

## The single-crystal structure of the organic superconductor $\beta_{\text{CO}}\text{-(BEDT-TTF)}_2\text{I}_3$ from a powder grain

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### Abstract

Synchrotron radiation diffraction data have been collected at 200 K on a microscopic single crystal (dimensions  $12 \times 10 \times 2 \mu\text{m}$ ) of the title compound, where BEDT-TTF is bis(ethylenedithio)tetrathiafulvalene,  $\text{C}_{10}\text{H}_8\text{S}_8$ . The quality of the diffraction data allowed a full structure refinement and enabled the determination of structural details such as the conformations of the ethylene groups as well as the occupancy of the triiodide sites. The compound was found to be slightly iodine-deficient and better described as  $\beta_{\text{CO}}\text{-(BEDT-TTF)}_2\text{I}_{3-x}$  [ $x = 0.014$  (3)]. One of the ethylene groups of the BEDT-TTF cation is disordered at this temperature and exists in two distinct conformations with occupancies which are identical within the standard uncertainty.

### 1. Introduction

Third-generation synchrotron sources such as the European Synchrotron Radiation Facility (ESRF) offer new possibilities for single-crystal diffraction on micrometre-sized crystals in materials science (Neder *et al.*, 1996; Fiedler, 1997; Burghammer, 1997) and in structural biology (Cusack *et al.*, 1998). Most of the previous studies on micrometre-sized crystals at second-generation synchrotron sources were performed on minerals (Bachmann *et al.*, 1985; Eisenberger *et al.*, 1984; Rieck *et al.*, 1988) though some were dedicated to chemical crystallography (Harding, 1995, 1996). It has recently been shown that the quality of the data collected on micrometre-sized crystals at the microfocuss beamline (ID13) at the ESRF is comparable with that of data collected on 'normal-sized' crystals (*i.e.* 0.1–0.5 mm) with sealed-tube sources (Neder *et al.*, 1996; Fiedler, 1997; Burghammer, 1997).

Superconducting radical cation salts derived from the donor molecule bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) constitute an important class of materials in the burgeoning field of molecular organic conductors. BEDT-TTF and iodine form a plethora of polymorphic phases, denoted by lower-case Greek

letters, the electrical conductivities of which range from semiconducting to metallic to superconducting (Williams *et al.*, 1992). The phases  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  (Kaminskii *et al.*, 1984),  $\theta\text{-(BEDT-TTF)}_2\text{I}_3$  (Kobayashi, Kato, Kobayashi, Nishio *et al.*, 1986) and  $\kappa\text{-(BEDT-TTF)}_2\text{I}_3$  (Kobayashi, Kato, Kobayashi, Nishio *et al.*, 1986; Kobayashi, Kato, Kobayashi, Moriyama *et al.*, 1986; Kobayashi *et al.*, 1995) are superconductors at ambient pressure with transition temperatures  $T_c$  of 1.4, 3.6 and 3.6 K, respectively. These compounds are prepared by an electrochemical technique. Individual batches may contain single crystals, sometimes quite large, of several different polymorphic phases. Recently, the non-electrochemical synthesis and structural characterization of the superconducting phase  $\beta_{\text{CO}}\text{-(BEDT-TTF)}_2\text{I}_3$  ( $T_c = 7\text{--}8$  K) was reported (Müller *et al.*, 1997). The subscript 'CO' refers to the fact that the compound is obtained by 'chemical oxidation' of BEDT-TTF with iodine and not by an anodic electrocrystallization. The redox synthesis provides  $\beta_{\text{CO}}\text{-(BEDT-TTF)}_2\text{I}_3$  as a phase-pure product as evidenced by ESR spectroscopy and X-ray powder diffraction. The compound can be obtained only as microcrystals and was found to be isostructural with  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  at ambient temperature by high-resolution powder-diffraction measurements. Despite their structural correspondence, the transition temperatures of  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  and of  $\beta_{\text{CO}}\text{-(BEDT-TTF)}_2\text{I}_3$  differ strikingly, a behaviour which is not yet understood.

