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A new polymorph of 2,6-dimethoxybenzoic acid

Gustavo Portalone

Chemistry Department, "Sapienza" University of Rome, P.le A. Moro, 5, I-00185 Rome, Italy
Correspondence e-mail: g.portalone@caspur.it

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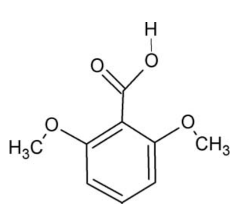
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.004 Å; R factor = 0.062; wR factor = 0.147; data-to-parameter ratio = 12.4.

A new crystalline form of 2,6-dimethoxybenzoic acid, $C_9H_{10}O_4$, crystallizing in a tetragonal unit cell has been identified during screening for co-crystals. The asymmetric unit comprises a non-planar independent molecule with a synplanar conformation of the carboxy group. The sterically bulky *o*-methoxy substituents force the carboxy group to be twisted away from the plane of the benzene ring by 65.72 (15)°. The carboxy group is disordered over two sites about the C—C bond [as indicated by the almost equal C—O distances of 1.254 (3) and 1.250 (3) Å], the occupancies of the disordered carboxym H atoms being 0.53 (5) and 0.47 (5). In the known orthorhombic form reported by Swaminathan *et al.* [*Acta Cryst.* (1976), B**32**, 1897–1900], due to the antiplanar conformation adopted by the OH group, the molecular components are associated in the crystal in chains stabilized by linear O—H⋯O hydrogen bonds. However, in the new tetragonal polymorph, molecules form dimeric units *via* pairs of O—H⋯O hydrogen bonds between the carboxy groups.

Related literature

For the orthorhombic polymorph of 2,6-dimethoxybenzoic acid, see: Swaminathan *et al.* (1976); Bryan & White (1982); Portalone (2009). For molecular packing modes of carboxylic acids, see: Leiserowitz (1976); Kanters *et al.* (1991); Moorthy *et al.* (2002). For analysis of benzene ring deformations induced by substitution, see: Schultz *et al.* (1993); Portalone *et al.* (1998); For computation of ring patterns formed by hydrogen bonds in crystal structures, see: Etter *et al.* (1990); Bernstein *et al.* (1995); Motherwell *et al.* (1999).



Experimental

Crystal data

$C_9H_{10}O_4$
M_r = 182.17
Tetragonal, $P4_12_12$
a = 8.1423 (3) Å
c = 27.6814 (18) Å
V = 1835.20 (15) Å^3
Z = 8
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 298 K
0.30 × 0.25 × 0.21 mm

Data collection

Oxford Diffraction Xcalibur S CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006).
T_{min} = 0.878, T_{max} = 0.999
11616 measured reflections
1653 independent reflections
1332 reflections with $I > 2\sigma(I)$
R_{int} = 0.042

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.147
S = 1.19
1653 reflections
133 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1⋯O1^{i}	0.77 (4)	1.87 (4)	2.632 (4)	168 (5)
O2—H2⋯O2^{i}	0.79 (5)	1.83 (5)	2.618 (4)	173 (5)

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU5390).

References

Altomare, A., Burla, M. C., Camalli, M., Cascarano, G. L., Giacovazzo, C., Guagliardi, A., Moliterni, A. G. G., Polidori, G. & Spagna, R. (1999). *J. Appl. Cryst.* **32**, 115–119.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Bryan, R. F. & White, D. H. (1982). *Acta Cryst.* B**38**, 1014–1016.
Etter, M. C., MacDonald, J. C. & Bernstein, J. (1990). *Acta Cryst.* B**46**, 256–262.
Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
Kanters, J. A., Kroon, J., Hooft, R., Schouten, A., van Scijndel, J. A. M. & Brandsen, J. (1991). *Croat. Chem. Acta*, **64**, 353–370.
Leiserowitz, L. (1976). *Acta Cryst.* B**32**, 775–802.
Moorthy, J. N., Natarajan, R., Mal, P. & Venugopalan, P. (2002). *J. Am. Chem. Soc.* **124**, 6530–6531.
Motherwell, W. D. S., Shields, G. P. & Allen, F. H. (1999). *Acta Cryst.* B**55**, 1044–1056.
Oxford Diffraction (2006). *CrysAlis CCD* and *CrysAlis RED*. Oxford Diffraction Ltd, Abingdon, England.
Portalone, G. (2009). *Acta Cryst.* E**65**, o327–o328.

