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Crystal structure of *cis-anti-cis*-dicyclohexane-18-crown-6 acetonitrile disolvate

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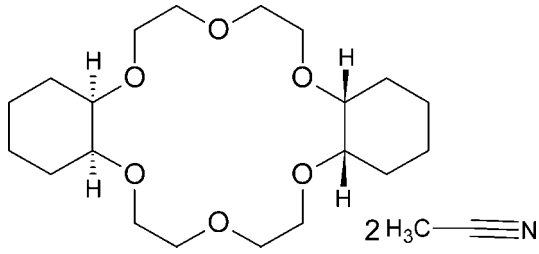
The title compound (systematic name: *cis-anti-cis*-2,5,8,15,18,21-hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane acetonitrile disolvate), $C_{20}H_{36}O_6\cdot 2CH_3CN$, crystallizes from an acetonitrile solution of dicyclohexane-18-crown-6 on evaporation. The molecule is arranged around a center of symmetry with half the crown ether molecule and one molecule of acetonitrile symmetry independent. All O—C—C—O torsion angles are *gauche* while all C—O—C—C angles are *trans*. The sequence of torsion angles is $[(tg^+t)(tg^-t)]_3$; the geometry of oxygen atoms is close to pseudo-D_{3d} with three atoms below and three atoms above the mean plane, with an average deviation of ±0.16 (1) Å from the mean plane. This geometry is identical to that observed in metal ion complexes of dicyclohexane-18-crown-6 but differs significantly from the conformation of a free unsolvated molecule. Each acetonitrile molecule connects to a crown ether molecule *via* two of its methyl group H atoms (C—H···O). Weaker interactions exist between the third H atom of the acetonitrile methyl group and an O atom of a neighbouring crown ether molecule (C—H···O); and between the N atom of the acetonitrile molecule and a H atom of another neighbouring crown ether molecule. All these intermolecular interactions create a three-dimensional network stabilizing the disolvate.

Keywords: crystal structure; dicyclohexane-18-crown-6; crown ether; acetonitrile; hydrogen bonding.

CCDC reference: 1405283

1. Related literature

The crystal structure of the *cis-anti-cis* isomer of dicyclohexane-18-crown-6 was reported by Dalley *et al.* (1975) (no atomic coordinates given), and later re-investigated by Nazarenko (2002). For the orthorhombic polymorph, see: Kravtsov *et al.* (2002). Synthesis and crystal structures of solvates of dicyclohexane-18-crown-6 with dinitriles have been investigated; see: structures with malononitrile by Damewood *et al.* (1988) and with succinonitrile by Dalley & Nazarenko (1999). The importance of the different behavior of isomers of dicyclohexane-18-crown-6 was first stressed by Pedersen (1967) and later studied in complexation, extraction, and transport reactions.



2. Experimental

2.1. Crystal data

$C_{20}H_{36}O_6\cdot 2C_2H_3N$
M_r = 454.59
Triclinic, $P\overline{1}$
a = 6.9428 (4) Å
b = 9.5286 (5) Å
c = 9.8927 (6) Å
α = 80.415 (2)°
β = 81.697 (2)°
γ = 80.927 (2)°
V = 632.53 (6) Å^3
Z = 1
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 173 K
0.49 × 0.34 × 0.28 mm

2.2. Data collection

Bruker PHOTON-100 CMOS diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
T_{min} = 0.956, T_{max} = 1.000
20203 measured reflections
3045 independent reflections
2476 reflections with $I > 2\sigma(I)$
R_{int} = 0.031

2.3. Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.104
S = 1.07
3045 reflections
229 parameters
All H-atom parameters refined
$\Delta\rho_{max}$ = 0.29 e Å^{-3}
$\Delta\rho_{min}$ = −0.19 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C11—H11A···O3^{i}	0.936 (19)	2.51 (2)	3.3528 (17)	150.8 (16)
C11—H11C···O1^{i}	0.97 (2)	2.56 (2)	3.4809 (16)	159.1 (15)

Symmetry code: (i) $-x+1, -y+1, -z+1$.

