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## Structure Reports

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3-(Bromoacetyl)coumarin: a second  $P2_1/c$  modification

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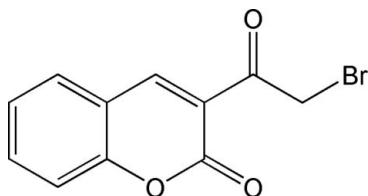
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Key indicators: single-crystal X-ray study;  $T = 120$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å;  
 $R$  factor = 0.023;  $wR$  factor = 0.061; data-to-parameter ratio = 21.2.

A new polymorph of 3-(bromoacetyl)coumarin,  $\text{C}_{11}\text{H}_7\text{BrO}_3$ , is reported in the monoclinic space group  $P2_1/c$ . The structure contains a number of short intermolecular  $\text{C}-\text{H}\cdots\text{O}$  contacts.

## Related literature

For the initial structure described in  $P2_1/n$ , see: Vasudevan *et al.* (1991). For additional related literature, see: Wolff *et al.* (2003); Testa *et al.* (2000); Taylor *et al.* (1982).



## Experimental

## Crystal data

$\text{C}_{11}\text{H}_7\text{BrO}_3$   
 $M_r = 267.08$   
Monoclinic,  $P2_1/c$   
 $a = 5.2932$  (1) Å  
 $b = 18.4568$  (5) Å  
 $c = 9.7473$  (3) Å  
 $\beta = 98.768$  (1)°

$V = 941.14$  (4) Å<sup>3</sup>  
 $Z = 4$   
Mo  $K\alpha$  radiation  
 $\mu = 4.35$  mm<sup>-1</sup>  
 $T = 120$  (2) K  
 $0.15 \times 0.14 \times 0.08$  mm

## Data collection

Bruker SMART 6K CCD detector  
diffractometer  
Absorption correction: multi-scan  
(*SADABS*; Sheldrick, 1998)  
 $T_{\min} = 0.608$ ,  $T_{\max} = 1.000$   
(expected range = 0.429–0.706)

14782 measured reflections  
2879 independent reflections  
2547 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.033$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.024$   
 $wR(F^2) = 0.061$   
 $S = 1.06$   
2879 reflections

136 parameters  
H-atom parameters constrained  
 $\Delta\rho_{\text{max}} = 0.47$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.39$  e Å<sup>-3</sup>

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{C4}-\text{H4}\cdots\text{O2}^{\text{ii}}$	0.95	2.45	3.3572 (19)	159
$\text{C5}-\text{H5}\cdots\text{O3}^{\text{ii}}$	0.95	2.52	3.3302 (18)	143
$\text{C7}-\text{H7}\cdots\text{O3}^{\text{ii}}$	0.95	2.38	3.2329 (17)	149

Symmetry codes: (i)  $-x + 1, y - \frac{1}{2}, -z + \frac{3}{2}$ ; (ii)  $-x + 2, -y + 1, -z + 1$ .

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NG2310).

## References

- Bruker (1998). *SMART* (Version 5.054) and *SAINT* (Version 6.45A). Bruker AXS Inc, Madison, Wisconsin, USA.  
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
Sheldrick, G. M. (1998). *SADABS*. University of Göttingen, Germany.  
Taylor, R. & Kennard, O. (1982). *J. Am. Chem. Soc.* **104**, 5063–5070.  
Testa, B., Gnerre, C., Catto, M., Leonetti, F., Weber, P., Carrupt, P.-A., Altomare, C. & Carotti, A. (2000). *J. Med. Chem.* **43**, 4747–4758.  
Vasudevan, K. T., Puttaraja, & Kulkarni, M. V. (1991). *Acta Cryst.* **C47**, 775–777.  
Wolff, T., Yu, A., Scheller, D. & Rademacher, O. (2003). *J. Org. Chem.* **68**, 7386–7399.

**supplementary materials**

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### 3-(Bromoacetyl)coumarin: a second $P2_1/c$ modification

H. A. Sparkes and J. A. K. Howard

#### Comment

Coumarin and its derivatives have attracted much interest due to their optical (Wolff *et al.*, 2003) and biological properties (Testa *et al.*, 2000). The structure of the title compound (form A) has previously been determined at 300 K (Vasudevan *et al.*, 1991), using crystals grown by evaporation from a chloroform solution. The new polymorph (form B) reported here was obtained unexpectedly during recrystallization from acetonitrile.

