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Norbornane-*exo*-*cis*-2,3-diyl 1′,2′-phenylene orthocarbonate

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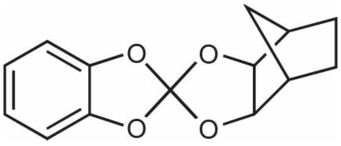
Key indicators: single-crystal X-ray study; T = 200 K; mean σ(C–C) = 0.002 Å; R factor = 0.045; wR factor = 0.119; data-to-parameter ratio = 15.7.

The title compound (systematic name: 4,7-methano-2,2′-spirobi[1,3-benzodioxole]), $C_{14}H_{14}O_4$, is an asymmetric spiro ester of orthocarbonic acid and two diols, *viz*. the aromatic benzene-1,2-diol and the aliphatic vicinal norbornane-*exo*-*cis*-2,3-diol. The orthocarbonate molecule is close to having non-crystallographic C_s symmetry. The five-membered ring stemming from the aliphatic diol has an envelope conformation. C—O bonds including the spiro-C atom span an approximately 0.07 Å range, but are within 0.02 Å of the respective distances in a density functional theory calculation, *i.e.* the distance difference is not caused by packing forces. Accordingly, the crystal packing is characterized by weak C—H⋯O and C—H⋯π interactions.

Related literature

For the synthesis of the title compound, see: Komatsu *et al.* (1992). For related compounds, see: Betz & Klüfers (2007*a*,*b*,*c*); Betz *et al.* (2007). Density functional theory calculations were performed by Betz & Klüfers (2008).



Experimental

Crystal data

$C_{14}H_{14}O_4$
M_r = 246.25
Monoclinic, $P2_1/n$
a = 7.9125 (3) Å
b = 9.5545 (5) Å
c = 15.2813 (6) Å
β = 101.490 (3)°
V = 1132.11 (9) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.11 mm^{-1}
T = 200 (2) K
0.30 × 0.25 × 0.16 mm

Data collection

Nonius KappaCCD diffractometer
Absorption correction: none
8399 measured reflections
2582 independent reflections
1716 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.054

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.119$
S = 1.05
2582 reflections
164 parameters
Only H-atom displacement parameters refined
$\Delta\rho_{\rm max}$ = 0.21 e Å^{-3}
$\Delta\rho_{\rm min}$ = −0.19 e Å^{-3}

Table 1
Selected bond lengths (Å).

O1—C1	1.367 (2)	O3—C1	1.412 (2)
O2—C1	1.370 (2)	O4—C1	1.435 (2)

Table 2
Hydrogen-bond geometry (Å, °).

Cg is the centroid of the C9–C14 phenylene ring.

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C3—H3⋯O4$^{\rm i}$	1.00	2.71	3.623 (2)	151
C7—H7A⋯O4$^{\rm i}$	0.99	2.76	3.663 (2)	151
C14—H14⋯O2$^{\rm ii}$	0.95	2.61	3.501 (2)	156
C14—H14⋯O4$^{\rm ii}$	0.95	2.88	3.514 (2)	125
C2—H2⋯$Cg^{\rm iii}$	1.00	2.86	3.563 (2)	128
C5—H5⋯$Cg^{\rm iv}$	1.00	2.66	3.568 (2)	152

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

Data collection: *COLLECT* (Nonius, 2004); cell refinement: *SCALEPACK* (Otwinowski & Minor 1997); data reduction: *DENZO* (Otwinowski & Minor 1997) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *PLATON* (Spek, 2003; 2006 version).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LX2027).

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supporting information

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Norbornane-*exo*-*cis*-2,3-diyl 1′,2′-phenylene orthocarbonate

Richard Betz and Peter Klüfers

S1. Comment

The title compound was prepared in order to compare its NMR-spectroscopic data with those of related silicon compounds.

