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### The Synthesis, Crystal Structure, Electrical Conductivity and Band Electronic Structure of (BPDT-TTF)<sub>2</sub>ICl<sub>2</sub>

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# The Synthesis, Crystal Structure, Electrical Conductivity and Band Electronic Structure of $(\text{BPDT-TTF})_2\text{ICl}_2$

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$(\text{BPDT-TTF})_2\text{ICl}_2$  is a synthetic metal salt composed of the electron donor molecule bis(propylenedithio)tetrathiafulvalene (BPDT-TTF,  $\text{C}_{12}\text{H}_{12}\text{S}_8$ ) and the linear iododichloride anion,  $\text{ICl}_2^-$ . The crystal structure of  $(\text{BPDT-TTF})_2\text{ICl}_2$ , determined at 298 K and 120 K, closely resembles those of the organic metals and semiconductors based on bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF,  $\text{C}_{10}\text{H}_8\text{S}_8$ ), in that all of these materials contain sheetlike donor molecule networks sandwiched between anion layers. In contrast to the  $(\text{BEDT-TTF})_2\text{X}$  salts, however, there is a total absence of  $\text{S} \cdots \text{S}$  contact distances less than  $\sim 3.6$  Å (the van der Waals radius sum) within the donor-molecule network of  $(\text{BPDT-TTF})_2\text{ICl}_2$ . In addition, each stack of BPDT-TTF molecules is also strongly dimerized. The lack of short  $\text{S} \cdots \text{S}$  contact distances at both 298 K and 120 K appears to be a consequence of the bulky propylene groups of BPDT-TTF compared to the smaller ethylene groups of the BEDT-TTF molecule. Based

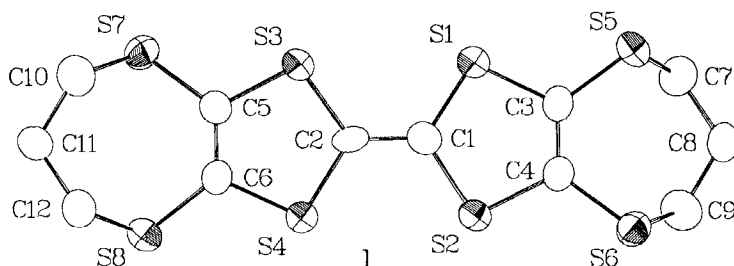
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upon four-probe a.c. resistivity measurements,  $(\text{BPDT-TTF})_2\text{ICl}_2$  is a semiconductor. From our tight-binding band calculations on  $(\text{BPDT-TTF})_2\text{ICl}_2$ , and the fact that this salt is nonmetallic, it is concluded that each  $(\text{BPDT-TTF})_2^+$  dimer cation carries an unpaired electron. The lack of short intermolecular  $\text{S} \cdots \text{S}$  contacts, and the strong dimerization in each BPDT-TTF stack, is considered to be a consequence of the crystal packing of the relatively bulky propylene groups of the BPDT-TTF molecule around each  $\text{ICl}_2^-$  anion resulting in semiconductive electrical properties.

**Keywords:** organic conductors, crystal structure, electrical properties, band electronic structure, BPDT-TTF

## INTRODUCTION

Ambient-pressure superconductivity has been reported for several  $(\text{BEDT-TTF})_2X$  synthetic metals, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene and  $X^-$  is a linear anion, namely,  $X^- = \text{I}_3^-$ ,<sup>1,2</sup> with  $T_c = 1.4$  K,  $X^- = \text{IBr}_2^-$ ,<sup>3</sup> with  $T_c = 2.8$  K and  $X^- = \text{AuI}_2^-$ ,<sup>4</sup> with  $T_c = 5$  K. Other metallic  $(\text{BEDT-TTF})_2X$  organic salts, viz., where  $X^- = \text{I}_2\text{Br}^-$ ,<sup>5</sup> and semiconductors, viz.,  $X^- = \text{AuCl}_2^-$ ,<sup>6</sup>  $\text{ICl}_2^-$ ,<sup>7</sup> or  $\text{BrICl}^-$ ,<sup>7</sup> have also been synthesized. The search for new electron-donor molecules with similar molecular and electronic properties to those of BEDT-TTF, for use in the development of new synthetic metals, requires knowledge of the structural features which bear directly on the physical properties of their derived salts. Such structural parameters for the BEDT-TTF-based salts include the size and symmetry of the anion,<sup>5,7</sup> the existence of short inter-donor  $\text{S} \cdots \text{S}$  contact distances less than the  $\text{S} \cdots \text{S}$  van der Waals radius sum of  $\sim 3.6$  Å, and sometimes short hydrogen  $\cdots$  anion ( $\text{H} \cdots X^-$ ) contact distances.<sup>20</sup> The syntheses of the propylene and methylene analogs of BEDT-TTF, which are bis(propylenedithio)tetrathiafulvalene<sup>9,13</sup> (BPDT-TTF, **1**) and bis(methylenedithio)tetrathiafulvalene<sup>8,9</sup> (BMDT-TTF), respectively, have been reported recently. The crystal structures of only a few  $(\text{BPDT-TTF})_nX_m$



salts have been reported, including  $(\text{BPDT-TTF})_3(\text{PF}_6)_2$ ,<sup>10,11</sup>  $(\text{BPDT-TTF})_2\text{I}_3$ ,<sup>12</sup> and  $(\text{BPDT-TTF})_2\text{IBr}_2$ .<sup>13</sup> These three BPDT-TTF materials are closely related, in that the  $X^- = \text{PF}_6^-$  and  $\text{I}_3^-$  salts have one-dimensional band electronic structures,<sup>14</sup> and the  $X^- = \text{I}_3^-$  and  $\text{IBr}_2^-$  salts are isomorphous.<sup>13</sup> With the increased number and types of  $(\text{BPDT-TTF})_nX_m$  salts that are currently being synthesized, correlations of their structural parameters to their observed physical properties are slowly being developed and in this report we discuss those for a new semiconducting salt,  $(\text{BPDT-TTF})_2\text{ICl}_2$ .

