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Electronic and Molecular Structure of the Composite Organic Metal $(BO)_{2.4}I_3$

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The iodide salt of BEDO–TTF (3,4;3′,4′-bis(ethylenedioxo)-2,2′,5,5′-tetrathiafulvalene) $(BEDO\text{–}TTF)_{2.4}I_3$, $M_r = 1154.85$, has an incommensurate composite structure with a different periodicity of the two sublattices in the *b*-axis direction. Cell parameters are as follows: iodine sublattice $a = 5.840$ (1), $b = 9.620$ (2), $c = 17.115$ (2) Å, $\alpha = 99.55$ (1)°, $\beta = 80.19$ (1)°, $\gamma = 115.67$ (1)°, $V(I) = 849.4$ Å^3; BEDO–TTF sublattice $a = 5.326$ (1), $b = 4.029$ (1), $c = 16.885$ (2) Å, $\alpha = 88.29$ (2)°, $\beta = 83.45$ (1)°, $\gamma = 81.21$ (2)°, $V(BEDO\text{–}TTF) = 355.7$ Å^3. Triclinic, space group $P\bar{1}$, $Z = 1$, $D_x = 2.263$ g/cm^3, $\lambda(Mo\ K\alpha) = 0.7103$ Å, $\mu = 3.4051$ mm^{-1}, $F(000) = 551$, $T = 295$ K, final *R* factor = 0.055 for 2173 unique observed reflections (1710 main reflections, 463 first-order satellites). Band structure calculations show the Fermi surface to be two-dimensional for both the average and the modulated structures. The effect of the modulation on the band structure is minor, unlike the case of the previously studied $(BEDT\text{–}TTF)Hg_{0.776}(SCN)_2$, in which the absence of a metal–insulator transition is attributed to the influence of the modulation on the band structure.

Introduction

The exponential development of solid-state chemistry has led to a large variety of new solids with interesting properties. Of particular interest are salts of BEDT–TTF (BEDT–TTF = 3,3;3′,4′-bis(ethylenedithio)-2,2′,5,5′-tetrathiafulvalene, referred to as ET) and related compounds, which are showing considerable promise as synthetic metals and superconductors. The synthesis of novel solids with more complicated stoichiometry has led to increasingly complex solid-state structures. The study of such complex structures is essential, since understanding of structure–property relationships can point the way in the design of new materials with desirable properties.

Composite structures are typified by the existence of two or more sublattices in the crystal. As a result the chemical composition is a function of the ratio of the sublattice volumes and is nonstoichiometric when this ratio is a nonrational number.[1] Several organic metals and related compounds have been found to crystallize as composite crystals, including BEDT–TTF Hg_3Br_8[2] and $(BEDT\text{–}TTF)_2HgBr_4$·trichloroethane.[3] More recently we have studied the composite structure of $(BEDT\text{–}TTF)Hg_{0.776}(SCN)_2$.[4] In the latter compound a strong modulation is introduced by the interaction between Hg and S in different sublattices. The modulation has a strong influence on the band structure and is responsible for the solid remaining an organic metal down to very low temperatures.[4,5]

The organic metal $(BEDO\text{–}TTF)_{2.4}I_3$ (BEDO–TTF = 3,3;3′,4′-bis(ethylenedioxo)-2,2′,5,5′-tetrathiafulvalene, referred to as BO) was synthesized by Wudl and co-workers.[6] Its physical properties and crystal structure have been described in a preliminary communication.[7] The nonstoichiometric ratio of BO and I_3^- follows from the ratio of volumes of the unit cells and corresponds to average net charge on BO cations of +0.42 e. We describe here the analysis of its composite structure and the electronic band structure, both with and without the modulations that occur due to the interaction of the two sublattices. A new method, first applied to TTF–TCNQ,[8] was used in the theoretical calculation.