Portalone, G., Ramondo, F., Domenicano, A. & Hargittai, I. (1998). *J. Organomet. Chem.* **560**, 183–190.
Schultz, Gy., Nagy, T., Portalone, G., Ramondo, F., Hargittai, I. & Domenicano, A. (1993). *Struct. Chem.* **4**, 183–190.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Swaminathan, S., Vimala, T. M. & Lotter, H. (1976). *Acta Cryst.* B**32**, 1897–1900.

supporting information

Acta Cryst. (2011). E**67**, o3394–o3395 [https://doi.org/10.1107/S1600536811049075]

A new polymorph of 2,6-dimethoxybenzoic acid

Gustavo Portalone

S1. Comment

In this paper it is reported the crystal structure of a new polymorph, (I), of 2,6-dimethoxybenzoic acid, produced unexpectedly during an attempt to synthesize cocrystals of boronic acid with of 2,6-dimethoxybenzoic acid. The known form, (II) (Fig. 3), of of 2,6-dimethoxybenzoic acid is orthorhombic in the space group $P2_12_12_1$ and crystallizes with one molecule in the asymmetric unit (Swaminathan *et al.*, 1976; Bryan & White, 1982; Portalone, 2009). In (II), due to the antiplanar conformation adopted by the OH group, the molecular components are associated in the crystal in chains stabilized by linear O—H···O hydrogen bonds.

The title new polymorph (I) is tetragonal in the space group $P4_12_12$. The asymmetric unit of (I) comprises a non-planar independent molecule, as the *o*-methoxy substituents force the carboxy group to be twisted away from the plane of the phenyl ring by 65.72 (15)° (Fig. 1). The carboxy group, which adopts a synplanar conformation, is almost completely disordered, as indicated by the equal C—O distances, 1.254 (3) and 1.250 (3) Å, the C—C—O angles, 118.9 (2) and 117.8 (2)°, and by the presence of disordered H atoms with occupancy factors of 0.53 (5) and 0.47 (5) in the O···O intermolecular hydrogen bond. The pattern of bond lengths and bond angles of the phenyl ring is consistent with that reported in the structure determination of (II), and a comparison of the present results with those obtained for similar benzene derivatives in the gas phase (Schultz *et al.*, 1993; Portalone *et al.*, 1998) shows no appreciable effects of the crystal environment on the ring deformation induced by substituents. Analysis of the crystal packing of (I), (Fig. 2), shows that the molecular components form the conventional dimeric units observed in benzoic acids (Leiserowitz, 1976; Kanters *et al.*, 1991; Moorthy *et al.*, 2002). Indeed, the structure is stabilized by usual intermolecular $C^2_2(8)$ O—H···O interactions (Etter *et al.*, 1990; Bernstein *et al.*, 1995; Motherwell *et al.*, 1999) (Table 1) which link the molecules into dimers through the disordered carboxy moieties [symmetry code: (i) $-y + 1$, $-x + 1$, $-z + 3/2$].

S2. Experimental

Polymorph (I) was formed during cocrystallization in a 1:1 molar ratio of 2,6-dimethoxybenzoic acid (1 mmol, Sigma Aldrich at 99% purity) and phenylboronic acid (1 mmol, Sigma Aldrich at 97% purity). The two components were dissolved in water (10 ml) and gently heated under reflux for 3 h. After cooling the solution to an ambient temperature, only one crystal suitable for single-crystal X-ray diffraction was grown by slow evaporation of the solvent after two weeks. Unfortunately, any attempts to produce more crystals of polymorph (I) by repeating the crystallization conditions were unsuccessful. Crystallization of 2,6-dimethoxybenzoic acid carried out under a wide range of different sets of conditions (different solvents, different molar ratio, different cosolute molecules) led systematically to the orthorhombic polymorph.

S3. Refinement

All H atoms were identified in difference Fourier maps, but for refinement all C-bound H atoms were placed in calculated positions, with C—H = 0.97 Å (phenyl) and 0.97–0.98 Å (methyl), and refined as riding on their carrier atoms. The U_{iso} values were kept equal to $1.2U_{eq}$(C, phenyl). and to $1.5U_{eq}$(C, methyl). The remaining two half H atoms of the carboxy group were freely refined and their occupancy factors constrained to sum to unity. In the absence of significant anomalous scattering in this light-atom study, Friedel pairs were merged.

