

Analysis of the Diffraction Pattern of a Twinned Crystal of (3,4;3',4'-Bis(ethylenedioxy)-2,2',5,5'-tetrathiafulvalene)₂.Ag(CN)₂

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Abstract

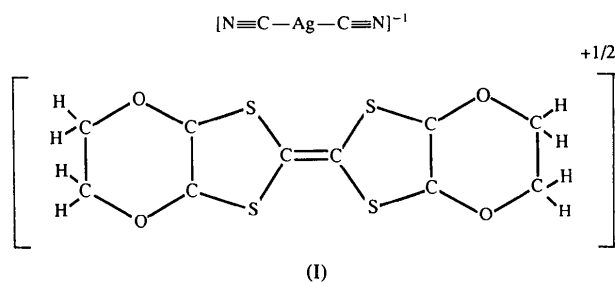
A strategy is described for recognition of partially overlapped reflections of a twinned crystal. Potentially overlapping reflections are identified by comparison of the Miller indices after transformation to a single basis set for all twin components. Overlapping reflections are subsequently rejected or accepted for structure determination based on their calculated separation in the ω -scanning angle. The method is applied to a twinned crystal of 6,6'-bi(2,3-dihydro[1,3]-dithiolo[5,4-*b*]-1,4-diox-6-ylidene)ium dicyanoargentate₂, [C₁₀H₈O₄S₄]₂⁺[Ag(CN)₂]₂⁻, $M_r = 800.76$, triclinic, $P1$, $a = 4.0355(1)$, $b = 16.7566(2)$, $c = 10.2335(1)$ Å, $\alpha = 82.49(1)$, $\beta = 81.12(1)$, $\gamma = 91.10(2)^\circ$, $V = 677.3(3)$ Å³, $Z = 1$, $D_{\text{calc}} = 1.963$ g cm⁻³, $\text{Mo } K\alpha = 0.71073$ Å, $\mu = 13.805$ cm⁻¹, $F(000) = 401$, room temperature, $R(F) = 0.0642$, for 1250 reflections. The structure consists of stacks of BEDO-TTF cations [BEDO-TTF = bis(ethylenedioxy)tetrathiafulvalene] parallel to *a*. Short S—S contacts of 3.433 and 3.500 Å occur between the BEDO-TTF molecules within sheets perpendicular to the stacking direction.

Introduction

The diffraction pattern of a twinned crystal in general contains fully overlapped, partially overlapped and fully separated reflections. It has long been recognized that the most difficult problem in the analysis of a twinned data set is the possibility of partially overlapping reflections (see van Smaalen & Petricek, 1992), which are defined as reflections that are closer together than the experimental resolution. Fully overlapped and fully separated reflections, on the other hand, can be recorded unambiguously, and should be included in an optimal structure analysis. The rapid identification of partially overlapped reflections is addressed in this paper.

The strategy developed is applied in the structure solution of a twinned crystal of (BEDO-TTF)₂.Ag(CN)₂ (Fig. 1). Organic salts based on BEDO-TTF have been

synthesized as alternatives to the well-investigated low-dimensional conducting salts of BEDT-TTF [bis(ethylenedithio)tetrathiafulvalene]. Some of the BEDO-TTF salts show low-temperature superconductivity (Suzuki, Yamochi, Srdanov, Hinkelmann & Wudl, 1989; Wudl *et al.*, 1990; Beno *et al.*, 1990). (BEDO-TTF)₂.Ag(CN)₂ is one of the salts prepared as part of this program.



General considerations

In the case of a twinned crystal, at least two identical objects are diffracting independently. The covariant direct-space translation vectors of two components of a twinned crystal are related by the twinning matrix **T**

$$\mathbf{A}_2 = \mathbf{T}\mathbf{A}_1 \quad (1)$$

where, for a periodic crystal, **T** is a 3 × 3 matrix.

