organic compounds

6,10,16,19-Tetraoxatrispiro[4.2.2.4.2.2]-nonadecane

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The asymmetric unit of the title compound, $C_{15}H_{24}O_4$, contains one half-molecule; a twofold rotation axis passes through the central C atom. The non-planar six- and five-membered rings adopt chair and envelope conformations, respectively. In the crystal structure, intermolecular C—H···O hydrogen bonds link the molecules.

Related literature

For general background, see: Jermy & Pandurangan (2005). For related literature, see: Sun *et al.* (2001). For ring conformation puckering parameters, see: Cremer & Pople (1975). For bond-length data, see: Allen *et al.* (1987).
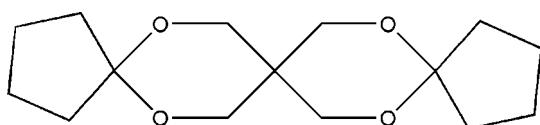
Experimental

Crystal data

$C_{15}H_{24}O_4$
$M_r = 268.34$
Monoclinic, $C2/c$
$a = 25.605$ (5) Å
$b = 5.5820$ (11) Å

$c = 10.337$ (2) Å
$\beta = 90.22$ (3)°
$V = 1477.4$ (5) Å^3
$Z = 4$
Mo $K\alpha$ radiation

$\mu = 0.09$ mm^{-1}
$T = 294$ (2) K

$0.30 \times 0.20 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{min} = 0.965$, $T_{max} = 0.982$
1547 measured reflections

1457 independent reflections
864 reflections with $I > 2\sigma(I)$
$R_{int} = 0.050$
3 standard reflections
frequency: 120 min
intensity decay: none

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.067$
$wR(F^2) = 0.173$
$S = 0.93$
1457 reflections

87 parameters
H-atom parameters constrained
$\Delta\rho_{max} = 0.26$ e Å^{-3}
$\Delta\rho_{min} = -0.21$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C6—H6B···O2^i	0.97	2.58	3.413 (4)	143

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

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *XCAD4* (Harms & Wocadlo, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *PLATON* (Spek, 2003).

References

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supplementary materials

6,10,16,19-Tetraoxatrispiro[4.2.2.4.2.2]nonadecane

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Comment

The title compound, (I), is an important intermediate in the synthesis of pesticides (Jermy & Pandurangan, 2005). The crystal structure determination of (I) has been carried out in order to elucidate the molecular conformation.

The asymmetric unit of the title compound, (I), contains one-half molecule (Fig. 1), in which the bond lengths are within normal ranges (Allen *et al.*, 1987).

Ring B (O1/O2/C5—C8) is not planar, having total puckering amplitude, Q_T, of 0.943 (3) Å. It adopts chair conformation [$\varphi = -32.96$ (2)° and $\theta = 58.52$ (3)°] (Cremer & Pople, 1975). Ring A has envelope conformation with atom C1 displaced by -0.222 (3) Å from the plane of the other ring atoms.

In the crystal structure, intermolecular C—H⋯O hydrogen bonds (Table 1) link the molecules, in which they may be effective in the stabilization of the structure.

Experimental

The title compound was prepared from a mixture of 2,2-bis-(hydroxymethyl) propane-1,3-diol (0.68 g, 5 mmol), cyclo-pentanone (10 mmol), freshly activated catalyst TiO2/SO4(2-)(0.6 g, 0.32 mmol) and cyclohexane (80 ml), heated with stirring at refluxing temperature for 2 h, using a Dean-Stark apparatus in a nitrogen atmosphere (Sun *et al.*, 2001). The progress of the reaction was monitored by thin-layer chromatography. After cooling to room temperature, the catalyst was filtered off, the crude product was isolated by distillation and the solid was recrystallized from ethanol. Crystals of (I) were obtained by dissolving the title compound (1.0 g) in toluene (15 ml) and evaporating the solvent slowly at room temperature for about 7 d.