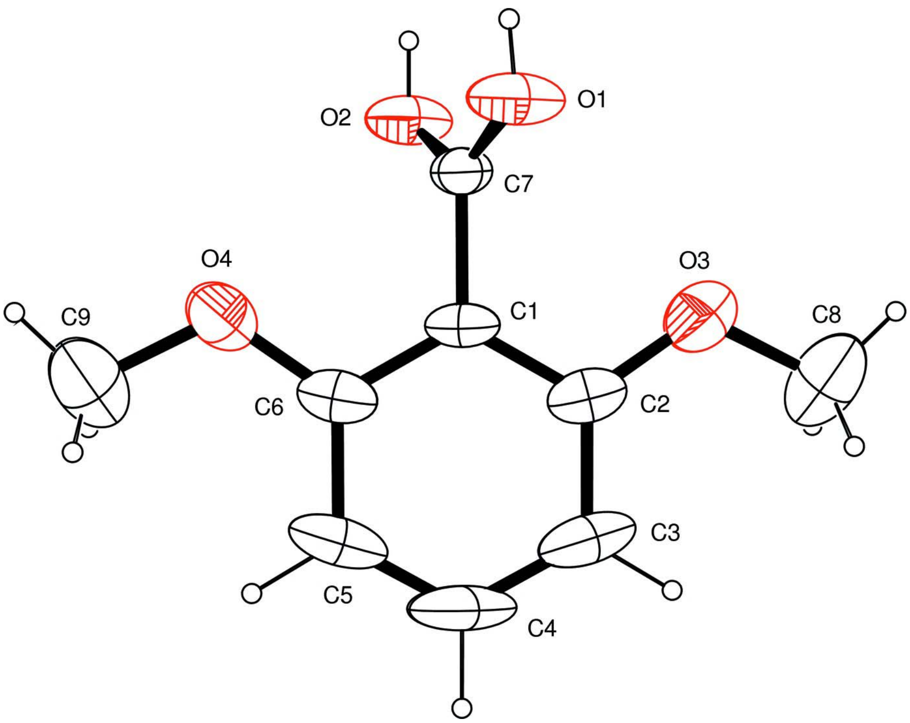


Figure 1

The molecular structure of (I), showing the atom-labelling scheme. Displacements ellipsoids are at the 50% probability level.

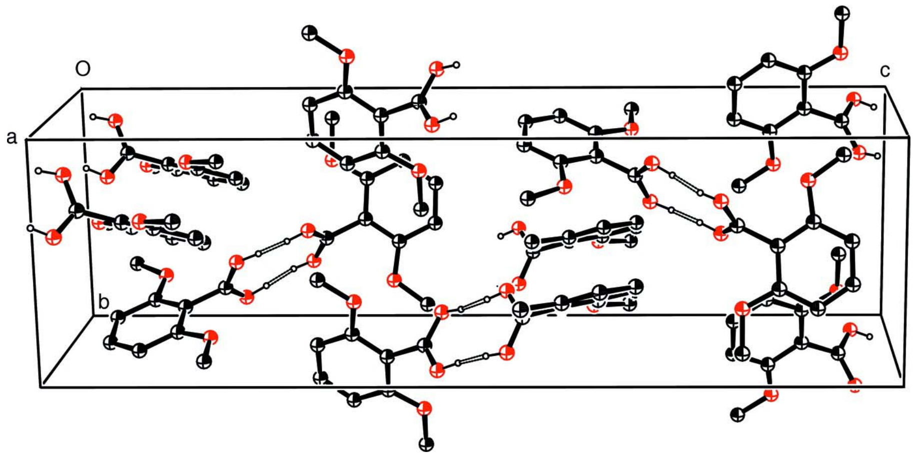


Figure 2

Crystal packing diagram for (I) viewed approximately down a. All atoms are shown as small spheres of arbitrary radii. For the sake of clarity, H atoms not involved in hydrogen bonding have been omitted. Hydrogen bonding is indicated by dashed lines.

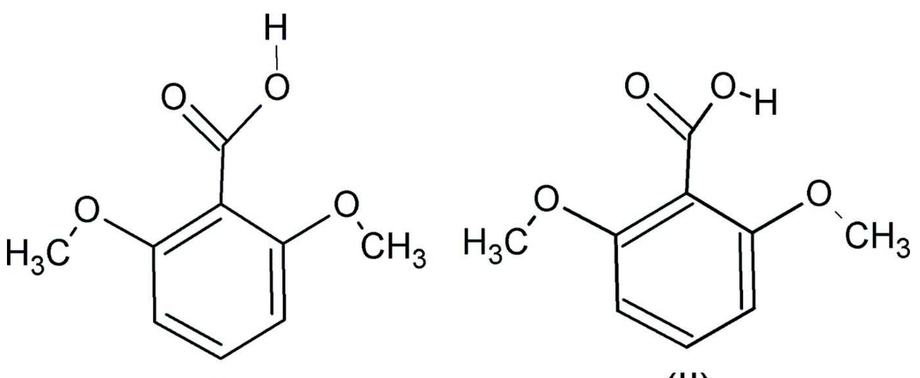


Figure 3

A scheme showing antiplanar and synplanar conformations of the carboxy group.