Data collection: *APEX2* (Bruker, 2013); cell refinement: *SAINT* (Bruker, 2013); data reduction: *SAINT*; program(s) used to solve structure: *SHELXT* (Sheldrick, 2015*a*); program(s) used to refine structure: *SHELXL2014* (Sheldrick, 2015*b*); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *OLEX2*.

Acknowledgements

Financial support from the State University of New York for acquisition of the X-ray diffractometer is gratefully acknowledged.

Supporting information for this paper is available from the IUCr electronic archives (Reference: ZL2627).

References

Bruker (2013). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2014). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Dalley, N. K., Lamb, J. D. & Nazarenko, A. Y. (1999). *J. Inclusion Phenom. Macrocycl. Chem.* **33**, 331–338.
Dalley, N. K., Smith, J. S., Larson, S. B., Christensen, J. J. & Izatt, R. M. (1975). *Chem. Commun.*, pp. 43–44.
Damewood, J. R., Urban, J. J., Williamson, T. C. & Rheingold, A. (1988). *J. Org. Chem.* **53**, 167–171.
Dolomanov, O. V., Bourhis, L. J., Gildea, R. J., Howard, J. A. K. & Puschmann, H. (2009). *J. Appl. Cryst.* **42**, 339–341.
Kravtsov, V. Ch., Fonari, M. S., Zaworotko, M. J. & Lipkowski, J. (2002). *Acta Cryst.* C**58**, o683–o684.
Nazarenko, A. Y. (2002). Private communication (refcode DCHXCS01). CCDC, Cambridge, England.
Pedersen, C. J. (1967). *J. Am. Chem. Soc.* **89**, 7017–7036.
Sheldrick, G. M. (2015*a*). *Acta Cryst.* A**71**, 3–8.
Sheldrick, G. M. (2015*b*). *Acta Cryst.* C**71**, 3–8.

supporting information

Acta Cryst. (2015). E**71**, o472–o473 [doi:10.1107/S2056989015011056]

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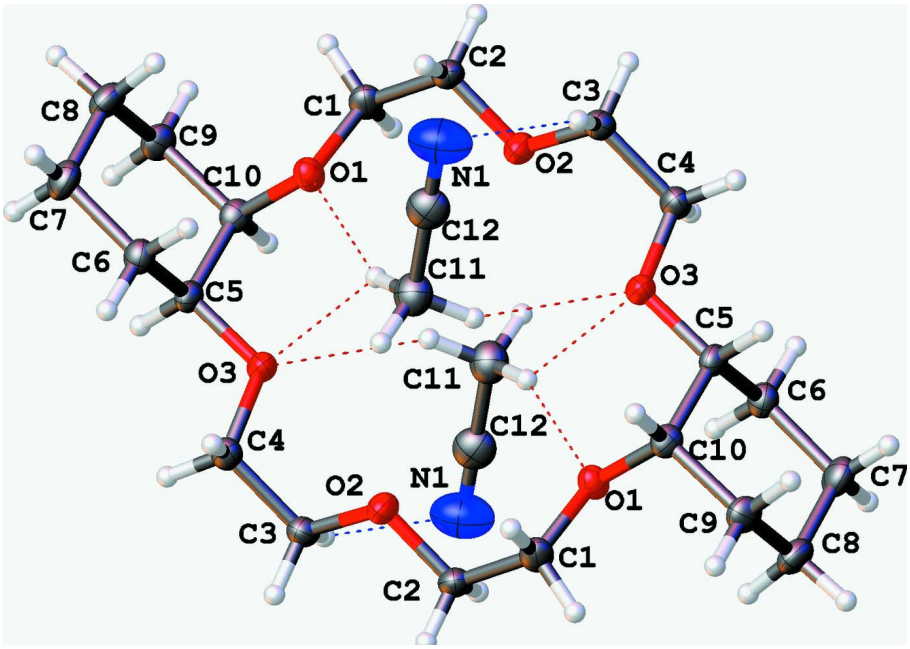

Figure 1

Structure of the title compound with atom labeling. The second half of the crown ether molecule and the second acetonitrile molecule molecule are created by an inversion center located at the center of the crown ether molecule (symmetry operator: 1 - *x*, 1 - y, 1 - *z*).