The  $(\text{BPDT-TTF})_2\text{ICl}_2$  salt was chosen for synthesis and structure-conductivity characterization because of materials design parameters learned from the  $(\text{BEDT-TTF})_2X$  series,<sup>27</sup> viz., the shorter the anion ( $X = \text{I}_3^- > \text{AuI}_2^- > \text{IBr}_2^- > \text{ICl}_2^-$ ) the shorter the sheet network  $\text{S} \cdots \text{S}$  distances. Since the  $\text{S} \cdots \text{S}$  network provides the pathway for electrical conduction in these materials, it is desirable to determine the precise metrical parameters of the network that optimize the electrical properties. Electrical properties measurements have indicated that  $(\text{BPDT-TTF})_2\text{I}_3$  is semiconductive,<sup>12</sup> but that its resistivity *decreases* with applied pressure (up to 10 kbar) until the room temperature value is approximately equal to that of the isostructural  $(\text{BEDT-TTF})_2\text{I}_3$  salt also at room temperature. Since applied pressure should shorten the  $\text{S} \cdots \text{S}$  contacts in  $(\text{BPDT-TTF})_2\text{I}_3$ , the same shortening might be accomplished simply by using a shorter anion such as the symmetric  $(\text{Cl-I-Cl})^-$ . We examine how the use of a shorter anion counteracts the bulkiness of the propylene groups in BPDT-TTF materials thereby gaining some insight into structure-conductivity relationships in  $(\text{BPDT-TTF})_2X$  salts.

## SYNTHESIS

The organic donor molecule BPDT-TTF was prepared as previously described.<sup>9,13</sup> The oxidation was performed by use of the electrocrystallization technique with 8.5 mg of BPDT-TTF (1.4 mM) and 240 mg of  $\text{NBu}_4\text{ICl}_2$  (36 mM) in 15 mL tetrahydrofuran at a current density of  $0.9 \mu\text{A}/\text{cm}^2$ . Black platelike crystals of  $(\text{BPDT-TTF})_2\text{ICl}_2$  were harvested after two weeks of crystal growth. All crystals gave room temperature ESR peak-to-peak linewidths of around 3.5 to 4.5 G which indicates the presence of a single phase.

## X-RAY DIFFRACTION

The x-ray diffraction data at 298 K and 120 K were collected on a Syntex P2<sub>1</sub> diffractometer, equipped with a nitrogen-cooled low-tem-

TABLE I  
Unit cell and data collection parameters and refinement results for  
(BPDT-TTF)<sub>2</sub>ICl<sub>2</sub>

unit cell (298/120K)		
<i>a</i> 15.950(6)/15.958(8) Å	β 100.84(5)/100.33(3)°	
<i>b</i> 6.930(1)/6.912(2) Å	<i>V</i> 1864(1)/1854(1) Å <sup>3</sup>	
<i>c</i> 17.170(8)/17.001(6) Å	<i>d</i> <sub>calc</sub> 1.823/1.842 g cm <sup>-3</sup>	
μ 18.8/19.0 cm <sup>-1</sup>	<i>T</i> <sub>min</sub> , <i>T</i> <sub>max</sub> 0.85, 0.88	
space group P2/c ( <i>Z</i> = 4)		
crystal dimensions	0.47 × 0.09 × 0.07 × 0.08 mm	
along the directions	[001], [100], [110], [1-10]	
wavelength (MoKα)	0.7107 Å (graphite monochromatized)	
scan widths, speeds	2.7 – 3.1°, 2 – 12° min <sup>-1</sup>	
θ-2θ scans		
data collection temperature	298 K	120 K
number of data collected	3812(0<2θ<50°)	6444 (0<2θ<55°)
<i>R</i> <sub>ave</sub> = Σ  <i>F</i> <sub>i</sub> - < <i>F</i> > /Σ  <i>F</i> <sub>i</sub>	0.019	0.024
number of unique data (NO)	3011	4213†
<i>R</i> ( <i>F</i> ) = Σ   <i>F</i> <sub>o</sub>   -   <i>F</i> <sub>c</sub>   /Σ  <i>F</i> <sub>o</sub>	0.077	0.064
<i>wR</i> ( <i>F</i> ) = [Σw(  <i>F</i> <sub>o</sub>   -   <i>F</i> <sub>c</sub>   ) <sup>2</sup> /Σw <i>F</i> <sub>o</sub> <sup>2</sup> ] <sup>1/2</sup>	0.042	0.029*
GOF = [Σw(  <i>F</i> <sub>o</sub>   -   <i>F</i> <sub>c</sub>   ) <sup>2</sup> /(NO-NV)] <sup>1/2</sup>	1.349	1.539
residuals (e <sup>-</sup> /Å <sup>3</sup> )	-1.1 to +0.9	-1.0 to +0.8

\*The function Σw(|*F*<sub>o</sub>| - |*F*<sub>c</sub>||)<sup>2</sup> was minimized in the least-squares refinement, using weights, *w* = [σ<sup>2</sup>(*F*<sub>o</sub>) + 0.0004*F*<sub>o</sub><sup>4</sup>]<sup>-1</sup>.

