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Prop-2-ynyl 3-methoxy-4-(prop-2-ynyloxy)benzoate

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Keywords: crystal structure; dimer; hydrogen bonding.

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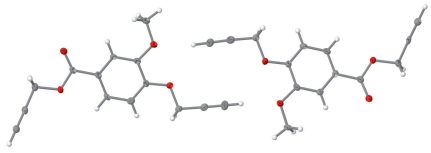
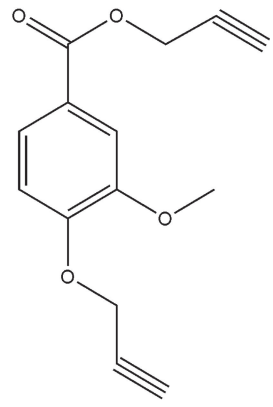
Structural data: full structural data are available from iucrdata.iucr.org

The title compound, $C_{14}H_{12}O_4$, comprises of two crystallographically independent molecules in the asymmetric unit, linked *via* C—H···O interactions to form dimeric entities. The allylic groups are twisted out of the phenyl planes with dihedral angles varying between 7.92 (13) and 25.42 (8)°. In the crystal, the packing follows a zigzag pattern along the *c*-axis direction. The absolute configuration of the sample could not be determined reliably.

3D view



Chemical scheme



Structure description

Vanillic acid (4-hydroxy-3-methoxybenzoic acid) is an aromatic phenolic acid widely used as a flavouring agent in the food industry. 4-Hydroxy-3-methoxybenzoic acid is naturally observed in some forms of vanilla and many other plant extracts, but may also be chemically synthesized (Calixto-Campos *et al.*, 2015). In addition to being a flavourant, this compound offers remarkable therapeutic (anticancer, antiobesity, antidiabetic, antibacterial, anti-inflammatory, and antioxidant) effects (Kaur *et al.*, 2022) and versatility for use in polymeric coatings (Silva *et al.*, 2016; El-Toni *et al.*, 2005), as an inclusion agent for encapsulants (Rajendiran & Jude Jenita, 2015; Hong *et al.*, 2008) and as a construct in metallomacrocyles (Xiong *et al.*, 2000). More recently, this compound has been reported as a promising linker precursor towards novel coordination polymers (Belay *et al.*, 2019). In this study, the title compound, $C_{14}H_{12}O_4$, was investigated as an intermediate toward hydroxamic acid-type linker systems and was prepared *via* the alkylation of 4-hydroxy-3-methoxybenzoic acid with propargyl bromide in the presence of K_2CO_3 (Buckley *et al.*, 2014; Hoogendoorn *et al.*, 2011).

The title compound crystallizes in the orthorhombic $Pca2_1$ (Z = 8) space group resulting in two independent molecules (*A* and *B*) in the asymmetric unit (Fig. 1) with all of the bond lengths and angles falling within the normal ranges. The differences between these two molecules are observed in the allyl groups attached to the carboxylate and *para*-hydroxy positions of 4-hydroxy-3-methoxybenzoic acid, respectively, which display dihedral angles varying between 7.91 (13) and 25.42 (8)° out of plane with each of the

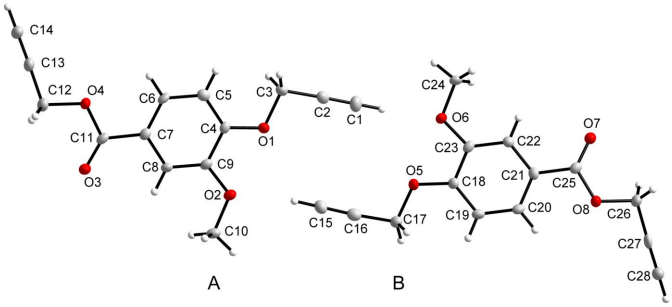


Figure 1
A view of the molecular structure of the title compound as two independent molecules (*A* and *B*) in the asymmetric unit, with the atom labelling. The displacement ellipsoids are drawn at the 50% probability level.

benzoate rings for *A* and *B*. This observation is best illustrated by superimposing the two molecules (Fig. 2).