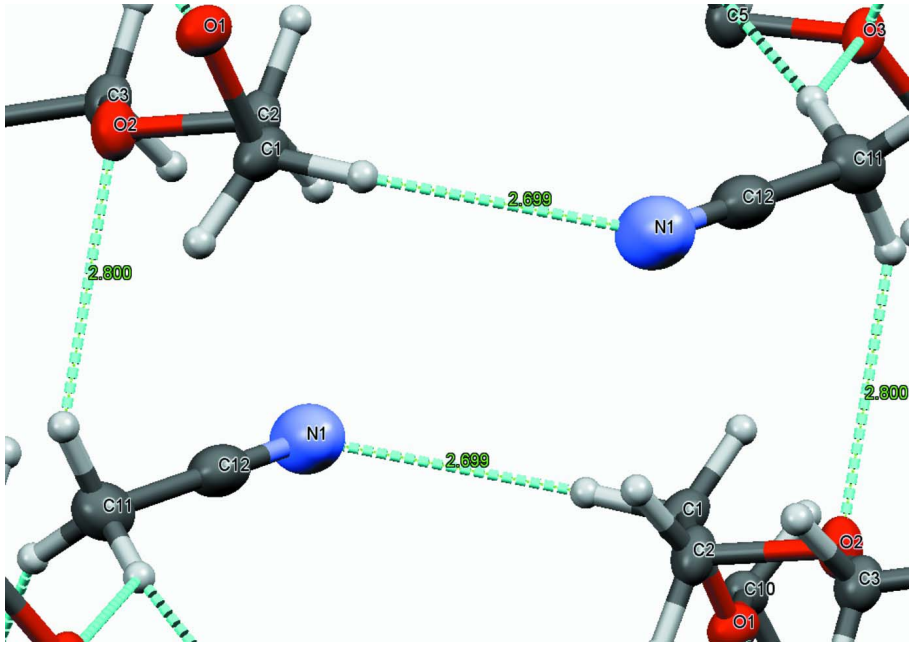

Figure 2

Intermolecular short contacts of acetonitrile molecules with neighboring crown ether molecules.

cis-anti-cis-2,5,8,15,18,21-Hexaoxatricyclo[20.4.0.0^{9,14}]hexacosane acetonitrile disolvate

Crystal data

$C_{20}H_{36}O_6 \cdot 2C_2H_3N$
$M_r = 454.59$
Triclinic, $P\overline{1}$
$a = 6.9428$ (4) Å
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$c = 9.8927$ (6) Å
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$\beta = 81.697$ (2)°
$\gamma = 80.927$ (2)°
$V = 632.53$ (6) Å^3
$Z = 1$
$F(000) = 248$
$D_x = 1.193$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 9918 reflections
$\theta = 3.0$–$33.2°$
$\mu = 0.09$ mm^{-1}
$T = 173$ K
Block, colourless
0.49 × 0.34 × 0.28 mm

Data collection

Bruker PHOTON-100 CMOS diffractometer
Detector resolution: 10 pixels mm^{-1}
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2014)
$T_{min} = 0.956$, $T_{max} = 1.000$
20203 measured reflections
3045 independent reflections
2476 reflections with $I > 2\sigma(I)$
$R_{int} = 0.031$
$\theta_{max} = 28.0°$, $\theta_{min} = 3.0°$
$h = -9 \rightarrow 9$
$k = -12 \rightarrow 12$
$l = -13 \rightarrow 13$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.104$
$S = 1.07$
3045 reflections
229 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Hydrogen site location: difference Fourier map
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0454P)^2 + 0.1761P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.29$ e Å^{-3}
$\Delta\rho_{min} = -0.19$ e Å^{-3}

Special details

Experimental. SADABS-2014/5 (Bruker, 2014) was used for absorption correction. wR2(int) was 0.0615 before and 0.0513 after correction. The Ratio of minimum to maximum transmission is 0.9562. The $\lambda/2$ correction factor is 0.00150.