Table I. Crystallographic Data for $(BO)_{2.4}I_3$

	BO cell	I cell
space group, *Z*	$P\bar{1}$ (No. 1)	$P\bar{1}$ (No. 1)
a, Å	5.326 (1)	5.840 (1)
b, Å	4.029 (1)	9.620 (2)
c, Å	16.885 (2)	17.115 (2)
α, deg	88.29 (2)	99.55 (1)
β, deg	83.45 (1)	80.19 (1)
γ, deg	81.21 (2)	115.67 (1)
V, Å^3	355.7	849.4
density (calc), g cm^{-3}	2.263	
diffractometer	CAD4	
radiation	Mo Kα (0.710 73 Å)	
monochromator	graphite	
data collection mode	ω–2θ	
θ range, deg	0–30	
absorption, mm^{-1}	3.405	
no. of unique reflns	2658	
no. of main reflns ($I > 2\sigma(I)$)	1710	
no. of satellite reflns ($I > 2\sigma(I)$)	463	
R(*F*), *R*(w*F*) for all obsd reflns	0.055, 0.069	
R(*F*), *R*(w*R*) for obsd satellite reflns	0.140, 0.170	

Experimental Section

A platelike, black single crystal (0.225 × 0.11 × 0.03 mm), prepared by electrocrystallization, was obtained from Prof. Wudl at UC Santa Barbara. Oscillation and Weissenberg photographs showed two lattices of strong reflections, in addition to weak satellite reflections representing the modulation of both lattices. The intensity data were collected on a CAD4 diffractometer using

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Table II. Atomic Fractional Coordinates and Thermal Parameters

atom	x	y	z	B_{eq},[a] Å^2
I(1)	0.0	0.0	0.0	2.68 (9)
I(2)	−0.0065 (4)	0.3022 (4)	0.0003 (1)	3.9 (2)
S(1)	0.6851 (2)	0.2997 (3)	0.3860 (1)	1.32 (3)
S(2)	0.2029 (2)	0.7526 (3)	0.4320 (1)	1.40 (3)
O(1)	0.5879 (7)	0.3572 (8)	0.2358 (2)	3.16 (8)
O(2)	0.1172 (7)	0.8030 (8)	0.2812 (2)	3.19 (8)
C(1)	0.4762 (9)	0.513 (1)	0.4616 (3)	2.1 (1)
C(3)	0.4989 (9)	0.454 (1)	0.3113 (3)	2.4 (1)
C(4)	0.2865 (9)	0.659 (1)	0.3322 (3)	2.3 (1)
C(7)	0.451 (1)	0.570 (2)	0.1791 (4)	3.8 (1)
C(8)	0.171 (1)	0.633 (2)	0.2054 (4)	3.7 (1)
H(71)	0.47 (1)	0.41 (1)	0.136 (4)	6 (1)[b]
H(72)	0.51 (1)	0.78 (1)	0.174 (3)	4 (1)[b]
H(81)	0.05 (1)	0.80 (1)	0.173 (3)	4 (1)[b]
H(82)	0.114 (9)	0.44 (1)	0.210 (3)	3 (1)[b]

[a] The equivalent isotropic thermal parameters are defined as $B_{eq} = {}^4/_3\sum_i\sum_j\beta_{ij}\mathbf{a}_i\cdot\mathbf{a}_j$.[18] [b] Isotropic thermal parameters.

Mo Kα radiation. Cell parameters for both sublattices, listed in Table I, were determined from setting angles of 25 reflections of each cell ($17 < 2\theta < 32°$). Intensities of 1710 main and 463 satellite reflections with $I > 2\sigma(I)$ were measured. Intensities of three standards ($\bar{2}01$, $10\bar{7}$, 030), monitored every 60 reflections, showed no significant variation; data were corrected for Lorentz and polarization effects. The details of data collection are summarized in Table I.

Starting parameters in both sublattices were obtained by using Patterson and Fourier methods. Hydrogen atoms were calculated assuming sp^3 hybridization of C atoms and then included in the refinement. The computer program COMPREF[1] was used in the simultaneous refinement of the main and satellite reflections of both lattices. The quantity minimized was $[\sum w(|F_o| - |F_c|)^2]$ with weights $w = 1/\sigma^2|F|$. Atomic scattering factors and anomalous dispersion terms for I, S, O, C, H were taken from the *International Tables for X-ray Crystallography*.[9] Final atomic positional and thermal parameters are given in Table II. The rigid-body model for the translational and rotational displacements of both molecules[10] was used in the analysis of the modulated structure. It included three harmonics for both translational and rotational displacements of the two molecules. The modulation of the iodine temperature factors was represented by two harmonics, to include phason and amplitudon contributions.[11] The final parameters are given in Table III.

