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Absolute Configuration of a Substituted Cyclohexanol

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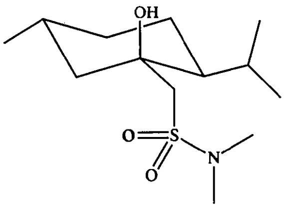
Abstract

The low-temperature X-ray structure of (−)-(1*S*,2*S*,5*R*)-1-(*N*,*N*-dimethylsulfamoylmethyl)-2-isopropyl-5-methylcyclohexan-1-ol, C$_{13}$H$_{27}$NO$_3$S [alternative IUPAC name: 1-hydroxy-2-isopropyl-5,*N*,*N*-trimethylcyclohexanemethanesulfonamide], is reported. There are two molecules in the asymmetric unit. The absolute configuration has been determined.

Comment

(−)-(1*S*,2*S*,5*R*)-1-(*N*,*N*-Dimethylsulfamoylmethyl)-2-isopropyl-5-methylcyclohexan-1-ol, (I), was prepared during the course of a synthetic programme to investigate the addition of α-metallated sulfonamides to cyclic ketones (Stanchev, Christov, Simova, Mladenova & Linden, 1995). (I) is obtained from the addition of α-lithiated dimethylmethanesulfonamide to (−)-*trans*-menthone.



(I)

The asymmetric unit contains two molecules of the same enantiomorph. Views of molecules *A* and *B*, showing the displacement ellipsoids, atomic numbering and the correct absolute configuration, are given in Fig. 1. The two independent molecules have very similar molecular dimensions and conformations. The main differences between the molecules are in the orientations of the isopropyl, sulfonamido and hydroxy groups. The conformation of molecule *B* is obtained by rotating the C(2)—C(11), S(1)—C(8), C(1)—C(8) and C(1)—O(1) bonds of molecule *A* by approximately 10, 13, −7 and 37°, respectively. All other torsion angles within the molecular skeleton differ by less than 7°. The large difference between the orientations of the H atoms of the hydroxy groups is probably the result of differences in the hydrogen-bonding interactions of each molecule, which are described below. The absolute configuration of each molecule was determined by refinement of the structure and the enantiopole parameter according to the method of Flack (1983).

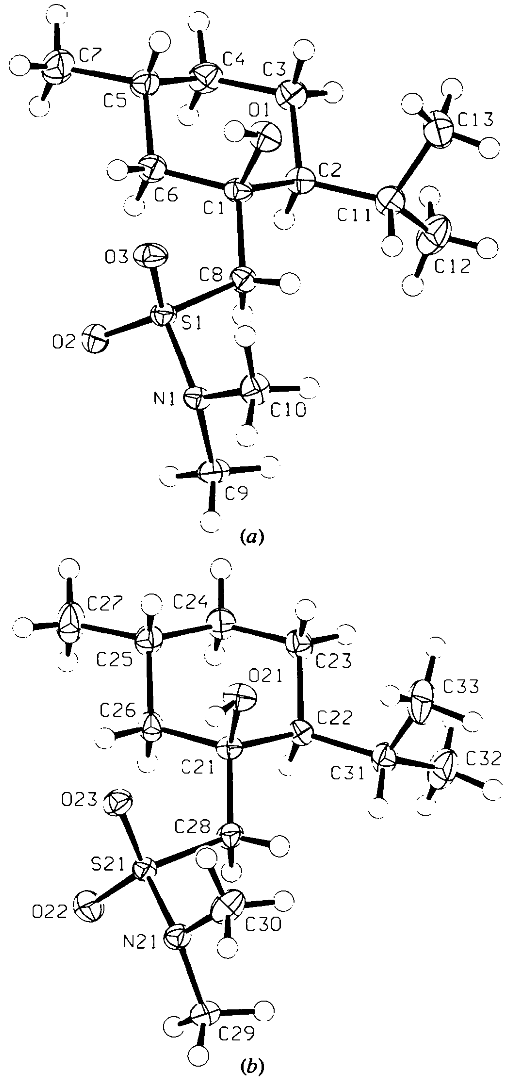


Fig. 1. Views of (*a*) molecule *A* and (*b*) molecule *B* showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

The cyclohexane ring has an undistorted chair conformation and most bond lengths and angles are within expected ranges. The S(1)—C(8) and S(21)—C(28) bonds are slightly elongated, being about 0.04 Å longer than the typical value for such bonds in a similar environment (Allen *et al.*, 1992). A similar elongation of about 0.06 Å was observed in the structures of the related compound (−)-(2*S*,5*R*)-2-[(1′*R*)-1′-(*N*,*N*-dimethylsulfamoyl)-2′-methyl-1′-phenylprop-2′-yl]-5-methylcyclohexan-1-one and its (+)-(1′*S*) enantiomer (Linden & Stanchev, 1995).

