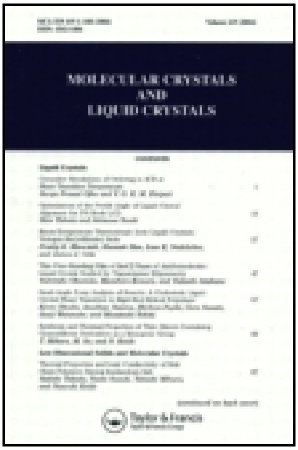

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

Novel Low Temperature Modulated Structure of the Ambient Pressure Superconductor $(BEDT\text{-}TTF)_2I_3$ and a Design Strategy for New Superconducting Polyhalide Phases

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To cite this article: Jack M. Williams , Peter C. W. Leung , Thomas J. Emge , Hau H. Wang , Mark A. Beno , Vaclav Petricek & Philip Coppens (1985): Novel Low Temperature Modulated Structure of the Ambient Pressure Superconductor $(BEDT\text{-}TTF)_2I_3$ and a Design Strategy for New Superconducting Polyhalide Phases, Molecular Crystals and Liquid Crystals, 119:1, 347-355

To link to this article: http://dx.doi.org/10.1080/00268948508075184

Mol. Cryst. Liq. Cryst. 1985, Vol. 119, pp. 347-355
0026-8941/85/1194-0347/$15.00/0

Printed in the United States of America

NOVEL LOW TEMPERATURE MODULATED STRUCTURE OF THE AMBIENT PRESSURE SUPERCONDUCTOR (BEDT-TTF)$_2$I$_3$ AND A DESIGN STRATEGY FOR NEW SUPERCONDUCTING POLYHALIDE PHASES

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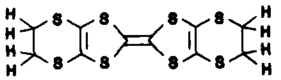
Abstract The first ambient pressure S-based organic superconductor (BEDT-TTF)$_2$I$_3$, abbreviated (ET)$_2$I$_3$, exhibits a novel modulated structure below ~ 200 K. At 125 K the ET molecules and I_3^- anions exhibit large displacements 0.124 (3) Å and 0.281 (1) Å, respectively, from their positions in the "average structure." New ambient pressure superconducting polyhalide derivatives such as (ET)$_2$IBr$_2$ are discussed with transition temperatures of 2.7 K, and in one sample, 4.2 K.

INTRODUCTION

With the very recent observation[1-3] of ambient pressure superconductivity in (ET)$_2$I$_3$ [1 is BEDT-TTF or "ET" = bis(ethylenedithio)tetrathiafulvalene] a new era in organic superconductor research appears certain. This suggestion is based on the findings that the T$_c$'s are from ~ 0.3-3.0 K higher than those of the (TMTSF)$_2$X, X = (monovalent anion) materials, and also because the crystal structures of the (ET)$_2$X materials exhibit greater variation than those of



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BEDT-TTF or **ET**

the $(TMTSF)_2X$ systems. This latter observation is important in that it provides great latitude in the design of new materials. In this article we focus on the crystal structures of $(ET)_2X$, $X = BrO_4^-$, ReO_4^-, and I_3^- and especially the novel low temperature modulated structure of $(ET)_2I_3$. In a companion article[4], we discuss the electrical properties of the $(ET)_2I_3$ phase (V_c = 855.9 Å^3, 298 K)[2] with a T_c = 1.40 ± 0.02 K.

THE STRUCTURES OF $(ET)_2X$, $X = BrO_4^-$, ReO_4^-, and I_3^-

Very recently it has been pointed out[5] that the $(ET)_2X$ systems, where $X = [BrO_4^-, ReO_4^-]$[5], $[ClO_4^-]$[6], and $[I_3^-]$[2,7] belong to a new structural class of organic conductors in which the interstack chalcogenide [S•••S] contacts are much shorter than the similar intrastack contacts. In general, the interstack S•••S contact distances are less than the van der Waals radius sum of 3.6 Å while the intrastack separations usually exceed 3.6 Å.

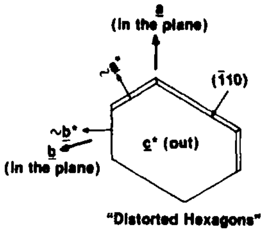

FIGURE 1
The crystal habit exhibited by $(ET)_2I_3$ electrocrystallized from 1,1,2-trichloroethane.

