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endo-3,3-Dimethyl-4-oxobicyclo[3.1.0]-hexan-2-yl methanesulfonate

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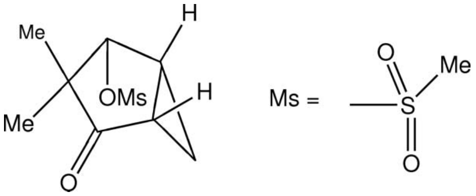
Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.002 Å; R factor = 0.046; wR factor = 0.130; data-to-parameter ratio = 26.4.

The relative configuration of the *endo* isomer of the title compound, $C_9H_{14}O_4S$, has been established and the conformation of the diastereoisomer is discussed. The five-membered ring adopts an envelope conformation. The conformation of the methanesulfonate substituent is stabilized by intermolecular C—H⋯O hydrogen bonds. The crystal packing results in alternating layers of polar methanesulfonates and stacked bicyclohexanyl rings parallel to *ab*.

Related literature

For related enantioselective syntheses, see: Krief (1994); Krief *et al.* (2000). For puckering parameters and theoretical torsion angles, see: Cremer & Pople (1975); Dunitz (1979).



Experimental

Crystal data

$C_9H_{14}O_4S$
M_r = 218.27
Triclinic, $P\overline{1}$
a = 5.8558 (3) Å
b = 7.7497 (4) Å
c = 12.2527 (6) Å
α = 84.290 (4)°
β = 79.531 (4)°
γ = 72.070 (5)°
V = 519.66 (5) $Å^3$
Z = 2
Mo $K\alpha$ radiation
μ = 0.30 mm^{-1}
T = 293 K
0.35 × 0.14 × 0.12 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Ruby (Gemini ultra Mo) detector
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)
T_{min} = 0.904, T_{max} = 0.966
6128 measured reflections
3432 independent reflections
2283 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.130
S = 0.99
3432 reflections
130 parameters
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.36 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.31 e $Å^{-3}$

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
C4—H4⋯O4^{i}	0.98	2.48	3.302 (4)	141
C9—H9B⋯O2^{ii}	0.96	2.54	3.485 (2)	169

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

Data collection: *CrysAlis PRO* (Oxford Diffraction, 2009); cell refinement: *CrysAlis PRO*; data reduction: *CrysAlis PRO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEPIII* (Burnett & Johnson, 1996) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97* .

This work was supported in part by the Fonds National de la Recherche Scientifique (FNRS, Belgium).

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: DN2550).

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supporting information

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endo-3,3-Dimethyl-4-oxobicyclo[3.1.0]hexan-2-yl methanesulfonate

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S1. Comment

In the course of a work involving the enantioselective synthesis of didesmethyl-deltametrinic acid (Krief *et al.*, 2000; Krief, 1994) both the *exo* and *endo* isomers of 3,3-dimethyl-4-oxobicyclo[3.1.0]hexan-2-yl methanesulfonate were synthesized and characterized.

The X-ray crystallography study reported here determined the relative stereochemistry of the *endo* diasteroisomer : C(1) *S*, C(4) *R*, and C(5) *R*. The compound crystallizing in a centrosymetric space group, one obtains the racemic mixture *S*,*R*,*R*/*R*,*S*,*S*.

The five-membered ring C1—C5 adopts an envelope conformation. Puckering parameter Phi is 260.1 (8)° and close to the expected value of k *x* 36° (Cremer & Pople, 1975), suggesting that the presence of a sp^2 carbon (C2) in the five-membered ring does not significantly distort its conformation. The observed values of torsion angles defining the C1—C5 ring (Table 1) fairly well follow the theoretical sequence of torsion angles $-\omega1$, $\omega2$, $-\omega2$, $\omega1$ and 0 (Dunitz, 1979) characteristic of an envelope conformation.

Atom C6 of the fused three-membered ring deviates by +1.250 (2) Å from the mean plane defined by the five atoms of the C1—C5 ring (Figure 1).

Steric effects resulting from C6 being in *cis* of the mesylate substituent on O2, constrain the conformation of the methanesulfonate group. Positions of the oxygen atoms O3 and O4 of the sulfonate group are further explained by intra and intermolecular CH···O hydrogen bondings. Indeed O3 forms an intramolecular H bond [O3···H4 = 2.81 Å] with H4 of C4 that carries the mesylate. An intermolecular H bond with H4 further involves O4 [C(4)—H4 ··· $O4_i$: D···A = 3.302 (4) Å; H···A = 2.48 Å; D - H···A = 141°, *i* = *x*-1,*y*,*z*].