In the molecule, a central carbon atom is chelated by a phenylene-1,2-dioxy and a norbornylene-*exo*-*cis*-2,3-dioxy moiety. The C—O bond lengths differ markedly (1.37 to 1.44 Å). About the same bond-length values were computed for the isolated molecule on the B3LYP/6–31+G(d,p) level of theory thus ruling out packing forces as the origin of the bond-length differences. The five-membered chelate ring stemming from the aliphatic diol adopts an envelope conformation on the spiro center C1 (puckering parameters: Q_2 = 0.1274 (16) Å, φ_2 = 42.6 (7)° for the O1—C1—O2—C4—C3 ring).

Accordingly, the crystal packing is characterized by weak C—H···*X* interactions whose H···*X* distances are close to the sum of the van-der-Waals radii (vdWr). In terms of the vdWr criterion, the shortest tabulated hydrogen-bond, the C14—H14···O2 interaction, is 0.11 \&A shorter than the radii sum. The weak interactions in (I) are thus less significant than those in the related 1-(ylomethyl)cyclopentyl 1′,2′-phenylene orthocarbonate, where C—H···O bonds are observed at the radii sum minus 0.35 Å (Betz & Klüfers, 2007*c*). Fig. 2 shows this interaction as well as the shortest C—H···*π* bond which has one of the norbornane-bridgehead C—H functions as the donor. The other bridgehead methylidyne function acts as a donor in a still weaker bond. Moreover, another weak C—H···O bond may be recognized with a diol-CH function as the donor (see the hydrogen bond table).

S2. Experimental

The title compound was prepared based on a published procedure (Komatsu *et al.*, 1992) upon reaction of norbornane-*exo*-*cis*-2,3-diol with 2,2-dichlorobenzo[1.3]dioxol in dichloromethane in the presence of pyridine. Crystals suitable for X-ray analysis were obtained after recrystallization from boiling ethyl acetate.

S3. Refinement

All H atoms were positioned geometrically and refined using a riding model, with C—H distances of 0.95, 0.99 and 1.00 Å, and with U_{iso}(H) = 1.2U_{eq}(C) for all H atoms.

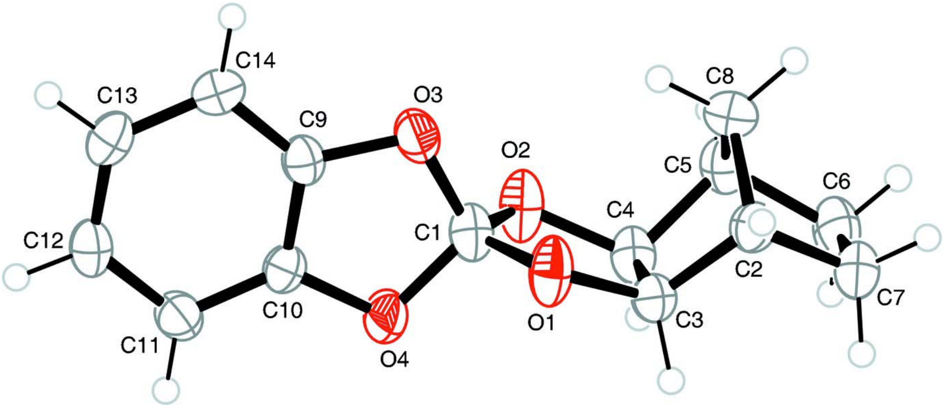

Figure 1

The molecular structure of the title compound, showing displacement ellipsoids drawn at the 50% probability level.