2,6-dimethoxybenzoic acid

Crystal data

$C_9H_{10}O_4$
M_r = 182.17
Tetragonal, $P4_12_12$
Hall symbol: P 4abw 2nw
a = 8.1423 (3) Å
c = 27.6814 (18) Å
V = 1835.20 (15) Å^3
Z = 8
F(000) = 768
D_x = 1.319 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71069 Å
Cell parameters from 4278 reflections
θ = 2.9–32.3°
μ = 0.11 mm^{-1}
T = 298 K
Tablets, colourless
0.30 × 0.25 × 0.21 mm

Data collection

Oxford Diffraction Xcalibur S CCD diffractometer
Radiation source: Enhance (Mo) X-ray source
Graphite monochromator
Detector resolution: 16.0696 pixels mm^{-1}
ω and φ scans
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2006).
T_{min} = 0.878, T_{max} = 0.999
11616 measured reflections
1653 independent reflections
1332 reflections with $I > 2\sigma(I)$
R_{int} = 0.042
θ_{max} = 30.0°, θ_{min} = 2.9°
$h = -11 \rightarrow 10$
$k = -8 \rightarrow 11$
$l = -38 \rightarrow 38$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.062$
$wR(F^2) = 0.147$
$S = 1.19$
1653 reflections
133 parameters
0 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0659P)^2 + 0.2634P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.17 e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.017 (3)

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.7090 (3)	0.1661 (3)	0.71019 (8)	0.0558 (6)	
H1	0.733 (5)	0.209 (5)	0.7340 (15)	0.023 (14)*	0.53 (5)
O2	0.5271 (3)	0.3665 (2)	0.70822 (7)	0.0508 (6)	
H2	0.566 (7)	0.393 (7)	0.7333 (17)	0.031 (18)*	0.47 (5)
O3	0.7742 (3)	0.2435 (3)	0.60828 (6)	0.0652 (7)	
O4	0.2838 (3)	0.1176 (3)	0.68526 (7)	0.0618 (6)	
C1	0.5250 (3)	0.1775 (3)	0.64409 (7)	0.0362 (6)	
C2	0.6221 (4)	0.1801 (3)	0.60276 (8)	0.0456 (7)	
C3	0.5579 (5)	0.1225 (4)	0.55922 (9)	0.0644 (9)	
H3	0.6230	0.1245	0.5299	0.077*	
C4	0.3993 (6)	0.0628 (5)	0.55889 (11)	0.0749 (11)	
H4	0.3547	0.0220	0.5287	0.090*	
C5	0.3025 (5)	0.0583 (4)	0.59895 (12)	0.0653 (9)	
H5	0.1917	0.0147	0.5972	0.078*	

C6	0.3652 (4)	0.1176 (3)	0.64256 (9)	0.0447 (7)
C7	0.5920 (3)	0.2410 (3)	0.69057 (7)	0.0329 (5)
C8	0.8729 (5)	0.2678 (4)	0.56701 (12)	0.0722 (11)
H8A	0.889 (3)	0.164 (2)	0.5507 (7)	0.108*
H8B	0.978 (3)	0.312 (3)	0.5767 (3)	0.108*
H8C	0.819 (2)	0.344 (3)	0.5453 (7)	0.108*
C9	0.1147 (5)	0.0710 (6)	0.68556 (15)	0.0917 (14)
H9A	0.0518 (15)	0.147 (3)	0.6655 (11)	0.138*
H9B	0.0730 (16)	0.074 (4)	0.7186 (7)	0.138*
H9C	0.1036 (7)	−0.040 (3)	0.6728 (11)	0.138*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0679 (14)	0.0562 (13)	0.0432 (9)	0.0162 (11)	−0.0267 (10)	−0.0181 (9)
O2	0.0616 (13)	0.0497 (12)	0.0412 (9)	0.0118 (10)	−0.0217 (10)	−0.0159 (9)
O3	0.0665 (15)	0.0862 (17)	0.0428 (10)	−0.0139 (13)	0.0104 (10)	−0.0077 (11)
O4	0.0504 (13)	0.0836 (16)	0.0513 (10)	−0.0242 (12)	−0.0085 (10)	0.0041 (11)
C1	0.0506 (15)	0.0330 (12)	0.0251 (9)	−0.0008 (11)	−0.0133 (10)	−0.0031 (9)
C2	0.0618 (18)	0.0448 (15)	0.0302 (10)	0.0038 (14)	−0.0069 (12)	−0.0045 (11)
C3	0.094 (3)	0.069 (2)	0.0306 (12)	0.014 (2)	−0.0103 (15)	−0.0175 (14)
C4	0.095 (3)	0.083 (2)	0.0461 (16)	0.007 (2)	−0.0347 (18)	−0.0298 (17)
C5	0.068 (2)	0.064 (2)	0.0636 (17)	−0.0076 (16)	−0.0356 (17)	−0.0177 (17)
C6	0.0530 (17)	0.0412 (14)	0.0400 (12)	−0.0028 (13)	−0.0173 (12)	−0.0035 (11)
C7	0.0373 (13)	0.0370 (13)	0.0242 (8)	−0.0047 (10)	−0.0050 (9)	−0.0023 (9)
C8	0.095 (3)	0.057 (2)	0.0641 (18)	−0.0006 (19)	0.0319 (19)	−0.0022 (17)
C9	0.063 (3)	0.123 (4)	0.089 (3)	−0.034 (2)	−0.007 (2)	0.003 (3)

