organic compounds

3,3,12,12-Tetramethyl-1,5,10,14-tetraoxadispiro[5.2.5.2]hexadecane

Yong-Jun He, Min-Hao Xie,* Pei Zou, Ya-Ling Liu and Jun Wu

Jiangsu Institute of Nuclear Medicine, Wuxi 214063, People's Republic of China
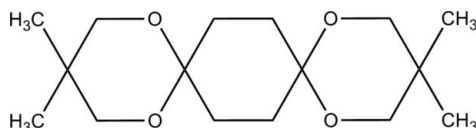Correspondence e-mail: yongjunhe001@hotmail.com

The molecule of the title compound, $C_{16}H_{28}O_4$, is centrosymmetric. The cyclohexane ring and both six-membered dioxane rings adopt chair conformations. In the crystal, the molecules lie in layers in the (100) planes and the shortest intermolecular contacts are H···H (2.30 Å).

Related literature

The title compound is an intermediate in the synthesis of Frovatriptan, a 5-HT$_1$-like agonist, see: Borrett *et al.* (1999). For details of the synthesis, see: Babler & Spina (1984); Borrett *et al.* (1999). For a related structure, see: Luger *et al.* (1972).

Experimental

Crystal data

$C_{16}H_{28}O_4$	$V = 772.1$ (9) Å^3
$M_r = 284.38$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 12.639$ (8) Å	$\mu = 0.09$ mm^{-1}
$b = 5.838$ (4) Å	$T = 93$ K
$c = 11.179$ (7) Å	$0.43 \times 0.37 \times 0.14$ mm
$\beta = 110.611$ (8)°	

Data collection

Rigaku SPIDER diffractometer	1752 independent reflections
Absorption correction: none	1243 reflections with $I > 2\sigma(I)$
5721 measured reflections	$R_{int} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.049$	93 parameters
$wR(F^2) = 0.095$	H-atom parameters constrained
$S = 1.00$	$\Delta\rho_{max} = 0.27$ e Å^{-3}
1752 reflections	$\Delta\rho_{min} = -0.19$ e Å^{-3}

Data collection: *RAPID-AUTO* (Rigaku 2004); cell refinement: *RAPID-AUTO*; data reduction: *RAPID-AUTO*; 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: *SHELXTL*.

References

Babler, J. H. & Spina, K. P. (1984). *Synth. Commun.* **14**, 39–44.
Borrett, G. T., Kitteringham, J., Porter, R. A., Shipton, M. R., Vimal, M. & Young, R. C. (1999). US Patent No. 5 962 501.
Luger, P., Plieth, K. & Ruban, G. (1972). *Acta Cryst.* B**28**, 706–710.
Rigaku (2004). *RAPID-AUTO*. Rigaku Corporation, Tokyo, Japan.
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supporting information

3,3,12,12-Tetramethyl-1,5,10,14-tetraoxadispiro[5.2.5.2]hexadecane

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S1. Comment

The title compound is useful as an intermediate in the synthesis of Frovatriptan, a 5-HT$_1$-like agonist (Babler & Spina, 1984; Borrett *et al.*, 1999). The molecular structure is shown in Fig. 1. Three six-membered rings exhibit chair conformations, with C—C bond lengths in the range 1.516 (2)–1.527 (2) Å and C—C—C angles in the range 106.59 (13)–112.55 (13)°; these agree well with the values in other cyclohexane derivatives described in the literature (Luger *et al.*, 1972).

S2. Experimental

The title compound was obtained by reaction of 1,4-cyclohexanedione (20 mmol), 2,2-dimethyl-1,3-propanediol (40 mmol) and sulfuric acid (0.1 mmol) in hexane (20 ml). The mixture was stirred for 6 h at 333 K. Colourless block-shaped crystals suitable for X-ray diffraction analysis were grown at the bottom of the vessel after 7 days slow evaporation of the solution at room temperature.

S3. Refinement

H atoms were placed in calculated positions with C—H = 0.99 and 0.98 Å for methylene and methyl H atoms, respectively, and refined as riding with U_{iso}(H) = 1.2 or 1.5U_{eq}(C).
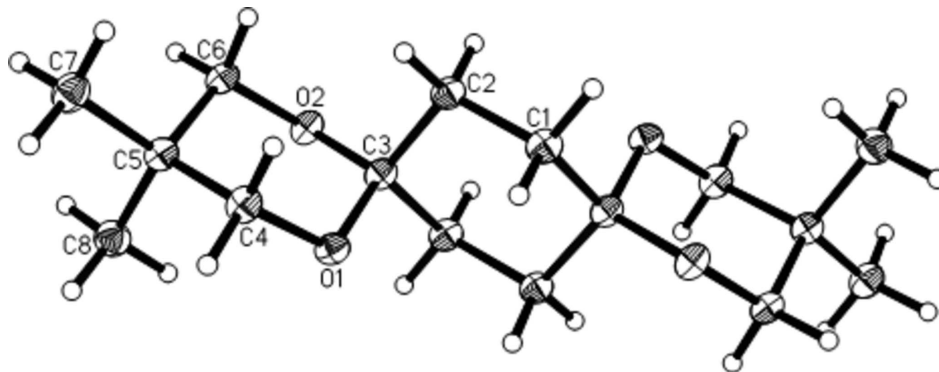