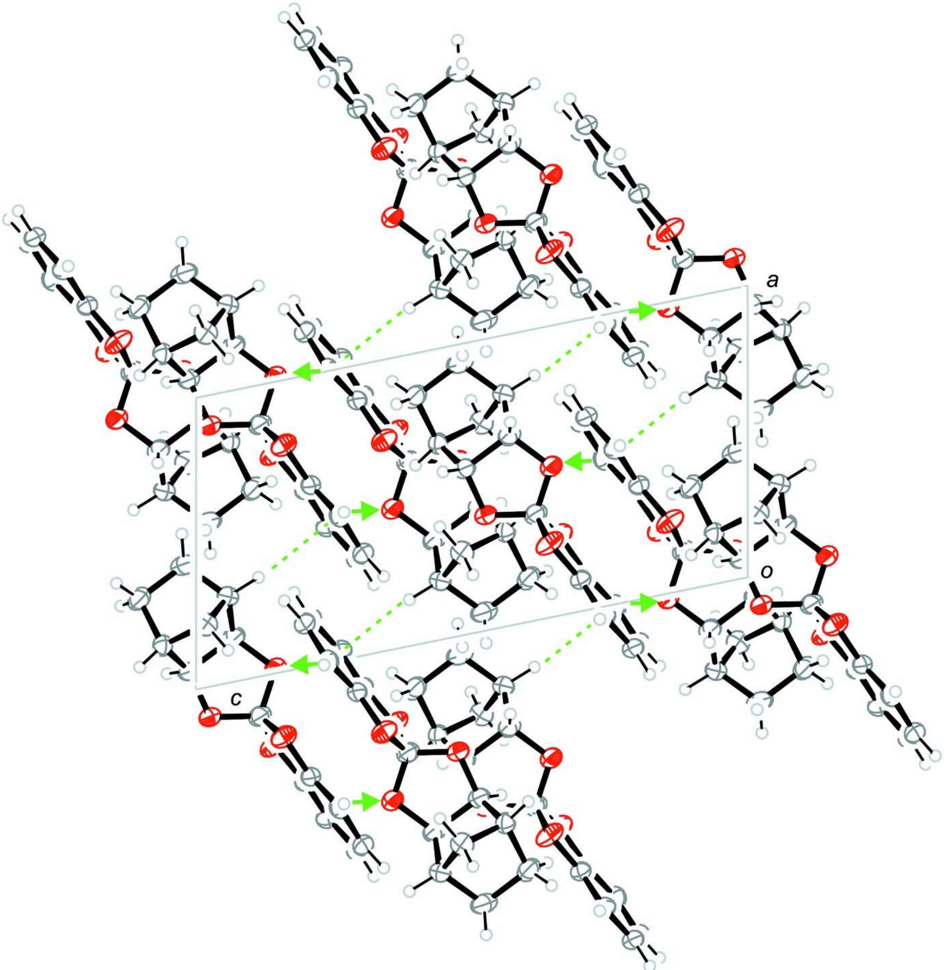

Figure 2

The crystal packing viewed along [0 1 0]. Green arrows: the strongest C—H···O interaction in terms of the H···O distance (C14—H14···O2). Green dotted lines: the strongest C—H···*π* interaction (C5—H5—*Cg*, *Cg* is the centroid of the phenylene residue).

4,7-methano-2,2′-spirobi[1,3-benzodioxole]

Crystal data

$C_{14}H_{14}O_4$
$M_r = 246.25$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 7.9125$ (3) Å
$b = 9.5545$ (5) Å
$c = 15.2813$ (6) Å
$\beta = 101.490$ (3)°
$V = 1132.11$ (9) Å^3
$Z = 4$

$F(000) = 520$
$D_x = 1.445$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 14429 reflections
$\theta = 2.7$–27.5°
$\mu = 0.11$ mm^{-1}
$T = 200$ K
Block, colourless
0.30 × 0.25 × 0.16 mm

Data collection

Nonius KappaCCD diffractometer
Radiation source: rotating anode
MONTEL, graded multilayered X-ray optics monochromator
CCD; rotation images; thick slices scans
8399 measured reflections

2582 independent reflections
1716 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.054$
$\theta_{\max} = 27.5°$, $\theta_{\min} = 3.2°$
$h = -9 \rightarrow 10$
$k = -12 \rightarrow 11$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.044$
$wR(F^2) = 0.119$
$S = 1.05$
2582 reflections
164 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
Only H-atom displacement parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0569P)^2 + 0.1349P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.21$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}

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 $F^2 > \sigma(F^2)$ 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}
O1	0.39573 (14)	0.24072 (14)	0.47478 (7)	0.0460 (3)
O2	0.51722 (14)	0.20489 (14)	0.35623 (7)	0.0463 (3)
O3	0.27667 (13)	0.34038 (12)	0.34119 (7)	0.0408 (3)
O4	0.25466 (14)	0.10405 (11)	0.35921 (8)	0.0441 (3)
C1	0.3646 (2)	0.22289 (18)	0.38424 (11)	0.0384 (4)