Geometric parameters (Å, º)

O1—C7	1.254 (3)	C3—C4	1.380 (6)
O1—H1	0.77 (4)	C3—H3	0.9700
O2—C7	1.250 (3)	C4—C5	1.361 (5)
O2—H2	0.79 (5)	C4—H4	0.9700
O3—C2	1.350 (4)	C5—C6	1.397 (4)
O3—C8	1.411 (4)	C5—H5	0.9700
O4—C6	1.355 (4)	C8—H8A	0.9684
O4—C9	1.428 (5)	C8—H8B	0.9684
C1—C2	1.391 (4)	C8—H8C	0.9684
C1—C6	1.391 (4)	C9—H9A	0.9766
C1—C7	1.490 (3)	C9—H9B	0.9766
C2—C3	1.395 (4)	C9—H9C	0.9766
C7—O1—H1	110 (3)	O4—C6—C1	115.5 (2)
C7—O2—H2	113 (4)	O4—C6—C5	125.1 (3)
C2—O3—C8	119.0 (2)	C1—C6—C5	119.3 (3)
C6—O4—C9	118.5 (3)	O2—C7—O1	123.3 (2)
C2—C1—C6	120.8 (2)	O2—C7—C1	117.8 (2)

C2—C1—C7	119.8 (2)	O1—C7—C1	118.9 (2)
C6—C1—C7	119.4 (2)	O3—C8—H8A	109.5
O3—C2—C1	115.7 (2)	O3—C8—H8B	109.5
O3—C2—C3	124.8 (3)	H8A—C8—H8B	109.5
C1—C2—C3	119.5 (3)	O3—C8—H8C	109.5
C4—C3—C2	118.4 (3)	H8A—C8—H8C	109.5
C4—C3—H3	120.8	H8B—C8—H8C	109.5
C2—C3—H3	120.8	O4—C9—H9A	109.5
C5—C4—C3	123.1 (3)	O4—C9—H9B	109.5
C5—C4—H4	118.5	H9A—C9—H9B	109.5
C3—C4—H4	118.5	O4—C9—H9C	109.5
C4—C5—C6	118.9 (3)	H9A—C9—H9C	109.5
C4—C5—H5	120.6	H9B—C9—H9C	109.5
C6—C5—H5	120.6		

C8—O3—C2—C1	−172.8 (3)	C9—O4—C6—C5	−7.4 (5)
C8—O3—C2—C3	5.7 (5)	C2—C1—C6—O4	178.5 (3)
C6—C1—C2—O3	178.9 (2)	C7—C1—C6—O4	−2.0 (4)
C7—C1—C2—O3	−0.6 (4)	C2—C1—C6—C5	0.4 (4)
C6—C1—C2—C3	0.3 (4)	C7—C1—C6—C5	179.9 (3)
C7—C1—C2—C3	−179.2 (3)	C4—C5—C6—O4	−178.6 (3)
O3—C2—C3—C4	−179.2 (3)	C4—C5—C6—C1	−0.8 (5)
C1—C2—C3—C4	−0.8 (5)	C2—C1—C7—O2	114.4 (3)
C2—C3—C4—C5	0.4 (6)	C6—C1—C7—O2	−65.0 (3)
C3—C4—C5—C6	0.3 (6)	C2—C1—C7—O1	−66.0 (3)
C9—O4—C6—C1	174.7 (3)	C6—C1—C7—O1	114.5 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1···O1^{i}	0.77 (4)	1.87 (4)	2.632 (4)	168 (5)
O2—H2···O2^{i}	0.79 (5)	1.83 (5)	2.618 (4)	173 (5)

Symmetry code: (i) −*y*+1, −*x*+1, −*z*+3/2.