In molecule *A*, the dihedral angles between the benzene ring (C4–C9) and the methoxy group (C9/O2/C10), the ester group (O4/C12–C14) and the ether group (O1/C1–C3) are 7.17 (15), 15.80 (12) and 11.48 (15)°, respectively. In molecule *B*, the corresponding angles between the benzene ring (C18–C22), the methoxy group (C23/O6/C24), the ester group (O8/C26–C28) and the ether group (O5/C15–C17) are 3.22 (16), 25.42 (8) and 7.92 (13)°, respectively.

Non-classical intermolecular hydrogen bonding is observed in the extended structure of the title compound. These interactions (Fig. 3) are summarized in Table 1 and a packing diagram of the title compound shows the molecules linked by infinite C—H···O chains along the *c*-axis direction (Fig. 4).

Synthesis and crystallization

A solution of 4-hydroxy-3-methoxybenzoic acid (2.0 g, 11.90 mmol) was treated with K_2CO_3 (2.50 g, 17.85 mmol) in acetone. The reaction mixture was stirred under reflux for approximately 30 minutes followed by the addition of propargyl bromide (3.0 ml, 23.8 mmol of 80 wt. % in toluene). After stirring for 4 h, the reaction mixture was concentrated under vacuum. The residue was extracted using ethyl acetate, washed successively (water and brine) and dried over anhydrous sodium sulfate. The crude product was then recrystallized from the mixed solvents of dichloromethane and hexane to provide the title compound as colourless needles.

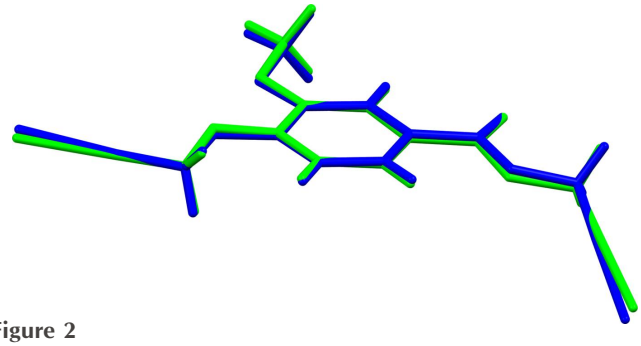


Figure 2
Superimposed view of the two independent molecules in the asymmetric unit (r.m.s. deviation = 0.113 Å, max displacement = 0.258 Å).

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O6	0.95	2.30	3.231 (5)	165
C14—H14···O3^{i}	0.95	2.28	3.231 (5)	177
C15—H15···O2	0.95	2.28	3.213 (5)	169
C28—H28···O7^{ii}	0.95	2.41	3.291 (5)	155

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

Analytical data: Melting point range: 65–68°C; ^{1}H NMR ($CDCl_3$, 400 MHZ): δ 7.69 (*d*, *J* = 8.4 Hz, 1H), 7.55 (*s*, 1H), 7.03 (*d*, *J* = 8.4 Hz, 1H), 4.88 (*d*, *J* = 2.4 Hz, 2H), 4.81 (*d*, *J* = 2.4 Hz, 2H), 3.91 (*s*, 3H), 2.52 (*t*, *J* = 2.4 Hz, 1H), 2.50 (*t*, *J* = 2.4 Hz, 1H); ^{13}C NMR ($CDCl_3$, 400 MHZ): δ 165.2, 150.9, 149.0, 123.4, 122.8, 112.5, 77.8, 74.8, 56.4, 55.9, 52.2.

