

Coumarin-3-carboxylic acid: a second $P2_1/c$ modification

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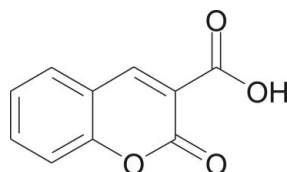
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 Key indicators: single-crystal X-ray study; $T = 120$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å;
 R factor = 0.041; wR factor = 0.111; data-to-parameter ratio = 12.6.

A second polymorph of coumarin-3-carboxylic acid (2-oxo-2*H*-1-benzopyran-3-carboxylic acid), $\text{C}_{10}\text{H}_6\text{O}_4$, is reported in the $P2_1/c$ space group. The structure shows intermolecular hydrogen bonding between the carboxyl groups on pairs of molecules related by an inversion centre, as well as a number of $\text{C}-\text{H}\cdots\text{O}$ contacts.

Related literature

For the initial structure described in $P2_1/n$, see: Dobson & Gerkin (1996). For additional related literature, see: Testa *et al.* (2000); Wolff *et al.* (2003); Taylor & Kennard (1982).



Experimental

Crystal data

$\text{C}_{10}\text{H}_6\text{O}_4$
 $M_r = 190.15$
 Monoclinic, $P2_1/c$
 $a = 9.8733$ (7) Å
 $b = 9.4382$ (7) Å

$c = 9.7356$ (6) Å
 $\beta = 118.785$ (2)°
 $V = 795.12$ (10) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

$\mu = 0.13$ mm⁻¹
 $T = 120$ (2) K

0.17 × 0.16 × 0.04 mm

Data collection

Bruker SMART 6K CCD detector
 diffractometer
 Absorption correction: none
 5128 measured reflections

1604 independent reflections
 1048 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.039$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$
 $wR(F^2) = 0.111$
 $S = 0.99$
 1604 reflections

127 parameters
 H-atom parameters constrained
 $\Delta\rho_{\text{max}} = 0.19$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.21$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{O3}-\text{H3A}\cdots\text{O4}^{\text{i}}$	0.84	1.80	2.6258 (19)	167
$\text{O4}-\text{H4A}\cdots\text{O3}^{\text{ii}}$	0.84	1.80	2.6258 (18)	167
$\text{C2}-\text{H2}\cdots\text{O2}^{\text{ii}}$	0.95	2.57	3.393 (2)	146
$\text{C4}-\text{H4}\cdots\text{O2}^{\text{iii}}$	0.95	2.57	3.384 (3)	144
$\text{C4}-\text{H4}\cdots\text{O3}^{\text{iii}}$	0.95	2.48	3.275 (3)	141
$\text{C5}-\text{H5}\cdots\text{O4}^{\text{iv}}$	0.95	2.53	3.419 (2)	156

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

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINTE* (Bruker, 1998); data reduction: *SAINTE*; 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: NG2309).

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supplementary materials

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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 coumarin-3-carboxylic acid (I) (form A) has previously been determined at 296 K by Dobson & Gerkin (1996), using crystals grown by evaporation from an ether solution. The new polymorph (form B) reported here was obtained unexpectedly during recrystallization of (I).

In form (B) (Figure 1) all bond lengths and angles fall within the expected ranges. The coumarin moiety (C1—C9/O1) is essentially planar with an r.m.s deviation for the fitted atoms of 0.008 (2) Å, while the carboxyl group is twisted just out of this plane with a torsion angle of 1.8 (3)° (O4, C10, C8, C7).

Hydrogen bonding was observed in both forms; in form (A) an intramolecular hydrogen bond (O2···H3A) was identified with an O2···O3 distance of 2.589 (2) Å and an O2···H3A—O3 angle of 153°. The position of the carboxyl group hydrogen atom (H3A/H4A) in (B) differs from that found in form (A) and as a result the hydrogen bonding is intermolecular, involving pairs of coumarin-3-carboxylic acid molecules related by an inversion centre; the O3···O4₁ (₁ = $x + 1, y, z$) separation distance is 2.623 (2) Å with an O3—H3A···O4₁ angle of 167° (Fig. 2).