†25 data eliminated because of bad backgrounds.

perature device.<sup>15</sup> The unit cell data derived from the setting angles of 25 centered reflections (10 < θ < 16°) are given in Table I along with other data collection parameters and refinement results. All of the unique diffraction data were corrected for Lorentz and polarization effects, and for absorption (the latter by a numerical grid method<sup>16</sup>). The crystal structure was solved by use of direct methods,<sup>17</sup> and the full-matrix least-squares refinement of the 195 variables (NV in Table I), which included the coordinates and anisotropic thermal parameters of all non-hydrogen atoms, gave the agreement factors listed in Table I. The hydrogen atoms were assigned fixed positions (with *B*<sub>iso</sub> values of 5.0 at 298 K and 3.0 at 120 K with C-H at 1.00 Å, using sp<sup>3</sup> geometry). Atomic scattering factors, including correction terms for anomalous dispersion, were obtained from *The International Tables for X-ray Crystallography* (1974). The fractional coordinates and the isotropic equivalent thermal parameters of all non-hydrogen atoms are given in Table II. The intramolecular bond distances and angles for non-hydrogen atoms of the BPDT-TTF molecule and the ICl<sub>2</sub><sup>-</sup> anion are given in Table III. A unit cell stereoview

TABLE II  
Fractional atomic coordinates and equivalent isotropic thermal parameters of  
(BPDT-TTF)<sub>2</sub>ICl<sub>2</sub> at 298 K/120 K

T = 298 K				
Atom	x	y	z	U <sub>eq</sub> 10 <sup>4</sup>
I	0.0000	0.17364(9)	0.2500	481(2)
Cl	0.02796(10)	0.1727(3)	0.10876(10)	567(7)
S1	0.62397(10)	0.6537(2)	0.47189(9)	379(5)
S2	0.57842(10)	0.2472(2)	0.44305(10)	407(6)
S3	0.45547(10)	0.7781(2)	0.34382(9)	372(6)
S4	0.41051(10)	0.3712(2)	0.31831(10)	401(6)
S5	0.78260(11)	0.5716(2)	0.58724(10)	438(6)
S6	0.72401(10)	0.0953(2)	0.55844(10)	423(6)
S7	0.32888(10)	0.9222(2)	0.20954(10)	435(6)
S8	0.27116(10)	0.4382(2)	0.18176(10)	421(6)
C1	0.5528(4)	0.4869(9)	0.4222(4)	362(22)
C2	0.4818(4)	0.5381(8)	0.3682(3)	364(22)
C3	0.6926(4)	0.4824(9)	0.5237(3)	331(22)
C4	0.6724(3)	0.2973(9)	0.5105(3)	365(22)
C5	0.3708(4)	0.7232(8)	0.2664(3)	340(22)
C6	0.3506(4)	0.5378(8)	0.2547(3)	328(21)
C7	0.8689(4)	0.4594(9)	0.5485(4)	470(25)
C8	0.8897(4)	0.2535(10)	0.5720(4)	493(25)
C9	0.8279(4)	0.1027(9)	0.5294(4)	499(26)
C10	0.2160(4)	0.9178(9)	0.2136(4)	474(25)
C11	0.1632(4)	0.7651(10)	0.1615(4)	499(26)
C12	0.1748(4)	0.5623(9)	0.1941(4)	458(25)
T = 120 K				
Atom	x	y	z	U <sub>eq</sub> 10 <sup>5</sup>
I	0.000	0.17078(4)	0.2500	2071(10)
Cl	0.02799(5)	0.17009(12)	0.10652(4)	2438(24)
S1	0.62352(5)	0.65726(11)	0.47262(4)	1693(23)
S2	0.57812(5)	0.24705(11)	0.44358(5)	1791(24)
S3	0.45499(5)	0.78143(11)	0.34319(4)	1621(23)
S4	0.41122(5)	0.36987(11)	0.31766(4)	1765(24)
S5	0.78238(5)	0.57425(11)	0.58916(4)	1910(24)
S6	0.72363(5)	0.09397(11)	0.56047(4)	1839(24)
S7	0.32786(5)	0.92557(11)	0.20828(4)	1839(24)
S8	0.27157(5)	0.43637(11)	0.17979(4)	1835(24)
C1	0.5521(2)	0.4890(4)	0.4224(2)	1678(93)
C2	0.4818(2)	0.5406(4)	0.3676(2)	1661(94)
C3	0.6925(2)	0.4847(4)	0.5253(2)	1598(93)
C4	0.6713(2)	0.2968(4)	0.5125(2)	1514(91)
C5	0.3704(2)	0.7255(4)	0.2656(2)	1543(92)
C6	0.3497(2)	0.5366(4)	0.2538(2)	1648(95)
C7	0.8695(2)	0.4619(5)	0.5495(2)	2202(101)
C8	0.8898(2)	0.2521(5)	0.5732(2)	2091(99)
C9	0.8276(2)	0.1034(5)	0.5305(2)	2202(101)
C10	0.2147(2)	0.9163(4)	0.2123(2)	2197(101)
C11	0.1628(2)	0.7647(5)	0.1600(2)	2314(104)
C12	0.1741(2)	0.5593(5)	0.1923(2)	2107(101)

\*The complete temperature factor is  $\exp(-8\pi^2 U_{eq} \sin^2 \theta / \lambda^2)$ , where  $U_{eq} = 1/3 \sum_i U_{ij} a_i^* a_j^* a_i a_j$  in units of  $\text{\AA}^2$ .