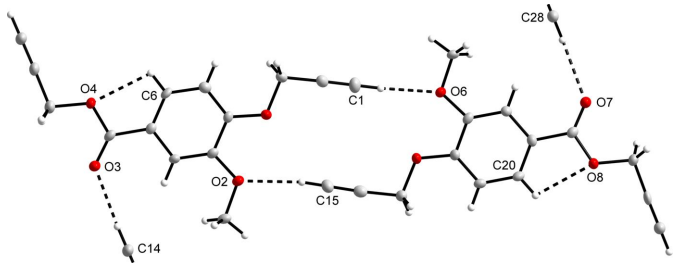


Figure 3
The non-classical C—H···O hydrogen-bonding interactions observed for the title compound, shown as dashed lines.

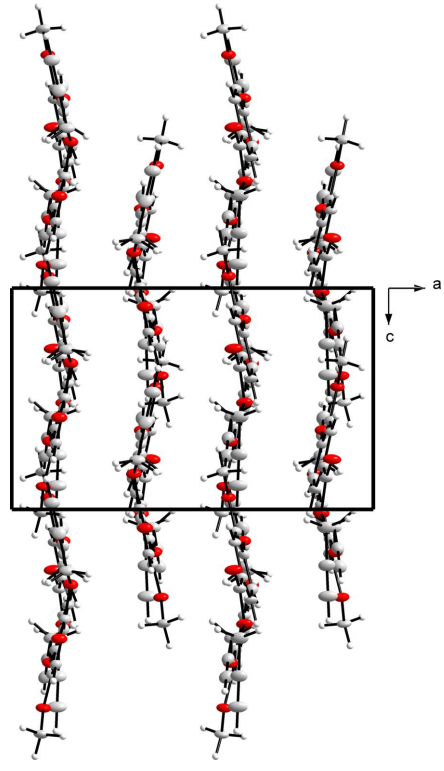


Figure 4
Packing diagram showing the title compound molecules linked by infinite one-dimensional C—H···O chains along the *c*-axis direction.

Refinement

Crystal data, data collection and structure refinement details are summarized in Table 2. Reflection (200) was removed as discrepant. The highest electron density of 0.22 e Å^{-3} is 0.75 Å away from C5, while the deepest electron density of −0.25 e Å^{-3} is 1.27 Å away from C25.

Acknowledgements

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Table 2
Experimental details.

Crystal data	
Chemical formula	$C_{14}H_{12}O_4$
M_r	244.24
Crystal system, space group	Orthorhombic, $Pca2_1$
Temperature (K)	100
a, b, c (Å)	13.7387 (12), 20.547 (2), 8.4283 (9)
V (Å^3)	2379.2 (4)
Z	8
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.10
Crystal size (mm)	0.40 × 0.07 × 0.03
Data collection	
Diffractometer	Bruker *APEX* DUO 4K CCD
Absorption correction	Multi-scan (*SADABS*; Krause *et al.*, 2015)
T_{min}, T_{max}	0.487, 0.749
No. of measured, independent and observed [$I > 2\sigma(I)$] reflections	12893, 5028, 3236
R_{int}	0.072
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.670
Refinement	
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.052, 0.111, 1.00
No. of reflections	5028
No. of parameters	326
No. of restraints	1
H-atom treatment	H-atom parameters constrained
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.22, −0.25
Absolute structure	Flack x determined using 833 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter	−1.6 (10)

Computer programs: *APEX2* (Bruker, 2011), *SAINT* and *XPREP* (Bruker, 2008), *SIR97* (Altomare *et al.*, 1999), *SHELXL2019/2* (Sheldrick, 2015), *DIAMOND* (Brandenburg & Putz, 2005) and *WinGX* publication routines (Farrugia, 2012).