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.

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

	x	*y*	*z*	U_{iso}*/U_{eq}
O3	0.32768 (12)	0.49496 (8)	0.76820 (8)	0.0246 (2)
O1	0.47462 (11)	0.27282 (8)	0.32574 (8)	0.02307 (19)
O2	0.24108 (12)	0.30700 (8)	0.59392 (8)	0.0258 (2)
C10	0.50905 (17)	0.66821 (12)	0.81733 (11)	0.0222 (2)
C5	0.31527 (17)	0.60704 (12)	0.84980 (11)	0.0217 (2)
C2	0.28223 (19)	0.18001 (13)	0.53071 (12)	0.0265 (3)
C1	0.29308 (18)	0.22030 (14)	0.37680 (13)	0.0275 (3)
C4	0.16935 (18)	0.41295 (13)	0.80064 (13)	0.0259 (3)
C3	0.22641 (18)	0.27499 (12)	0.73991 (12)	0.0244 (3)
C6	0.14216 (17)	0.72519 (13)	0.82817 (13)	0.0245 (2)
C9	0.50976 (19)	0.78031 (13)	0.91167 (13)	0.0278 (3)
C8	0.3383 (2)	0.90062 (13)	0.89292 (14)	0.0312 (3)
C7	0.1431 (2)	0.84186 (14)	0.91736 (14)	0.0319 (3)
C12	0.25068 (19)	0.76690 (15)	0.34942 (15)	0.0356 (3)
N1	0.2335 (2)	0.87640 (16)	0.28169 (17)	0.0589 (4)
C11	0.2721 (2)	0.62716 (15)	0.43442 (15)	0.0346 (3)
H5	0.3067 (19)	0.5644 (13)	0.9475 (14)	0.021 (3)*
H6A	0.1510 (18)	0.7665 (14)	0.7324 (14)	0.022 (3)*
H8A	0.357 (2)	0.9525 (15)	0.7989 (16)	0.032 (4)*
H1A	0.183 (2)	0.2961 (15)	0.3529 (14)	0.031 (4)*
H2A	0.408 (2)	0.1246 (15)	0.5572 (15)	0.032 (4)*
H10	0.618 (2)	0.5904 (14)	0.8319 (13)	0.024 (3)*
H3A	0.356 (2)	0.2254 (14)	0.7689 (13)	0.023 (3)*
H9A	0.499 (2)	0.7318 (15)	1.0061 (16)	0.032 (4)*
H2B	0.179 (2)	0.1217 (15)	0.5635 (14)	0.029 (3)*
H4A	0.140 (2)	0.3869 (15)	0.9035 (16)	0.031 (4)*
H3B	0.124 (2)	0.2113 (14)	0.7749 (14)	0.026 (3)*
H6B	0.015 (2)	0.6841 (15)	0.8527 (14)	0.028 (3)*
H9B	0.636 (2)	0.8182 (15)	0.8941 (15)	0.032 (4)*
H7A	0.121 (2)	0.8002 (16)	1.0119 (17)	0.035 (4)*
H1B	0.281 (2)	0.1362 (17)	0.3363 (15)	0.036 (4)*
H8B	0.337 (2)	0.9694 (16)	0.9556 (16)	0.038 (4)*
H4B	0.053 (2)	0.4659 (16)	0.7635 (15)	0.033 (4)*