The diffraction spots from the different twin parts have to be indexed in a unique manner, which can be accomplished using additional basis vectors in analogy to the treatment of composite structures (van Smaalen & Petricek, 1992), or as discussed here, by a three-dimensional approach. Since the Miller indices are

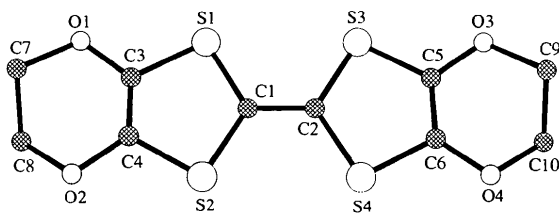


Fig. 1. Molecular diagram of BEDO-TTF showing the labeling of the atoms; thermal ellipsoids are 50% probability surfaces.

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covariant, the indices of twin component 1 in \mathbf{A}_1 and in \mathbf{A}_2 are also related by the twinning matrix

$$\begin{pmatrix} h'_1 \\ k'_1 \\ l'_1 \end{pmatrix} = \mathbf{T} \begin{pmatrix} h_1 \\ k_1 \\ l_1 \end{pmatrix}. \quad (2)$$

If all coefficients of the twinning matrix are rational (*commensurate twinning*), all reflection indices are rational when referred to only three basis vectors in the case of periodic crystals. When \mathbf{T} contains nonrational elements (*incommensurate twinning*), the transformed indices h'_i , k'_i and l'_i are not rational, but can be approximated by rational numbers, as illustrated below. In the full data set, reflections of the second subsystem and completely overlapped reflections of the first subsystem have integer indices in the basis \mathbf{A}_2 , while all other reflections of the first subsystem have noninteger indices in this basis.

Identification of partially overlapped reflections

Accidental overlapping of reflections occurs when two diffraction spots are separated by less than the experimental resolution. The proximity of two reflections originating from different twin components can be described by their distance δ in reciprocal space, which in the basis \mathbf{A}_2 is given by

$$\delta = |(h_2 - h'_1)\mathbf{a}_2^* + (k_2 - k'_1)\mathbf{b}_2^* + (l_2 - l'_1)\mathbf{c}_2^*|, \quad (3)$$

where h_2 , k_2 , l_2 refer to the Miller indices of a reflection of the second subsystem.

The angular difference between the vectors \mathbf{H}_2 and \mathbf{H}_1 is a measure of the ease of resolving the two reflections, and is given by

$$\delta' = \cos^{-1} \{ \mathbf{H}_2 \cdot \mathbf{H}_1 / (|\mathbf{H}_2||\mathbf{H}_1|) \} \quad (4)$$

Use of (4) requires a check of all pairs of reflections, and does not discriminate against pairs of reflections on the same or close to the same central reciprocal lattice row, although the latter occurrence seems rare for common types of twinning.

Expressions (3) and (4) can be used for two successive tests to identify partially overlapping reflections. In the case of (BEDO-TTF)₂Ag(CN)₂, the twin is a rotation twin and the twinning matrix has the form

$$\mathbf{T} = \begin{pmatrix} -1 & 0 & 0 \\ t_{21} & 1 & t_{23} \\ 0 & 0 & -1 \end{pmatrix}, \quad (5)$$

where t_{21} and t_{23} are irrational numbers. The twin plane is the *ac* plane, which is also the composition plane shared by both components.

For commensurate twinning, the elements of \mathbf{T} can be expressed as fractions, such as $t_{21} = n_1/n_2$, and $t_{23} = m_1/m_2$. In the incommensurate case, these equal-

ities become approximations which can still be used. Substitution into (5) and multiplication of the second row elements by $m_2/m_2 = n_2/n_2 = 1$ gives

$$\mathbf{T} = \begin{pmatrix} -1 & 0 & 0 \\ n_1 m_2 & n_2 m_2 & n_2 m_1 \\ n_2 m_2 & n_2 m_2 & n_2 m_2 \\ 0 & 0 & -1 \end{pmatrix}. \quad (6)$$