Although the conformation of coumarin-3-carboxylic acid in both structures is very similar, the packing is significantly different. In (A), alternate molecules are rotated with respect to each other (Fig. 3(i)) creating an angle of 60.31 (4)° between the mean planes calculated through the coumarin moiety of symmetry related fragments. Unlike the situation in (A), all of the molecules in (B) are aligned, forming parallel sheets through the structure in which the angle between the mean planes calculated through the coumarin moieties in symmetry related fragment ($x, 1/2 - y, z - 1/2$) in alternate sheets is 8.09 (4)° (Fig. 3(ii)).

It was noted in the initial structure report on (I) (Dobson & Gerkin, 1996) that there were a number of short attractive C—H···O interactions in form (A), and the authors postulated that these interactions accounted for the higher than expected density of the structure. Form (B) has a similar calculated density to that of (A), along with a number of short C—H···O contacts that satisfy the criteria postulated by Taylor & Kennard (1982).

Experimental

Coumarin-3-carboxylic acid was purchased from Aldrich (99%) and recrystallized by evaporation at room temperature from a solution of acetone and water.

Refinement

Hydrogen atoms were positioned geometrically in (aromatic C—H = 0.95 Å and O—H = 0.84 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_{eq} of the parent atom. The

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hydrogen atom of the CO₂H group was modelled at 50% occupancy on both O3 and O4, as peaks were identified in the fourier map at both positions and the associated C—O bond lengths were essentially equivalent at (1.265 (2) Å (C10—O3) and 1.271 (2) Å (C10—O4)).

Figures

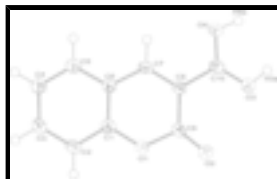


Fig. 1. Molecular structure of form (B). Ellipsoids are depicted at the 50% probability level.

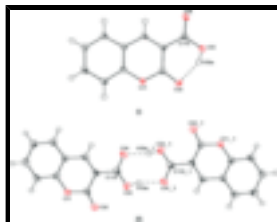


Fig. 2. Illustration of hydrogen bonding (dashed lines) in the two forms with ellipsoids depicted at the 50% probability level (i) form (A) (Dobson & Gerkin, 1996), (ii) form (B) [$_1 = -x + 1, -y, -z$]. Only one position of the CO₂H hydrogen atom in form (B) is shown for clarity.

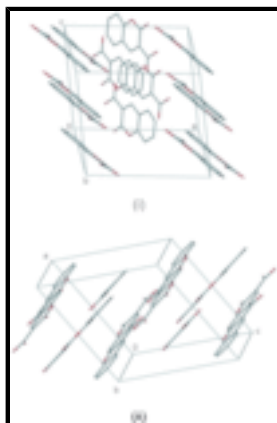


Fig. 3. Comparison of the packing in (i) form (A) (Dobson & Gerkin, 1996), (ii) form (B). Hydrogen atoms are omitted for clarity.

2-oxo-2H-1-benzopyran-3-carboxylic acid

Crystal data

C₁₀H₆O₄

$M_r = 190.15$

Monoclinic, $P2_1/c$

Hall symbol: $-P\ 2_1/c$

$a = 9.8733$ (7) Å

$b = 9.4382$ (7) Å

$c = 9.7356$ (6) Å

$\beta = 118.785$ (2)°

$V = 795.12$ (10) Å³

$Z = 4$

$F_{000} = 392$

$D_x = 1.588$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 1039 reflections