In (I) (Fig. 1) all bond lengths and angles fall within the expected ranges. The coumarin moiety is essentially planar with a dihedral angle between the mean planes of the two rings (C(1) to C(6) and C(1) to O(1)) of  $1.4 (1)^\circ$ . Br(1) and O(3) are *cis* to each other with a torsion angle Br(1)—C(11)—C(10)—O(3) of  $-2.0 (2)^\circ$ .

The initial structure (A) was reported in the monoclinic space group  $P2_1/n$  with the following cell parameters:  $a = 21.555 (2)$ ,  $b = 4.229 (2)$ ,  $c = 10.784 (1) \text{ \AA}$ ,  $\beta = 93.89 (1)^\circ$  and  $V = 980.8 \text{ \AA}^3$  (Vasudevan *et al.*, 1991). In view of the fact that the structures of (A) and (B) were determined at 300 K and 120 K respectively, the possibility that the structural differences were the result of a temperature induced phase transition, was examined using differential scanning calorimetry; no phase transition was observed over the temperature range 102 to 323 K.

Although the molecular conformation of (I) in both structures is very similar, there are significant differences between the packing of the two forms. The molecules in alternate layers of (A) are rotated with respect to each other creating an angle of  $74^\circ$  between mean planes calculated through the coumarin moieties (C2—C10/O1) in the asymmetric unit and the symmetry related fragment ( $1/2 - x, 1/2 + y, 1/2 - z$ ) (Fig. 2(i)). While in (B) the molecules of (I) are inclined away from each other resulting in an angle of  $28^\circ$  between the mean planes calculated through the coumarin moieties (C1—C9/O1) in the asu and the adjacent symmetry related fragment ( $1 - x, y - 1/2, 3/2 - z$ ) (Fig. 2(ii)).

In the initial structure report for (A) the authors noted the presence of weak C—H $\cdots$ O interactions which link the molecules to create one dimensional chains through the crystal. The new polymorph also contains a number of short attractive C—H $\cdots$ O contacts, which fulfil the criteria proposed by Taylor *et al.* (1982), and result in the interacting molecules essentially forming two dimensional non-planar sheets.

#### Experimental

3-(Bromoacetyl) coumarin was purchased from Aldrich (97%), and recrystallized by evaporation at room temperature from acetonitrile.

## Refinement

Hydrogen atoms were positioned geometrically (aromatic C—H = 0.95 Å and methylene C—H = 0.99 Å) and refined using a riding model. The hydrogen atom isotropic displacement parameters were fixed to  $U_{\text{iso}}(\text{H}) = 1.2$  times  $U_{\text{eq}}$  of the parent carbon atom.

Differential Scanning Calorimetry (DSC): Data were collected on a Perkin Elmer Pyris 1 DSC with 3 cycles recorded over the temperature range 102 to 323 K at a rate of 10 K/min.

## Figures

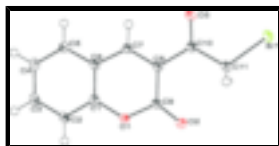


Fig. 1. Molecular structure of (I). Ellipsoids are depicted at the 50% probability level.

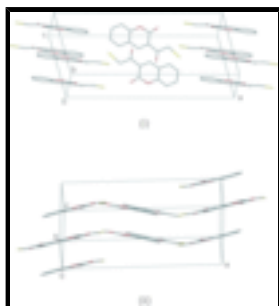


Fig. 2. Comparison of the packing of the two polymorphs (i) form (A), (Vasudevan *et al.*, 1991) (ii) form (B). Hydrogen atoms are omitted for clarity.

## 3-(Bromoacetyl)coumarin

### Crystal data

$\text{C}_{11}\text{H}_7\text{BrO}_3$   
 $M_r = 267.08$

Monoclinic,  $P2_1/c$

Hall symbol: -P 2ybc  
 $a = 5.29320$  (10) Å  
 $b = 18.4568$  (5) Å  
 $c = 9.7473$  (3) Å  
 $\beta = 98.7680$  (10)°  
 $V = 941.14$  (4) Å<sup>3</sup>  
 $Z = 4$

$F_{000} = 528$

$D_x = 1.885$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation  
 $\lambda = 0.71073$  Å