Defining $M = n_1 m_2$, $N = n_2 m_2$ and $P = n_2 m_1$, the new indices in the second coordinate system are

$$\begin{pmatrix} h'_1 \\ k'_1 \\ l'_1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ M/N & N/N & P/N \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} h_1 \\ k_1 \\ l_1 \end{pmatrix}, \quad (7)$$

which can be rearranged to give

$$\begin{aligned} \begin{pmatrix} h''_1 \\ k''_1 \\ l''_1 \end{pmatrix} &= \begin{pmatrix} h'_1 \\ Nk'_1 \\ l'_1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ M & N & P \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} h_1 \\ k_1 \\ l_1 \end{pmatrix} \\ &= \mathbf{T}' \begin{pmatrix} h_1 \\ k_1 \\ l_1 \end{pmatrix}. \end{aligned} \quad (8)$$

In general N , M and P can be divided by their common denominator.

According to (8), the indices (h_1, k_1, l_1) of the first subsystem are transferred into the indices h''_1, k''_1 and l''_1 of the second subsystem. To be consistent with the new indices of the first subsystem k_2 , the index of the second subsystem must be multiplied by the coefficient N

$$\begin{pmatrix} h''_2 \\ k''_2 \\ l''_2 \end{pmatrix} = \begin{pmatrix} h_2 \\ Nk_2 \\ l_2 \end{pmatrix}. \quad (9)$$

Thus, $k''_1 = Nk'_1 = Mh_1 + Nk_1 + Pl_1$, and $k''_2 = Nk_2$. Substitution shows that when

$$Mh_1 + Pl_1 = Nn \quad (n = 0, \pm 1, \pm 2, \dots), \quad (10)$$

the difference between k''_1 and k''_2 is an integer multiple of N , and given by

$$k''_1 - k''_2 = Nn' \quad (n' = 0, \pm 1, \pm 2, \dots). \quad (11)$$

When (11) is fulfilled, a reflection of the first component is completely overlapped with a reflection of the second twin component. Partially overlapped reflections are recognized by the condition

$$\Delta k'' = |k''_1 - k''_2| = m \leq \delta'' \quad (m = 1, 2, 3, \dots), \quad (12)$$

where the dimensionless quantity δ'' is obtained from the reciprocal space separation δ [in \AA^{-1} , (3)] by $N\delta/|\mathbf{b}^*|$, or an equivalent expression for other twin matrices. If δ'' is chosen too small, some partially overlapped reflections will be included in the set of accepted data. On the other

hand, if its value is too large, some of the well separated reflections are excluded. The δ'' criterion is useful for obtaining a set of potentially overlapped reflections, to be subjected to the second test based on the angular separation.

Defining the setting angles of \mathbf{H}_1 by χ_1, φ_1 and ω_1 , and those for \mathbf{H}_2 at ω_1 (which will be zero for the bisecting position) by χ_2 and φ_2 , rotation around the scattering vector will bring \mathbf{H}_2 into the diffraction position at ω_2 , leading to an angular separation $\Delta\omega$ given by

$$\Delta\omega = \omega_2 - \omega_1 = \arcsin[-\sin(\varphi_2 - \varphi_1) \cos \chi] \quad (13)$$

(*International Tables for X-ray Crystallography*, 1974, Vol. IV, p. 279). An average value of χ is used in (13), as justified by the broadness of the reflection profile in a χ scan. A limiting value ε is selected, such that for $\Delta\omega < \varepsilon$, the reflection pair cannot be properly separated. The choice of ε depends on the width of the profiles of the individual reflections. Some of the reflections flagged by the δ'' analysis can now be accepted in the structure analysis. Thus, the δ'' criterion is used as an initial guideline to determine which reflection pairs are to be examined by (13).

Once the overlap pattern is determined, the original indices of the first subsystem are used in the refinement. Since there is no interaction between the twin components, the combined squared 'structure factor' of the overlapping reflections is the sum of structure factors of each subsystem, taking into account the twin ratio ν

$$F^2(\text{twin}) = \nu F^2(\mathbf{H}_1) + (1 - \nu) F^2(\mathbf{H}_2). \quad (14)$$

Only one component contributes to the well-separated reflections, or

$$F^2(\text{twin}) = \nu F^2(\mathbf{H}_1) \quad (15a)$$

$$F^2(\text{twin}) = (1 - \nu) F^2(\mathbf{H}_2), \quad (15b)$$

respectively, for the two twin components.