$\theta = 2.4$ – 26.3 °

$\mu = 0.13$ mm⁻¹

$T = 120$ (2) K

Plate, colourless

$0.17 \times 0.16 \times 0.04$ mm

Data collection

Bruker SMART 6K CCD detector diffractometer	1604 independent reflections
Radiation source: fine-focus sealed tube	1048 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.039$
Detector resolution: 8 pixels mm^{-1}	$\theta_{\text{max}} = 26.3^\circ$
$T = 120(2)$ K	$\theta_{\text{min}} = 4.2^\circ$
ω scans	$h = -12 \rightarrow 12$
Absorption correction: none	$k = -11 \rightarrow 11$
5128 measured reflections	$l = -12 \rightarrow 11$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.041$	H-atom parameters constrained
$wR(F^2) = 0.111$	$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2]$
$S = 0.99$	where $P = (F_o^2 + 2F_c^2)/3$
1604 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
127 parameters	$\Delta\rho_{\text{max}} = 0.19 \text{ e } \text{\AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.21 \text{ e } \text{\AA}^{-3}$
	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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
O1	0.84754 (15)	0.31858 (13)	0.55156 (15)	0.0262 (4)	
O2	0.80372 (17)	0.09130 (14)	0.50285 (17)	0.0373 (4)	
O3	0.61410 (15)	0.00992 (14)	0.20082 (17)	0.0310 (4)	
H3A	0.5633	-0.0405	0.1211	0.037*	0.50
O4	0.52464 (15)	0.18083 (14)	0.01970 (16)	0.0299 (4)	
H4A	0.4841	0.1108	-0.0393	0.036*	0.50

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C1	0.8303 (2)	0.45875 (19)	0.5069 (2)	0.0240 (4)
C2	0.9047 (2)	0.5584 (2)	0.6240 (2)	0.0264 (5)
H2	0.9648	0.5306	0.7304	0.032*
C3	0.8890 (2)	0.6988 (2)	0.5815 (2)	0.0286 (5)
H3	0.9388	0.7687	0.6604	0.034*
C4	0.8017 (2)	0.7415 (2)	0.4254 (3)	0.0298 (5)
H4	0.7932	0.8391	0.3986	0.036*
C5	0.7282 (2)	0.6407 (2)	0.3108 (3)	0.0280 (5)
H5	0.6687	0.6688	0.2044	0.034*
C6	0.7408 (2)	0.4964 (2)	0.3505 (2)	0.0226 (4)
C7	0.6668 (2)	0.38576 (19)	0.2395 (2)	0.0237 (5)
H7	0.6047	0.4096	0.1321	0.028*
C8	0.6823 (2)	0.2480 (2)	0.2821 (2)	0.0225 (5)
C9	0.7781 (2)	0.2081 (2)	0.4468 (2)	0.0253 (5)
C10	0.6020 (2)	0.1388 (2)	0.1607 (2)	0.0242 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0305 (7)	0.0232 (8)	0.0180 (7)	-0.0008 (6)	0.0062 (6)	-0.0007 (6)
O2	0.0499 (10)	0.0247 (8)	0.0248 (8)	0.0020 (7)	0.0081 (7)	0.0021 (7)
O3	0.0339 (8)	0.0240 (7)	0.0257 (8)	-0.0016 (6)	0.0068 (6)	-0.0017 (6)
O4	0.0314 (8)	0.0306 (8)	0.0183 (8)	-0.0027 (6)	0.0046 (6)	-0.0014 (6)
C1	0.0239 (10)	0.0230 (10)	0.0238 (11)	0.0005 (8)	0.0103 (8)	0.0006 (9)
C2	0.0252 (10)	0.0307 (11)	0.0188 (11)	-0.0007 (8)	0.0070 (8)	-0.0019 (9)
C3	0.0285 (11)	0.0284 (11)	0.0265 (12)	-0.0040 (9)	0.0113 (9)	-0.0067 (9)
C4	0.0304 (11)	0.0258 (11)	0.0298 (12)	-0.0006 (8)	0.0119 (9)	-0.0005 (9)
C5	0.0278 (11)	0.0279 (11)	0.0237 (11)	-0.0003 (8)	0.0086 (9)	0.0003 (9)
C6	0.0222 (10)	0.0235 (10)	0.0188 (10)	-0.0002 (8)	0.0072 (8)	-0.0007 (8)
C7	0.0228 (10)	0.0282 (11)	0.0166 (10)	0.0018 (8)	0.0065 (8)	0.0007 (8)
C8	0.0236 (10)	0.0244 (10)	0.0183 (11)	-0.0009 (7)	0.0091 (8)	-0.0018 (8)
C9	0.0273 (11)	0.0243 (11)	0.0205 (11)	-0.0010 (8)	0.0083 (8)	-0.0036 (9)
C10	0.0211 (10)	0.0287 (11)	0.0217 (11)	-0.0001 (8)	0.0094 (8)	-0.0005 (9)