Description of the Structure

Intramolecular distances and angles for BO (Figure 1) are given in Table IVa. It is well-known that for ET and TTF (tetrathiafulvalene) molecules the central C–C bond lengthens and the adjacent S–C bonds shorten on oxidation.[12] In BO the S–C bonds adjacent to the central bond average to 1.762 (2) Å for the four independent bonds in the neutral molecule,[6] and 1.741 (4) Å for the two bonds in $BO_{2.4}I_3$, thus showing a similar trend. The central C–C bond, however, is 1.357 (6) Å in the neutral and 1.347 (7) Å in the positively charged molecule of $BO_{2.4}I_3$, whereas a *lengthening* of about 0.01–0.02 Å would have been expected on the basis of the analogy with ET and TTF. We note that such a lengthening is observed in $(BO)_2ClO_4$ in which the central C–C bond is 1.371 (9) Å.[13]

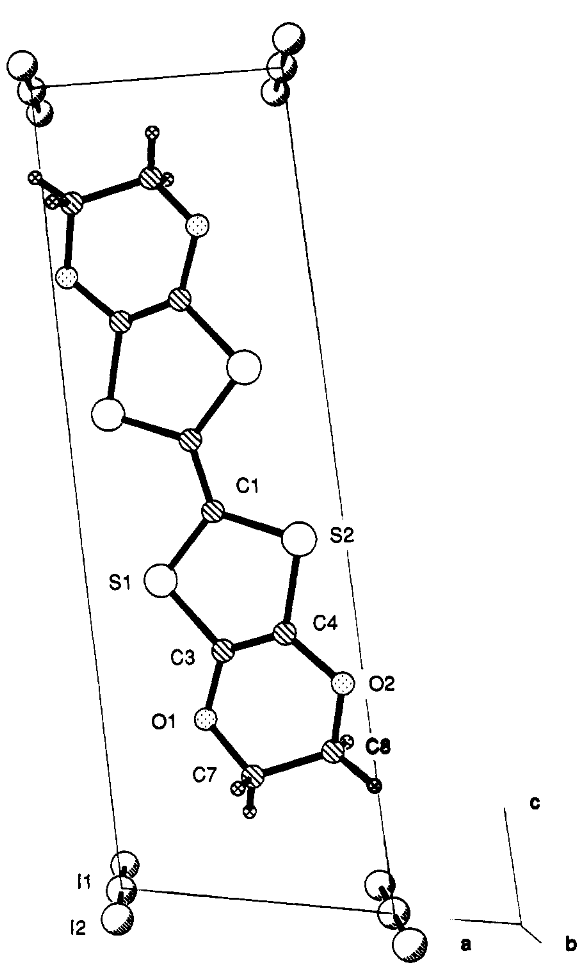

Figure 1. View of the structure $BO_{2.4}I_3$ along the common *b* axis and numbering of the atoms.

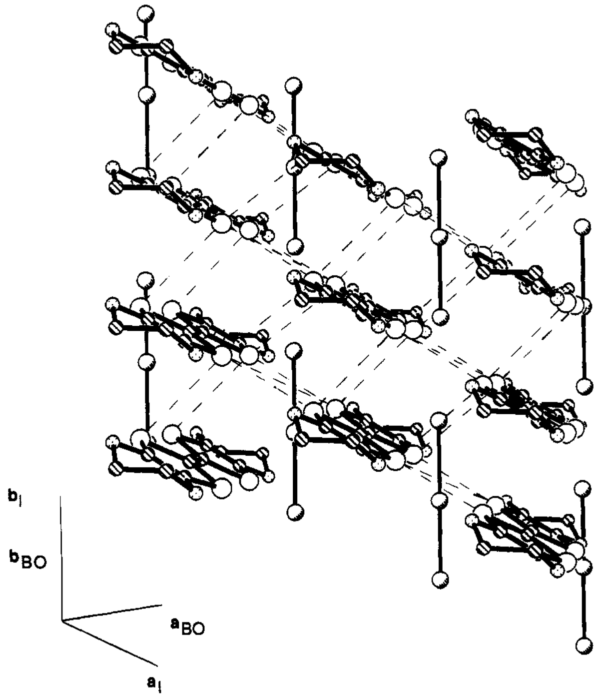

Figure 2. Packing of the BO and I_3^- molecules in the *a*, *b* plane; the shortest S–S contacts are indicated.