The structure can now be refined using both the completely overlapped and well separated reflections from both subsystems, thus allowing optimal use of the available experimental information.

The three-dimensional approach described above has been incorporated in the *JANA93* program system for the refinement of modulated, composite and twinned crystals (Petricek, 1993).

Application to (BEDO)₂Ag(CN)₂

Experimental

A needle-shaped crystal elongated along the a -axis (dimensions $0.525 \times 0.08 \times 0.05$ mm) was mounted on a glass fiber. The twinning is schematically illustrated in Fig. 2.

Table 1. *Crystallographic information on (BO)₂[Ag(CN)₂] and details of data collection*

| | | |
|---|---------------------------------|-------------------|
| a (Å) | 4.0355 (1) | |
| b (Å) | 16.7566 (2) | |
| c (Å) | 10.2335 (1) | |
| α (°) | 82.49 (1) | |
| β (°) | 81.12 (1) | |
| γ (°) | 91.10 (2) | |
| V (Å ³) | 677.3 (3) | |
| Z | 1 | |
| D_{calc} (g mm ⁻³) | 1.963×10^{-3} | |
| μ (mm ⁻¹) | 1.3805 | |
| λ (Å) | 0.71073 | |
| M_r | 800.76 | |
| $F(000)$ | 401 | |
| Twin ratio | 0.458 (1) | |
| Crystal dimensions (mm) | $0.525 \times 0.08 \times 0.05$ | |
| Transmission | 0.895–0.936 | |
| Diffractometer | Enraf–Nonius CAD-4 | |
| Criterion for observed reflections | $\sigma/I \leq 0.3$ | |
| | Cell (I) | Cell (II) |
| Range of hkl | 0→4; -19→19; -12→12 | 0→3; -16→16; -9→9 |
| No. of measured reflections | 1852 | 1593 |
| No. of unique reflections | 1040 | 891 |
| θ range (°) | $1 < \theta < 25$ | $1 < \theta < 20$ |
| R (merge) | 0.016 | 0.019 |

Room-temperature intensity data were collected on a CAD-4 diffractometer with the $\omega/2\theta$ scan technique and graphite-monochromated Mo $K\alpha$ radiation. Three standard reflections monitored throughout the data collection showed less than 3% change in intensity. Crystallographic information and data collection details are listed in Table 1. Both sets were processed using programs by Blessing (1987); numerical absorption corrections were applied.

Analysis of the twinning

The twinning matrix was determined from the orientation matrices of the two components as

$$\mathbf{T} = \begin{pmatrix} -1 & 0 & 0 \\ 0.333 & 1 & -0.444 \\ 0 & 0 & -1 \end{pmatrix}. \quad (16)$$

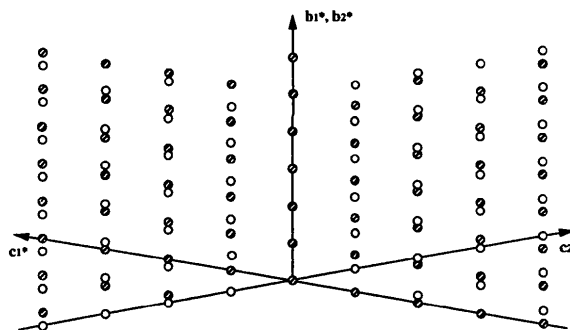


Fig. 2. Diffraction pattern within the Ok_l plane. Striped circles represent the reflections of the first twin component; open circles represent the reflections of the second component.