### 2. Experimental

#### 2.1. Experimental set-up

The measurement of Bragg intensities on a micrometre-sized crystal requires a combination of high flux density and low background sample environment (Cusack *et al.*, 1998; Neder *et al.*, 1996; Engström *et al.*, 1995). The high flux density ( $10^6\text{--}10^7$  photons  $\text{s}^{-1} \mu\text{m}^{-2}$ ) at ID13, ESRF, is generated by X-ray optics consisting of a low- $\beta$  undulator, an Si(111) double-crystal monochromator and an ellipsoidal-shaped mirror as main components. The natural beam size ( $20 \times 40 \mu\text{m}$ ) at the

focal spot is further reduced by a 10  $\mu\text{m}$  collimator. Parasitic air scattering is usually the main contribution to the background signal. We have therefore minimized the unshielded beam path around the sample using a very small beamstop (400  $\mu\text{m}$  in diameter) and an additional aperture, which was placed between the collimator and the sample. The aperture and the beamstop were placed a few millimetres in front of and behind the sample, respectively. The wavelength was calibrated by recording absorption spectra of a Zr foil. The crystal-to-detector distance, 41.89 mm, was calibrated with an Si powder. We used the technique described by Rieck *et al.* (1988) to mount the crystals. The area detector used was a Princeton CCD detector (1024  $\times$  1024 pixels/100  $\times$  100 mm). The detector was mounted on a support structure so that it could be tilted out of the horizontal plane.

## 2.2. Data collection

Several microcrystals were tested to select a single crystal of suitable quality. Each sample was mounted on a very thin glass fibre with Araldite glue. The crystals of highest quality were  $\sim 10$   $\mu\text{m}$  in size whereas the quality of larger crystals was significantly poorer. The crystal used in the data collection is shown in Fig. 1.

The measurement was carried out at a fixed temperature of 200 (2) K using an Oxford Cryostream device. A full sphere of data was collected with the  $\varphi$ -oscillation method to a resolution of 0.75  $\text{\AA}$  with two positions of the Princeton CCD detector (tilt angles of 0 and 30 $^\circ$ ). The data collection lasted about 1.5 h per tilt angle. 92 frames of 6 $^\circ$  oscillation range were used, starting at 0, 4 $^\circ$  *etc.* in  $\varphi$ . The frames were indexed and the reflections integrated using *DENZO* (Otwinowski & Minor, 1997) and subsequently scaled using *SCALA* (Evans, 1997) in the *CCP4* program suite (Collaborative Computational Project, Number 4, 1994). The unit cell was determined using *SCALEPACK* (Otwinowski & Minor, 1997) by a refinement on the setting angles of the medium to strong reflections on frames with 0 $^\circ$  tilt angle.

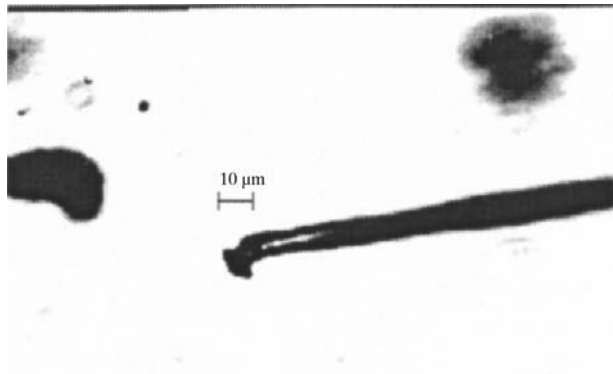


Fig. 1. The microcrystal is mounted on a very thin glass fibre using a micromanipulator and an inverted-geometry optical microscope.