Figure 1

The molecular structure with displacement ellipsoids drawn at the 30% probability level for non-H atoms. Non-labelled atoms are related to labelled atoms by the symmetry operator: 1 - *x*, 1 - *y*, 1 - *z*.

3,3,12,12-Tetramethyl-1,5,10,14-tetraoxadispiro[5.2.5.2]hexadecane

Crystal data

$C_{16}H_{28}O_4$	$F(000) = 312$
$M_r = 284.38$	$D_x = 1.223$ Mg m^{-3}
Monoclinic, $P2_1/c$	Melting point: 430 K
Hall symbol: -P 2ybc	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 12.639$ (8) Å	Cell parameters from 2071 reflections
$b = 5.838$ (4) Å	$\theta = 3.3–27.5°$
$c = 11.179$ (7) Å	$\mu = 0.09$ mm^{-1}
$\beta = 110.611$ (8)°	$T = 93$ K
$V = 772.1$ (9) Å^3	Block, colourless
$Z = 2$	$0.43 \times 0.37 \times 0.14$ mm

Data collection

Rigaku SPIDER diffractometer	1243 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.048$
Radiation source: Rotating Anode	$\theta_{max} = 27.5°$, $\theta_{min} = 3.4°$
Graphite monochromator	$h = -16 \rightarrow 16$
ω scans	$k = -7 \rightarrow 7$
5721 measured reflections	$l = -13 \rightarrow 14$
1752 independent reflections	

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.049$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.095$	
$S = 1.00$	H-atom parameters constrained
1752 reflections	$w = 1/[\sigma^2(F_o^2) + (0.0116P)^2 + 0.36P]$
93 parameters	where $P = (F_o^2 + 2F_c^2)/3$
0 restraints	$(\Delta/\sigma)_{max} < 0.001$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{max} = 0.27$ 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	0.68024 (9)	0.62454 (18)	0.57453 (10)	0.0219 (3)
O2	0.66546 (9)	0.37232 (18)	0.73088 (10)	0.0221 (3)
C1	0.43232 (13)	0.7060 (3)	0.48564 (15)	0.0224 (4)
H1A	0.3649	0.7851	0.4912	0.027*
H1B	0.4768	0.8194	0.4574	0.027*

C2	0.50381 (13)	0.6171 (3)	0.61780 (15)	0.0220 (4)
H2A	0.5299	0.7478	0.6774	0.026*
H2B	0.4570	0.5166	0.6505	0.026*
C3	0.60572 (13)	0.4836 (3)	0.61294 (15)	0.0204 (4)
C4	0.74097 (14)	0.7887 (3)	0.66956 (15)	0.0232 (4)
H4A	0.6868	0.8977	0.6843	0.028*
H4B	0.7928	0.8768	0.6380	0.028*
C5	0.80864 (13)	0.6730 (3)	0.79466 (15)	0.0217 (4)
C6	0.72591 (14)	0.5256 (3)	0.83191 (15)	0.0222 (4)
H6A	0.7677	0.4360	0.9093	0.027*
H6B	0.6715	0.6257	0.8526	0.027*
C7	0.85930 (15)	0.8559 (3)	0.89653 (16)	0.0284 (4)
H7A	0.9083	0.9571	0.8691	0.034*
H7B	0.9038	0.7820	0.9773	0.034*
H7C	0.7983	0.9459	0.9085	0.034*
C8	0.90174 (14)	0.5242 (3)	0.77798 (16)	0.0288 (4)
H8A	0.8680	0.4097	0.7113	0.035*
H8B	0.9430	0.4466	0.8587	0.035*
H8C	0.9541	0.6206	0.7532	0.035*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0275 (6)	0.0188 (6)	0.0206 (6)	−0.0030 (5)	0.0099 (5)	−0.0001 (5)
O2	0.0292 (6)	0.0154 (6)	0.0197 (6)	−0.0016 (5)	0.0060 (5)	0.0013 (5)
C1	0.0282 (9)	0.0151 (8)	0.0240 (9)	0.0018 (6)	0.0093 (7)	−0.0016 (7)
C2	0.0262 (9)	0.0184 (8)	0.0217 (9)	0.0008 (6)	0.0087 (7)	−0.0019 (7)
C3	0.0254 (9)	0.0167 (8)	0.0188 (8)	−0.0007 (6)	0.0074 (7)	0.0024 (7)
C4	0.0289 (9)	0.0160 (8)	0.0240 (9)	−0.0042 (7)	0.0083 (7)	0.0000 (7)
C5	0.0258 (9)	0.0182 (8)	0.0209 (9)	−0.0010 (7)	0.0083 (7)	0.0002 (7)
C6	0.0277 (9)	0.0207 (8)	0.0175 (9)	0.0002 (7)	0.0073 (7)	0.0003 (7)
C7	0.0331 (10)	0.0254 (9)	0.0253 (10)	−0.0041 (8)	0.0084 (8)	−0.0010 (8)
C8	0.0281 (9)	0.0291 (10)	0.0293 (10)	0.0016 (7)	0.0105 (8)	0.0008 (8)

