Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0388$
$wR(F^2) = 0.1062$
$S = 1.058$
910 reflections
74 parameters
H atoms riding, C—H 0.96 Å
$w = 1/[\sigma^2(F_o^2) + (0.0614P)^2 + 0.3167P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.185$ e Å^{-3}
$\Delta\rho_{\min} = -0.129$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0041 (23)
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
O1	0.58121 (12)	0.25180 (14)	0.67443 (14)	0.0675 (5)
N1	0.36106 (13)	−0.08875 (14)	0.62923 (15)	0.0490 (4)
N2	0.41118 (11)	0.10724 (13)	0.55889 (13)	0.0393 (4)
C1	0.44285 (14)	0.0133 (2)	0.6744 (2)	0.0400 (4)
C2	0.2722 (2)	−0.0609 (2)	0.4803 (2)	0.0498 (5)
C3	0.30004 (14)	0.0569 (2)	0.4352 (2)	0.0452 (4)
C4	0.48132 (15)	0.2270 (2)	0.5628 (2)	0.0441 (4)
C5	0.4223 (2)	0.3111 (2)	0.4235 (2)	0.0558 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1—C4	1.196 (2)	N2—C4	1.424 (2)
N1—C1	1.307 (2)	C1—C1ⁱ	1.468 (3)
N1—C2	1.381 (2)	C2—C3	1.338 (2)
N2—C1	1.387 (2)	C4—C5	1.481 (2)
N2—C3	1.391 (2)		
C1—N1—C2	105.76 (14)	N2—C1—C1ⁱ	127.72 (11)
C1—N2—C3	105.91 (12)	C3—C2—N1	111.07 (14)
C1—N2—C4	127.30 (12)	C2—C3—N2	106.16 (13)
C3—N2—C4	126.71 (13)	O1—C4—N2	119.23 (15)
N1—C1—N2	111.09 (13)	O1—C4—C5	125.2 (2)
N1—C1—C1ⁱ	120.96 (11)	N2—C4—C5	115.56 (13)

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

Data collection: *P3/P4/PC Diffractometer Program* (Siemens, 1991*a*). Cell refinement: *P3/P4/PC Diffractometer Program*. Data reduction: *XDISK* (Siemens, 1991*b*). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990*a*). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC* (Sheldrick, 1990*b*). Software used to prepare material for publication: *SHELXTL/PC*, *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HA1165). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Methyl 2-Benzoyloxy-3-oxo-3-phenylpropanoate

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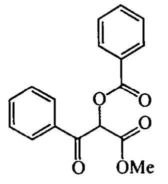
Abstract

The title compound, $C_{17}H_{14}O_5$, was obtained as a by-product from a procedure to regioselectively hydroxylate homochiral acid derivatives. Structural analysis confirmed its identity and showed it to be achiral.

Comment

The title compound, (I), was investigated as part of a study into the regioselective hydroxylation of 2-hydroxy-3-phenylpropanoic acid derivatives (Shaw & Tan, 1996). This structure determination was undertaken to confirm the structure of an oxidation product of the reaction, which presumably arose from the 2,3-dibromo-3-phenylpropanoate derivative. Compound (I), prepared from a chiral starting material, crystallized from a dichloromethane/hexane mix in the space group $P2_1/n$, thus requiring it to be achiral. An interesting



(I)

aspect of the structure is the near coplanarity of the methyl ester and benzoyl substituents attached to C3 (C4 in the crystallographic numbering scheme) with the angle between the planes defined by O5,C11,O3,C3 and O1,C2,O2,C3 being 8.84 (14)°. All bond lengths and angles within the identical fragments of (I) and methyl (*S*)-2-benzoyloxy-4-bromo-4-methylpentanoate are the same within 3 e.s.d.'s, with the exception of the angle C3—O3—C11 [114.62 (14) *versus* 118.0 (4)° in the latter compound (Shaw, Tan & Blackman, 1995)].