Geometric parameters (\AA , $^\circ$)

O1—C1	1.377 (2)	C3—C4	1.398 (3)
O1—C9	1.387 (2)	C3—H3	0.9500
O2—C9	1.202 (2)	C4—C5	1.377 (3)
O3—C10	1.265 (2)	C4—H4	0.9500
O3—H3A	0.8400	C5—C6	1.404 (3)
O4—C10	1.271 (2)	C5—H5	0.9500
O4—H4A	0.8400	C6—C7	1.426 (3)
C1—C2	1.384 (3)	C7—C8	1.351 (3)
C1—C6	1.390 (3)	C7—H7	0.9500
C2—C3	1.375 (3)	C8—C9	1.465 (3)
C2—H2	0.9500	C8—C10	1.479 (3)
C1—O1—C9	123.23 (15)	C6—C5—H5	119.8

C10—O3—H3A	109.5	C1—C6—C5	118.37 (18)
C10—O4—H4A	109.5	C1—C6—C7	117.81 (17)
O1—C1—C2	117.19 (17)	C5—C6—C7	123.82 (18)
O1—C1—C6	120.57 (16)	C8—C7—C6	122.10 (18)
C2—C1—C6	122.24 (18)	C8—C7—H7	118.9
C3—C2—C1	117.99 (19)	C6—C7—H7	118.9
C3—C2—H2	121.0	C7—C8—C9	120.09 (18)
C1—C2—H2	121.0	C7—C8—C10	119.17 (18)
C2—C3—C4	121.75 (19)	C9—C8—C10	120.74 (17)
C2—C3—H3	119.1	O2—C9—O1	115.75 (18)
C4—C3—H3	119.1	O2—C9—C8	128.05 (18)
C5—C4—C3	119.32 (19)	O1—C9—C8	116.20 (17)
C5—C4—H4	120.3	O3—C10—O4	123.52 (18)
C3—C4—H4	120.3	O3—C10—C8	119.23 (18)
C4—C5—C6	120.3 (2)	O4—C10—C8	117.25 (17)
C4—C5—H5	119.8		

Hydrogen-bond geometry (Å, °)

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O3—H3A...O4 ⁱ	0.84	1.80	2.6258 (19)	167
O4—H4A...O3 ⁱ	0.84	1.80	2.6258 (18)	167
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C4—H4...O3 ⁱⁱⁱ	0.95	2.48	3.275 (3)	141
C5—H5...O4 ^{iv}	0.95	2.53	3.419 (2)	156