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full crystallographic data

IUCrData (2024). **9**, x240163 [https://doi.org/10.1107/S2414314624001639]

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Crystal data

$C_{14}H_{12}O_4$
M_r = 244.24
Orthorhombic, $Pca2_1$
a = 13.7387 (12) Å
b = 20.547 (2) Å
c = 8.4283 (9) Å
V = 2379.2 (4) Å^3
Z = 8
$F(000)$ = 1024
D_x = 1.364 Mg m^{-3}
Mo $K\alpha$ radiation, λ = 0.71073 Å
Cell parameters from 13397 reflections
θ = 0.1–28.4°
μ = 0.10 mm^{-1}
T = 100 K
Needle, colourless
0.40 × 0.07 × 0.03 mm

Data collection

Bruker APEX DUO 4K CCD diffractometer
Radiation source: Sealed tube
Detector resolution: 8.4 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (SADABS; Krause *et al.*, 2015)
T_{min} = 0.487, T_{max} = 0.749
12893 measured reflections
5028 independent reflections
3236 reflections with $I > 2\sigma(I)$
R_{int} = 0.072
θ_{max} = 28.4°, θ_{min} = 1.0°
h = −18→16
k = −23→27
l = −7→11

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.111
S = 1.00
5028 reflections
326 parameters
1 restraint
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0426P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.25 e Å^{-3}
Absolute structure: Flack x determined using 833 quotients $[(I^+)-(I^-)]/[(I^+)+(I^-)]$ (Parsons *et al.*, 2013)
Absolute structure parameter: −1.6 (10)

Special details

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

Refinement. The hydrogen atoms were refined isotropically in their idealized geometrical positions while riding on their anisotropic parent atoms with $U_{iso} = 1.2U_{eq}$ for the aromatic and methine protons, and $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl protons, the latter groups were refined as a fixed rotor and adjusted to match the hydrogen atoms electron density from the Fourier difference map.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.8623 (3)	0.4803 (2)	0.5854 (5)	0.0277 (10)
H1	0.865272	0.441594	0.523834	0.033*
C2	0.8586 (3)	0.5283 (2)	0.6621 (5)	0.0216 (9)
C3	0.8542 (3)	0.58880 (19)	0.7541 (5)	0.0218 (9)
H3A	0.792808	0.590809	0.815537	0.026*
H3B	0.909534	0.591193	0.829057	0.026*
C4	0.8578 (3)	0.70289 (19)	0.7050 (4)	0.0172 (8)
C5	0.8355 (3)	0.7179 (2)	0.8601 (5)	0.0218 (9)
H5	0.818301	0.684249	0.932124	0.026*
C6	0.8381 (3)	0.78228 (18)	0.9115 (4)	0.0201 (9)
H6	0.822973	0.792274	1.018751	0.024*
C7	0.8625 (3)	0.8317 (2)	0.8079 (4)	0.0184 (9)
C8	0.8831 (3)	0.8172 (2)	0.6488 (4)	0.0178 (9)
H8	0.898778	0.851112	0.576445	0.021*
C9	0.8806 (3)	0.7534 (2)	0.5981 (4)	0.0189 (9)
C10	0.9142 (3)	0.78343 (19)	0.3294 (5)	0.0242 (9)
H10A	0.969498	0.810891	0.359604	0.036*
H10B	0.855279	0.810159	0.322386	0.036*
H10C	0.927149	0.763268	0.226153	0.036*
C11	0.8692 (3)	0.9007 (2)	0.8589 (5)	0.0212 (9)
C12	0.8697 (3)	0.9719 (2)	1.0807 (5)	0.0299 (11)
H12A	0.931613	0.990641	1.041645	0.036*
H12B	0.815584	1.000530	1.047077	0.036*
C13	0.8716 (3)	0.9661 (2)	1.2525 (5)	0.0278 (10)
C14	0.8750 (3)	0.9624 (2)	1.3921 (5)	0.0325 (11)
H14	0.877700	0.959484	1.504519	0.039*
C15	0.9067 (3)	0.5981 (2)	0.2571 (5)	0.0260 (9)
H15	0.910724	0.635494	0.322918	0.031*
C16	0.9016 (3)	0.5515 (2)	0.1751 (5)	0.0239 (9)
C17	0.8920 (3)	0.49179 (19)	0.0811 (5)	0.0226 (9)
H17A	0.829561	0.491684	0.022371	0.027*
H17B	0.945988	0.488156	0.003873	0.027*
C18	0.8798 (3)	0.3775 (2)	0.1339 (4)	0.0177 (9)
C19	0.8565 (3)	0.3629 (2)	−0.0221 (4)	0.0203 (9)
H19	0.848605	0.396833	−0.097637	0.024*
C20	0.8446 (3)	0.29830 (19)	−0.0673 (5)	0.0197 (9)
H20	0.828592	0.288233	−0.174173	0.024*
C21	0.8561 (3)	0.24841 (19)	0.0419 (5)	0.0175 (8)
C22	0.8783 (3)	0.2632 (2)	0.2010 (5)	0.0183 (9)
H22	0.885351	0.229252	0.276632	0.022*