C2	0.67414 (19)	0.32183 (17)	0.56079 (10)	0.0333 (4)
H2	0.6161	0.3766	0.6022	0.0490 (13)*
C3	0.56971 (19)	0.20081 (17)	0.51341 (10)	0.0342 (4)
H3	0.5742	0.1165	0.5526	0.0490 (13)*
C4	0.65286 (19)	0.17354 (18)	0.43193 (10)	0.0368 (4)
H4	0.6964	0.0755	0.4305	0.0490 (13)*
C5	0.7973 (2)	0.28116 (18)	0.44257 (11)	0.0378 (4)
H5	0.8407	0.3025	0.3869	0.0490 (13)*
C6	0.9350 (2)	0.2320 (2)	0.52188 (12)	0.0458 (5)
H6A	1.0433	0.2857	0.5259	0.0490 (13)*
H6B	0.9600	0.1310	0.5171	0.0490 (13)*
C7	0.8509 (2)	0.26146 (19)	0.60315 (11)	0.0439 (4)
H7A	0.8387	0.1743	0.6364	0.0490 (13)*
H7B	0.9196	0.3298	0.6443	0.0490 (13)*
C8	0.7165 (2)	0.40464 (17)	0.48246 (10)	0.0384 (4)
H8A	0.6123	0.4412	0.4420	0.0490 (13)*
H8B	0.7995	0.4814	0.5018	0.0490 (13)*
C9	0.12113 (18)	0.29423 (16)	0.29208 (9)	0.0307 (4)
C10	0.10837 (18)	0.15188 (16)	0.30274 (9)	0.0307 (4)
C11	−0.03269 (19)	0.07732 (17)	0.26098 (10)	0.0365 (4)
H11	−0.0406	−0.0211	0.2681	0.0490 (13)*
C12	−0.16353 (19)	0.15365 (18)	0.20764 (10)	0.0367 (4)
H12	−0.2643	0.1064	0.1778	0.0490 (13)*
C13	−0.1506 (2)	0.29664 (18)	0.19700 (10)	0.0375 (4)
H13	−0.2426	0.3454	0.1600	0.0490 (13)*
C14	−0.0054 (2)	0.37112 (17)	0.23937 (10)	0.0350 (4)
H14	0.0049	0.4693	0.2320	0.0490 (13)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0254 (6)	0.0743 (9)	0.0367 (7)	0.0025 (5)	0.0027 (5)	−0.0082 (6)
O2	0.0296 (6)	0.0719 (9)	0.0354 (6)	0.0024 (6)	0.0016 (5)	−0.0142 (6)
O3	0.0331 (6)	0.0367 (7)	0.0486 (7)	−0.0050 (5)	−0.0018 (5)	−0.0036 (5)
O4	0.0333 (6)	0.0351 (7)	0.0556 (7)	0.0031 (5)	−0.0107 (5)	0.0028 (5)
C1	0.0293 (9)	0.0449 (10)	0.0388 (9)	0.0000 (7)	0.0014 (7)	−0.0057 (7)
C2	0.0337 (8)	0.0357 (9)	0.0301 (8)	0.0013 (7)	0.0053 (6)	−0.0024 (6)
C3	0.0283 (8)	0.0362 (9)	0.0369 (8)	−0.0013 (6)	0.0034 (6)	0.0023 (7)
C4	0.0305 (8)	0.0389 (9)	0.0389 (9)	0.0032 (7)	0.0016 (6)	−0.0092 (7)
C5	0.0297 (8)	0.0489 (10)	0.0358 (9)	−0.0022 (7)	0.0089 (6)	−0.0042 (7)
C6	0.0283 (9)	0.0509 (11)	0.0552 (11)	0.0031 (7)	0.0015 (7)	−0.0084 (8)
C7	0.0365 (9)	0.0506 (11)	0.0401 (10)	−0.0041 (8)	−0.0031 (7)	0.0004 (8)
C8	0.0419 (9)	0.0320 (9)	0.0419 (9)	−0.0018 (7)	0.0096 (7)	0.0023 (7)
C9	0.0267 (8)	0.0362 (9)	0.0293 (8)	−0.0017 (6)	0.0059 (6)	−0.0036 (6)
C10	0.0261 (8)	0.0336 (9)	0.0315 (8)	0.0037 (6)	0.0033 (6)	0.0010 (6)
C11	0.0320 (8)	0.0335 (9)	0.0432 (9)	−0.0027 (7)	0.0057 (6)	−0.0007 (7)
C12	0.0261 (8)	0.0478 (11)	0.0351 (8)	−0.0012 (7)	0.0030 (6)	−0.0050 (7)
C13	0.0318 (8)	0.0468 (11)	0.0326 (8)	0.0083 (7)	0.0035 (6)	0.0031 (7)