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Fig. 1

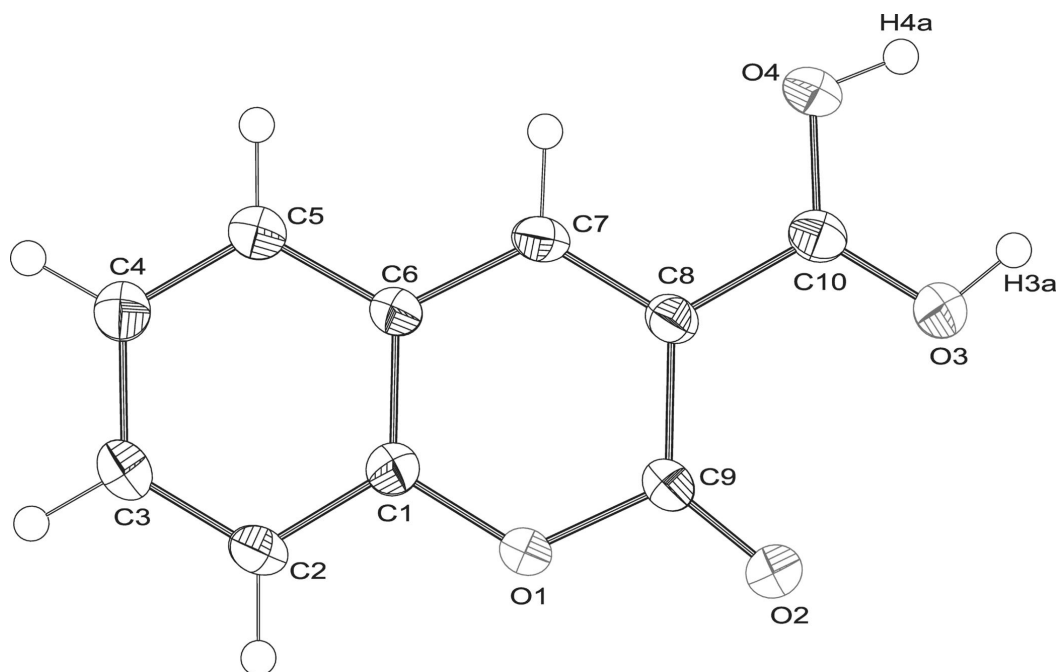


Fig. 2