The angles C(1)—C(2)—C(11), C(2)—C(11)—C(13), C(21)—C(22)—C(31) and C(22)—C(31)—C(33) are about 5–8° larger than the normally expected tetrahedral value, which gives rise to slightly distorted isopropyl groups. This effect may be due to steric repulsion between one of the methyl groups of this substituent and the adjacent hydroxy group. The dihedral angles O(1)—C(1)···C(11)—C(13) and O(21)—C(21)···C(31)—C(33) are −18.4 (2) and −4.9 (2)°, respectively, which indicate the eclipsed nature of these groups. The contact distances between the hydroxy O atom and the nearest methyl C atom of the isopropyl group [O(1)···C(13) = 3.126 (3), O(21)···C(33) = 3.093 (3) Å] are about 0.11 Å shorter than the sum of the van der Waals radii of these atoms (Bondi, 1964). This suggests that the distortion of the bond angles at C(2), C(11), C(22) and C(31) is indeed the result of steric repulsion.

The symmetry-independent molecules are linked into dimeric units by intermolecular hydrogen bonds (Fig. 2, Table 3). The hydroxy group of molecule *A* acts as a donor, with the O atom of the hydroxy group of molecule *B* acting as the acceptor. The hydroxy group of molecule *B* forms bifurcated hydrogen bonds, having an intermolecular interaction with one of the O atoms of the sulfonyl group of molecule *A*, and, additionally, an intramolecular interaction with one of the O atoms of the sulfonyl group within molecule *B*. The angle at the bifurcated H atom, O(3)···H(21)···O(23), is 91.0 (7)°.

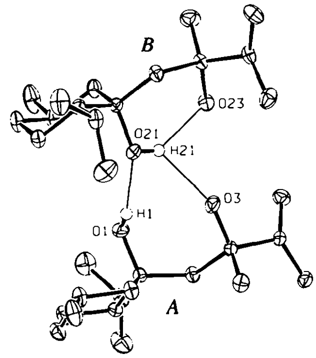


Fig. 2. The hydrogen-bonded dimeric unit of (I) viewed down *b*. Most H atoms have been omitted for clarity.

Experimental

(I) was prepared as described by Stanchev, Christov, Simova, Mladenova & Linden (1995). Suitable crystals were obtained by recrystallization from $CHCl_3$/hexane.

Crystal data

$C_{13}H_{27}NO_3S$
$M_r = 277.42$
Monoclinic
$P2_1$
$a = 10.609\ (3)$ Å
$b = 10.879\ (3)$ Å
$c = 13.419\ (1)$ Å
$\beta = 100.14\ (1)°$
$V = 1524.7\ (6)$ Å^3
$Z = 4$
$D_x = 1.207$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 12.0$–$13.0°$
$\mu = 0.204$ mm^{-1}
$T = 173\ (1)$ K
Prism
0.50 × 0.33 × 0.25 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
9774 measured reflections
8886 independent reflections
7862 observed reflections [$I > 2\sigma(I)$]
$R_{\rm int} = 0.012$

$\theta_{\rm max} = 30°$
$h = -14 \rightarrow 14$
$k = -15 \rightarrow 15$
$l = -18 \rightarrow 18$
3 standard reflections monitored every 150 reflections intensity decay: insignificant

Refinement

Refinement on F
$R = 0.0335$
$wR = 0.0309$
$S = 1.705$
7862 reflections
540 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$

