appreciably as a function of the anion size and temperature.<sup>3,7</sup> To quantitatively evaluate how such structural changes affect the electronic structures of  $\beta$ -(ET)<sub>2</sub>X, we carried our band electronic structure calculations on  $\beta$ -(ET)<sub>2</sub>X (X = I<sub>3</sub><sup>-</sup>, IBr<sub>2</sub><sup>-</sup>) for the crystal structure determined at both 298 and 125 K<sup>3,7</sup> employing the tight binding band scheme<sup>13,14</sup> based upon the extended Hückel method.<sup>15</sup> In order to better represent the interstack S...S interactions, double- $\zeta$  Slater-type orbitals were used for the *s* and *p* orbitals of carbon and sulfur.<sup>16,17</sup>

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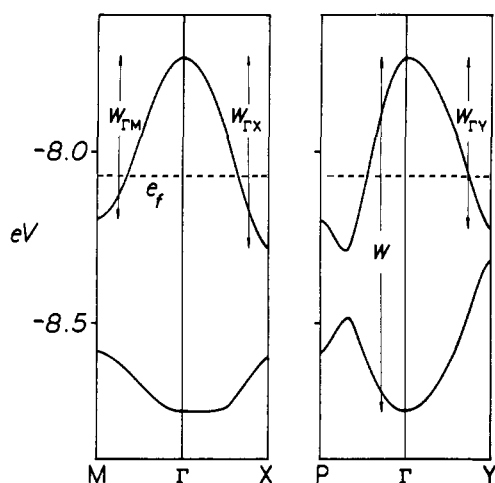
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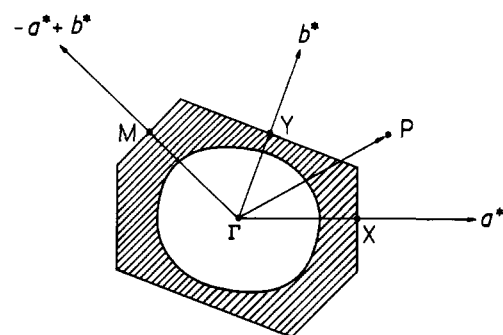
**Figure 1.** Dispersion of the  $\psi_+$  and  $\psi_-$  bands (the lower and upper bands, respectively) along some wavevector directions, where the dashed line refers to the Fermi level. The wavevector points  $\Gamma$ ,  $X$ ,  $Y$ ,  $M$ , and  $P$  are defined as follows:  $\Gamma = (0,0)$ ,  $X = (a^*/2,0)$ ,  $Y = (0,b^*/2)$ ,  $M = (-a^*/2,b^*/2)$ , and  $P = (a^*/2,b^*/2)$ .

$\beta$ -(ET) $_2$ X systems have two ET molecules per unit cell, the HOMO's of which interact to give the bonding and antibonding levels  $\psi_+$  and  $\psi_-$ , respectively. Thus  $\beta$ -(ET) $_2$ X metals have two highest occupied bands derived largely from  $\psi_+$  and  $\psi_-$  of each unit cell, which will be referred to as the  $\psi_+$  and  $\psi_-$  bands, respectively. As a representative example of how these two bands vary along some wavevector directions, Figure 1 shows the  $\psi_+$  and  $\psi_-$  bands (the lower and upper bands, respectively) calculated using the 298 K structural data of  $\beta$ -(ET) $_2$ I $_3$ . A number of important features of the calculated band structures of  $\beta$ -(ET) $_2$ X salts ( $X^- = I_3^-, IBr_2^-$ ) can be summarized as follows: (a) The  $\psi_-$  band does not overlap with the  $\psi_+$  band, which is different from the band electronic structure observed in (TMTSF) $_2$ X.<sup>13,14,16</sup> With the formal oxidation state of (ET) $_2^+$  per unit cell, the  $\psi_+$  band is completely filled and the  $\psi_-$  band is half-filled. Therefore,  $\beta$ -(ET) $_2$ X should not be considered as a system with a  $1/4$ -empty band but as one with  $1/2$ -filled band. This distinction is particularly important in connection with the Peierls instability of pseudo-one-dimensional conductors.<sup>19</sup> For instance, the Peierls distortion expected for a  $1/2$ -filled band is dimerization but that for a  $1/4$ -empty band is tetramerization. (b) The  $\psi_-$  band crosses the Fermi level in all wavevector directions of the  $a^*b^*$  plane, so that the resulting Fermi surface is closed as shown in Figure 2 for the 298 K structure of  $\beta$ -(ET) $_2$ I $_3$ . (c) The width of the  $\psi_-$  band along the interstack direction  $a$  (i.e.,  $W_{\Gamma X}$ ) is comparable in magnitude with that along the interstack direction  $-a + b$  (i.e.,  $W_{\Gamma M}$ ) or that along the  $b$  direction (i.e.,  $W_{\Gamma Y}$ ). Consequently, the Fermi surface is nearly isotropic in two dimensions. (d) The  $\psi_-$  band dispersion along the stacking direction  $a + b$  is given by that component along  $\Gamma \rightarrow P$  in Figure 1 (note in Figure 2 that the point  $P$  lies outside the first Brillouin zone). Comparison of the  $\psi_-$  band dispersions along  $\Gamma \rightarrow X$  and  $\Gamma \rightarrow P$  shows that the widths of the  $\psi_-$  band along the interchain direction  $a$  and the stacking direction  $a + b$  are nearly the same (see Figure 1).