TABLE III

Intramolecular bond distances (Å) and angles (°) for (BPDT-TTF)<sub>2</sub>ICl<sub>2</sub> at 298/120 K

## Interatomic Distances (Å)

T = 298 K					
Atoms	Distance	Atoms	Distance	Atoms	Distance
I-C1	2.547(2)	S1-C1	1.729(6)	S1-C3	1.741(6)
S2-C1	1.732(6)	S2-C4	1.748(6)	S3-C2	1.747(6)
S3-C5	1.749(6)	S4-C2	1.732(6)	S4-C6	1.746(6)
S5-C3	1.745(6)	S5-C7	1.813(7)	S6-C4	1.749(6)
S6-C9	1.819(6)	S7-C5	1.748(6)	S7-C10	1.815(6)
S8-C6	1.747(6)	S8-C12	1.807(6)	C1-C2	1.369(8)
C3-C4	1.331(8)	C5-C6	1.331(7)	C7-C8	1.502(9)
C8-C9	1.526(8)	C10-C11	1.531(8)	C11-C12	1.511(8)

T = 120 K					
Atoms	Distance	Atoms	Distance	Atoms	Distance
S1-C1	1.742(3)	S1-C3	1.756(3)	S2-C1	1.745(3)
S2-C4	1.754(3)	S3-C2	1.750(3)	S3-C5	1.754(3)
S4-C2	1.743(3)	S4-C6	1.757(3)	S5-C3	1.750(3)
S5-C7	1.824(3)	S6-C4	1.756(3)	S6-C9	1.823(3)
S7-C5	1.756(3)	S7-C10	1.820(3)	S8-C6	1.748(3)
S8-C12	1.819(3)	C1-C2	1.370(4)	C3-C4	1.350(4)
C5-C6	1.352(4)	C7-C8	1.525(4)	C8-C9	1.520(4)
C10-C11	1.520(4)	C11-C12	1.521(4)	C1-I	2.557(1)

## Bond Angles (deg)

T = 298 K					
Atoms	Angle	Atoms	Angle	Atoms	Angle
C1-I-C1	179.71(9)	C1-S1-C3	95.0(3)	C1-S2-C4	94.9(3)
C2-S3-C5	95.2(3)	C2-S4-C6	95.7(3)	C3-S5-C7	102.2(3)
C4-S6-C9	102.7(3)	C5-S7-C10	104.1(3)	C6-S8-C12	104.3(3)
C2-C1-S1	122.9(5)	C2-C1-S2	121.5(5)	S1-C1-S2	115.6(3)
C1-C2-S4	123.0(5)	C1-C2-S3	122.7(5)	S4-C2-S3	114.3(3)
C4-C3-S1	117.5(4)	C4-C3-S5	126.3(5)	S1-C3-S5	116.2(4)
C3-C4-S2	117.0(5)	C3-C4-S6	127.9(5)	S2-C4-S6	114.9(4)
C6-C5-S7	128.4(5)	C6-C5-S3	117.1(4)	S7-C5-S3	114.4(3)
C5-C6-S4	117.1(5)	C5-C6-S8	127.7(5)	S4-C6-S8	115.2(3)
C8-C7-S5	117.0(5)	C7-C8-C9	115.5(5)	C8-C9-S6	115.3(4)
C11-C10-S7	115.4(5)	C12-C11-C10	114.3(5)	C11-C12-S8	116.5(5)

T = 120 K					
C1-I-C1	179.79(4)	C1-S1-C3	95.27(15)	C1-S2-C4	95.30(14)
C2-S3-C5	95.23(14)	C2-S4-C6	95.59(14)	C3-S5-C7	102.34(14)
C4-S6-C9	102.85(14)	C5-S7-C10	103.80(14)	C6-S8-C12	104.22(14)
C2-C1-S1	122.9(2)	C2-C1-S2	121.7(2)	S1-C1-S2	115.3(2)
C1-C2-S4	122.2(2)	C1-C2-S3	123.0(2)	S4-C2-S3	114.8(2)
C4-C3-S5	126.5(2)	C4-C3-S1	117.1(2)	S5-C3-S1	116.4(2)
C3-C4-S2	117.0(2)	C3-C4-S6	127.5(2)	S2-C4-S6	115.4(2)
C6-C5-S3	117.3(2)	C6-C5-S7	128.2(2)	S3-C5-S7	114.4(2)
C5-C6-S8	127.8(2)	C5-C6-S4	116.6(2)	S8-C6-S4	115.6(2)
C8-C7-S5	116.6(2)	C9-C8-C7	115.3(3)	C8-C9-S6	116.1(2)
C11-C10-S7	116.2(2)	C10-C11-C12	114.6(3)	C11-C12-S8	116.2(2)



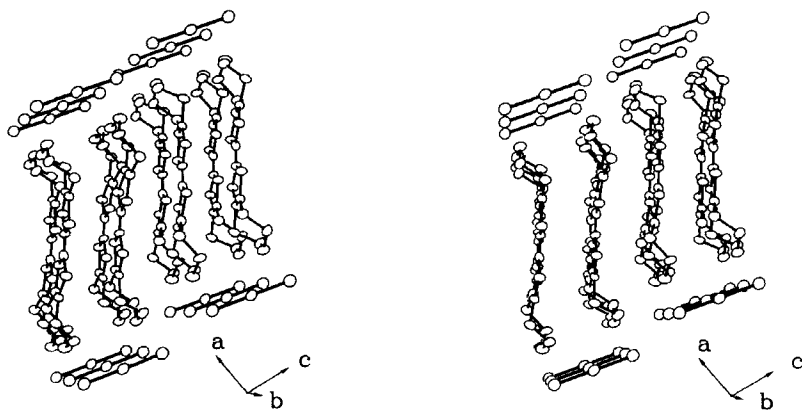


FIGURE 1 Stereoview of the crystal structure of  $(\text{BPDT-TTF})_2\text{ICl}_2$ , viewed approximately along the  $b$ -axis, with thermal ellipsoids drawn at the 50% probability level (298 K).<sup>19</sup>

of  $(\text{BPDT-TTF})_2\text{ICl}_2$ , viewed nearly along the  $b$ -axis, is shown in Figure 1.