Table 2. Number of reflections and *R* factor at variant ε

| ε | No. of reflections | <i>R</i> (%) | <i>wR</i> (%) | Goodness of fit |
|---------------|--------------------|--------------|---------------|-----------------|
| 0.8 | 1068 | 6.31 | 8.03 | 2.495 |
| 0.7 | 1167 | 6.34 | 8.13 | 2.508 |
| 0.6 | 1250 | 6.42 | 8.36 | 2.571 |
| 0.5 | 1354 | 6.63 | 8.85 | 2.731 |
| 0.4 | 1500 | 6.88 | 9.41 | 2.867 |
| 0.3 | 1620 | 7.30 | 10.09 | 3.064 |
| 0.2 | 1731 | 8.21 | 12.05 | 3.653 |
| 0.1 | 1840 | 9.41 | 14.40 | 4.376 |
| 0.0 | 1931 | 10.45 | 16.04 | 4.880 |

 Table 3. Fractional coordinates and equivalent isotropic thermal parameters (\AA^2) with *e.s.d.*'s in parentheses

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{eq}}/U_{\text{iso}}^\dagger$ |
|-----|------------|-------------|------------|--|
| Ag | 0 | 0 | 0 | 0.0683 (9)† |
| S1 | 0.2799 (8) | 0.5503 (2) | 0.3654 (2) | 0.024 (1)† |
| S2 | 0.7384 (7) | 0.5500 (2) | 0.1100 (2) | 0.024 (1)† |
| S3 | 0.2453 (8) | 0.3584 (2) | 0.4070 (3) | 0.025 (1)† |
| S4 | 0.7112 (8) | 0.3577 (2) | 0.1541 (3) | 0.026 (1)† |
| O1 | 0.318 (2) | 0.7093 (5) | 0.3314 (6) | 0.029 (2) |
| O2 | 0.768 (2) | 0.7098 (5) | 0.0788 (6) | 0.030 (2) |
| O3 | 0.232 (2) | 0.1997 (6) | 0.4451 (7) | 0.036 (2) |
| O4 | 0.693 (2) | 0.1985 (5) | 0.1958 (6) | 0.032 (2) |
| N | 0.082 (3) | -0.0491 (9) | 0.296 (1) | 0.076 (4) |
| C | 0.048 (4) | -0.0350 (9) | 0.193 (1) | 0.047 (4) |
| C1 | 0.496 (3) | 0.4958 (8) | 0.249 (1) | 0.019 (3) |
| C2 | 0.488 (3) | 0.4130 (8) | 0.269 (1) | 0.022 (3) |
| C3 | 0.431 (3) | 0.6419 (7) | 0.276 (1) | 0.022 (3) |
| C4 | 0.630 (3) | 0.6440 (7) | 0.161 (1) | 0.020 (3) |
| C5 | 0.368 (3) | 0.2644 (7) | 0.3608 (9) | 0.019 (3) |
| C6 | 0.576 (3) | 0.2667 (7) | 0.248 (1) | 0.023 (3) |
| C7 | 0.534 (3) | 0.7783 (9) | 0.264 (1) | 0.036 (3) |
| C8 | 0.596 (3) | 0.7809 (8) | 0.117 (1) | 0.036 (3) |
| C9 | 0.412 (3) | 0.1280 (9) | 0.410 (1) | 0.048 (4) |
| C10 | 0.480 (3) | 0.1298 (9) | 0.264 (1) | 0.045 (4) |

† $U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$; atom refined anisotropically.

This leads, according to (8), to

$$\begin{pmatrix} h'_1 \\ 9k'_1 \\ l'_1 \end{pmatrix} = \begin{pmatrix} -1 & 0 & 0 \\ 3 & 9 & -4 \\ 0 & 0 & -1 \end{pmatrix} \begin{pmatrix} h_1 \\ k_1 \\ l_1 \end{pmatrix}. \quad (17)$$

Therefore, when $3h_1 - 4l_1 = 9n$ (n integer), the difference between k'_2 and k'_1 is an integer multiple of 9, or $k'_2 = k'_1 + 9n'$, and the reflection of the first subsystem is fully overlapped with a reflection of the second subsystem.