Kobayashi et al.[6] pointed this out in their prototypical study of solvated $(ET)_2(ClO_4)(C_2H_3Cl_3)_{0.5}$.

The Structure of $(ET)_2I_3$ at 298 K

Crystals of $(ET)_2I_3$ were prepared in 1,1,2-trichloroethane[2] (Figure 1). X-ray energy dispersive analysis of the $(\underline{n}\text{-}Bu_4N)I_3$ reveals exceedingly high purity with nondetectable Br content compared to standardized samples with <1-2 ppm Br. In $(ET)_2I_3$ the ET molecules form loosely connected "stacks" approximately along the crystallographic [110] diagonal axis as illustrated in Figure 2.

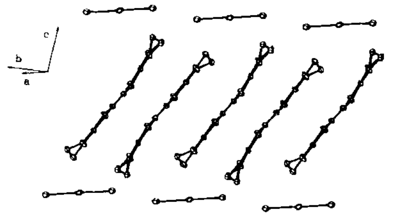

FIGURE 2
Packing of ET molecules and linear (centrosymmetric) I_3^- anions in $(ET)_2I_3$.

The ET molecule and interstack S•••S contact labeling scheme is given in Figure 3.

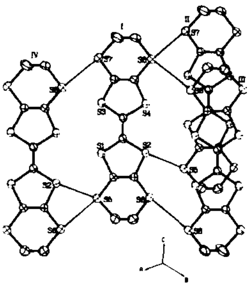

FIGURE 3
The short interstack S•••S contacts (d <3.60 Å) in $(ET)_2I_3$ at 298 K.

The cation molecules are nonplanar and two of the peripheral carbon atoms are in crystallographic disorder (at 298 and 125 K). The centrosymmetric and well-ordered I_3^- anions [I-I = 2.912(1) Å] form ribbons with a relatively short intermolecular I•••I distance of 4.211(1) Å. The intrastack S•••S distances (298 K) exceed 3.60 Å (shortest distance 3.759(1) Å) while the four shortest interstack distances range from 3.574 (1) to 3.600 (1) Å [S2•••S5 = 3.574(2) Å; S6•••S8 = 3.593(2) Å; S7•••S8 = 3.598(2) Å; S5•••S6 = 3.600(2) Å].

Surprising structural changes occur when $(ET)_2I_3$ is cooled below ~ 200 K, i.e., pairs of satellite reflections surround each Bragg reflection which is an indication of a displacive structural modulation (vide infra).

The Incommensurate Structural Modulation in $(ET)_2I_3$ at 125 K

In the $(TMTSF)_2X$ systems below the anion-ordering phase transitions the superlattices are commensurate with those at high temperature. However, in $(ET)_2I_3$ symmetrically placed, but incommensurate, satellite reflections develop with $\pm q = 0.08a^* + 0.27b^* + 0.205c^*$. The transition at ~ 200 K is quite sharp and does not depend on the thermal cycling rate. The nonequivalent satellite peak intensities can be less, or greater, than the fundamental peak indicating a displacive structural modulation occurs. The satellite data were analyzed using a new program (JANA)[8] which allows the intensities to be described in terms of one or more sinusoidal displacement waves with associated phases. We have assumed that the I_3^- and ET moieties behave as rigid bodies with respect to the modulation waves and that the center of symmetry is preserved in the four-dimensional super-space group. In the least-squares analysis the positional and temperature parameters within the rigidly displaced bodies were varied for all non-hydrogen atoms. Low temperature data were collected well below the structural transition temperature of ~ 200 K, using graphite-monochromatized MoKα radiation and a Syntex $P2_1$ diffractometer. A total of 3767 main Bragg and 7045 satellite reflection intensities were measured and 3346/1041, respectively, were used in the data analysis [R_F (Bragg + satellite) = 0.060]. The triclinic crystal ($P\bar{1}$, Z = 1) has cell dimensions (125 K) of: $\underline{a}$ = 6.561(1) Å, $\underline{b}$ = 9.010(2) Å, $\underline{c}$ = 15.173(2) Å, α = 95.09(1)°, β = 95.95(1)°, γ = 110.27(1)°, V_c = 829.4(2) Å^3.