Table 1. *Experimental details*

Crystal data	
Chemical formula	$\text{C}_{10}\text{H}_8\text{S}_8\cdot 1.5\text{I}$
Chemical formula weight	574.99
Cell setting	Triclinic
Space group	$P\bar{1}$
$a$ ( $\text{\AA}$ )	6.585 (2)
$b$ ( $\text{\AA}$ )	9.038 (2)
$c$ ( $\text{\AA}$ )	15.205 (2)
$\alpha$ ( $^\circ$ )	94.90 (1)
$\beta$ ( $^\circ$ )	95.74 (1)
$\gamma$ ( $^\circ$ )	110.00 (1)
$V$ ( $\text{\AA}^3$ )	839.1
$Z$	2
$D_x$ ( $\text{Mg m}^{-3}$ )	2.276
Radiation type	Synchrotron
Wavelength ( $\text{\AA}$ )	0.6887
No. of reflections for cell parameters	896
$\theta$ range ( $^\circ$ )	2.8–24.9
$\mu$ ( $\text{mm}^{-1}$ )	3.807
Temperature (K)	200 (2)
Crystal form	Plate
Crystal size (mm)	0.012 $\times$ 0.010 $\times$ 0.002
Crystal colour	Brown
Data collection	
Data collection method	See text
Absorption correction	None
No. of measured reflections	13 912
No. of independent reflections	3230
No. of observed reflections	2746
Criterion for observed reflections	$I > 2\sigma(I)$
$R_{\text{int}}$	0.032
$\theta_{\text{max}}$ ( $^\circ$ )	27.33
Refinement	
Refinement on	$F^2$
$R[F^2 > 2\sigma(F^2)]$	0.0371
$wR(F^2)$	0.0812
$S$	1.076
No. of reflections used in refinement	3230
No. of parameters used	198
H-atom treatment	Mixed
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.0097P)^2 + 5.7148P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\text{max}}$	0.002
$\Delta\rho_{\text{max}}$ ( $\text{e \AA}^{-3}$ )	2.283
$\Delta\rho_{\text{min}}$ ( $\text{e \AA}^{-3}$ )	−1.719
Extinction method	None
Source of atomic scattering factors	<i>International Tables for Crystallography</i> (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)
Computer programs	
Cell refinement	<i>DENZO</i> (Otwinowski & Minor, 1997)
Data reduction	<i>DENZO</i> (Otwinowski & Minor, 1997), <i>CCP4</i> ( <i>SCALA</i> ; Evans, 1997)
Structure solution	<i>SHELXS97</i> (Sheldrick, 1990)
Structure refinement	<i>SHELXL97</i> (Sheldrick, 1997)

*SCALEPACK* does not provide standard uncertainties (s.u.s) on the determined cell parameters but, since the refined mosaicity was 0.17 $^\circ$ , we estimate the s.u.s to be of

the order of a few thousandths of an angstrom on  $a$ ,  $b$  and  $c$  and a few hundredths of a degree on  $\alpha$ ,  $\beta$  and  $\gamma$ . Further experimental details are summarized in Table 1.

### 2.3. Structure refinement

The atomic coordinates from a recent powder-diffraction study at RT (Müller *et al.*, 1997) were used as starting values for the structure refinement of the single-crystal data using *SHELXL97* (Sheldrick, 1997) assuming the space group  $P\bar{1}$ . After a few least-squares cycles, anisotropic displacement parameters were employed on all I, S and C atoms. Atoms C8 and C9 of one terminal ethylene group ( $C_2H_4$ ) of the BEDT-TTF cation showed large displacement parameters indicating disorder. The six-membered dithiin ( $C_4H_4S_2$ ) rings of the neutral donor BEDT-TTF molecule are non-planar (Kobayashi, Kobayashi *et al.*, 1986) with several distinct conformations. As illustrated in Fig. 2, the ethylene groups of the BEDT-TTF cations can adopt either a staggered (*A*) or an eclipsed (*B*) conformation when viewed along the long molecular axis. The structural model improved significantly, according to Hamilton's ratio test (Hamilton, 1965), by including the occupancy of the triiodide anion as a parameter in refinement. The final value was 0.986 (3), thus slightly deviating from the ideal stoichiometry.