$(\Delta/\sigma)_{\rm max} = 0.0006$
$\Delta\rho_{\rm max} = 0.35$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
S(1)	0.05566 (3)	0.22420	0.97473 (3)	0.0179 (1)
O(1)	0.1076 (1)	0.1211 (1)	0.7450 (1)	0.0258 (4)
O(2)	−0.0371 (1)	0.3178 (1)	0.98341 (9)	0.0256 (4)
O(3)	0.1778 (1)	0.2612 (1)	0.95233 (9)	0.0263 (4)
N(1)	0.0840 (1)	0.1528 (2)	1.0829 (1)	0.0182 (4)
C(1)	−0.0160 (2)	0.1446 (2)	0.7691 (1)	0.0199 (5)
C(2)	−0.1095 (2)	0.0533 (2)	0.7037 (1)	0.0206 (5)
C(3)	−0.1255 (2)	0.0890 (2)	0.5914 (1)	0.0265 (6)
C(4)	−0.1711 (2)	0.2207 (2)	0.5715 (1)	0.0286 (5)
C(5)	−0.0768 (2)	0.3106 (2)	0.6316 (1)	0.0259 (6)
C(6)	−0.0582 (2)	0.2781 (2)	0.7446 (1)	0.0242 (5)
C(7)	−0.1198 (3)	0.4436 (2)	0.6136 (2)	0.0386 (8)
C(8)	−0.0152 (2)	0.1140 (2)	0.8825 (1)	0.0207 (5)
C(9)	−0.0281 (2)	0.1076 (2)	1.1225 (1)	0.0247 (6)
C(10)	0.1965 (2)	0.0712 (2)	1.1036 (2)	0.0249 (6)
C(11)	−0.0777 (2)	−0.0849 (2)	0.7213 (1)	0.0250 (5)
C(12)	−0.2011 (2)	−0.1604 (2)	0.7040 (2)	0.0382 (7)
C(13)	0.0157 (2)	−0.1361 (2)	0.6570 (2)	0.0365 (7)
S(21)	0.56935 (4)	0.22598 (5)	0.98059 (3)	0.0188 (1)
O(21)	0.3214 (1)	0.2829 (1)	0.80256 (9)	0.0239 (4)
O(22)	0.6881 (1)	0.1668 (1)	0.9743 (1)	0.0308 (4)
O(23)	0.4564 (1)	0.1510 (1)	0.97722 (9)	0.0233 (4)
N(21)	0.5869 (1)	0.3016 (2)	1.0870 (1)	0.0221 (4)
C(21)	0.4497 (2)	0.2980 (2)	0.7828 (1)	0.0178 (5)
C(22)	0.4445 (2)	0.3991 (2)	0.7017 (1)	0.0184 (5)
C(23)	0.3583 (2)	0.3566 (2)	0.6032 (1)	0.0239 (5)
C(24)	0.4046 (2)	0.2365 (2)	0.5640 (1)	0.0276 (5)
C(25)	0.4135 (2)	0.1344 (2)	0.6428 (1)	0.0257 (6)
C(26)	0.4957 (2)	0.1769 (2)	0.7423 (1)	0.0233 (5)

C(27)	0.4663 (3)	0.0161 (2)	0.6047 (2)	0.0412 (8)
C(28)	0.5371 (2)	0.3390 (2)	0.8812 (1)	0.0215 (5)
C(29)	0.7001 (2)	0.3814 (2)	1.1124 (2)	0.0301 (6)
C(30)	0.4685 (2)	0.3549 (2)	1.1125 (2)	0.0316 (7)
C(31)	0.4117 (2)	0.5305 (2)	0.7331 (1)	0.0247 (5)
C(32)	0.4582 (3)	0.6258 (2)	0.6640 (2)	0.0396 (8)
C(33)	0.2703 (2)	0.5529 (2)	0.7354 (2)	0.0420 (8)

Table 2. *Selected geometric parameters* (Å, °)

S(1)—O(2)	1.435 (1)	S(21)—O(22)	1.431 (1)
S(1)—O(3)	1.438 (1)	S(21)—O(23)	1.444 (1)
S(1)—N(1)	1.628 (1)	S(21)—N(21)	1.630 (2)
S(1)—C(8)	1.790 (2)	S(21)—C(28)	1.802 (2)
O(1)—C(1)	1.427 (2)	O(21)—C(21)	1.441 (2)
C(1)—C(2)	1.560 (2)	C(21)—C(22)	1.542 (2)
C(1)—C(6)	1.538 (3)	C(21)—C(26)	1.538 (2)
C(1)—C(8)	1.557 (2)	C(21)—C(28)	1.540 (2)
C(2)—C(3)	1.536 (3)	C(22)—C(23)	1.540 (2)
C(2)—C(11)	1.551 (3)	C(22)—C(31)	1.546 (3)
C(3)—C(4)	1.521 (3)	C(23)—C(24)	1.522 (3)
C(4)—C(5)	1.524 (3)	C(24)—C(25)	1.525 (3)
C(5)—C(6)	1.536 (3)	C(25)—C(26)	1.532 (3)
O(2)—S(1)—O(3)	118.27 (8)	O(22)—S(21)—O(23)	118.58 (8)
N(1)—S(1)—C(8)	106.64 (8)	N(21)—S(21)—C(28)	106.35 (9)
S(1)—N(1)—C(9)	116.6 (1)	S(21)—N(21)—C(29)	117.6 (1)
S(1)—N(1)—C(10)	118.1 (1)	S(21)—N(21)—C(30)	115.5 (1)
O(1)—C(1)—C(2)	106.1 (1)	O(21)—C(21)—C(22)	107.1 (1)
O(1)—C(1)—C(6)	111.4 (1)	O(21)—C(21)—C(26)	109.6 (1)
O(1)—C(1)—C(8)	109.6 (1)	O(21)—C(21)—C(28)	108.8 (1)
C(2)—C(1)—C(6)	110.4 (1)	C(22)—C(21)—C(26)	109.6 (1)
C(2)—C(1)—C(8)	107.9 (1)	C(22)—C(21)—C(28)	109.9 (1)
C(6)—C(1)—C(8)	111.2 (1)	C(26)—C(21)—C(28)	111.7 (1)
C(1)—C(2)—C(3)	109.9 (1)	C(21)—C(22)—C(23)	109.5 (1)
C(1)—C(2)—C(11)	115.6 (1)	C(21)—C(22)—C(31)	116.7 (1)
C(3)—C(2)—C(11)	112.2 (2)	C(23)—C(22)—C(31)	112.5 (1)
S(1)—C(8)—C(1)	117.5 (1)	S(21)—C(28)—C(21)	116.4 (1)
C(2)—C(11)—C(12)	109.9 (2)	C(22)—C(31)—C(32)	110.5 (2)
C(2)—C(11)—C(13)	114.3 (2)	C(22)—C(31)—C(33)	115.0 (2)
C(12)—C(11)—C(13)	110.0 (2)	C(32)—C(31)—C(33)	109.1 (2)