C23	0.8897 (3)	0.3272 (2)	0.2463 (4)	0.0186 (8)
C24	0.9196 (3)	0.2979 (2)	0.5156 (4)	0.0224 (9)
H24A	0.936300	0.317677	0.617786	0.034*
H24B	0.857032	0.275307	0.524575	0.034*
H24C	0.970282	0.266625	0.485517	0.034*
C25	0.8537 (3)	0.1789 (2)	−0.0043 (4)	0.0199 (9)
C26	0.8474 (3)	0.1063 (2)	−0.2232 (5)	0.0248 (9)
H26A	0.786129	0.081748	−0.207870	0.030*
H26B	0.900466	0.083150	−0.167331	0.030*
C27	0.8699 (3)	0.1123 (2)	−0.3932 (5)	0.0233 (10)
C28	0.8893 (3)	0.1151 (2)	−0.5294 (5)	0.0271 (10)
H28	0.904872	0.117410	−0.639094	0.032*
O1	0.8587 (2)	0.64180 (14)	0.6418 (3)	0.0215 (7)
O2	0.90058 (19)	0.73376 (13)	0.4462 (3)	0.0223 (6)
O3	0.8860 (2)	0.94679 (15)	0.7732 (3)	0.0289 (7)
O4	0.8561 (2)	0.90620 (14)	1.0171 (3)	0.0245 (7)
O5	0.89505 (19)	0.43864 (13)	0.1930 (3)	0.0218 (6)
O6	0.91275 (19)	0.34757 (13)	0.3969 (3)	0.0224 (6)
O7	0.8687 (2)	0.13363 (14)	0.0841 (3)	0.0246 (7)
O8	0.83739 (18)	0.17221 (13)	−0.1617 (3)	0.0222 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.031 (2)	0.021 (2)	0.031 (2)	−0.0013 (19)	−0.003 (2)	−0.0048 (19)
C2	0.024 (2)	0.019 (2)	0.022 (2)	−0.0013 (18)	−0.0033 (17)	0.0021 (18)
C3	0.031 (2)	0.016 (2)	0.018 (2)	−0.0008 (17)	−0.0018 (17)	0.0027 (16)
C4	0.020 (2)	0.016 (2)	0.0157 (19)	0.0005 (16)	−0.0027 (15)	−0.0032 (16)
C5	0.025 (2)	0.020 (2)	0.020 (2)	−0.0004 (17)	0.0000 (16)	0.0021 (17)
C6	0.027 (2)	0.023 (2)	0.0110 (19)	0.0011 (17)	0.0023 (15)	−0.0049 (16)
C7	0.021 (2)	0.019 (2)	0.015 (2)	0.0025 (17)	0.0001 (15)	−0.0030 (16)
C8	0.025 (2)	0.017 (2)	0.0116 (17)	0.0020 (17)	−0.0006 (15)	0.0012 (16)
C9	0.024 (2)	0.020 (2)	0.0129 (19)	0.0031 (17)	−0.0022 (16)	−0.0005 (17)
C10	0.034 (2)	0.024 (2)	0.0141 (19)	0.0052 (19)	0.0022 (17)	0.0027 (17)
C11	0.029 (2)	0.022 (2)	0.0126 (19)	0.0030 (18)	0.0000 (16)	−0.0034 (17)
C12	0.051 (3)	0.018 (3)	0.021 (2)	−0.001 (2)	0.000 (2)	−0.004 (2)
C13	0.045 (3)	0.017 (3)	0.021 (2)	−0.0024 (19)	−0.0012 (19)	−0.0043 (18)
C14	0.059 (3)	0.019 (2)	0.019 (2)	−0.001 (2)	0.000 (2)	−0.002 (2)
C15	0.033 (2)	0.019 (2)	0.026 (2)	−0.0012 (19)	0.0044 (19)	0.0004 (19)
C16	0.026 (2)	0.023 (2)	0.023 (2)	0.0020 (18)	0.0028 (17)	0.0034 (18)
C17	0.034 (2)	0.017 (2)	0.0170 (19)	0.0020 (17)	0.0018 (18)	−0.0003 (16)
C18	0.023 (2)	0.014 (2)	0.0160 (19)	0.0024 (16)	0.0014 (15)	−0.0015 (17)
C19	0.026 (2)	0.021 (2)	0.0134 (18)	0.0003 (18)	−0.0002 (16)	0.0026 (16)
C20	0.024 (2)	0.022 (2)	0.0128 (19)	−0.0022 (17)	0.0021 (15)	0.0004 (17)
C21	0.0187 (19)	0.014 (2)	0.0202 (19)	0.0011 (17)	0.0005 (15)	−0.0016 (17)
C22	0.022 (2)	0.016 (2)	0.0163 (19)	−0.0011 (16)	0.0016 (15)	0.0007 (17)
C23	0.020 (2)	0.021 (2)	0.0144 (18)	0.0009 (16)	−0.0013 (15)	−0.0039 (17)
C24	0.034 (2)	0.022 (2)	0.0118 (18)	−0.0010 (19)	−0.0026 (16)	0.0028 (16)