C14	0.0388 (9)	0.0328 (9)	0.0346 (8)	0.0043 (7)	0.0102 (7)	0.0046 (7)

Geometric parameters (Å, º)

O1—C1	1.367 (2)	C5—H5	1.0000
O1—C3	1.438 (2)	C6—C7	1.547 (3)
O2—C1	1.370 (2)	C6—H6A	0.9900
O2—C4	1.444 (2)	C6—H6B	0.9900
O3—C9	1.380 (2)	C7—H7A	0.9900
O3—C1	1.412 (2)	C7—H7B	0.9900
O4—C10	1.377 (2)	C8—H8A	0.9900
O4—C1	1.435 (2)	C8—H8B	0.9900
C2—C3	1.518 (2)	C9—C14	1.367 (2)
C2—C8	1.527 (2)	C9—C10	1.376 (2)
C2—C7	1.532 (2)	C10—C11	1.370 (2)
C2—H2	1.0000	C11—C12	1.390 (2)
C3—C4	1.542 (2)	C11—H11	0.9500
C3—H3	1.0000	C12—C13	1.382 (2)
C4—C5	1.522 (2)	C12—H12	0.9500
C4—H4	1.0000	C13—C14	1.396 (2)
C5—C8	1.526 (2)	C13—H13	0.9500
C5—C6	1.533 (2)	C14—H14	0.9500

C1—O1—C3	110.32 (12)	C5—C6—H6A	111.1
C1—O2—C4	109.66 (12)	C7—C6—H6A	111.1
C9—O3—C1	107.62 (12)	C5—C6—H6B	111.1
C10—O4—C1	107.09 (12)	C7—C6—H6B	111.1
O1—C1—O2	109.88 (12)	H6A—C6—H6B	109.1
O1—C1—O3	110.18 (13)	C2—C7—C6	103.41 (13)
O2—C1—O3	109.73 (14)	C2—C7—H7A	111.1
O1—C1—O4	110.22 (14)	C6—C7—H7A	111.1
O2—C1—O4	110.04 (13)	C2—C7—H7B	111.1
O3—C1—O4	106.75 (11)	C6—C7—H7B	111.1
C3—C2—C8	101.79 (12)	H7A—C7—H7B	109.0
C3—C2—C7	106.20 (13)	C5—C8—C2	95.02 (13)
C8—C2—C7	101.65 (13)	C5—C8—H8A	112.7
C3—C2—H2	115.2	C2—C8—H8A	112.7
C8—C2—H2	115.2	C5—C8—H8B	112.7
C7—C2—H2	115.2	C2—C8—H8B	112.7
O1—C3—C2	112.31 (13)	H8A—C8—H8B	110.2
O1—C3—C4	103.94 (12)	C14—C9—C10	122.58 (14)
C2—C3—C4	103.56 (12)	C14—C9—O3	128.15 (15)
O1—C3—H3	112.1	C10—C9—O3	109.27 (13)
C2—C3—H3	112.1	C11—C10—C9	122.08 (14)
C4—C3—H3	112.1	C11—C10—O4	128.66 (14)
O2—C4—C5	111.59 (13)	C9—C10—O4	109.27 (12)
O2—C4—C3	104.08 (12)	C10—C11—C12	116.29 (15)
C5—C4—C3	103.40 (12)	C10—C11—H11	121.9