Cell parameters from 6159 reflections

$\theta = 2.4$ – $30.5$ °

$\mu = 4.35$  mm<sup>-1</sup>

$T = 120$  (2) K

Plate, colourless

$0.15 \times 0.14 \times 0.08$  mm

### Data collection

Bruker SMART 6K CCD detector  
diffractometer

2879 independent reflections

Radiation source: fine-focus sealed tube

2547 reflections with  $I > 2\sigma(I)$

Monochromator: graphite  $R_{\text{int}} = 0.033$   
 Detector resolution: 8 pixels  $\text{mm}^{-1}$   $\theta_{\text{max}} = 30.5^\circ$   
 $T = 120(2)$  K  $\theta_{\text{min}} = 2.2^\circ$   
 $\omega$  scans  $h = -7 \rightarrow 7$   
 Absorption correction: multi-scan (SADABS; Sheldrick, 1998)  $k = -26 \rightarrow 26$   
 $T_{\text{min}} = 0.608$ ,  $T_{\text{max}} = 1.000$   $l = -13 \rightarrow 13$   
 14782 measured reflections

### Refinement

Refinement on  $F^2$  Secondary atom site location: difference Fourier map  
 Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites  
 $R[F^2 > 2\sigma(F^2)] = 0.024$  H-atom parameters constrained  
 $wR(F^2) = 0.061$   $w = 1/[\sigma^2(F_o^2) + (0.0323P)^2 + 0.2289P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $S = 1.06$   $(\Delta/\sigma)_{\text{max}} = 0.001$   
 2879 reflections  $\Delta\rho_{\text{max}} = 0.47 \text{ e } \text{\AA}^{-3}$   
 136 parameters  $\Delta\rho_{\text{min}} = -0.38 \text{ e } \text{\AA}^{-3}$   
 Primary atom site location: structure-invariant direct methods Extinction correction: none

### Special details

**Geometry.** All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement.** Refinement of  $F^2$  against ALL reflections. The weighted  $R$ -factor  $wR$  and goodness of fit  $S$  are based on  $F^2$ , conventional  $R$ -factors  $R$  are based on  $F$ , with  $F$  set to zero for negative  $F^2$ . The threshold expression of  $F^2 > 2\sigma(F^2)$  is used only for calculating  $R$ -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement.  $R$ -factors based on  $F^2$  are statistically about twice as large as those based on  $F$ , and  $R$ -factors based on ALL data will be even larger. Crystallized from acetonitrile.

### Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
Br1	1.01135 (3)	0.757563 (8)	0.371259 (15)	0.02027 (6)
O1	0.3366 (2)	0.59926 (6)	0.76010 (11)	0.0182 (2)
O2	0.4139 (2)	0.70306 (6)	0.66504 (12)	0.0212 (2)
O3	0.9830 (2)	0.60442 (6)	0.46858 (12)	0.0231 (2)
C1	0.3813 (3)	0.52704 (8)	0.78488 (14)	0.0154 (3)
C2	0.2347 (3)	0.49236 (8)	0.87179 (15)	0.0196 (3)
H2	0.1061	0.5180	0.9099	0.024*
C3	0.2795 (3)	0.41990 (9)	0.90167 (16)	0.0206 (3)
H3	0.1803	0.3956	0.9608	0.025*
C4	0.4698 (3)	0.38162 (9)	0.84573 (17)	0.0211 (3)

## supplementary materials

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H4	0.5004	0.3320	0.8680	0.025*
C5	0.6117 (3)	0.41663 (8)	0.75828 (16)	0.0188 (3)
H5	0.7394	0.3908	0.7196	0.023*
C6	0.5684 (3)	0.49013 (8)	0.72614 (14)	0.0153 (3)
C7	0.7075 (3)	0.53040 (8)	0.63710 (15)	0.0158 (3)
H7	0.8342	0.5064	0.5946	0.019*
C8	0.6642 (3)	0.60189 (8)	0.61151 (14)	0.0147 (3)
C9	0.4701 (3)	0.64004 (8)	0.67601 (15)	0.0157 (3)
C10	0.8224 (3)	0.63904 (8)	0.51699 (14)	0.0159 (3)
C11	0.7784 (3)	0.71852 (8)	0.48718 (15)	0.0180 (3)
H11A	0.7992	0.7455	0.5760	0.022*
H11B	0.6006	0.7257	0.4405	0.022*

### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
Br1	0.01892 (9)	0.02206 (9)	0.02101 (9)	-0.00114 (5)	0.00687 (6)	0.00582 (5)
O1	0.0192 (5)	0.0161 (5)	0.0220 (5)	0.0033 (4)	0.0116 (4)	0.0032 (4)
O2	0.0230 (5)	0.0160 (5)	0.0269 (6)	0.0034 (4)	0.0115 (4)	0.0012 (4)
O3	0.0254 (6)	0.0190 (5)	0.0289 (6)	0.0028 (4)	0.0172 (5)	0.0006 (4)
C1	0.0153 (6)	0.0151 (6)	0.0165 (6)	-0.0006 (5)	0.0044 (5)	0.0004 (5)
C2	0.0180 (7)	0.0220 (7)	0.0210 (7)	0.0001 (6)	0.0099 (6)	0.0020 (5)
C3	0.0202 (7)	0.0210 (7)	0.0220 (7)	-0.0031 (6)	0.0082 (6)	0.0031 (5)
C4	0.0229 (8)	0.0163 (7)	0.0249 (7)	-0.0022 (6)	0.0065 (6)	0.0019 (5)
C5	0.0194 (7)	0.0155 (7)	0.0224 (7)	-0.0004 (5)	0.0066 (6)	-0.0012 (5)
C6	0.0144 (6)	0.0157 (6)	0.0165 (6)	-0.0009 (5)	0.0051 (5)	-0.0004 (5)
C7	0.0148 (6)	0.0160 (6)	0.0178 (6)	-0.0009 (5)	0.0066 (5)	-0.0014 (5)
C8	0.0134 (6)	0.0160 (6)	0.0161 (6)	-0.0004 (5)	0.0064 (5)	-0.0006 (5)
C9	0.0145 (6)	0.0171 (7)	0.0165 (6)	0.0000 (5)	0.0056 (5)	-0.0005 (5)
C10	0.0168 (6)	0.0154 (6)	0.0163 (6)	-0.0013 (5)	0.0051 (5)	-0.0008 (5)
C11	0.0192 (7)	0.0168 (6)	0.0197 (7)	-0.0001 (5)	0.0089 (6)	0.0020 (5)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

Br1—C11	1.9343 (14)	C4—H4	0.9500
O1—C1	1.3688 (17)	C5—C6	1.403 (2)
O1—C9	1.3836 (17)	C5—H5	0.9500
O2—C9	1.2014 (18)	C6—C7	1.4293 (19)
O3—C10	1.2146 (17)	C7—C8	1.3559 (19)
C1—C2	1.3895 (19)	C7—H7	0.9500
C1—C6	1.3949 (19)	C8—C9	1.4638 (19)
C2—C3	1.382 (2)	C8—C10	1.5020 (19)
C2—H2	0.9500	C10—C11	1.507 (2)
C3—C4	1.407 (2)	C11—H11A	0.9900
C3—H3	0.9500	C11—H11B	0.9900
C4—C5	1.380 (2)		
C1—O1—C9	122.97 (11)	C8—C7—C6	121.96 (13)
O1—C1—C2	117.30 (13)	C8—C7—H7	119.0

O1—C1—C6	121.17 (12)	C6—C7—H7	119.0
C2—C1—C6	121.53 (13)	C7—C8—C9	119.96 (12)
C3—C2—C1	118.72 (13)	C7—C8—C10	117.54 (12)
C3—C2—H2	120.6	C9—C8—C10	122.50 (13)
C1—C2—H2	120.6	O2—C9—O1	115.94 (12)
C2—C3—C4	120.96 (14)	O2—C9—C8	127.45 (13)
C2—C3—H3	119.5	O1—C9—C8	116.61 (12)
C4—C3—H3	119.5	O3—C10—C8	119.14 (13)
C5—C4—C3	119.60 (14)	O3—C10—C11	122.28 (13)
C5—C4—H4	120.2	C8—C10—C11	118.58 (12)
C3—C4—H4	120.2	C10—C11—Br1	112.44 (10)
C4—C5—C6	120.33 (14)	C10—C11—H11A	109.1
C4—C5—H5	119.8	Br1—C11—H11A	109.1
C6—C5—H5	119.8	C10—C11—H11B	109.1
C1—C6—C5	118.85 (13)	Br1—C11—H11B	109.1
C1—C6—C7	117.32 (13)	H11A—C11—H11B	107.8
C5—C6—C7	123.82 (13)		
Br1—C11—C10—O3	-2.04 (19)	Br1—C11—C10—C8	177.10 (10)

*Hydrogen-bond geometry* ( $\text{\AA}$ ,  $^\circ$ )

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
C4—H4 $\cdots$ O2 <sup>i</sup>	0.95	2.45	3.3572 (19)	159
C5—H5 $\cdots$ O3 <sup>ii</sup>	0.95	2.52	3.3302 (18)	143
C7—H7 $\cdots$ O3 <sup>ii</sup>	0.95	2.38	3.2329 (17)	149

Symmetry codes: (i)  $-x+1, y-1/2, -z+3/2$ ; (ii)  $-x+2, -y+1, -z+1$ .