### MOLECULAR STRUCTURES OF BPDT-TTF AND $\text{ICl}_2^-$

The BPDT-TTF molecules in  $(\text{BPDT-TTF})_2\text{ICl}_2$  (Figure 1) have the chair conformation, which is also found in  $(\text{BPDT-TTF})_2\text{I}_3$ ,<sup>12</sup>  $(\text{BPDT-TTF})_2\text{IBr}_2$ ,<sup>13</sup> and  $(\text{BPDT-TTF})_3(\text{PF}_6)_2$ .<sup>14</sup> This chair conformation imparts a considerable "bulkiness" to the BPDT-TTF molecule, compared to a closely related, but more planar donor molecule such as BEDT-TTF. Furthermore, unlike the ethylene groups of the BEDT-TTF molecules in many of the  $(\text{BEDT-TTF})_2\text{X}$  salts, the terminal propylene groups of the BPDT-TTF molecule in  $(\text{BPDT-TTF})_2\text{ICl}_2$  are well ordered, and the carbon atoms of these groups do not have large thermal motion at either 298K or 120K (Table II).

In an attempt to quantify a relative molecular volume of BPDT-TTF to compare to that of BEDT-TTF, we calculated the volumes of the BPDT-TTF and BEDT-TTF molecules in their 2:1 salts with the  $\text{ICl}_2^-$  anion, i.e.,  $(\text{BPDT-TTF})_2\text{ICl}_2$  and  $\beta\text{-(BEDT-TTF)}_2\text{ICl}_2$ .<sup>7</sup> The relative molecular volume of each donor molecule is computed by subtracting the volume of the anions in a given salt from the crystallographic unit cell volume, and then by dividing this difference by the number of donor molecules in the unit cell. The anion volumes used here are the cylinders defined by the maximum van der Waals<sup>18</sup>

radius (2.15 Å for the I atom) and the van der Waals length of the anion, which is  $\sim 8.70$  Å for  $\text{ICl}_2^-$ .<sup>7</sup> Thus, the net volumes of the BPDT-TTF and BEDT-TTF molecules are  $(1864 - 2 \times 126)/4 = 403$  Å<sup>3</sup> and  $(814 - 126)/2 = 344$  Å<sup>3</sup>, respectively. Thus, there is about a 15% increase in molecular volume for BPDT-TTF compared to BEDT-TTF in their 2:1  $\text{ICl}_2^-$  salts.

In the BPDT-TTF salt, the  $\text{ICl}_2^-$  anion is centered on the two-fold symmetry axis of the monoclinic unit cell and, hence, is not required to be linear. However, the Cl-I-Cl angle is within  $0.3^\circ$  of  $180^\circ$  at 298 K and 120 K. The I-Cl bond lengths of 2.55 Å (298 K) and 2.56 Å (120 K) are also nearly identical to that in  $\beta\text{-(BEDT-TTF)}_2\text{ICl}_2^-$  at both 298 K and 120 K.

## CRYSTAL STRUCTURE OF $(\text{BPDT-TTF})_2\text{ICl}_2$

Crystals of  $(\text{BPDT-TTF})_2\text{ICl}_2$  are *not* isostructural to those of  $(\text{BPDT-TTF})_2\text{I}_3$ <sup>12</sup> and  $(\text{BPDT-TTF})_2\text{IBr}_2$ .<sup>13</sup> This situation is different from that for the  $\beta\text{-(BEDT-TTF)}_2\text{X}$  salts with  $\text{X}^- = \text{ICl}_2^-$ ,  $\text{IBr}_2^-$ ,  $\text{AuI}_2^-$ ,  $\text{I}_2\text{Br}^-$  and  $\text{I}_3^-$ , which are members of a nearly isostructural series of organic conductors. There is, however, one major characteristic common to both families of salts i.e., the presence of *sheetlike networks* of donor molecules that are separated by layers of anions, as represented in Figure 1 for  $(\text{BPDT-TTF})_2\text{ICl}_2$ .

The stereoview of the packing of the BPDT-TTF molecules and  $\text{ICl}_2^-$  anions for  $(\text{BPDT-TTF})_2\text{ICl}_2$  (Figure 1) illustrates two important features of this salt which impact on its electrical properties: (i) the presence of a sheetlike network of BPDT-TTF molecules that, surprisingly, contains no  $\text{S} \cdots \text{S}$  interdonor distances shorter than the van der Waals radii<sup>18</sup> sum of 3.6 Å; and (ii) the presence of H-bonding donor-anion contacts that link the two dimensional (2-D) donor molecule network and the anion layer. In the following discussion, the above structural characteristics are compared with analogous features in the metallic  $(\text{BEDT-TTF})_2\text{X}$  salts.