Packing is also reinforced by van der Waals interactions resulting in alterning layers of polar methanesulfonates and stacked bicyclohexanyl rings parallel to the *ab* cell planes.

S2. Experimental

Synthesis of the compound will be detailed elsewhere.

Crystals were obtained by evaporation at 5°C of solutions in diethylether.

S3. Refinement

All H atoms were placed at idealized positions and allowed to ride on their parent atoms, with C—H = 0.97 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ for methylene groups and $U_{iso}(H) = 1.5U_{eq}(C)$ for the methyl group.

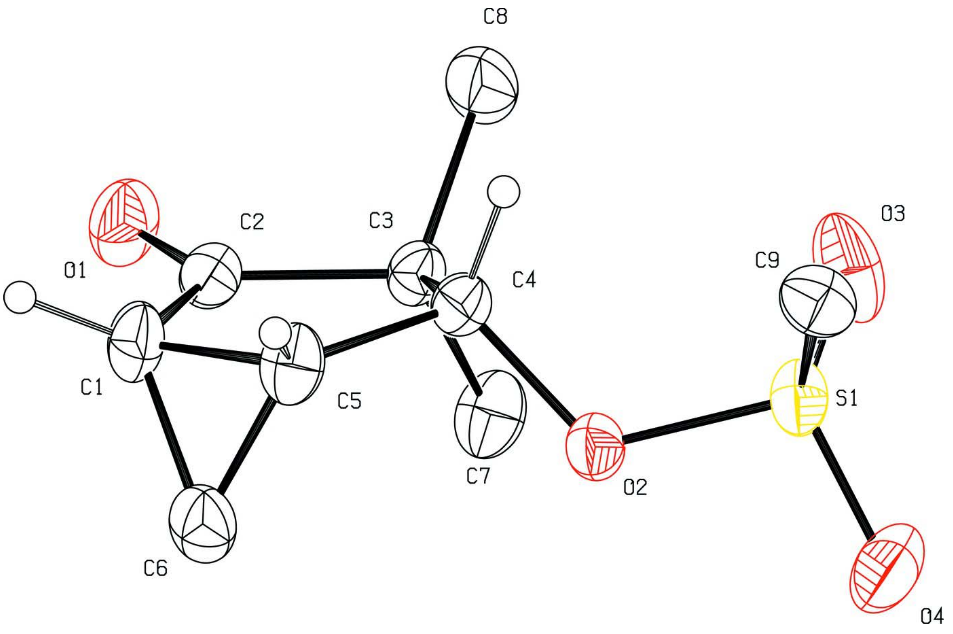

Figure 1

Conformation (*ORTEP* view) of the title compound. Only H atoms on chiral carbons have been retained for clarity. Displacement ellipsoids for non-H atoms are drawn at the 30% probability level.

endo-3,3-Dimethyl-4-oxobicyclo[3.1.0]hexan-2-yl methanesulfonate

Crystal data

$C_9H_{14}O_4S$
$M_r = 218.27$
Triclinic, $P\bar{1}$
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$a = 5.8558$ (3) Å
$b = 7.7497$ (4) Å
$c = 12.2527$ (6) Å
$\alpha = 84.290$ (4)°
$\beta = 79.531$ (4)°
$\gamma = 72.070$ (5)°
$V = 519.66$ (5) Å^3

$Z = 2$
$F(000) = 232$
$D_x = 1.395$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2686 reflections
$\theta = 3.2$–32.6°
$\mu = 0.30$ mm^{-1}
$T = 293$ K
Prism, colorless
0.35 × 0.14 × 0.12 mm

Data collection

Oxford Diffraction Xcalibur diffractometer with a Ruby (Gemini ultra Mo) detector
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 10.3712 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (*CrysAlis PRO*; Oxford Diffraction, 2009)

$T_{\min} = 0.904$, $T_{\max} = 0.966$
6128 measured reflections
3432 independent reflections
2283 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.019$
$\theta_{\max} = 32.6°$, $\theta_{\min} = 3.2°$
$h = -8 \rightarrow 8$
$k = -8 \rightarrow 11$
$l = -18 \rightarrow 18$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.130$
$S = 0.99$
3432 reflections
130 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
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0721P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.36$ e Å^{-3}
$\Delta\rho_{min} = -0.31$ e Å^{-3}