Refinement

H atoms were positioned geometrically, with C—H = 0.97 Å for methylene H, and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$.

supplementary materials

Figures
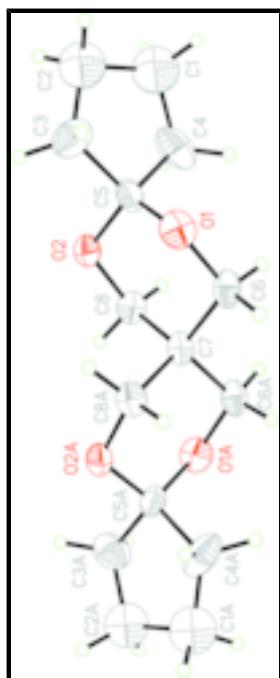
Fig. 1. The molecular structure of the title molecule, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (A) $1 - x, y, 1/2 - z$.]
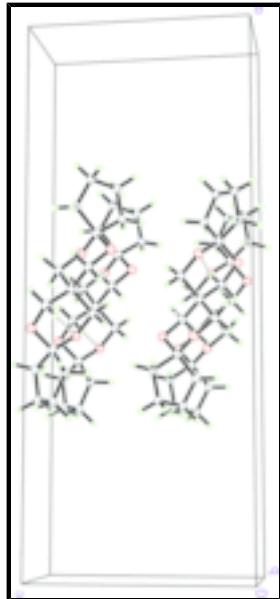
Fig. 2. A packing diagram of (I). Hydrogen bonds are shown as dashed lines.

6,10,16,19-Tetraoxatrispiro[4.2.2.4.2.2]nonadecane

Crystal data

$C_{15}H_{24}O_4$	$F_{000} = 584$
$M_r = 268.34$	$D_x = 1.206$ Mg m^{-3}
Monoclinic, $C2/c$	Melting point: 401 K
Hall symbol: -C 2yc	Mo $K\alpha$ radiation

$a = 25.605\ (5)$ Å

$b = 5.5820\ (11)$ Å

$c = 10.337\ (2)$ Å

$\beta = 90.22\ (3)°$

$V = 1477.4\ (5)$ Å^3

$Z = 4$

$\lambda = 0.71073$ Å

Cell parameters from 25 reflections

$\theta = 10–13°$

$\mu = 0.09$ mm^{-1}

$T = 294\ (2)$ K

Block, colorless

$0.30 \times 0.20 \times 0.10$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$R_{int} = 0.050$
Radiation source: fine-focus sealed tube	$\theta_{max} = 26.0°$
Monochromator: graphite	$\theta_{min} = 1.6°$
$T = 294(2)$ K	$h = -31 \rightarrow 31$
$\omega/2\theta$ scans	$k = 0 \rightarrow 6$
Absorption correction: ψ scan (North *et al.*, 1968)	$l = 0 \rightarrow 12$
$T_{min} = 0.965$, $T_{max} = 0.982$	3 standard reflections
1547 measured reflections	every 120 min
1457 independent reflections	intensity decay: none
864 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.067$	H-atom parameters constrained
$wR(F^2) = 0.173$	$w = 1/[\sigma^2(F_o^2) + (0.06P)^2 + 4.5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.93$	$(\Delta/\sigma)_{max} < 0.001$
1457 reflections	$\Delta\rho_{max} = 0.26$ e Å^{-3}
87 parameters	$\Delta\rho_{min} = -0.21$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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 > 2sigma(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	0.43380 (7)	0.3857 (4)	0.41870 (16)	0.0381 (5)
O2	0.42692 (7)	0.0861 (3)	0.26166 (16)	0.0324 (5)
C1	0.30826 (17)	0.3438 (9)	0.3294 (5)	0.0889 (15)
H1A	0.2819	0.3125	0.2638	0.107*
H1B	0.2974	0.4816	0.3797	0.107*
C2	0.31481 (15)	0.1237 (9)	0.4179 (4)	0.0803 (13)
H2A	0.2973	0.1514	0.4996	0.096*
H2B	0.2993	−0.0159	0.3773	0.096*
C3	0.36848 (12)	0.0842 (7)	0.4393 (3)	0.0503 (9)
H3A	0.3768	−0.0835	0.4262	0.060*
H3B	0.3777	0.1271	0.5274	0.060*
C4	0.35773 (13)	0.3897 (7)	0.2697 (3)	0.0567 (10)
H4A	0.3662	0.5588	0.2750	0.068*
H4B	0.3567	0.3436	0.1792	0.068*
C5	0.39900 (11)	0.2397 (5)	0.3435 (3)	0.0336 (7)
C6	0.46853 (11)	0.5234 (5)	0.3396 (2)	0.0342 (7)
H6A	0.4922	0.6138	0.3945	0.041*
H6B	0.4484	0.6366	0.2884	0.041*
C7	0.5000	0.3637 (7)	0.2500	0.0278 (8)
C8	0.46173 (10)	0.2072 (5)	0.1738 (2)	0.0337 (7)
H8A	0.4417	0.3060	0.1145	0.040*
H8B	0.4809	0.0901	0.1235	0.040*