(17) For sulfur and carbon, each atomic orbital was represented by a linear combination of two Slater-type orbitals of exponents  $\zeta_u$  and  $\zeta_v$  with the weighting coefficients  $c_u$  and  $c_v$ , respectively (Clementi, E.; Roetti, C. *At. Data Nucl. Data Tables* 1974, 14, 177). The  $\zeta_u$ ,  $\zeta_v$ ,  $c_u$ ,  $c_v$ , and  $H_{uv}$  (valence-shell ionization potential) values employed in our study are respectively 2.662, 1.688, 0.5564, 0.4874, and -20.0 eV for S 3s, 2.338, 1.333, 0.5212, 0.5443, and -13.3 eV for S 3p, 1.831, 1.153, 0.7616, 0.2630, and -21.4 eV for C 2s, and 2.730, 1.257, 0.2595, 0.8025, and -11.4 eV for C 2p. A modified Wolfsberg-Helmholz formula<sup>18</sup> was used to calculate  $H_{uv}$ .

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**Figure 2.** Fermi surface associated with the half-filled  $\psi_-$  band. The wavevectors in the shaded and unshaded regions of the first Brillouin zone lead to the occupied and unoccupied levels of the  $\psi_-$  band, respectively. The boundary separating those two regions, which is closed and nearly circular, is the Fermi surface.

The band structure calculated in the present work is consistent with the observed 2D metallic properties  $\beta$ -(ET) $_2$ I $_3$ .<sup>6,10</sup> An additional band parameter that characterizes the  $\psi_+$  and  $\psi_-$  bands is the combined bandwidth  $W$  defined in Figure 1. The  $W_{\Gamma X}$ ,  $W_{\Gamma M}$ ,  $W_{\Gamma Y}$ , and  $W$  values calculated for the 298 (125) K structure of  $\beta$ -(ET) $_2$ I $_3$  are 0.56 (0.64), 0.47 (0.49), 0.51 (0.57), and 1.03 (1.20) eV, respectively. The corresponding values for the 298 (125) K structure of  $\beta$ -(ET) $_2$ IBr $_2$  are 0.64 (0.68), 0.48 (0.52), 0.55 (0.59), and 1.10 (1.18) eV, respectively. Therefore, the temperature lowering from 298 to 125 K and the replacement of I $_3^-$  anion with IBr $_2^-$  slightly enhance the magnitudes of the bandwidths in  $\beta$ -(ET) $_2$ X. These trends are related to the findings of the structural studies<sup>3,7</sup> that the interstack S...S distances decrease with decreasing temperature and that these contacts are generally shorter in  $\beta$ -(ET) $_2$ IBr $_2$  than in  $\beta$ -(ET) $_2$ I $_3$ .

The above observations pose an interesting question: why is the superconducting transition temperature  $T_c$  higher, by a factor of 2, in  $\beta$ -(ET) $_2$ IBr $_2$  than in  $\beta$ -(ET) $_2$ I $_3$ ? Since the  $\psi_-$  band is wider in  $\beta$ -(ET) $_2$ IBr $_2$  than in  $\beta$ -(ET) $_2$ I $_3$ , the density of states at the Fermi level,  $n(e_f)$ , is expected to be smaller for  $\beta$ -(ET) $_2$ IBr $_2$ . More exactly, according to the simple relationship<sup>20</sup>  $T_c \propto \exp[-1/n(e_f)]$ , it is at first expected that  $\beta$ -(ET) $_2$ I $_3$  would have a higher  $T_c$  than  $\beta$ -(ET) $_2$ IBr $_2$ , which is in marked disagreement with the experimental observations.<sup>1-8</sup> To account for this discrepancy, it is necessary to investigate how the phonon (lattice vibration) structures of  $\beta$ -(ET) $_2$ X are modified by the anion  $X^-$ .<sup>8</sup> An important factor to consider might be the structural modulation that occurs in  $\beta$ -(ET) $_2$ I $_3$ .<sup>21,22</sup> This structural disorder, which does not occur in the IBr $_2$  derivative, could suppress an otherwise high value of  $T_c$  for the I $_3$  derivative. Recently, it has been found that an applied pressure of 1.2–1.3 kbar increases the onset of superconductivity in  $\beta$ -(ET) $_2$ I $_3$  to about 8 K,<sup>23,24</sup> a value greater than that in  $\beta$ -(ET) $_2$ IBr $_2$  under ambient pressure (2.3–2.8 K). Consequently, it is suggested that the primary role of the applied pressure in  $\beta$ -(ET) $_2$ I $_3$  is to suppress the effect of the structural disorder.

**Acknowledgment.** This work was in part supported by the Camille and Henry Dreyfus Foundation through a Teacher-Scholar Award to M.-H.W. Research at Argonne National Laboratory is sponsored by the U.S. Department of Energy (DOE), Division of Materials Sciences, under Contract W-31-109-Eng-38. We express our appreciation for computing time made available by DOE on the ER-CRAY.

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