Refinement was also carried out in the space group  $P1$  but resulted in no significant differences in atom positions or the occupancies of the triiodide ion or the two conformations of the BEDT-TTF cation. We therefore conclude that the correct space group is  $P\bar{1}$ . The populations of the two conformations of the BEDT-TTF cation are 0.490 (17) for *A* and 0.510 (17) for *B*. The H atoms were placed in idealized positions with  $C-H = 1.08$  Å during the refinement. The chemically equivalent  $C-C$  and  $C-S$  bonds in the three terminal ethylene groups were restrained to each other with an s.u. of 0.005 Å. The atoms S7, S8, C8A, C8B, C9A and C9B had a rigid bond restraint on the anisotropic displacement parameters.

Further details on the structure refinement are given in Table 1; fractional coordinates and equivalent displacement parameters are listed in Table 2.†

### 3. Discussion

The unit cell of  $\beta_{CO}-(BEDT-TTF)_2I_3$  is shown in Fig. 3. The BEDT-TTF cations form layers parallel to the  $ab$  plane so that a two-dimensional array of  $S \cdots S$  contacts results which stabilizes metallic conductivity down to low temperatures where a superconducting transition occurs. The triiodide anions are arranged above and

Table 2. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{Å}^2$ )

$$U_{eq} = (1/3)\Sigma_i \Sigma_j U^{ij} a^i a^j \mathbf{a}_i \cdot \mathbf{a}_j.$$

	$x$	$y$	$z$	$U_{eq}$
I1	0	0	0	0.03994 (17)
I2	0.40573 (8)	0.25157 (6)	-0.01721 (3)	0.05150 (16)
S1	0.0963 (2)	-0.14611 (17)	0.43081 (8)	0.0288 (3)
S2	0.4627 (2)	-0.26148 (17)	0.44813 (8)	0.0263 (3)
S3	0.2085 (3)	0.0071 (2)	0.27059 (10)	0.0392 (4)
S4	0.6385 (3)	-0.1389 (2)	0.28793 (10)	0.0394 (4)
S5	0.2814 (2)	-0.43049 (16)	0.61967 (7)	0.0249 (3)
S6	-0.0835 (2)	-0.31358 (17)	0.59826 (7)	0.0256 (3)
S7	0.1971 (2)	-0.54159 (18)	0.79329 (8)	0.0322 (3)
S8	-0.2374 (2)	-0.39674 (18)	0.76841 (8)	0.0322 (3)
C1	0.2268 (8)	-0.2543 (6)	0.4878 (3)	0.0217 (10)
C2	0.2721 (8)	-0.1055 (6)	0.3496 (3)	0.0237 (11)
C3	0.4092 (8)	0.0204 (8)	0.1965 (3)	0.0376 (14)
C4	0.6299 (9)	0.0335 (6)	0.2389 (4)	0.0350 (13)
C5	0.4378 (9)	-0.1576 (6)	0.3580 (3)	0.0251 (11)
C6	0.1496 (8)	-0.3259 (6)	0.5590 (3)	0.0214 (10)
C7	0.1177 (8)	-0.4523 (6)	0.7054 (3)	0.0205 (10)
C8A	-0.0351 (15)	-0.5828 (13)	0.8529 (8)	0.030 (3)
C9A	-0.106 (2)	-0.4432 (14)	0.8670 (5)	0.031 (3)
C8B	0.0429 (15)	-0.4891 (17)	0.8747 (5)	0.038 (4)
C9B	-0.1946 (15)	-0.5298 (13)	0.8437 (8)	0.032 (3)
C10	-0.0491 (8)	-0.3979 (6)	0.6958 (3)	0.0210 (10)

below the cation stacks thus forming a layered highly anisotropic structure. The atomic arrangement observed for the title compound resembles closely that of the known superconductor  $\beta-(BEDT-TTF)_2I_3$  (Shibaeva *et al.*, 1984), although the iodine-deficiency observed for  $\beta_{CO}-(BEDT-TTF)_2I_3$  suggests slightly different stoichiometries. Unfortunately, none of the independently performed structure determinations on  $\beta-(BEDT-TTF)_2I_3$  reported in the literature disclose detailed information on the occupancy of the anion sites and thus on the actual composition (Williams *et al.*, 1984; Mori *et al.*, 1984).