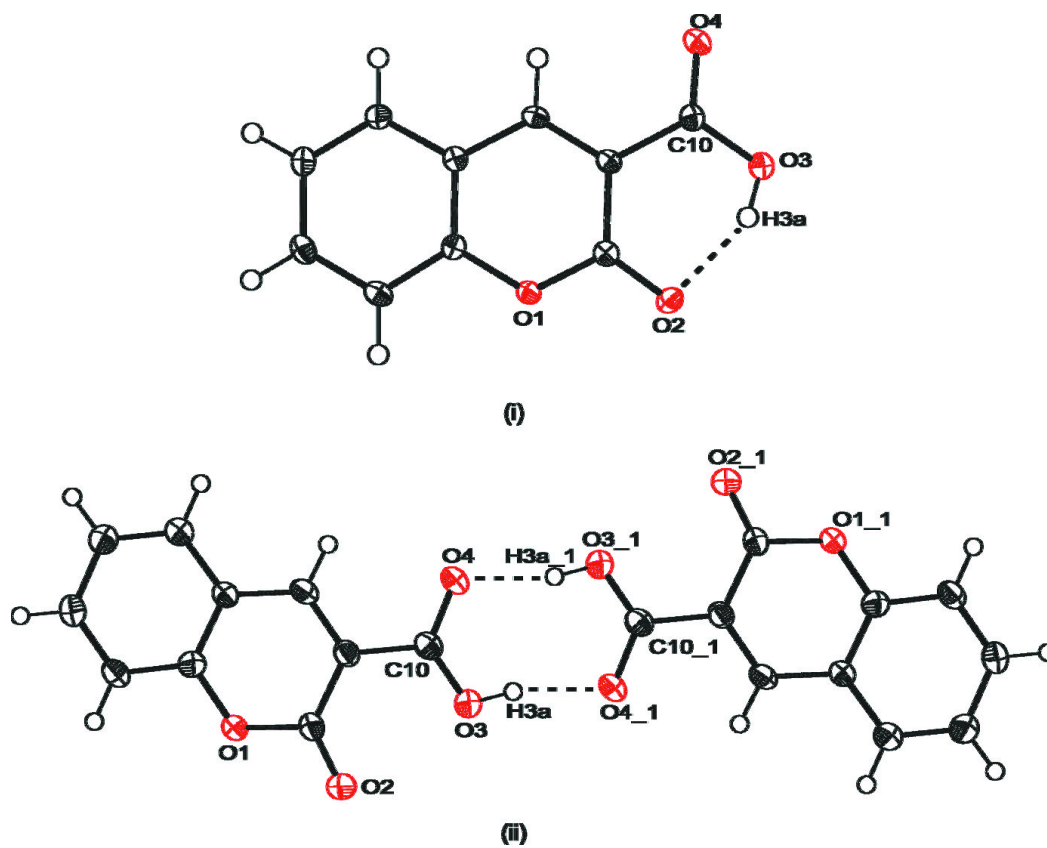
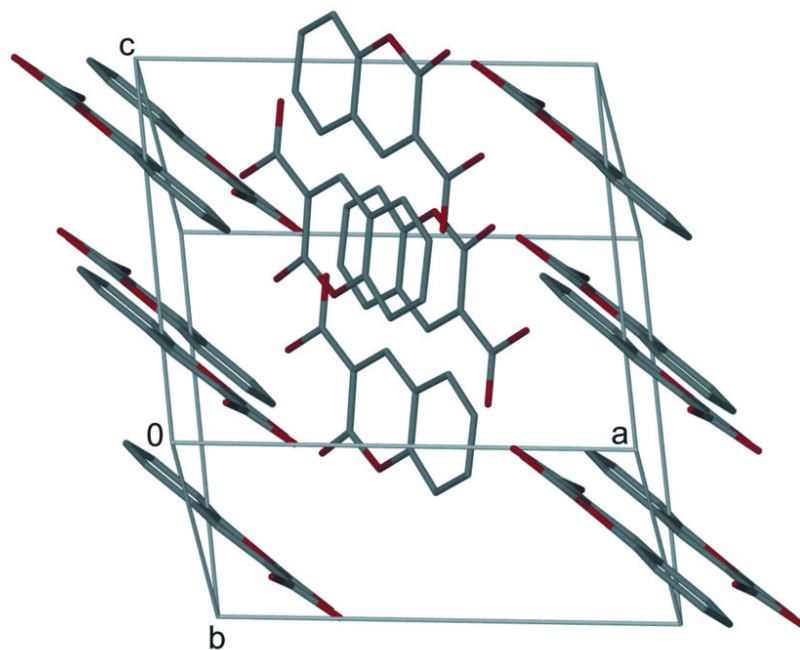
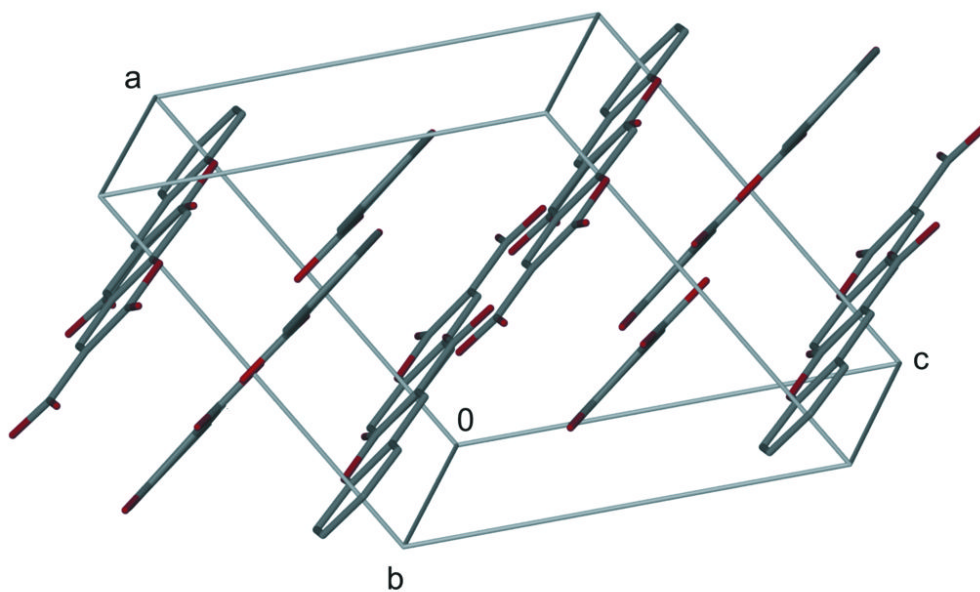


Fig. 3



(i)



(ii)