Atomic displacement parameters ($Å^2$)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0461 (12)	0.0405 (12)	0.0275 (9)	0.0017 (10)	−0.0016 (8)	−0.0038 (9)
O2	0.0368 (10)	0.0236 (10)	0.0368 (10)	−0.0008 (9)	0.0005 (8)	−0.0038 (8)
C1	0.076 (3)	0.098 (4)	0.093 (3)	0.005 (3)	−0.001 (2)	0.016 (3)
C2	0.069 (3)	0.089 (3)	0.083 (3)	−0.005 (3)	0.006 (2)	0.009 (3)
C3	0.052 (2)	0.053 (2)	0.0460 (17)	−0.0121 (17)	0.0100 (15)	−0.0008 (16)
C4	0.057 (2)	0.052 (2)	0.061 (2)	0.0252 (18)	−0.0165 (17)	−0.0025 (17)
C5	0.0338 (14)	0.0256 (15)	0.0413 (15)	0.0057 (12)	−0.0035 (12)	−0.0032 (12)
C6	0.0469 (16)	0.0252 (15)	0.0306 (13)	−0.0021 (13)	−0.0012 (12)	−0.0044 (11)
C7	0.040 (2)	0.023 (2)	0.0204 (16)	0.000	−0.0036 (15)	0.000
C8	0.0393 (15)	0.0322 (16)	0.0296 (13)	−0.0017 (13)	−0.0019 (12)	−0.0004 (12)

Geometric parameters (Å, °)

O1—C5	1.434 (3)	C3—H3B	0.9700
O1—C6	1.434 (3)	C4—C5	1.547 (4)
O2—C5	1.402 (3)	C4—H4A	0.9700
O2—C8	1.443 (3)	C4—H4B	0.9700
C1—C4	1.434 (5)	C6—C7	1.519 (3)
C1—C2	1.540 (6)	C6—H6A	0.9700

C1—H1A	0.9700	C6—H6B	0.9700
C1—H1B	0.9700	C7—C6^i	1.519 (3)
C2—C3	1.408 (5)	C7—C8	1.529 (3)
C2—H2A	0.9700	C7—C8^i	1.529 (3)
C2—H2B	0.9700	C8—H8A	0.9700
C3—C5	1.533 (4)	C8—H8B	0.9700
C3—H3A	0.9700		
C5—O1—C6	112.37 (19)	H4A—C4—H4B	108.6
C5—O2—C8	114.2 (2)	O2—C5—O1	110.9 (2)
C4—C1—C2	107.7 (4)	O2—C5—C3	107.8 (2)
C4—C1—H1A	110.2	O1—C5—C3	106.8 (2)
C2—C1—H1A	110.2	O2—C5—C4	112.5 (2)
C4—C1—H1B	110.2	O1—C5—C4	112.4 (2)
C2—C1—H1B	110.2	C3—C5—C4	106.0 (3)
H1A—C1—H1B	108.5	O1—C6—C7	111.4 (2)
C3—C2—C1	108.8 (4)	O1—C6—H6A	109.4
C3—C2—H2A	109.9	C7—C6—H6A	109.4
C1—C2—H2A	109.9	O1—C6—H6B	109.4
C3—C2—H2B	109.9	C7—C6—H6B	109.4
C1—C2—H2B	109.9	H6A—C6—H6B	108.0
H2A—C2—H2B	108.3	C6—C7—C6^i	108.1 (3)
C2—C3—C5	108.0 (3)	C6—C7—C8	107.99 (15)
C2—C3—H3A	110.1	C6^i—C7—C8	111.22 (14)
C5—C3—H3A	110.1	C6—C7—C8^i	111.22 (14)
C2—C3—H3B	110.1	C6^i—C7—C8^i	107.99 (15)
C5—C3—H3B	110.1	C8—C7—C8^i	110.3 (3)
H3A—C3—H3B	108.4	O2—C8—C7	109.86 (18)
C1—C4—C5	107.1 (3)	O2—C8—H8A	109.7
C1—C4—H4A	110.3	C7—C8—H8A	109.7
C5—C4—H4A	110.3	O2—C8—H8B	109.7
C1—C4—H4B	110.3	C7—C8—H8B	109.7
C5—C4—H4B	110.3	H8A—C8—H8B	108.2

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C6—H6B···O2^{ii}	0.97	2.58	3.413 (4)	143

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

Fig. 1

Fig. 2