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. 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}
C1	0.1819 (3)	0.4668 (2)	0.66360 (15)	0.0492 (4)
H1	0.0668	0.4050	0.6508	0.059*
C2	0.1965 (3)	0.6346 (2)	0.59887 (13)	0.0422 (3)
C3	0.2668 (3)	0.75983 (19)	0.66753 (13)	0.0377 (3)
C4	0.2405 (3)	0.6746 (2)	0.78727 (12)	0.0383 (3)
H4	0.0950	0.7502	0.8323	0.046*
C5	0.2143 (3)	0.4885 (2)	0.78131 (14)	0.0474 (4)
H5	0.1187	0.4400	0.8439	0.057*
C6	0.4088 (4)	0.3618 (2)	0.70955 (15)	0.0534 (4)
H6A	0.4345	0.2330	0.7265	0.064*
H6B	0.5558	0.3956	0.6814	0.064*
C7	0.5212 (3)	0.7725 (3)	0.61787 (15)	0.0556 (5)
H7A	0.6366	0.6539	0.6194	0.083*
H7B	0.5646	0.8515	0.6606	0.083*
H7C	0.5216	0.8202	0.5425	0.083*
C8	0.0812 (4)	0.9504 (2)	0.66350 (19)	0.0642 (5)
H8A	0.1226	1.0300	0.7066	0.096*
H8B	−0.0787	0.9425	0.6935	0.096*
H8C	0.0843	0.9972	0.5879	0.096*
C9	0.2608 (3)	0.7738 (2)	1.04091 (14)	0.0503 (4)
H9A	0.2548	0.8619	1.0920	0.075*
H9B	0.3173	0.6540	1.0740	0.075*
H9C	0.1012	0.7930	1.0235	0.075*
O1	0.1502 (3)	0.67456 (18)	0.50596 (10)	0.0606 (4)
O2	0.4535 (2)	0.64888 (14)	0.84223 (9)	0.0421 (3)

O3	0.3691 (3)	0.97232 (17)	0.87030 (11)	0.0717 (4)
O4	0.7018 (2)	0.7375 (2)	0.94357 (12)	0.0761 (5)
S1	0.45905 (8)	0.79673 (6)	0.91953 (3)	0.04398 (14)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0598 (11)	0.0458 (9)	0.0546 (10)	−0.0288 (8)	−0.0180 (8)	−0.0019 (7)
C2	0.0405 (8)	0.0438 (8)	0.0452 (8)	−0.0140 (7)	−0.0116 (6)	−0.0025 (7)
C3	0.0408 (8)	0.0344 (7)	0.0426 (8)	−0.0156 (6)	−0.0133 (6)	0.0027 (6)
C4	0.0353 (7)	0.0398 (8)	0.0421 (8)	−0.0143 (6)	−0.0058 (6)	−0.0031 (6)
C5	0.0589 (10)	0.0487 (9)	0.0438 (9)	−0.0314 (8)	−0.0089 (7)	0.0059 (7)
C6	0.0680 (12)	0.0369 (8)	0.0601 (11)	−0.0172 (8)	−0.0211 (9)	0.0017 (7)
C7	0.0600 (11)	0.0673 (12)	0.0508 (10)	−0.0390 (10)	−0.0052 (8)	0.0036 (9)
C8	0.0767 (14)	0.0400 (9)	0.0783 (13)	−0.0074 (9)	−0.0359 (11)	−0.0025 (9)
C9	0.0526 (10)	0.0515 (10)	0.0414 (8)	−0.0116 (8)	0.0001 (7)	−0.0030 (7)
O1	0.0771 (9)	0.0638 (8)	0.0499 (7)	−0.0244 (7)	−0.0290 (6)	0.0015 (6)
O2	0.0476 (6)	0.0399 (6)	0.0409 (6)	−0.0116 (5)	−0.0131 (5)	−0.0061 (4)
O3	0.1261 (14)	0.0447 (7)	0.0544 (8)	−0.0425 (8)	−0.0113 (8)	0.0004 (6)
O4	0.0484 (8)	0.1248 (13)	0.0661 (9)	−0.0348 (8)	−0.0039 (6)	−0.0363 (9)
S1	0.0507 (3)	0.0491 (2)	0.0385 (2)	−0.02405 (19)	−0.00324 (16)	−0.00920 (16)

Geometric parameters (Å, º)