H7B	0.034 (2)	0.9160 (17)	0.9006 (16)	0.040 (4)*
H11A	0.360 (3)	0.5628 (19)	0.3858 (19)	0.055 (5)*
H11B	0.147 (3)	0.5936 (19)	0.4572 (19)	0.057 (5)*
H11C	0.326 (3)	0.635 (2)	0.517 (2)	0.069 (6)*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O3	0.0272 (4)	0.0223 (4)	0.0253 (4)	−0.0080 (3)	0.0043 (3)	−0.0085 (3)
O1	0.0231 (4)	0.0282 (4)	0.0189 (4)	−0.0070 (3)	−0.0018 (3)	−0.0040 (3)
O2	0.0344 (5)	0.0210 (4)	0.0222 (4)	−0.0053 (3)	0.0006 (3)	−0.0055 (3)
C10	0.0249 (6)	0.0223 (5)	0.0196 (5)	−0.0013 (4)	−0.0055 (4)	−0.0028 (4)
C5	0.0283 (6)	0.0208 (5)	0.0163 (5)	−0.0032 (4)	−0.0013 (4)	−0.0047 (4)
C2	0.0308 (6)	0.0222 (6)	0.0276 (6)	−0.0095 (5)	0.0034 (5)	−0.0072 (5)
C1	0.0263 (6)	0.0324 (6)	0.0273 (6)	−0.0117 (5)	−0.0003 (5)	−0.0099 (5)
C4	0.0262 (6)	0.0266 (6)	0.0257 (6)	−0.0081 (5)	0.0030 (5)	−0.0072 (5)
C3	0.0286 (6)	0.0229 (6)	0.0222 (6)	−0.0086 (5)	0.0009 (5)	−0.0034 (4)
C6	0.0241 (6)	0.0259 (6)	0.0237 (6)	−0.0022 (4)	−0.0010 (4)	−0.0065 (5)
C9	0.0335 (7)	0.0308 (6)	0.0221 (6)	−0.0079 (5)	−0.0054 (5)	−0.0078 (5)
C8	0.0408 (7)	0.0249 (6)	0.0303 (7)	−0.0046 (5)	−0.0029 (5)	−0.0119 (5)
C7	0.0329 (7)	0.0292 (6)	0.0335 (7)	0.0011 (5)	0.0009 (5)	−0.0137 (5)
C12	0.0277 (7)	0.0402 (8)	0.0411 (8)	−0.0068 (5)	−0.0073 (5)	−0.0080 (6)
N1	0.0539 (9)	0.0474 (8)	0.0755 (11)	−0.0121 (7)	−0.0197 (7)	0.0062 (7)
C11	0.0317 (7)	0.0371 (7)	0.0340 (7)	−0.0009 (6)	−0.0032 (6)	−0.0063 (6)

Geometric parameters (Å, º)

O3—C5	1.4274 (13)	C4—H4B	0.969 (15)
O3—C4	1.4169 (14)	C3—H3A	1.005 (13)
O1—C10^{i}	1.4285 (13)	C3—H3B	0.993 (14)
O1—C1	1.4230 (14)	C6—C7	1.5313 (16)
O2—C2	1.4241 (13)	C6—H6A	0.961 (13)
O2—C3	1.4177 (14)	C6—H6B	1.006 (14)
C10—O1^{i}	1.4285 (13)	C9—C8	1.5256 (18)
C10—C5	1.5210 (16)	C9—H9A	0.969 (15)
C10—C9	1.5319 (16)	C9—H9B	0.983 (15)
C10—H10	0.982 (13)	C8—C7	1.5196 (19)
C5—C6	1.5248 (16)	C8—H8A	0.980 (15)
C5—H5	0.981 (13)	C8—H8B	0.972 (16)
C2—C1	1.5009 (17)	C7—H7A	0.953 (16)
C2—H2A	0.994 (15)	C7—H7B	0.964 (16)
C2—H2B	0.964 (15)	C12—N1	1.1414 (19)
C1—H1A	0.992 (15)	C12—C11	1.450 (2)
C1—H1B	0.974 (16)	C11—H11A	0.934 (19)
C4—C3	1.5086 (16)	C11—H11B	0.959 (19)
C4—H4A	1.005 (15)	C11—H11C	0.97 (2)
C4—O3—C5	114.40 (8)	O2—C3—H3B	110.1 (8)