As previously noted in the two-dimensional BPDT-TTF network of  $(\text{BPDT-TTF})_2\text{ICl}_2$ , there are no intermolecular  $\text{S} \cdots \text{S}$  distances less than 3.60 Å, and only five  $\text{S} \cdots \text{S}$  distances are less than or equal to 3.70 Å, as listed in Table IV. The lack of short  $\text{S} \cdots \text{S}$  distances in this salt, even though the sheetlike network of donor molecules is maintained, is apparently the result of two unique structural features: (i) the bulkiness of the BPDT-TTF molecules with respect to that of BEDT-TTF molecules, and (ii) the relative separations and rotations of pairs of donor molecules in  $(\text{BPDT-TTF})_2\text{ICl}_2$ , which are quite

TABLE IV

Noteworthy Intermolecular Distances in the Crystal Structure of (BPDT-TTF)<sub>2</sub>ICl<sub>2</sub>

A. Donor-Donor S · · S distances less than 3.8 Å within the BPDT-TTF molecular network at 298/120 K (labels refer to 1):\*

S1 · · S6 <sup>b</sup>	3.637(2)/3.613(2) Å	S3 · · S3 <sup>c</sup>	3.758(2)/3.705(2) Å
S1 · · S8 <sup>c</sup>	3.694(2)/3.660(2) Å	S4 · · S5 <sup>d</sup>	3.762(2)/3.736(2) Å
S1 · · S4 <sup>d</sup>	3.749(2)/3.711(2) Å	S5 · · S6 <sup>b</sup>	3.757(2)/3.724(2) Å
S2 · · S8 <sup>c</sup>	3.747(2)/3.696(2) Å	S7 · · S4 <sup>b</sup>	3.735(2)/3.711(2) Å
S3 · · S6 <sup>d</sup>	3.686(2)/3.637(2) Å	S7 · · S8 <sup>b</sup>	3.702(2)/3.653(2) Å

B. Donor-Anion H<sup>†</sup> · · Cl distances less than 3.0 Å between each BPDT-TTF molecule and the surrounding ICl<sub>2</sub><sup>-</sup> anions.

H7A · · Cl <sup>e</sup>	2.55/2.54 Å	H10A · · Cl <sup>b</sup>	2.83/2.82 Å
H8B · · Cl <sup>c</sup>	2.99/2.93 Å	H11B · · Cl <sup>b</sup>	2.84/2.82 Å
H9A · · Cl <sup>c</sup>	2.99/2.96 Å	H12B · · Cl <sup>a</sup>	2.65/2.64 Å
H9B · · Cl <sup>f</sup>	2.90/2.90 Å	H8B · · Cl <sup>f</sup>	3.04/2.99 Å

\*The estimated standard deviations for the S · · S distances are enclosed in parentheses. The symmetry for the second atom is one of the following:

a  $x, y, z$ b  $x, 1 + y, z$ c  $1 - x, y, 1/2 - z$ d  $1 - x, 1 - y, 1 - z$ e  $1 + x, 1 - y, 1/2 + z$ f  $1 + x, -y, 1/2 + z$ 

†Calculated C—H bond distance 1.09 Å.

different from those in  $\beta$ -(BEDT-TTF)<sub>2</sub>ICl<sub>2</sub>. Along the stack, there are dimers of BPDT-TTF molecules that contain two parallel (inversion related) molecules. Each dimer is rotated by  $\sim 30^\circ$  with respect to an adjacent dimer along the stack, as shown in Figure 2. The inter-

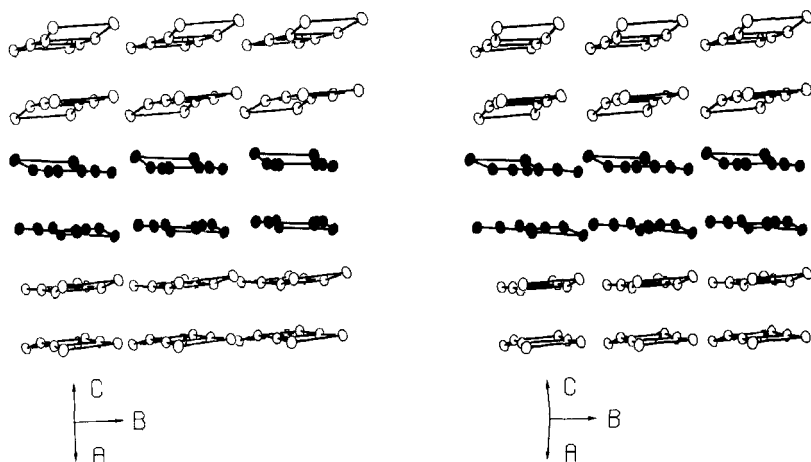
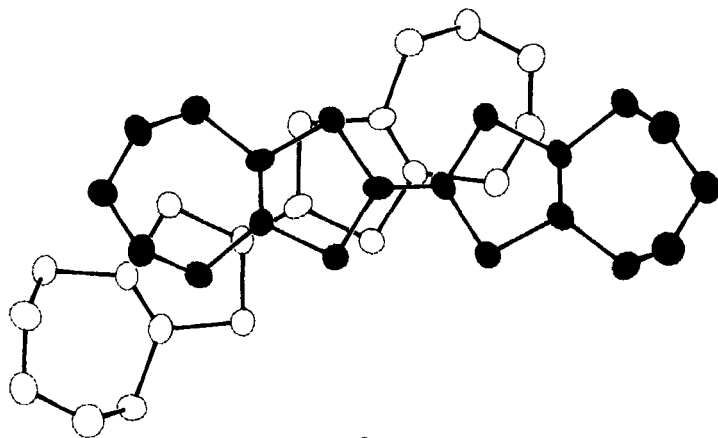
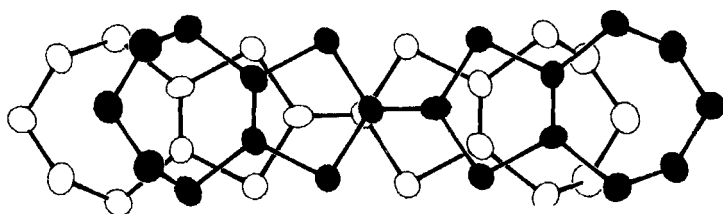


FIGURE 2 Representation of the BPDT-TTF molecule network in (BPDT-TTF)<sub>2</sub>ICl<sub>2</sub>. The stereoview is approximately along the  $c$ -axis. The solid and open ellipsoids are S atoms (connected for each molecule) of alternating sets of BPDT-TTF dimers along the molecular stacks, which are rotated nearly  $30^\circ$  from each other.