The BO molecules constitute a 2-dimensional network in the *a–b* plane, with short contacts in the *a*, *b*, and *a–b* directions (see Figure 2). The shortest intermolecular S--S distance in the average structure is 3.402 (2) Å in the *a–b*

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Table III. Rigid-Body Modulation Parameters[a]

(a) Components of Displacement Vectors in Fractions of the Unit Cell Edges

	U_1^x, R_1^x	U_2^x, R_2^x	U_3^x, R_3^x	U_1^y, R_1^y	U_2^y, R_2^y	U_3^y, R_3^y
I_3^-						
1 harm.	0.0112 (6), 0.0	0.0000 (5), 0.0	0.0053 (2), 0.0	0.0, −0.0148 (2)	0.0, 0.0	0.0, 0.0056 (1)
2 harm.	0.003 (2), 0.0	0.0063 (9), 0.0	−0.0003 (5), 0.0	0.0, −0.0008 (7)	0.0, 0.0	0.0, 0.0001 (3)
3 harm.	0.002 (3), 0.0	−0.004 (1), 0.0	−0.0053 (9), 0.0	0.0, −0.001 (1)	0.0, 0.0	0.0, 0.0026 (5)
BO						
1 harm.	0.0015 (4), 0.0	0.0003 (7), 0.0	0.0028 (1), 0.0	0.0, 0.0001 (2)	0.0, 0.0003 (1)	0.0, −0.0000 (1)
2 harm.	0.0001 (3), 0.0	0.0005 (7), 0.0	−0.0002 (1), 0.0	0.0, −0.0006 (1)	0.0, 0.0006 (2)	0.0, 0.0000 (1)
3 harm.	0.0019 (4), 0.0	−0.0030 (7), 0.0	0.0041 (1), 0.0	0.0, 0.0028 (2)	0.0, 0.0017 (2)	0.0, −0.0002 (1)

(b) Magnitudes and Principal Directions in Molecular Inertial Systems, with Axis 1 Corresponding to the Lowest Moment of Inertia

	$\|U\|$, Å	r_1	r_2	r_3	$\|R\|$, deg	r_1	r_2	r_3
I_3^-								
1 harm.	0.122	−0.366	0.742	0.562	6.7	0.194	0.794	−0.576
2 harm.	0.056	0.964	−0.081	0.255	0.27	0.350	0.462	−0.815
3 harm.	0.094	−0.305	−0.952	0.003	2.47	−0.116	0.993	0.005
BO								
1 harm.	0.049	0.995	−0.069	0.068	0.08	−0.414	0.108	0.904
2 harm.	0.004	−0.905	−0.151	0.398	0.22	−0.345	−0.938	0.039
3 harm.	0.070	0.994	0.009	−0.109	0.99	0.079	0.493	0.867

[a] Molecular displacement is described by translational **U** and rotational **R** vectors.[19] An atomic displacement is defined as $\mathbf{u} = \mathbf{U} + \mathbf{R} \times (\mathbf{r}_n - \mathbf{A})$, where $\mathbf{r}_n$ is the position of the n atom and **A** is the center of mass of the molecule. **U** and **R** are harmonic functions of the position of molecule in a crystal: $\mathbf{U} = \mathbf{U}_i^x \sin(\mathbf{q}\cdot(\mathbf{A} + \mathbf{n}) + \mathrm{U}_i^y \cos(\mathbf{q}\cdot(\mathbf{A} + \mathbf{n})$; **q** is the modulation vector, **n** is the location of the unit cell, U_1^x, U_2^x, and U_3^x are fractional amplitudes along **a**,**b**,**c** for the sine wave, respectively, U_1^y, U_2^y, and U_3^y are fractional amplitudes along **a**,**b**,**c** for the cosine wave, respectively (R_i^x and R_i^y are similar coordinates for the rotational vector). $|U|$ and $|R|$ are the magnitudes of the displacement vectors.