Fig. 1

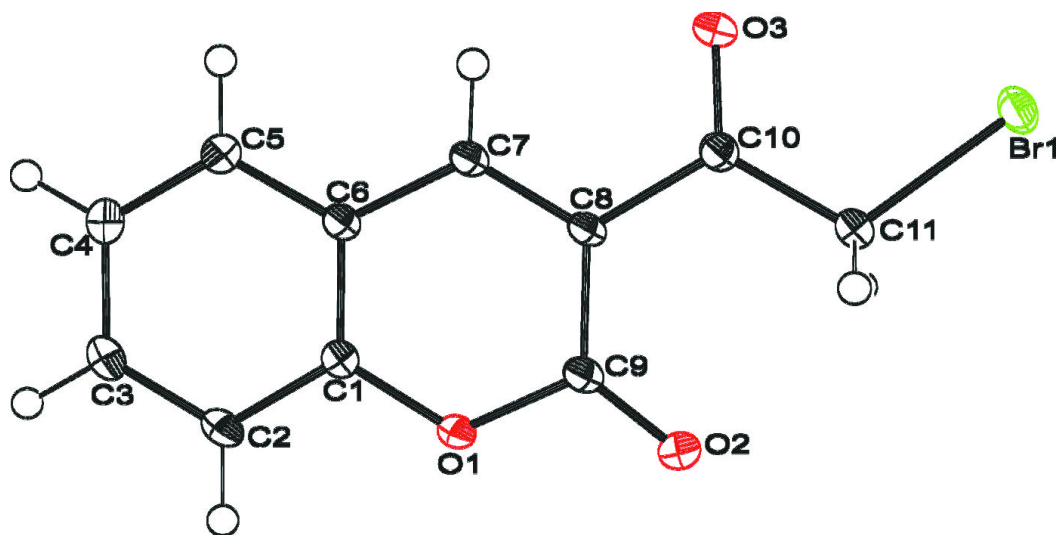
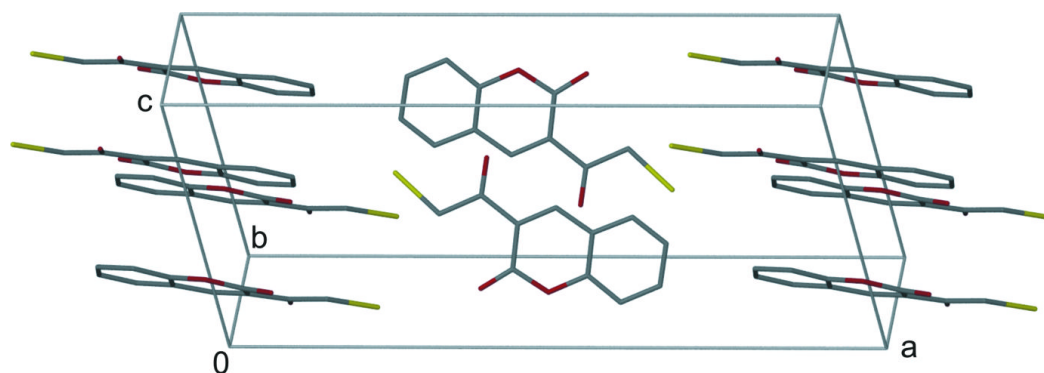
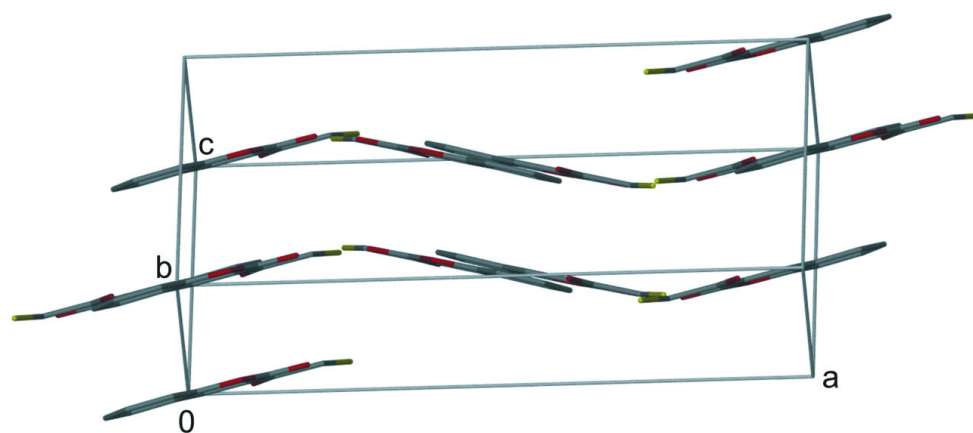




Fig. 2



(i)



(ii)