The transition temperature  $T_c$  of  $\beta-(BEDT-TTF)_2I_3$  is 1.4 K at ambient pressure and rises with applied pressure (1.5 kbar) to 8 K, whereas  $\beta_{CO}-(BEDT-TTF)_2I_3$  exhibits an onset of the superconducting transition at 8 K and ambient pressure (Müller *et al.*, 1997).

The observation of a more than sixfold increase in  $T_c$  of  $\beta-(BEDT-TTF)_2I_3$  under pressure has been explained by a pressure-induced ordering process of the ethylene groups of the BEDT-TTF cation. This interpretation has been corroborated by neutron diffraction data obtained on a large single crystal of  $\beta-(BEDT-TTF)_2I_3$  at 4.5 K and ambient pressure as well as under a pressure of 1.5 kbar (Schultz *et al.*, 1986). Pressure-induced ordering of the ethylene groups of  $\beta-(BEDT-TTF)_2I_3$  has also been observed by X-ray diffraction at ambient temperature (Molchanov *et al.*, 1986). In the present crystal at 200 K and ambient pressure, one of the ethylene groups of the BEDT-TTF cation is similarly disordered, taking one of the conformations *A* or *B* (Fig. 2).

† Supplementary data for this paper are available from the IUCr electronic archives (Reference: HA0183). Services for accessing these data are described at the back of the journal.

Table 3. Selected intermolecular distances ( $\text{\AA}$ ) in  $\beta_{\text{CO}}\text{-(BEDT-TTF)}_2\text{I}_3$ 

S1...S4 <sup>i</sup>	3.559 (3)	S3...S6 <sup>iv</sup>	3.643 (2)
S1...S5 <sup>ii</sup>	3.746 (2)	S3...S7 <sup>iv</sup>	3.564 (2)
S2...S6 <sup>iii</sup>	3.762 (2)	S4...S7 <sup>v</sup>	3.582 (3)
S2...S6 <sup>ii</sup>	3.756 (2)	S5...S8 <sup>iii</sup>	3.611 (2)
S3...S4 <sup>i</sup>	3.573 (3)	S5...S6 <sup>ii</sup>	3.715 (2)
S7...S8 <sup>iii</sup>	3.571 (2)	I2...H9C <sup>vi</sup>	2.85
I2...H9B <sup>iv</sup>	3.02	I2...H3B	3.06
H3A...H8A <sup>ii</sup>	2.20		

Symmetry codes: (i)  $x - 1, y, z$ ; (ii)  $-x, -y - 1, 1 - z$ ; (iii)  $1 + x, y, z$ ; (iv)  $-x, -y, 1 - z$ ; (v)  $1 - x, -1 - y, 1 - z$ ; (vi)  $1 + x, 1 + y, z - 1$ .

The observed pressure-induced ordering of the ethylene groups in  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  has been attributed to the presence of extremely short energetically unfavourable I...H as well as H...H contacts, arising from the coexistence of two BEDT-TTF conformers over a temperature range between 293 and  $\sim 200$  K. The I2...H9C distance was calculated to be 2.84  $\text{\AA}$  at ambient temperature and pressure for  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  whereas a value of 2.15  $\text{\AA}$  was found for the H3A...H8A distance (Whangbo *et al.*, 1987).