2



3

and intradimer molecular overlap geometries in  $(\text{BPDT-TTF})_2\text{ICl}_2$  are shown in 2 and 3, respectively. There is a relative shift of about 3.0 Å between dimers along the long in-plane axis of the BPDT-TTF molecule. Within a dimer the shift between BPDT-TTF molecules is about 1.5 Å. In contrast, the stacks of BEDT-TTF molecules in the  $(\text{BEDT-TTF})_2\text{X}$  salts contain only parallel molecules, with minor shifts between adjacent molecules within a given stack. Thus, the presence of the alternating shifts and rotations between adjacent  $(\text{BPDT-TTF})_2$  dimers *along* the stacks of donor molecules contributes significantly to the lack of short  $\text{S} \cdots \text{S}$  contacts in the donor-molecule networks of  $(\text{BPDT-TTF})_2\text{ICl}_2$ . The structure at 120 K is essentially the same as that at 298 K except for the expected thermal contractions. The unit cell volume at 120 K is only reduced by ~1% compared to that at 298 K, which is not sufficient to introduce any short  $\text{S} \cdots \text{S}$  contacts.

One structural feature of  $(\text{BPDT-TTF})_2\text{ICl}_2$  that is strikingly similar to  $\beta\text{-(BEDT-TTF)}_2\text{ICl}_2$  is the presence of *five* short contacts between the propylene group hydrogen H atoms of the donor molecule and the Cl atoms of  $\text{ICl}_2^-$ . These five short  $\text{H} \cdots \text{Cl}$  distances (calculated

at 298 K and observed at 120 K) are in the range  $2.5 - 2.9 \text{ \AA}$ , as listed in Table IV. There are no  $\text{H} \cdots \text{I}$  contact distances less than the van der Waals radii sum of  $3.35 \text{ \AA}$  for this pair of atoms. Thus, the only significantly close interactions in the crystal structure of  $(\text{BPDT-TTF})_2\text{ICl}_2$  are the donor-anion type rather than the donor-donor type as previously noted in many  $(\text{BEDT-TTF})_2\text{X}$  materials.<sup>27</sup>

## RESISTIVITY MEASUREMENTS

The temperature dependence of the electrical resistivity of  $(\text{BPDT-TTF})_2\text{ICl}_2$  was measured by the use of the 4-probe method with low-frequency a.c. currents and phase-sensitive detection. The probes consisted of gold wires attached by gold conducting paste, and they were aligned along the donor stacking axis (i.e.,  $a$ -axis). Currents of  $\sim 2 \mu\text{A}$  at  $\sim 37 \text{ Hz}$  were used. The measurements were carried out on two different crystal specimens over the range of 300 K to 200 K or slightly lower. The data indicate semiconducting behavior with a strict exponential temperature dependence, as illustrated in Figure 3. The terminal activation energy was found to be  $0.14 \text{ eV}$ . The room temperature resistivity ( $\rho$  at 300 K) was estimated from the crystal dimensions to be  $\sim 65 \Omega\text{cm}$ . For comparison, the room temperature resistivity of  $(\text{BPDT-TTF})_2\text{I}_3$  is  $\sim 0.5 \Omega\text{cm}$  at ambient pressure and  $\sim 0.05 \Omega\text{cm}$  at  $p = 10 \text{ kbar}$ .<sup>12</sup>

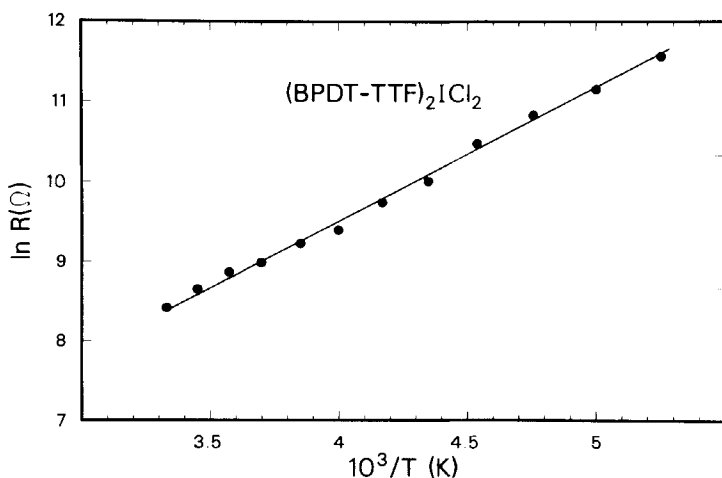


FIGURE 3 Plot of the natural logarithm of the resistance as a function of the reciprocal temperature for single crystal specimens of  $(\text{BPDT-TTF})_2\text{ICl}_2$ .