The average crystal structure at 125 K differs mainly from that at 298 K in that the intermolecular S•••S distances are contracted by about 2% as shown in Table I.

TABLE I. Interstack S•••S Distances (Å) in $(BEDT\text{-}TTF)_2I_3$*

	298 K	125 K	
		Average†	Range
S(3)•••S(8)	3.651(2)	3.578(2)	3.527 - 3.633
S(5)•••S(2)	3.574(2)	3.556(2)	3.503 - 3.613
S(5)•••S(6)	3.600(2)	3.548(2)	3.505 - 3.589
S(7)•••S(8)	3.598(2)	3.532(2)	3.493 - 3.575
S(5)•••S(7)	3.628(2)	3.547(2)	3.542 - 3.554
S(4)•••S(6)	3.691(2)	3.625(2)	3.553 - 3.698
S(8)•••S(6)	3.593(2)	3.553(2)	3.474 - 3.636
I(2)•••I(2)	4.211(1)	4.204(1)	4.189 - 4.275

*Only the S•••S interactions whose average distances at 125 K are less than the van der Waals sum of 3.6 Å are shown. All such distances are of the interstack type.

†The average structure refers to the refined atomic parameters using both fundamental and satellite reflections. These atomic distances are affected by the sinusoidal modulation resulting in a range of distances which are calculated by use of equation 1 (see text).

Even after lattice shrinkage (298 → 125 K) all but one of the intrastack S•••S distances exceeds 3.60 Å. A significant finding is that the I_3^- anion and ET molecule displacement vectors are of <u>different</u> directions and magnitudes. The former is large [0.281(1) Å] and directed along the *a*-axis [components in fractional coordinates are: 0.0428(2), 0.0008(2), -0.0022(1)], while the latter is somewhat smaller [0.124(3) Å; 0.0151(3), -0.0047(3), 0.0022(1)] and directed almost exactly along one of the inertial axes of the ET molecule as illustrated in Figures 4 and 5.

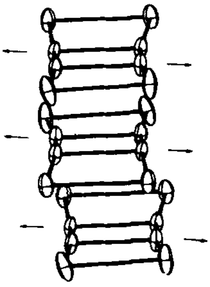

FIGURE 4

The ET cation column in $(ET)_2I_3$ including only the framework S-atoms of each ET molecule. Arrows indicate the allowed modulation displacement vectors of each molecule whose length is approximately 5 times the magnitude of the observed displacements.

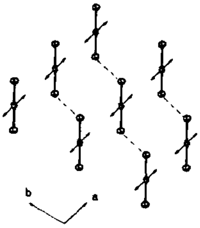

FIGURE 5

Crystal packing of the I_3^- anions on the a-b plane. All I_3^- anions are related by unit cell translations on the a-b plane. Pairs of arrows illustrate the allowed modulated displacements of I_3^- as described in Figure 4.

The local displacement ($\Delta\underset{\sim}{X}$) of each individual anion and ET molecule is described completely by the relation $\Delta\underset{\sim}{X} = \underset{\sim}{u} \sin (2\pi\underset{\sim}{q}\cdot\underset{\sim}{r} - \phi)$ (eq. 1) in which $\underset{\sim}{u}$ is the displacement vector, $\underset{\sim}{r}$ is the center-of-mass of a molecule relative to an origin, and ϕ is the phase angle. The phase angles are 0° and 13.8(9)° for the I_3^- and ET species, respectively.