C1—O1—C10^{i}	114.05 (8)	C4—C3—H3A	109.8 (7)
C3—O2—C2	111.74 (9)	C4—C3—H3B	108.8 (8)
O1^{i}—C10—C5	106.49 (9)	H3A—C3—H3B	109.1 (10)
O1^{i}—C10—C9	112.88 (9)	C5—C6—C7	110.51 (10)
O1^{i}—C10—H10	108.5 (8)	C5—C6—H6A	109.1 (8)
C5—C10—C9	109.33 (9)	C5—C6—H6B	110.4 (8)
C5—C10—H10	109.5 (8)	C7—C6—H6A	109.7 (8)
C9—C10—H10	110.0 (8)	C7—C6—H6B	109.2 (8)
O3—C5—C10	107.36 (9)	H6A—C6—H6B	107.8 (11)
O3—C5—C6	114.17 (9)	C10—C9—H9A	107.7 (8)
O3—C5—H5	108.6 (7)	C10—C9—H9B	110.2 (8)
C10—C5—C6	110.98 (9)	C8—C9—C10	110.82 (10)
C10—C5—H5	106.1 (8)	C8—C9—H9A	110.1 (9)
C6—C5—H5	109.4 (7)	C8—C9—H9B	111.4 (8)
O2—C2—C1	109.38 (10)	H9A—C9—H9B	106.6 (12)
O2—C2—H2A	109.3 (8)	C9—C8—H8A	108.6 (8)
O2—C2—H2B	109.0 (8)	C9—C8—H8B	110.4 (9)
C1—C2—H2A	110.7 (8)	C7—C8—C9	111.38 (11)
C1—C2—H2B	109.7 (8)	C7—C8—H8A	109.9 (8)
H2A—C2—H2B	108.7 (11)	C7—C8—H8B	109.5 (9)
O1—C1—C2	109.04 (10)	H8A—C8—H8B	107.0 (12)
O1—C1—H1A	109.4 (8)	C6—C7—H7A	108.0 (9)
O1—C1—H1B	111.4 (9)	C6—C7—H7B	108.9 (9)
C2—C1—H1A	110.0 (8)	C8—C7—C6	111.85 (10)
C2—C1—H1B	108.9 (9)	C8—C7—H7A	108.5 (9)
H1A—C1—H1B	108.1 (12)	C8—C7—H7B	112.3 (9)
O3—C4—C3	109.11 (9)	H7A—C7—H7B	106.9 (13)
O3—C4—H4A	110.3 (8)	N1—C12—C11	179.47 (16)
O3—C4—H4B	110.7 (9)	C12—C11—H11A	109.2 (11)
C3—C4—H4A	107.7 (8)	C12—C11—H11B	109.6 (11)
C3—C4—H4B	109.4 (9)	C12—C11—H11C	108.9 (12)
H4A—C4—H4B	109.6 (12)	H11A—C11—H11B	109.9 (15)
O2—C3—C4	109.08 (9)	H11A—C11—H11C	108.5 (17)
O2—C3—H3A	110.0 (7)	H11B—C11—H11C	110.8 (16)

O3—C5—C6—C7	−178.84 (9)	C5—C10—C9—C8	−58.39 (13)
O3—C4—C3—O2	−68.55 (12)	C5—C6—C7—C8	54.14 (14)
O1^{i}—C10—C5—O3	62.59 (10)	C2—O2—C3—C4	−176.21 (10)
O1^{i}—C10—C5—C6	−62.81 (11)	C4—O3—C5—C10	171.48 (9)
O1^{i}—C10—C9—C8	59.93 (13)	C4—O3—C5—C6	−65.05 (12)
O2—C2—C1—O1	75.52 (12)	C3—O2—C2—C1	179.16 (10)
C10^{i}—O1—C1—C2	−172.39 (9)	C9—C10—C5—O3	−175.17 (9)
C10—C5—C6—C7	−57.34 (13)	C9—C10—C5—C6	59.43 (12)
C10—C9—C8—C7	55.90 (14)	C9—C8—C7—C6	−53.72 (15)
C5—O3—C4—C3	−163.53 (9)		

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C11—H11*A*···O3^{i}	0.936 (19)	2.51 (2)	3.3528 (17)	150.8 (16)
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