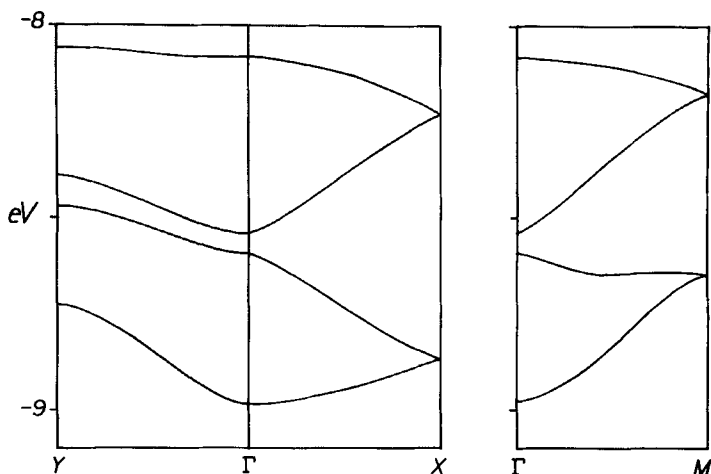
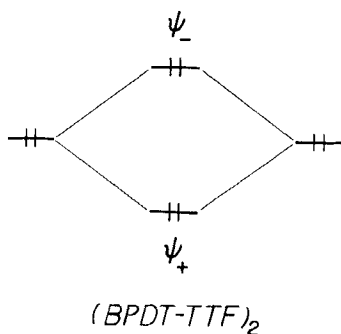


FIGURE 4 Dispersion of the four highest occupied bands of  $(\text{BPDT-TTF})_2\text{ICl}_2$  calculated for a single layer of donor molecules, and based on the 120 K structure, where  $\Gamma = (0,0)$   $X = (c^*/2, 0)$ ,  $Y = (0, b^*/2)$ , and  $M = (c^*/2, b^*/2)$ .

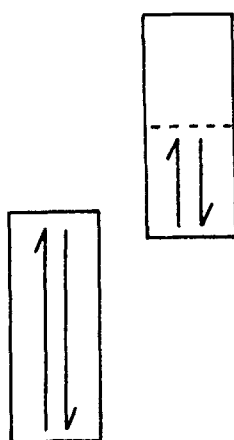
## BAND ELECTRONIC STRUCTURE

The electronic structure of the  $(\text{BPDT-TTF})_2\text{ICl}_2$  salt was examined by performing tight-binding band calculations.<sup>21</sup> Since there are four BPDT-TTF molecules per unit cell, it is expected that there occur four bands derived primarily from the HOMO of each BPDT-TTF molecule. Due to the symmetry of a glide plane with translational component along the stacking axis, however, these four bands merge into two separate bands as shown in Figure 4 for the 120 K crystal structure.

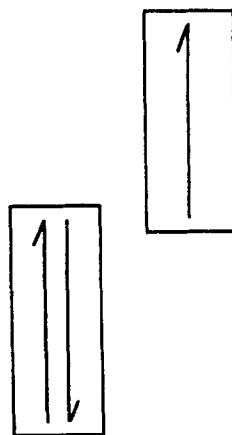
In each  $(\text{BPDT-TTF})_2$  dimer, the HOMO's of the BPDT-TTF molecules interact to give the bonding level  $\psi_+$  and the antibonding level  $\psi_-$ , as depicted in 4. The lower and upper bands of Figure 4 have the orbital character of  $\psi_+$  and  $\psi_-$ , respectively. With a formal oxidation state of  $(\text{BPDT-TTF})_2^+(\text{ICl}_2^-)$ , the  $\psi$  level is singly occupied in each  $(\text{BPDT-TTF})_2^+$  dimer cation. Therefore, the upper band of Figure 4 is half-filled. There are two ways of filling this half-filled band,<sup>26</sup> as indicated in **5a** and **5b**. The 'low-spin' band filling in **5a** leads to a metallic state, and the 'high-spin' band filling to a magnetic insulating state. The electron-localized state **5b** refers to all states in which an unpaired electron resides on each  $(\text{BPDT-TTF})_2^+$  dimer cation, regardless of whether or not a long range magnetic order exists between such unpaired electrons. Since  $(\text{BPDT-TTF})_2\text{ICl}_2$  is not metallic, its band filling should, therefore, be represented by **5b**.



4



5a



5b

Electrical conduction in a localized state such as **5b** requires electron hopping from one dimer cation site to another, which gives rise to the thermally activated electrical conductivity observed for  $(BPDT-TTF)_2ICl_2$ . For the reasons similar to those given for  $(BPDT-TTF)_2ICl_2$ , the 2:1 salts of BEDT-TTF, namely,  $\beta$ -(BEDT-TTF) $_2ICl_2$  and  $\beta$ -(BEDT-TTF) $_2AuCl_2$ ,<sup>6</sup> are found to be nonmetallic.

## CONCLUDING REMARKS

Synthetic metals and superconductors based upon 2:1 salts of BEDT-TTF contain relatively uniform stacks of BEDT-TTF molecules, which form numerous intermolecular  $S \cdots S$  contacts less than 3.6 Å. In the 2:1 salt of BPDT-TTF, i.e.,  $(BPDT-TTF)_2ICl_2$ , studied in the present work, however, stacks of BPDT-TTF are strongly dimerized, and there exist no intermolecular  $S \cdots S$  contacts less than 3.6 Å. Consequently, unpaired electrons on the  $(BPDT-TTF)_2^+$  dimer cations remain localized in the  $(BPDT-TTF)_2ICl_2$  salt. The lack of short intermolecular  $S \cdots S$  contacts, and the resulting rotation between dimers in each BPDT-TTF stack, may be considered as a consequence of packing the relatively bulky propylene groups of the BPDT-TTF molecule around each  $ICl_2^-$  anion. Finally, because of the bulkiness of the propylene groups in BPDT-TTF, it may be difficult to prepare new phases containing trihalide anions and having short  $S \cdots S$  contact distances.

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## Supplementary Material Available

Tables of calculated and observed structure factors, anisotropic thermal parameters of the non-H atoms and calculated H atom parameters at 298 and 120 K may be obtained by contacting Gordon and Breach, 50 West 23rd St., New York, NY, 10010.

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