A structural modulation, as observed for  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  at temperatures below 200 K (Nogami *et al.*, 1986), is believed to be an effective way of reducing such non-favourable intermolecular contacts at ambient pressure (Whangbo *et al.*, 1987), but does not prevent the compound from condensing in a structurally disordered state associated with a transition temperature of 1.4 K, unless pressure is applied. Upon application of pressure ( $\sim 0.5$  kbar), a structural phase transition occurs and all the BEDT-TTF molecules eventually

adopt a staggered conformation associated with a  $T_c$  of 8 K. The resulting ordered structure is stable at ambient pressure up to a temperature of  $\sim 130$  K, where it transforms into the disordered  $\beta$ -phase with both eclipsed and staggered ethylene groups (Schultz *et al.*, 1986).

In the case of  $\beta_{\text{CO}}\text{-(BEDT-TTF)}_2\text{I}_3$ , the populations of both conformations at 200 K and ambient pressure are identical (0.5) within the s.u. The non-bonded I2...H9C and H3A...H8A contacts are 2.85 and 2.20  $\text{\AA}$ , respectively. The values resemble closely those found for  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  at 293 K. A comparison of the intermolecular S...S contacts of  $\beta_{\text{CO}}\text{-(BEDT-TTF)}_2\text{I}_3$  (200 K;  $P = 0.001$  kbar) with those of  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  (4.5 K;  $P = 1.5$  kbar) reveals a significant shortening upon cooling and pressurization only for the contacts S3...S4 ( $\Delta = -0.122$   $\text{\AA}$ ) and S7...S8 ( $\Delta = -0.151$   $\text{\AA}$ ), whereas all other S...S contacts (*cf.* Table 3) decrease significantly less ( $\sim 0.05$   $\text{\AA}$ ). Taking into account that atoms S3, S4 and S7, S8 constitute together with atoms C3, C4 as well as C8A(B), C9A(B) the conformationally flexible dithiin rings of the BEDT-TTF cations, these findings underline the importance of minute structural details on the physical properties of the material under investigation.

In view of the structural analogies of  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  and  $\beta_{\text{CO}}\text{-(BEDT-TTF)}_2\text{I}_3$  in the temperature range between 290 and 200 K, it is possible that a structural modulation followed by conformational flipping of the eclipsed ethylene groups as observed for  $\beta\text{-(BEDT-TTF)}_2\text{I}_3$  (Leung *et al.*, 1984) occurs as well in  $\beta_{\text{CO}}\text{-(BEDT-TTF)}_2\text{I}_3$  at temperatures below 200 K and thus accounts for the physical properties of the latter

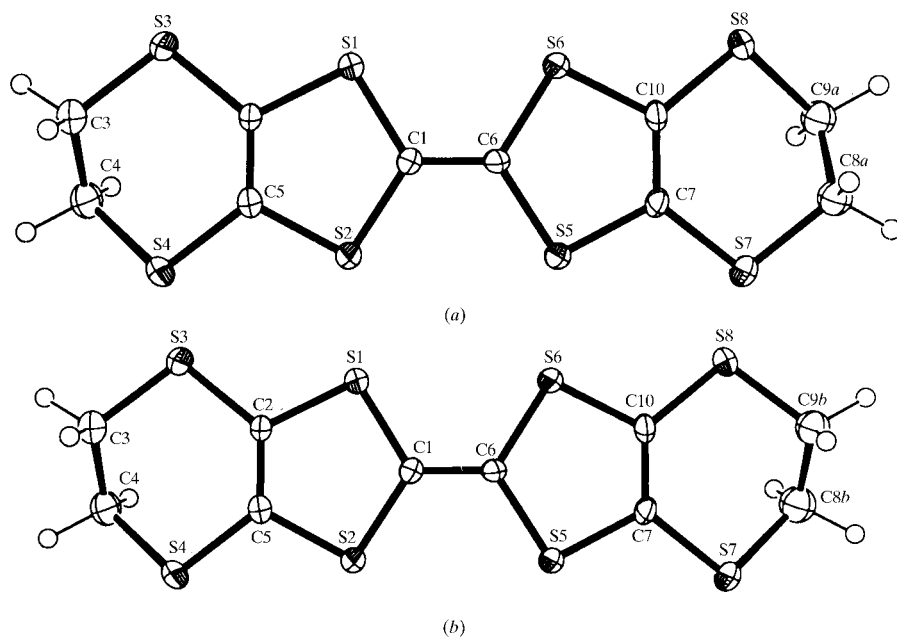


Fig. 2. ORTEP drawing showing the labelling scheme in the cation in  $\beta_{\text{CO}}\text{-(BEDT-TTF)}_2\text{I}_3$  with the (a) staggered and (b) eclipsed conformations of the disordered ethylene group (C8, C9) shown separately. The ellipsoids enclose 50% probability.