Geometric parameters (Å, º)

O1—C3	1.4258 (19)	C4—H4A	0.990
O1—C4	1.4362 (19)	C4—H4B	0.990
O2—C3	1.4248 (19)	C5—C6	1.521 (2)
O2—C6	1.4328 (19)	C5—C8	1.526 (2)
C1—C3[i]	1.516 (2)	C5—C7	1.527 (2)
C1—C2	1.526 (2)	C6—H6A	0.990
C1—H1A	0.990	C6—H6B	0.990
C1—H1B	0.990	C7—H7A	0.980
C2—C3	1.523 (2)	C7—H7B	0.980
C2—H2A	0.990	C7—H7C	0.980
C2—H2B	0.990	C8—H8A	0.980
C3—C1[i]	1.516 (2)	C8—H8B	0.980

C4—C5	1.517 (2)	C8—H8C	0.980
C3—O1—C4	113.58 (12)	H4A—C4—H4B	108.0
C3—O2—C6	113.98 (12)	C4—C5—C6	106.59 (13)
C3^i—C1—C2	112.55 (13)	C4—C5—C8	110.46 (14)
C3^i—C1—H1A	109.1	C6—C5—C8	110.18 (14)
C2—C1—H1A	109.1	C4—C5—C7	109.17 (14)
C3^i—C1—H1B	109.1	C6—C5—C7	109.84 (14)
C2—C1—H1B	109.1	C8—C5—C7	110.50 (14)
H1A—C1—H1B	107.8	O2—C6—C5	111.39 (13)
C3—C2—C1	111.07 (13)	O2—C6—H6A	109.3
C3—C2—H2A	109.4	C5—C6—H6A	109.3
C1—C2—H2A	109.4	O2—C6—H6B	109.3
C3—C2—H2B	109.4	C5—C6—H6B	109.3
C1—C2—H2B	109.4	H6A—C6—H6B	108.0
H2A—C2—H2B	108.0	C5—C7—H7A	109.5
O2—C3—O1	110.54 (12)	C5—C7—H7B	109.5
O2—C3—C1^i	105.59 (13)	H7A—C7—H7B	109.5
O1—C3—C1^i	106.05 (13)	C5—C7—H7C	109.5
O2—C3—C2	112.32 (13)	H7A—C7—H7C	109.5
O1—C3—C2	111.86 (13)	H7B—C7—H7C	109.5
C1^i—C3—C2	110.12 (13)	C5—C8—H8A	109.5
O1—C4—C5	111.45 (13)	C5—C8—H8B	109.5
O1—C4—H4A	109.3	H8A—C8—H8B	109.5
C5—C4—H4A	109.3	H8A—C8—H8C	109.5
O1—C4—H4B	109.3	C5—C8—H8C	109.5
C5—C4—H4B	109.3	H8A—C8—H8C	109.5
		H8B—C8—H8C	109.5
C3^i—C1—C2—C3	56.01 (19)	C1—C2—C3—C1^i	−54.63 (18)
C6—O2—C3—O1	54.99 (16)	C3—O1—C4—C5	57.12 (17)
C6—O2—C3—C1^i	169.25 (12)	O1—C4—C5—C6	−54.38 (17)
C6—O2—C3—C2	−70.72 (16)	O1—C4—C5—C8	65.32 (17)
C4—O1—C3—O2	−55.06 (16)	O1—C4—C5—C7	−172.97 (13)
C4—O1—C3—C1^i	−169.04 (12)	C3—O2—C6—C5	−56.61 (17)
C4—O1—C3—C2	70.90 (16)	C4—C5—C6—O2	54.05 (17)
C1—C2—C3—O2	−172.00 (12)	C8—C5—C6—O2	−65.83 (17)
C1—C2—C3—O1	63.02 (16)	C7—C5—C6—O2	172.21 (13)

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