C25	0.023 (2)	0.021 (2)	0.015 (2)	−0.0011 (18)	−0.0005 (16)	−0.0016 (17)
C26	0.041 (2)	0.017 (2)	0.0164 (18)	−0.0010 (19)	0.0006 (17)	−0.0035 (17)
C27	0.034 (2)	0.009 (2)	0.027 (2)	−0.0001 (18)	−0.0019 (18)	−0.0042 (17)
C28	0.043 (3)	0.018 (2)	0.021 (2)	0.0003 (19)	0.0010 (18)	−0.0010 (19)
O1	0.0349 (16)	0.0147 (16)	0.0150 (14)	0.0010 (12)	−0.0007 (12)	0.0013 (12)
O2	0.0337 (16)	0.0194 (16)	0.0138 (13)	0.0032 (12)	0.0009 (11)	0.0000 (11)
O3	0.053 (2)	0.0189 (18)	0.0153 (14)	−0.0030 (14)	0.0028 (13)	−0.0003 (13)
O4	0.0438 (17)	0.0150 (16)	0.0146 (14)	−0.0022 (13)	0.0017 (12)	−0.0031 (11)
O5	0.0365 (16)	0.0124 (15)	0.0165 (13)	0.0005 (13)	−0.0019 (12)	−0.0009 (11)
O6	0.0366 (16)	0.0172 (15)	0.0135 (12)	−0.0014 (12)	−0.0023 (11)	−0.0003 (11)
O7	0.0398 (18)	0.0174 (17)	0.0165 (14)	−0.0004 (13)	−0.0008 (12)	−0.0006 (12)
O8	0.0365 (17)	0.0136 (15)	0.0165 (13)	0.0000 (12)	−0.0022 (12)	−0.0006 (12)

Geometric parameters (Å, º)