The derived intermolecular contact distances resulting from the displacive structural modulations are crucially dependent on the phase angles in eq. 1. Since the ET molecule displacement vector is parallel to the molecular plane, local variations can occur in molecular stacking and in the intermolecular overlap integrals. Thus, the interstack S•••S distances fluctuate by as much as 0.16 Å in different unit cells (Table I) with a local shortening of up to 0.08 Å. For the I_3^- columns the modulations have a larger magnitude, but are directed such that the I_3^- anions slip relative to each other and the shortest intermolecular I•••I distances change by as much as 0.07 Å. Finally, the local fluctuations of the interatomic distances are very significant and, therefore, any theoretical treatment of the transport properties of $(ET)_2I_3$ below 200 K must include these local variations in geometry. Neutron scattering data taken at 10 K confirm the incommensurate modulation exists at that temperature.[9]

The S•••S Networks in $(ET)_2X$ Conductors

It is especially noteworthy that the short interstack S•••S interactions (d < 3.60 Å) that occur in $(ET)_2X$, X = $[BrO_4^-, ReO_4^-]$,[5] $[I_3^-]$,[2] form an extensive "corrugated sheet" network (see Figure 6).[2] The network is quite different from that observed[10] in $(TMTSF)_2X$ materials. At low temperature (125 K), the network of ET molecules becomes truly 2-dimensional as all the cation sheets are connected by short S•••S contacts. Since the S•••S network provides the pathway for electrical conduction it is not surprising that these materials exhibit highly two-dimensional electrical conductivity.

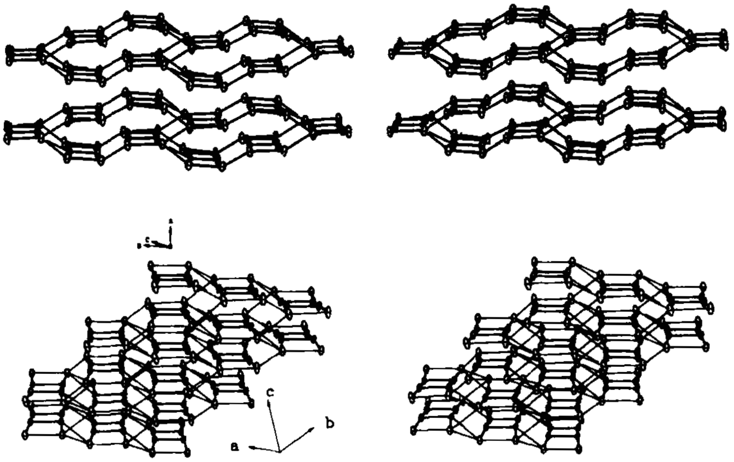

FIGURE 6

Stereoviews of the "corrugated sheet" network of interstack (d < 3.60 Å) S•••S interactions in $(ET)_2X$, X = BrO_4^- and ReO_4^- (top, 125 K) and $(ET)_2I_3$ (bottom, 125 K). Note that the network is much more highly developed in $(ET)_2I_3$.

The I_3^- Anion Environment In $(ET)_2I_3$ And A Strategy For New Materials Design

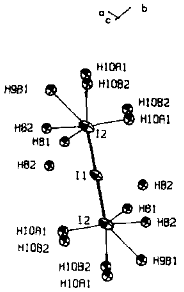

FIGURE 7

The hydrogen atoms surrounding the I_3^- anion in $(ET)_2I_3$. The anion resides in a cavity created by the $-CH_2$ groups of ET and can be replaced by similar polyhalide species. Disordered H-atoms are HA and HB.

As illustrated in Figure 7 the immediate environment of the linear $(I-I-I)^-$ anion comprises H-atoms from the $-CH_2$ groups of ET. By analogy with the correlations[10] developed for the $(TMTSF)_2X$ systems, the S•••S interstack distances, and the electrical properties of $(ET)_2X$ materials, can be altered by inserting different triatomic polyhalide anions in the $(ET)_2X$ framework cavity. For example, using X = IBr_2^-, I_2Br^-, or ICl_2^-, we have prepared many new $(ET)_yX_n$ phases.[2,11] For the IBr_2^- anion, purposely chosen because it is ~ 5% shorter than I_3^-, we have several phases which are ambient pressure superconductors (rf penetration depth measurements) with T_c's of 2.7 K and, in one sample, 4.2 K. These T_c's are the highest yet reported for any organic superconductor.

Acknowledgment Work performed under the auspices of the Office of Basic Energy Sciences, Division of Materials Sciences, of the U.S. Department of Energy, under Contract W-31-109-Eng-38. Support of the work at Buffalo by the National Science Foundation (CHE7905897) and the Donors of the Petroleum Research Fund administered by the American Chemical society (PRF15451AC67C) is gratefully acknowledged.

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