Table IV

(a) Intramolecular Distances of BO and I_3^- (Å)

I(1)–I(2)	2.924 (3)				
S(1)–C(1)	1.747 (5)	O(1)–C(3)	1.358 (6)	C(1)–C(1)[i]	1.347 (7)
S(2)–C(1)	1.735 (5)	O(2)–C(4)	1.371 (6)	C(3)–C(4)	1.312 (7)
S(1)–C(3)	1.735 (5)	O(1)–C(7)	1.451 (8)	C(7)–C(8)	1.489 (9)
S(2)–C(4)	1.731 (4)	O(2)–C(8)	1.449 (7)		

C(3)–S(1)–C(1)	93.8 (2)	S(1)–C(1)–S(2)	116.1 (3)
C(1)–S(2)–C(4)	93.6 (2)	S(1)–C(3)–O(1)	116.9 (4)
C(3)–O(1)–C(7)	110.1 (4)	S(1)–C(3)–C(4)	117.7 (4)
C(4)–O(2)–C(8)	109.5 (4)	O(1)–C(3)–C(4)	125.4 (5)
S(2)–C(4)–O(6)	115.7 (4)	O(1)–C(7)–C(8)	111.4 (5)
S(2)–C(4)–C(3)	118.9 (4)	O(2)–C(8)–C(7)	111.5 (5)
O(2)–C(4)–C(3)	125.4 (5)		

(b) Intermolecular Distances (Å)

atoms	av	min–max
I(2)–I(2)[a]	3.774 (4)	3.69 (3)–3.92 (3)
S(1)–S(2)[b]	3.405 (2)	3.362 (6)–3.452 (6)
S(1)–O(2)[b]	3.210 (4)	3.150 (8)–3.270 (8)
S(2)–S(2)[c]	3.426 (2)	3.412 (6)–3.442 (6)
S(1)–S(2)[d]	3.637 (2)	3.622 (6)–3.659 (6)
S(1)–S(2)[e]	3.694 (2)	3.645 (6)–3.749 (6)
I(1)–H(81)[d]	2.96 (6)–3.25 (6)	2.96 (6)–3.36 (5)
I(2)–H(81)	2.96 (6)–3.24 (6)	2.88 (6)–3.28 (6)

[a] The symmetry operations for the second atom are as follows: (*a*) $-x, 1 - y, -z$; (*b*) $1 + x, y - 1, z$; (*c*) $-x, 2 - y, 1 - z$; (*d*) $x, y - 1, z$; (*e*) $1 + x, y, z$; (*i*) $1 - x, 1 - y, 1 - z$.

direction (Table IVb). The triiodide ions form an almost linear chain along the *b*-axis direction; the distance between adjacent ions (3.774 (4) Å) is considerably shorter than the sum of the van der Waals distances (4.2 Å). These distances are affected by the modulation of the sublattices (Table IVb). For the BO molecule the major translational and rotational modulation amplitudes are the first and third harmonic components with amplitudes 0.122 Å, 0.094 Å and 6.7°, 2.5°, respectively. The translations are almost exactly along, and the rotations about, the long axis of the molecule, which means that the S--S distances are not very strongly affected by the modulation (Figure 3). The iodide displacement directions are less regular, but are of the same magnitude (Table III).

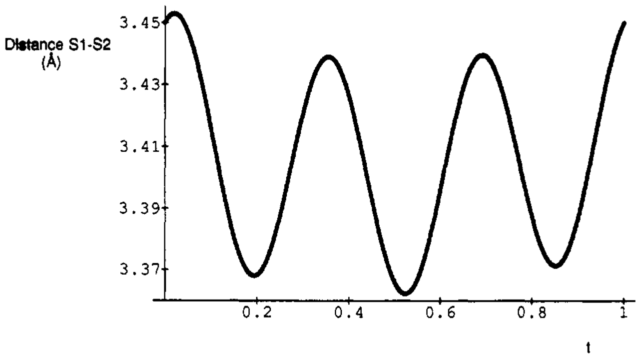

Figure 3. Variation of interstack S(1)–S(2) distances in the crystal including the modulation.