According to (12), the closeness of two partially overlapped reflections depends on the difference between k'_1 and k'_2 . With $\delta'' = 2$, the rejection condition for partially overlapped reflections becomes

$$\Delta k'' = |k'_1 - k'_2| = 1, 2. \quad (18)$$

Accordingly, 654 out of 1040 reflections of the first twin component were accepted, and used in the initial structure determination. As the Ag atom is located at the origin of the unit cell, determination of the structure is straightforward. All atoms except Ag and S were refined isotropically using the full-matrix refinement program *LINEX84* (1984). The function $\Sigma[w(|F_{\text{obs}}| - k|F_{\text{cal}}|)]$

 Table 4. Bond lengths (\AA) and angles ($^\circ$)

| | | | |
|-----------|-----------|-----------|-----------|
| Ag—C | 2.03 (1) | C—N | 1.08 (2) |
| S1—C1 | 1.73 (1) | S1—C3 | 1.73 (1) |
| S2—C1 | 1.74 (1) | S2—C4 | 1.76 (1) |
| S3—C2 | 1.73 (1) | S3—C5 | 1.76 (1) |
| S4—C2 | 1.74 (1) | S4—C6 | 1.72 (1) |
| O1—C3 | 1.38 (1) | O1—C7 | 1.46 (2) |
| O2—C4 | 1.35 (1) | O2—C8 | 1.46 (2) |
| O3—C5 | 1.34 (1) | O3—C9 | 1.47 (2) |
| O4—C6 | 1.39 (1) | O4—C10 | 1.45 (2) |
| C1—C2 | 1.38 (2) | C3—C4 | 1.31 (1) |
| C5—C6 | 1.31 (1) | C7—C8 | 1.48 (2) |
| C9—C10 | 1.48 (2) | | |
| C1—S2—C4 | 93.3 (5) | C1—S1—C3 | 93.1 (5) |
| C2—S4—C6 | 93.0 (6) | C2—S3—C5 | 94.0 (5) |
| C4—O2—C8 | 109.1 (8) | C3—O1—C7 | 107.8 (8) |
| C6—O4—C10 | 108.1 (8) | C5—O3—C9 | 108.9 (8) |
| S1—C1—C2 | 121.6 (7) | S1—C1—S2 | 117.3 (7) |
| S3—C2—S4 | 116.7 (7) | S2—C1—C2 | 121.0 (8) |
| S4—C2—C1 | 122.0 (7) | S3—C2—C1 | 121.4 (8) |
| S1—C3—C4 | 120 (1) | S1—C3—O1 | 115.6 (7) |
| S2—C4—O2 | 116.1 (7) | O1—C3—C4 | 124 (1) |
| O2—C4—C3 | 128 (1) | S2—C4—C3 | 116.4 (9) |
| S3—C5—C6 | 116.0 (9) | S3—C5—O3 | 115.5 (7) |
| S4—C6—O4 | 116.0 (7) | O3—C5—C6 | 129 (1) |
| O4—C6—C5 | 124 (1) | S4—C6—C5 | 120 (1) |
| O2—C8—C7 | 111 (1) | O1—C7—C8 | 113 (1) |
| O4—C10—C9 | 113 (1) | O3—C9—C10 | 110 (1) |
| | | Ag—C—N | 176 (1) |

 Table 5. Intermolecular S—S distances (\AA) less than 3.8 \AA

| | | | |
|--------------------------|-----------|--------------------------|-----------|
| S1 <i>K</i> —S1 <i>L</i> | 3.500 (4) | S1 <i>K</i> —S1 <i>M</i> | 3.741 (4) |
| S1 <i>K</i> —S3 <i>L</i> | 3.433 (4) | S1 <i>K</i> —S3 <i>M</i> | 3.692 (4) |
| S1 <i>L</i> —S2 <i>M</i> | 3.657 (4) | S3 <i>L</i> —S4 <i>M</i> | 3.616 (4) |

K, *L* and *M* refer to BEDO-TTF molecules in Fig. 4.

was minimized, where $w = 1/\sigma^2(F)$, $\sigma(F) = \sigma(F^2)/2F$, $\sigma(F^2) = [\sigma_{\text{counting}}^2 + (0.02|F|^2)^2]^{1/2}$.