C1—C2	1.472 (2)	C6—H6B	0.9700
C1—C6	1.503 (2)	C7—H7A	0.9600
C1—C5	1.521 (2)	C7—H7B	0.9600
C1—H1	0.9800	C7—H7C	0.9600
C2—O1	1.2066 (19)	C8—H8A	0.9600
C2—C3	1.534 (2)	C8—H8B	0.9600
C3—C7	1.532 (2)	C8—H8C	0.9600
C3—C8	1.543 (2)	C9—S1	1.7429 (17)
C3—C4	1.549 (2)	C9—H9A	0.9600
C4—O2	1.4747 (17)	C9—H9B	0.9600
C4—C5	1.506 (2)	C9—H9C	0.9600
C4—H4	0.9800	O2—S1	1.5687 (11)
C5—C6	1.467 (3)	O3—S1	1.4156 (14)
C5—H5	0.9800	O4—S1	1.4287 (14)
C6—H6A	0.9700		
C2—C1—C6	114.72 (14)	C1—C6—H6A	117.6
C2—C1—C5	107.13 (13)	C5—C6—H6B	117.6
C6—C1—C5	58.06 (11)	C1—C6—H6B	117.6
C2—C1—H1	120.3	H6A—C6—H6B	114.7
C6—C1—H1	120.3	C3—C7—H7A	109.5
C5—C1—H1	120.3	C3—C7—H7B	109.5
O1—C2—C1	125.52 (15)	H7A—C7—H7B	109.5
O1—C2—C3	123.47 (14)	C3—C7—H7C	109.5

C1—C2—C3	110.94 (13)	H7A—C7—H7C	109.5
C7—C3—C2	109.53 (13)	H7B—C7—H7C	109.5
C7—C3—C8	109.33 (15)	C3—C8—H8A	109.5
C2—C3—C8	108.62 (13)	C3—C8—H8B	109.5
C7—C3—C4	115.62 (13)	H8A—C8—H8B	109.5
C2—C3—C4	103.93 (11)	C3—C8—H8C	109.5
C8—C3—C4	109.53 (14)	H8A—C8—H8C	109.5
O2—C4—C5	106.44 (12)	H8B—C8—H8C	109.5
O2—C4—C3	113.84 (11)	S1—C9—H9A	109.5
C5—C4—C3	108.08 (12)	S1—C9—H9B	109.5
O2—C4—H4	109.5	H9A—C9—H9B	109.5
C5—C4—H4	109.5	S1—C9—H9C	109.5
C3—C4—H4	109.5	H9A—C9—H9C	109.5
C6—C5—C4	116.56 (15)	H9B—C9—H9C	109.5
C6—C5—C1	60.38 (11)	C4—O2—S1	120.23 (9)
C4—C5—C1	108.34 (13)	O3—S1—O4	119.56 (10)
C6—C5—H5	119.1	O3—S1—O2	110.12 (7)
C4—C5—H5	119.1	O4—S1—O2	103.74 (8)
C1—C5—H5	119.1	O3—S1—C9	108.61 (9)
C5—C6—C1	61.56 (12)	O4—S1—C9	108.62 (9)
C5—C6—H6A	117.6	O2—S1—C9	105.24 (8)

C6—C1—C2—O1	127.22 (19)	C8—C3—C4—C5	128.36 (15)
C5—C1—C2—O1	−170.65 (18)	O2—C4—C5—C6	−66.42 (17)
C6—C1—C2—C3	−55.74 (19)	C3—C4—C5—C6	56.24 (18)
C5—C1—C2—C3	6.39 (18)	O2—C4—C5—C1	−131.81 (14)
O1—C2—C3—C7	−70.5 (2)	C3—C4—C5—C1	−9.15 (18)
C1—C2—C3—C7	112.43 (15)	C2—C1—C5—C6	−108.87 (16)
O1—C2—C3—C8	48.9 (2)	C2—C1—C5—C4	1.83 (19)
C1—C2—C3—C8	−128.22 (16)	C6—C1—C5—C4	110.70 (16)
O1—C2—C3—C4	165.44 (17)	C4—C5—C6—C1	−96.92 (16)
C1—C2—C3—C4	−11.67 (17)	C2—C1—C6—C5	95.46 (16)
C7—C3—C4—O2	10.41 (18)	C5—C4—O2—S1	−146.30 (11)
C2—C3—C4—O2	130.47 (12)	C3—C4—O2—S1	94.74 (13)
C8—C3—C4—O2	−113.62 (15)	C4—O2—S1—O3	−42.98 (13)
C7—C3—C4—C5	−107.61 (15)	C4—O2—S1—O4	−172.07 (11)
C2—C3—C4—C5	12.45 (16)	C4—O2—S1—C9	73.90 (12)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C4—H4···O4^{i}	0.98	2.48	3.302 (4)	141
C9—H9*B*···O2^{ii}	0.96	2.54	3.485 (2)	169

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