S(1)—C(8)—C(1)—O(1)	78.3 (2)
S(1)—C(8)—C(1)—C(2)	−166.6 (1)
S(1)—C(8)—C(1)—C(6)	−45.4 (2)
O(2)—S(1)—C(8)—C(1)	82.7 (1)
O(3)—S(1)—C(8)—C(1)	−47.6 (2)
N(1)—S(1)—C(8)—C(1)	−162.5 (1)
C(1)—C(2)—C(3)—C(4)	−56.2 (2)
C(1)—C(2)—C(11)—C(12)	148.5 (2)
C(1)—C(2)—C(11)—C(13)	−87.2 (2)
C(1)—C(6)—C(5)—C(4)	55.2 (2)
C(2)—C(1)—C(6)—C(5)	−53.3 (2)
C(2)—C(3)—C(4)—C(5)	59.1 (2)
C(3)—C(2)—C(1)—C(6)	51.9 (2)
C(3)—C(2)—C(11)—C(12)	−84.4 (2)
C(3)—C(2)—C(11)—C(13)	39.9 (2)
C(3)—C(4)—C(5)—C(6)	−56.3 (2)
C(2)—C(1)—O(1)—H(1)	167 (2)
C(6)—C(1)—O(1)—H(1)	47 (2)
C(8)—C(1)—O(1)—H(1)	−77 (2)
S(21)—C(28)—C(21)—O(21)	69.7 (2)
S(21)—C(28)—C(21)—C(22)	−173.4 (1)
S(21)—C(28)—C(21)—C(26)	−51.5 (2)
O(22)—S(21)—C(28)—C(21)	95.5 (1)
O(23)—S(21)—C(28)—C(21)	−34.4 (2)
N(21)—S(21)—C(28)—C(21)	−148.2 (1)
C(21)—C(22)—C(23)—C(24)	−57.7 (2)
C(21)—C(22)—C(31)—C(32)	158.6 (2)
C(21)—C(22)—C(31)—C(33)	−77.4 (2)
C(21)—C(26)—C(25)—C(24)	54.6 (2)
C(22)—C(21)—C(26)—C(25)	−56.4 (2)
C(22)—C(23)—C(24)—C(25)	56.9 (2)
C(23)—C(22)—C(21)—C(26)	56.1 (2)
C(23)—C(22)—C(31)—C(32)	−73.6 (2)
C(23)—C(22)—C(31)—C(33)	50.4 (2)
C(23)—C(24)—C(25)—C(26)	−53.7 (2)
C(22)—C(21)—O(21)—H(21)	−157 (2)
C(26)—C(21)—O(21)—H(21)	84 (2)
C(28)—C(21)—O(21)—H(21)	−38 (2)

Table 3. *Hydrogen-bonding geometry* (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(1)—H(1)···O(21)	0.72 (2)	2.17 (2)	2.868 (2)	165 (3)
O(21)—H(21)···O(3)	0.80 (2)	2.19 (2)	2.737 (2)	126 (2)
O(21)—H(21)···O(23)	0.80 (2)	2.23 (2)	2.902 (2)	143 (2)

The data collection was extended to include the measurement of the intensities of the Friedel opposites of all unique reflections. Friedel pairs were not averaged during the data reduction so that the effects of anomalous dispersion could be used for the determination of the absolute configuration. For this purpose the *CRYSTALS* program system (Watkin, Carruthers & Betteridge, 1985) was used to refine the final atomic coordinates together with the enantiopole parameter (Flack, 1983). The refined value of the enantiopole parameter was −0.06 (5), thus confirming that the atomic coordinates for each structure represented the correct enantiomorph.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1991). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN PROCESS* (Molecular Structure Corporation, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *TEXSAN LS*. Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *TEXSAN FINISH*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: BM1004). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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