O2—C4—H4	112.4	C12—C11—H11	121.9
C5—C4—H4	112.4	C13—C12—C11	121.58 (14)
C3—C4—H4	112.4	C13—C12—H12	119.2
C4—C5—C8	101.52 (13)	C11—C12—H12	119.2
C4—C5—C6	106.13 (14)	C12—C13—C14	121.51 (14)
C8—C5—C6	102.10 (13)	C12—C13—H13	119.2
C4—C5—H5	115.1	C14—C13—H13	119.2
C8—C5—H5	115.1	C9—C14—C13	115.96 (15)
C6—C5—H5	115.1	C9—C14—H14	122.0
C5—C6—C7	103.11 (13)	C13—C14—H14	122.0

C3—O1—C1—O2	−14.26 (19)	O2—C4—C5—C6	−177.46 (13)
C3—O1—C1—O3	−135.27 (13)	C3—C4—C5—C6	71.25 (15)
C3—O1—C1—O4	107.18 (14)	C4—C5—C6—C7	−72.05 (16)
C4—O2—C1—O1	15.22 (19)	C8—C5—C6—C7	33.89 (17)
C4—O2—C1—O3	136.51 (13)	C3—C2—C7—C6	70.90 (16)
C4—O2—C1—O4	−106.32 (14)	C8—C2—C7—C6	−35.19 (16)
C9—O3—C1—O1	−119.98 (13)	C5—C6—C7—C2	0.83 (17)
C9—O3—C1—O2	118.91 (13)	C4—C5—C8—C2	54.90 (14)
C9—O3—C1—O4	−0.31 (16)	C6—C5—C8—C2	−54.59 (14)
C10—O4—C1—O1	120.17 (13)	C3—C2—C8—C5	−54.54 (14)
C10—O4—C1—O2	−118.49 (14)	C7—C2—C8—C5	54.98 (14)
C10—O4—C1—O3	0.52 (17)	C1—O3—C9—C14	−179.57 (15)
C1—O1—C3—C2	118.72 (15)	C1—O3—C9—C10	−0.02 (16)
C1—O1—C3—C4	7.43 (17)	C14—C9—C10—C11	0.0 (2)
C8—C2—C3—O1	−77.54 (15)	O3—C9—C10—C11	−179.53 (14)
C7—C2—C3—O1	176.46 (13)	C14—C9—C10—O4	179.94 (14)
C8—C2—C3—C4	33.98 (15)	O3—C9—C10—O4	0.36 (17)
C7—C2—C3—C4	−72.02 (14)	C1—O4—C10—C11	179.34 (16)
C1—O2—C4—C5	−120.76 (14)	C1—O4—C10—C9	−0.54 (17)
C1—O2—C4—C3	−9.90 (17)	C9—C10—C11—C12	−0.6 (2)
O1—C3—C4—O2	1.48 (16)	O4—C10—C11—C12	179.57 (14)
C2—C3—C4—O2	−116.04 (13)	C10—C11—C12—C13	0.5 (2)
O1—C3—C4—C5	118.21 (13)	C11—C12—C13—C14	0.0 (2)
C2—C3—C4—C5	0.68 (15)	C10—C9—C14—C13	0.5 (2)
O2—C4—C5—C8	76.19 (15)	O3—C9—C14—C13	179.99 (14)
C3—C4—C5—C8	−35.11 (15)	C12—C13—C14—C9	−0.5 (2)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3···O4$^{\mathrm{i}}$	1.00	2.71	3.623 (2)	151
C7—H7*A*···O4$^{\mathrm{i}}$	0.99	2.76	3.663 (2)	151
C14—H14···O2$^{\mathrm{ii}}$	0.95	2.61	3.501 (2)	156
C14—H14···O4$^{\mathrm{ii}}$	0.95	2.88	3.514 (2)	125

C2—H2···Cg^{iii}	1.00	2.86	3.563 (2)	128
C5—H5···Cg^{iv}	1.00	2.66	3.568 (2)	152

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