phase. This view is corroborated by the observation of an increase in  $T_c$  from 1.5 to  $\sim 8$  K in  $\beta$ -(BEDT-TTF) $_2$ I $_3$  upon low-temperature annealing at ambient pressure, although no structural evidence for an ordering process was provided (Kanoda *et al.*, 1990). In this context it is also tempting to speculate on a possible link of the triiodide deficiency and the enhanced transition temperature observed for  $\beta_{CO}$ -(BEDT-TTF) $_2$ I $_3$ . The  $T_c$  onset of  $\sim 8$  K, followed by a broad transition curve between 8 and 2 K, is clearly suggestive of some degree of structural ordering. The superconducting volume fraction with a  $T_c$  of  $\sim 8$  K is small and has been estimated from DC-magnetization measurements to values of  $\sim 1\%$  of the total sample volume (Müller *et al.*, 1999). It appears therefore not unreasonable to presume that the observed non-stoichiometric triiodide occupancy reduces unfavourable intermolecular interactions to some extent. The coexistence of a small fraction of ordered together with disordered BEDT-TTF cations could explain the observed physical properties of  $\beta_{CO}$ -(BEDT-TTF) $_2$ I $_3$  and is compatible with the crystallographic evidence presented in this study.

#### 4. Conclusions

The high flux from a third-generation synchrotron source was necessary in the present study to obtain the good quality diffraction data from a micrometre-sized crystal of an organic sample. This opens new possibilities in the field of chemical crystallography where detailed structural information is of interest for the properties of a given compound and only micrometre-sized crystals can be obtained.

The single-crystal structure of the organic superconducting radical cation salt  $\beta_{CO}$ -(BEDT-TTF) $_2$ I $_3$  ( $T_c$

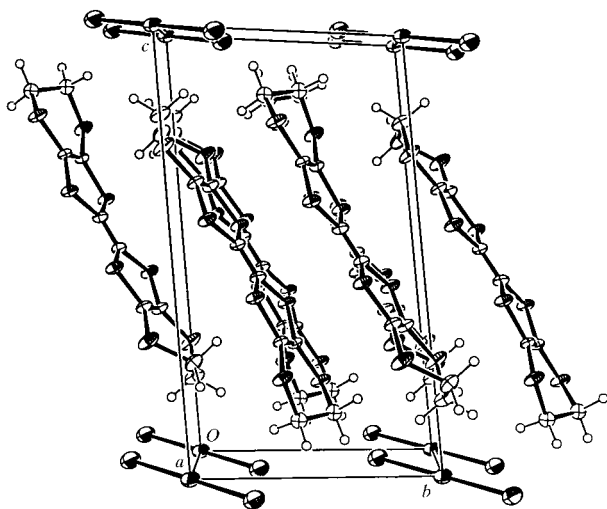


Fig. 3. View along the crystallographic  $a$ -axis of the stacking of the anions and cations. Only the staggered ( $A$ ) conformation is shown for the cation.

7–8 K) has been determined on a micrometre-sized single crystal at 200 K. The compound is slightly iodine-deficient and better described by the formula  $\beta_{CO}$ -(BEDT-TTF) $_2$ I $_{3-x}$  [ $x = 0.014$  (3)]. It appears possible that the observed deviation from the ideal stoichiometry is the reason for the more than sixfold increase in  $T_c$  when compared with the isostructural superconductor  $\beta$ -(BEDT-TTF) $_2$ I $_3$ .

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