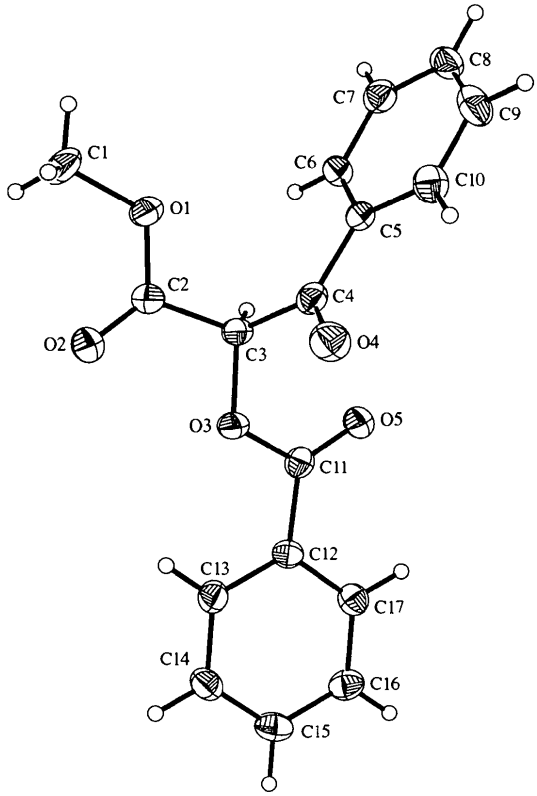


Fig. 1. *ORTEP* (Johnson, 1965) drawing of (I) showing displacement ellipsoids drawn at the 50% probability level.

Experimental

A mixture of methyl (*S*)-2-benzoyloxy-3-phenylpropanoate (3.85 g, 13.5 mmol) and *N*-bromosuccinimide (4.81 g, 27.0 mmol) in CCl_4 was heated at reflux under N_2 overnight, with reaction being initiated by a 160 W mercury lamp. The reaction mixture was then cooled, filtered and evaporated under reduced pressure. The residue was then stirred for 2 weeks in an acetone/water solution containing excess $AgNO_3$. The solvent was removed by rotary evaporation and the remaining residue was dissolved in CH_2Cl_2, dried ($MgSO_4$) and filtered. Purification of the β-hydroxy product by column chromatography also isolated the title compound which was recrystallized from CH_2Cl_2/hexane.

Crystal data

$C_{17}H_{14}O_5$
$M_r = 298.28$
Monoclinic
$P2_1/n$
$a = 6.070$ (2) Å
$b = 12.824$ (3) Å
$c = 18.457$ (5) Å
$\beta = 93.14$ (3)°
$V = 1434.5$ (6) Å^3
$Z = 4$
$D_x = 1.381$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 27 reflections
$\theta = 5$–14°
$\mu = 0.102$ mm^{-1}
$T = 151$ (2) K
Block
0.52 × 0.26 × 0.24 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
2260 measured reflections
2245 independent reflections
1470 observed reflections [$I > 2\sigma(I)$]
$R_{\text{int}} = 0.0147$

$\theta_{\max} = 24.00°$
$h = -6 \rightarrow 0$
$k = 0 \rightarrow 14$
$l = -20 \rightarrow 21$
3 standard reflections monitored every 97 reflections intensity decay: <2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0332$
$wR(F^2) = 0.0665$
$S = 0.831$
2245 reflections
200 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0291P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.150$ e Å^{-3}
$\Delta\rho_{\min} = -0.153$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
O1	−0.4124 (2)	0.48828 (9)	0.89600 (7)	0.0300 (3)
O2	−0.1443 (2)	0.38118 (10)	0.86161 (8)	0.0365 (4)
O3	0.0746 (2)	0.53973 (9)	0.80772 (7)	0.0260 (3)
O4	0.1160 (2)	0.61582 (10)	0.94630 (7)	0.0351 (4)
O5	0.1079 (2)	0.70868 (10)	0.77920 (7)	0.0313 (4)
C8	−0.5010 (3)	0.86417 (15)	0.98486 (11)	0.0316 (5)
C6	−0.4142 (3)	0.73463 (14)	0.89817 (11)	0.0261 (5)
C11	0.1704 (3)	0.61984 (15)	0.77371 (10)	0.0234 (4)
C3	−0.1168 (3)	0.56736 (14)	0.84473 (10)	0.0234 (5)
C4	−0.0566 (3)	0.63397 (14)	0.91217 (10)	0.0247 (5)
C5	−0.2122 (3)	0.71606 (14)	0.93523 (10)	0.0223 (4)
C12	0.3554 (3)	0.58501 (14)	0.73089 (10)	0.0224 (4)
C13	0.4065 (3)	0.47992 (15)	0.72300 (10)	0.0269 (5)
C17	0.4844 (3)	0.66015 (15)	0.69954 (10)	0.0253 (5)
C1	−0.5392 (3)	0.40056 (15)	0.92035 (11)	0.0360 (5)
C16	0.6648 (3)	0.6311 (2)	0.66151 (10)	0.0292 (5)
C7	−0.5585 (3)	0.80844 (15)	0.92314 (11)	0.0299 (5)
C9	−0.2982 (3)	0.8473 (2)	1.02144 (11)	0.0354 (5)
C2	−0.2211 (3)	0.4662 (2)	0.86771 (10)	0.0251 (5)
C10	−0.1552 (3)	0.77348 (14)	0.99697 (11)	0.0304 (5)
C15	0.7161 (3)	0.5264 (2)	0.65479 (10)	0.0326 (5)
C14	0.5869 (3)	0.4512 (2)	0.68546 (10)	0.0311 (5)