The relation between the two sublattices is given by the expression

$$\begin{bmatrix} a_{BO} \\ b_{BO} \\ c_{BO} \end{bmatrix} = \sigma \begin{bmatrix} a_I \\ b_I \\ c_I \end{bmatrix} = \begin{bmatrix} 1 & 0.347\,60 & 0 \\ 0 & 0.428\,80 & 0 \\ 0 & 0.347\,60 & 1 \end{bmatrix} \begin{bmatrix} a_I \\ b_I \\ c_I \end{bmatrix}$$

which shows the incommensurate direction to be *b*, with *a* and *c* of the BO lattice in the *ab* and *bc* plane of the iodine lattice, respectively. This form of the *interlattice matrix* σ is typical for column composite structures.[1]

As a consequence of the composite nature of the crystal, there is a continuous variation in intersublattice distances for unit cells displaced along the incommensurate direction. It is possible, however, to plot all distances occurring in the crystal as a function of the four-dimensional coordinate *t*, which is periodic modulus 1. Such plots are shown in Figures 3 and 4. The shortest H···I contact in the average structure is 2.96 (6) Å (using the X-ray hydrogen positions). The shortest distances are not lengthened by the modulation (Table IVb, Figure 4), even though the H···I contact distances are much shorter than the minimum of the nonbonded H···I potential curve at 3.36 Å.[14] It appears, however, from Figure 4 that the number

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[14] Coppens, P. In *Extended Linear Chain Compounds*; Miller, J. S., Ed.; Plenum: New York; 1982; Vol 1, p 333-356.

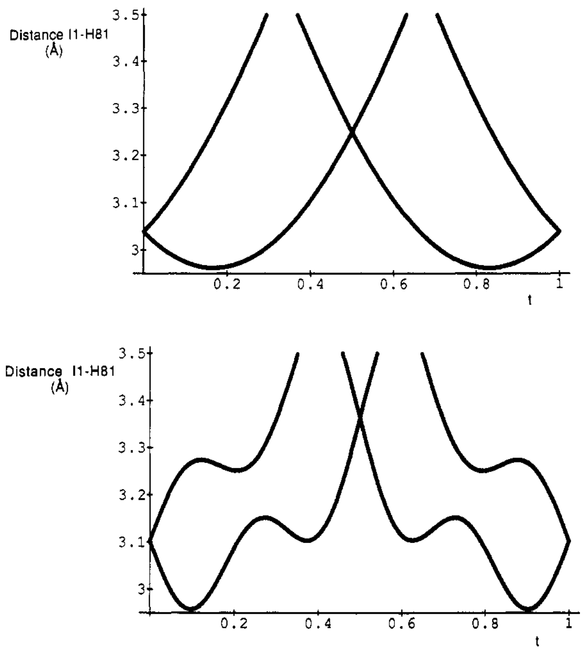

Figure 4. (a) Distances I(1)–H(81) as a function of position of the cell in the crystal for the average structure. Each cell belongs to one value of t in the interval ⟨0,1⟩. Distances between the closest atoms vary from 2.96 to 3.27 Å. (b) as in (a), including the modulation.

of unit cells in which the very short distances occur is reduced by the modulation. The short contacts are similar to those found in the modulated structure of $\beta(\mathrm{ET})_2\mathrm{I}_3$ (2.83, 3.00 and 3.05 Å, without the modulation, and minimum values of 2.64, 2.73, and 2.99 Å taking the modulation into account).[15]

Band Structure

The VEH (valence effective Hamiltonian) method,[16] applied in this work, was previously used to calculate the band structure for the related solid (BEDT-TTF)$\mathrm{Hg}_{0.776}(\mathrm{SCN})_2$[5] and to analyze the Peierls transition in TTF–TCNQ.[17]

The dispersion relation for the average structure of the BO sheets is

$$\epsilon(k_x,k_y) = h_{00} + 2h_{0a}\cos(2\pi k_x) + 2h_{0b}\cos(2\pi k_y) + 2h_{0(a-b)}\cos(2\pi(k_y - k_x))$$