C1—C2	1.181 (6)	C15—C16	1.182 (6)
C1—H1	0.9500	C15—H15	0.9500
C2—C3	1.466 (5)	C16—C17	1.467 (6)
C3—O1	1.444 (5)	C17—O5	1.444 (5)
C3—H3A	0.9900	C17—H17A	0.9900
C3—H3B	0.9900	C17—H17B	0.9900
C4—O1	1.364 (4)	C18—O5	1.367 (5)
C4—C5	1.378 (5)	C18—C19	1.386 (5)
C4—C9	1.410 (5)	C18—C23	1.409 (5)
C5—C6	1.392 (5)	C19—C20	1.391 (6)
C5—H5	0.9500	C19—H19	0.9500
C6—C7	1.381 (5)	C20—C21	1.387 (5)
C6—H6	0.9500	C20—H20	0.9500
C7—C8	1.403 (5)	C21—C22	1.408 (6)
C7—C11	1.484 (6)	C21—C25	1.481 (6)
C8—C9	1.379 (6)	C22—C23	1.379 (6)
C8—H8	0.9500	C22—H22	0.9500
C9—O2	1.370 (4)	C23—O6	1.373 (4)
C10—O2	1.430 (4)	C24—O6	1.433 (4)
C10—H10A	0.9800	C24—H24A	0.9800
C10—H10B	0.9800	C24—H24B	0.9800
C10—H10C	0.9800	C24—H24C	0.9800
C11—O3	1.213 (5)	C25—O7	1.209 (5)
C11—O4	1.350 (4)	C25—O8	1.353 (4)
C12—C13	1.453 (6)	C26—O8	1.456 (5)
C12—O4	1.464 (5)	C26—C27	1.471 (6)
C12—H12A	0.9900	C26—H26A	0.9900
C12—H12B	0.9900	C26—H26B	0.9900
C13—C14	1.180 (6)	C27—C28	1.180 (6)
C14—H14	0.9500	C28—H28	0.9500
C2—C1—H1	180.0	O5—C17—H17A	110.5
C1—C2—C3	178.8 (5)	C16—C17—H17A	110.5

O1—C3—C2	106.9 (3)	O5—C17—H17B	110.5
O1—C3—H3A	110.3	C16—C17—H17B	110.5
C2—C3—H3A	110.3	H17A—C17—H17B	108.7
O1—C3—H3B	110.3	O5—C18—C19	125.4 (4)
C2—C3—H3B	110.3	O5—C18—C23	114.5 (3)
H3A—C3—H3B	108.6	C19—C18—C23	120.1 (4)
O1—C4—C5	125.3 (4)	C18—C19—C20	119.6 (4)
O1—C4—C9	115.2 (3)	C18—C19—H19	120.2
C5—C4—C9	119.4 (4)	C20—C19—H19	120.2
C4—C5—C6	120.1 (4)	C21—C20—C19	120.7 (4)
C4—C5—H5	119.9	C21—C20—H20	119.6
C6—C5—H5	119.9	C19—C20—H20	119.7
C7—C6—C5	120.5 (3)	C20—C21—C22	119.8 (4)
C7—C6—H6	119.7	C20—C21—C25	122.4 (4)
C5—C6—H6	119.7	C22—C21—C25	117.6 (3)
C6—C7—C8	119.8 (4)	C23—C22—C21	119.6 (4)
C6—C7—C11	122.3 (3)	C23—C22—H22	120.2
C8—C7—C11	117.9 (4)	C21—C22—H22	120.2
C9—C8—C7	119.5 (4)	O6—C23—C22	125.0 (4)
C9—C8—H8	120.2	O6—C23—C18	114.8 (3)
C7—C8—H8	120.2	C22—C23—C18	120.2 (4)
O2—C9—C8	124.4 (3)	O6—C24—H24A	109.5
O2—C9—C4	115.1 (4)	O6—C24—H24B	109.5
C8—C9—C4	120.5 (4)	H24A—C24—H24B	109.5
O2—C10—H10A	109.5	O6—C24—H24C	109.5
O2—C10—H10B	109.5	H24A—C24—H24C	109.5
H10A—C10—H10B	109.5	H24B—C24—H24C	109.5
O2—C10—H10C	109.5	O7—C25—O8	123.7 (4)
H10A—C10—H10C	109.5	O7—C25—C21	125.1 (4)
H10B—C10—H10C	109.5	O8—C25—C21	111.1 (4)
O3—C11—O4	123.3 (4)	O8—C26—C27	106.8 (3)
O3—C11—C7	125.8 (4)	O8—C26—H26A	110.4
O4—C11—C7	111.0 (3)	C27—C26—H26A	110.4
C13—C12—O4	106.9 (4)	O8—C26—H26B	110.4
C13—C12—H12A	110.3	C27—C26—H26B	110.4
O4—C12—H12A	110.3	H26A—C26—H26B	108.6
C13—C12—H12B	110.3	C28—C27—C26	177.9 (5)
O4—C12—H12B	110.3	C27—C28—H28	180.0
H12A—C12—H12B	108.6	C4—O1—C3	116.0 (3)
C14—C13—C12	178.4 (5)	C9—O2—C10	117.3 (3)
C13—C14—H14	180.0	C11—O4—C12	114.9 (3)
C16—C15—H15	180.0	C18—O5—C17	116.9 (3)
C15—C16—C17	176.5 (5)	C23—O6—C24	116.3 (3)
O5—C17—C16	106.1 (3)	C25—O8—C26	115.3 (3)