Table 2. *Selected geometric parameters (Å, °)*

O1—C2	1.330 (2)	O5—C11	1.207 (2)
O1—C1	1.448 (2)	C11—C12	1.477 (2)
O2—C2	1.193 (2)	C3—C2	1.515 (3)
O3—C11	1.352 (2)	C3—C4	1.537 (3)
O3—C3	1.424 (2)	C4—C5	1.492 (2)
O4—C4	1.215 (2)		
C2—O1—C1	116.54 (15)	O4—C4—C3	118.3 (2)
C11—O3—C3	114.62 (14)	C5—C4—C3	119.8 (2)
O5—C11—O3	122.2 (2)	C10—C5—C4	118.5 (2)
O5—C11—C12	125.6 (2)	C6—C5—C4	122.4 (2)
O3—C11—C12	112.2 (2)	C17—C12—C11	118.4 (2)
O3—C3—C2	106.60 (14)	C13—C12—C11	121.9 (2)
O3—C3—C4	111.26 (15)	O2—C2—O1	125.9 (2)
C2—C3—C4	109.51 (14)	O2—C2—C3	125.8 (2)
O4—C4—C5	121.9 (2)	O1—C2—C3	108.4 (2)

Data collection: *SHELXTL-Plus* (Sheldrick, 1991). Cell refinement: *SHELXTL-Plus*. Data reduction: *SHELXTL-Plus*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965).

We thank Professor W. T. Robinson (University of Canterbury, New Zealand) for data collection. This work is supported by a University of Otago Division of Sciences Research Grant.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: TA1103). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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2-Butyne-1,4-diol

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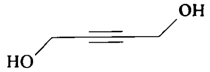
Abstract

A crystallographic twofold axis passes through the central C≡C triple bond of the title molecule, $C_4H_6O_2$. The conformation is markedly non-planar with the two O—C1—C2 planes almost perpendicular to one another. The hydroxyl groups form infinite cooperative hydrogen-bond chains.

Comment

Several crystal structures have been published where 2-butyne-1,4-diol, (1), is complexed by organic hosts or is used as a ligand in organometallic compounds (see below). The crystal structure of (1) itself has not been reported as yet and is therefore presented here.



(1)

The conformation of (1) is non-planar with an O—C1···C1′—O1′ torsion angle of −94.7 (3)°, *i.e.* the two O—C1—C2 planes are roughly perpendicular to one another. The OH group is *gauche* with respect to the C1—C2 bond [C2—C1—O—H −77 (2)°] (Fig. 1).

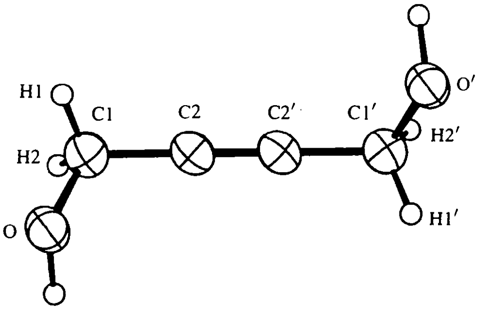


Fig. 1. The molecular structure and atom labelling of the title compound. Projection is along the twofold axis intersecting the C≡C triple bond. Displacement ellipsoids are drawn at the 30% probability level.

The hydroxyl groups form infinite chains of cooperative O—H···O—H···O hydrogen bonds, with O···O($x-\frac{1}{2}$, $y-\frac{1}{4}$, $-z+\frac{1}{4}$) separations of 2.681 (2) Å (Fig. 2). Based on a normalized H-atom position (O—H 0.98 Å), the H···O separation is 1.70 Å, the O—H···O angle 174° and the H···O—C angle 117° [experimental values: O—H 1.04 (3), H···O 1.65 (3) Å, O—H···O 174 (3) and H···O—C 116.6 (9)°]. The hydrogen bond chains at $z/c = \frac{1}{8}$ and $z/c = \frac{3}{8}$ run in the $[1\bar{1}0]$ and $[\bar{1}10]$ directions, respectively, *i.e.* in the directions of the different diagonals of the *ab* plane. The apparently cyclic motifs in Fig. 2 are, therefore, in fact, screw axes; this is indicated by broken hydrogen bonds in the chain at $z/c = \frac{3}{8}$. Note that the projection of Fig. 2 is along the polar axis of the crystal structure; in this projection, all O-atom lone pairs point away from the viewer, whereas all C—H2 bonds point towards the viewer. On the macroscopic level, this must lead to different polarities and growth characteristics of the (100) and $(\bar{1}00)$