Here h_{00} is the energy of the BEDO–TTF HOMO (highest occupied molecular orbital), and h_{0x} are the transfer integrals in the a, b, and $a-b$ directions between pairs of BO molecules. For the average structure, values of the transfer integrals that are the average over the modulated structure are used. They are the $m = 0$ components of the Fourier expansion of the transfer integrals in terms of the fourth-dimension coordinate t, where m is the index of the harmonics in the expansion. Numerical values of the magnitude of the largest coefficients are given in Table V. For $m > 0$, the integrals have complex values. It is clear that the magnitudes of the transfer integrals are much larger in the a and $a - b$ directions than in the b direction. The band structure in the average structure is therefore not one-dimensional, as was the case for (BEDT-TTF)$\mathrm{Hg}_{0.776}(\mathrm{SCN})_2$.[5]

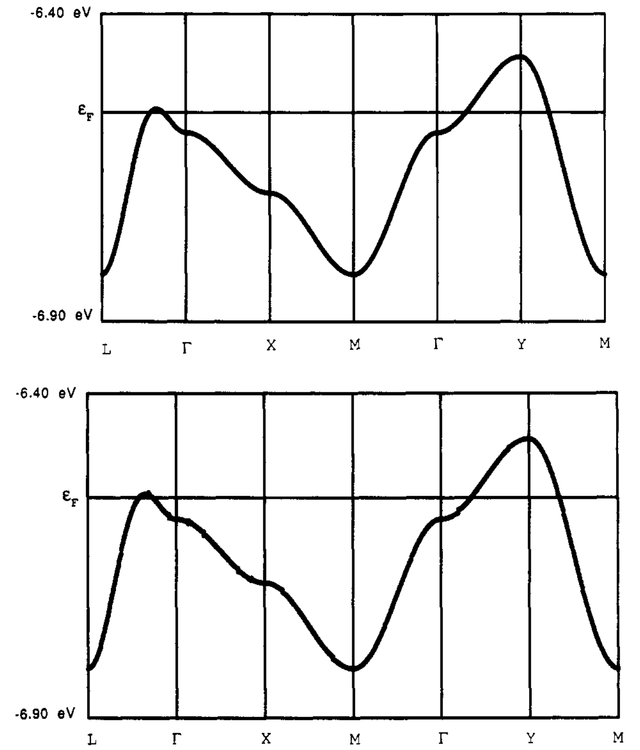

Figure 5. Structure of the valence band along various directions in the Brillouin zone. Γ (0,0), X (πa^*,0), Y (πb^*,0), L ($-\pi a^*,\pi b^*$), M ($\pi a^*,\pi b^*$). Vertical axis: energy (electronvolts).

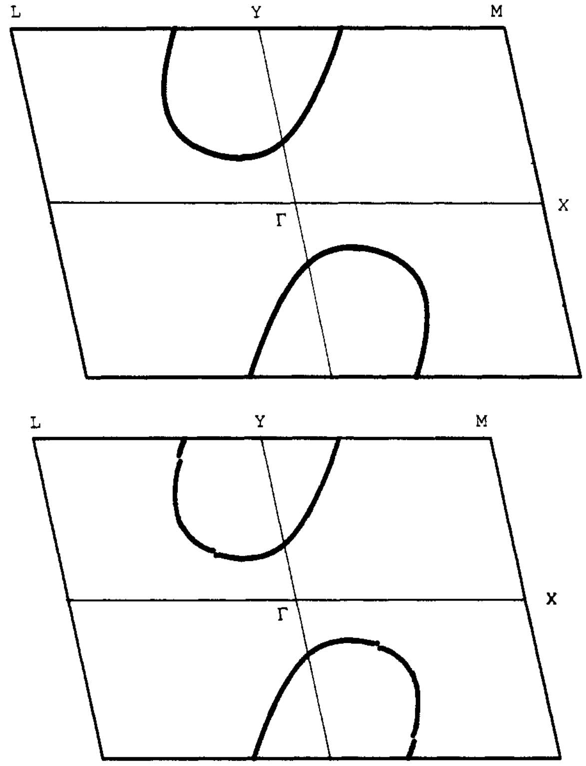

Figure 6. Fermi surface in the two-dimensional (a^*b^*) Brillouin zone of the BO sublattice: (a) for the average structure; (b) including the modulation.

As third-order harmonics were included in the modulation refinement of BEDO–TTF, transfer integrals to at least the third order ($m = 3$) should be taken into account in the calculation. In this work the fourth order terms ($m = 4$) were also retained.