O1—C4—C5—C6	179.3 (4)	C21—C22—C23—C18	−0.4 (5)
C9—C4—C5—C6	−1.8 (6)	O5—C18—C23—O6	0.2 (5)
C4—C5—C6—C7	0.3 (6)	C19—C18—C23—O6	−179.9 (3)

C5—C6—C7—C8	1.2 (6)	O5—C18—C23—C22	−178.6 (3)
C5—C6—C7—C11	−178.0 (4)	C19—C18—C23—C22	1.4 (5)
C6—C7—C8—C9	−1.2 (6)	C20—C21—C25—O7	175.5 (4)
C11—C7—C8—C9	178.1 (3)	C22—C21—C25—O7	0.5 (6)
C7—C8—C9—O2	−179.2 (3)	C20—C21—C25—O8	−1.2 (5)
C7—C8—C9—C4	−0.3 (6)	C22—C21—C25—O8	−176.2 (3)
O1—C4—C9—O2	−0.2 (5)	C5—C4—O1—C3	−12.5 (6)
C5—C4—C9—O2	−179.3 (3)	C9—C4—O1—C3	168.5 (3)
O1—C4—C9—C8	−179.2 (3)	C2—C3—O1—C4	−178.5 (3)
C5—C4—C9—C8	1.8 (6)	C8—C9—O2—C10	−7.4 (5)
C6—C7—C11—O3	−176.6 (4)	C4—C9—O2—C10	173.7 (3)
C8—C7—C11—O3	4.2 (6)	O3—C11—O4—C12	−3.7 (6)
C6—C7—C11—O4	4.8 (5)	C7—C11—O4—C12	175.0 (3)
C8—C7—C11—O4	−174.4 (3)	C13—C12—O4—C11	−169.1 (3)
O5—C18—C19—C20	178.8 (3)	C19—C18—O5—C17	−3.7 (5)
C23—C18—C19—C20	−1.1 (6)	C23—C18—O5—C17	176.2 (3)
C18—C19—C20—C21	−0.1 (6)	C16—C17—O5—C18	175.1 (3)
C19—C20—C21—C22	1.0 (5)	C22—C23—O6—C24	−3.7 (5)
C19—C20—C21—C25	−173.9 (4)	C18—C23—O6—C24	177.6 (3)
C20—C21—C22—C23	−0.8 (5)	O7—C25—O8—C26	−5.1 (6)
C25—C21—C22—C23	174.3 (3)	C21—C25—O8—C26	171.7 (3)
C21—C22—C23—O6	−179.0 (3)	C27—C26—O8—C25	−155.7 (3)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C1—H1···O6	0.95	2.30	3.231 (5)	165
C14—H14···O3^{i}	0.95	2.28	3.231 (5)	177
C15—H15···O2	0.95	2.28	3.213 (5)	169
C28—H28···O7^{ii}	0.95	2.41	3.291 (5)	155

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*, *y*, *z*−1.