In the second stage, (13) was applied. The final *R*-factors and number of reflections accepted as a function of ε are given in Table 2. The final positional and temperature parameters obtained with $\varepsilon = 0.6$ are listed in Table 3, while interatomic distances and angles are given in Tables 4 and 5. H-atom parameters were calculated and used in the structure-factor calculation. The twin ratio ν was found to be 0.458 (1). Parameter shifts in the final least-squares cycles were smaller than 0.02σ .*

Discussion

The packing diagram is shown in Fig. 3. The cell contains two crystallographically equivalent BEDO-TTF cations and one $\text{Ag}(\text{CN})_2^{-1}$ anion. The BEDO-TTF molecules form stacks along the *a*-direction with the

* Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the IUCr (Reference: BK0014). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

long molecular axis oriented along **b**. S—S contacts shorter than the sum of the van der Waals radii (3.6 Å) occur between the stacks from S1 (molecule *K*) to S3 (molecule *L*) and from S1 (*K*) to S1 (*L*); they are 3.433(4) and 3.500(4) Å, respectively (Fig. 4). S—S contacts between two BEDO-TTF molecules within the unit cell (*K* and *M*) have a length of *ca* 3.7 Å (Table 5). In terms of the classification of ET molecules by Williams *et al.* (1987), the intrastack packing mode of the BO molecule is type *b* with $\Delta X_{ij} \approx 2$ Å, and the interstack arrangement is described by the *L*-mode.

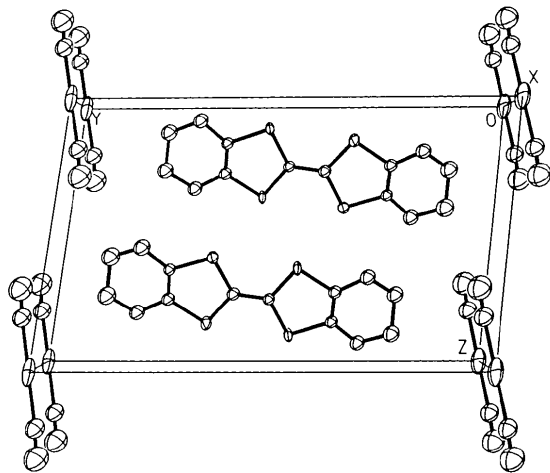


Fig. 3. Packing diagram of the unit cell.

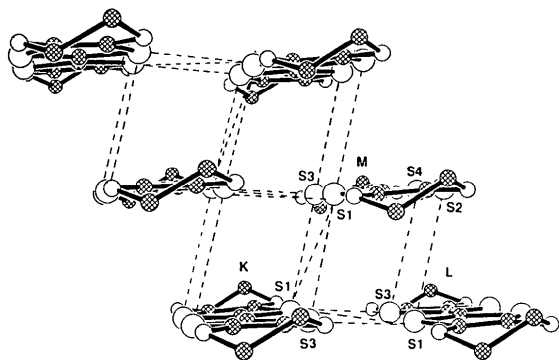


Fig. 4. Arrangement of the BEDO-TTF molecules. Intermolecular S—S contacts are indicated by dashed lines.

The bond lengths between the S and the central C atoms, and the central C=C bond are comparable with other salts of BEDO-TTF with the same stoichiometry, such as (BEDO-TTF)₂ClO₄, in which the S—C bond length equals 1.738 Å and the central C=C bond length is 1.371 Å (Beno *et al.*, 1990). Comparison between the neutral BEDO-TTF molecule and (BEDO-TTF)₂Ag(CN)₂, in which the BEDO-TTF molecules carry a formal charge of +0.5, indicates that the geometry varies with the electron population of the BEDO-TTF molecule, as expected (Mori, Wang, Imaeda, Enoki & Inokuchi, 1987; Umland, Allie, Kuhlmann & Coppens, 1988). However, the bond lengths in the present structure are not sufficiently accurate for a reliable prediction of the charge transfer.

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