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Table V. Absolute Value of Transfer Integrals $>10^{-4}$ (electronvolts) for the *a*, *b*, and *a*–*b* direction in the BEDO-TTF Subcell as a Function of Satellite Index *m*

m	*h*(*a*)	*h*(*b*)	*h*(*b*–*a*)
0	0.0564	0.0011	0.0320
1	0.0014	0.0002	
2			
3	0.0009	0.0001	0.0008

[a] The energy of the HOMO of the BEDO–TTF molecule is calculated as −6.6451 eV.

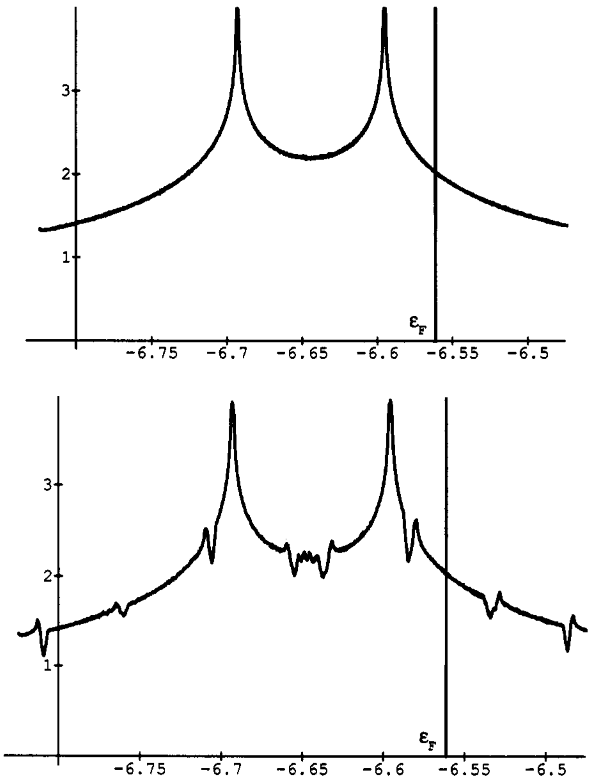

Figure 7. Density of states vs energy: (a) without modulation; (b) with modulation.

The band structures in the *ab* plane directions $L \rightarrow \Gamma \rightarrow X \rightarrow M \rightarrow \Gamma \rightarrow Y \rightarrow M$ {Γ (0,0), *X* (πa^*,0), *Y* (πb^*,0), *L* ($-\pi a^*,\pi b^*$), *M* ($\pi a^*,\pi b^*$)} are shown in Figure 5 for the average and modulated structures of the BO lattice. The Fermi energy is given by the horizontal line at $\epsilon_F = -6.5612$ eV. Along the directions plotted several small gaps occur as a result of the modulation, the largest of which is 0.007 eV wide at $k = (-0.625\pi a^*, 0.625\pi b^*)$.

The Fermi surface is hardly affected by the modulation (see Figure 6), except for small gaps at ($0.313\pi a^*$, $-0.287\pi b^*$) and ($0.380\pi a^*$,$-0.859\pi b^*$), of 0.006 eV width. The minor influence of the modulation on the band structure and the closed nature of the Fermi surface are in agreement with conductivity measurements that show metallic behavior down to 1.2 K.[6] The two-dimensionality evident from the features of the Fermi surface is also in good agreement with the observed T^{-2} dependence of the conductivity.[6]

The density of states for the average and modulated structures are shown in parts a and b of Figure 7, respectively. Both have a symmetrical distribution around the energy of the HOMO of the BEDO–TTF molecule (−6.645 eV).

The lack of influence of the modulation on the band structure is in contrast to the behavior of ET $Hg_{0.776}(SCN)_2$, in which the drastic modification of the one-dimensional Fermi surface due to the modulation provides an explanation for the absence of a metal–insulator transition on cooling.[4]

Concluding Remarks

Though the number of known low-dimensional organic solids with composite structures is increasing rapidly, the energy relations causing their occurrence are not yet properly understood. The actual stoichiometry is a function of the stability of a particular composite arrangement, which is influenced by the electronic and Madelung energies of the sublattices, the ionization potential of the donor and electron affinity of the acceptor, and the van der Waals forces between molecules within and between sublattices. A larger number of composite solids must be analyzed to obtain more insight into the relative importance of each of these factors.

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