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Absolute Configurations of Two Enantiomers of a Substituted Cyclohexanone

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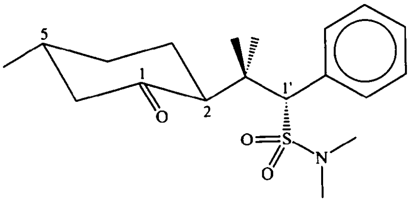
Abstract

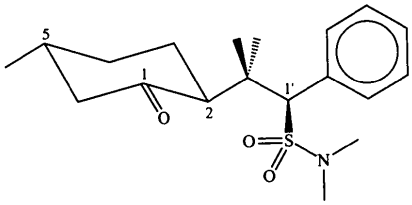
The low-temperature X-ray structures of (−)-(2*S*,5*R*)-2-[(1′*R*)-1′-(*N*,*N*-dimethylsulfamoyl)-2′-methyl-1′-phenylprop-2′-yl]-5-methylcyclohexan-1-one, $C_{19}H_{29}NO_3S$, and its (+)-(1′*S*) enantiomer are reported [alternative IUPAC name: β,β,*N*,*N*,4-pentamethyl-2-oxo-α-phenylcyclohexaneethanesulfonamide]. The absolute configuration of each molecule has been determined.

Comment

(−)-(2*S*,5*R*)-2-[(1′*R*)-1′-(*N*,*N*-dimethylsulfamoyl)-2′-methyl-1′-phenylprop-2′-yl]-5-methylcyclohexan-1-one, (I), and its (+)-(1′*S*) enantiomer, (II), were 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). The enantiomers (I) and (II) are both obtained from the addition of α-lithiated phenylmethanesulfonamide to (+)-(*R*)-pulegone.



(I)



(II)

Views of (I) and (II), showing the displacement ellipsoids, atomic numbering and the correct absolute configuration are given in Figs. 1 & 2, respectively. The absolute configuration of each molecule was determined by refinement of the structure and the enantiopole parameter according to the method of Flack (1983). There are no significant differences between the corresponding bond lengths and angles of molecules (I) and (II). Most bond lengths and angles are within expected ranges. The C(2)—C(8), C(8)—C(11) and C(11)—S(12) bonds are slightly elongated in both structures; the C—S bonds are about 0.06 Å longer than the typical value for such bonds in a similar environment (Allen *et al.*, 1992). A similar elongation of about 0.04 Å was observed in the structure of the related compound, (−)-(1*S*,2*S*,5*R*)-1-(*N*,*N*-dimethylsulfamoylmethyl)-2-iso-

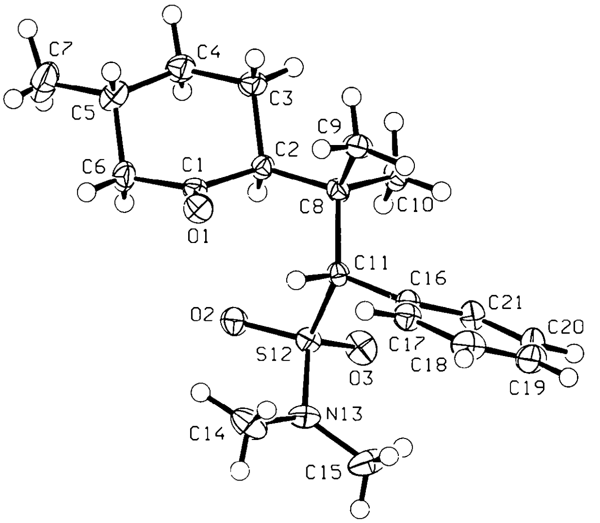


Fig. 1. View of the molecule of (I) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

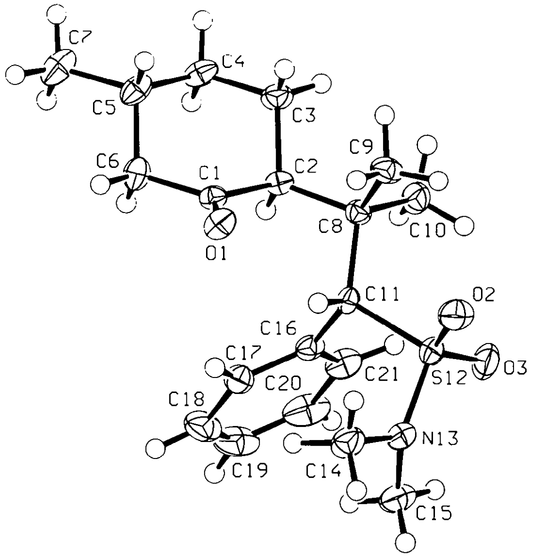


Fig. 2. View of the molecule of (II) showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by spheres of arbitrary size.

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propyl-5-methylcyclohexan-1-ol (Linden & Stanchev, 1995). The cyclohexanone ring has a virtually undistorted chair conformation. The sp^2 C atom, C(1), does not cause any significant distortion of the ring conformation.

Allowing for the interchange of the Ph and Me_2NSO_2 substituents, the torsion angles about C(2)—C(8) and C(8)—C(11) are very similar in (I) and (II), showing that this interchange does not affect the preferred conformation of the molecule.

Experimental

Compounds (I) and (II) were prepared as described by Stanchev, Christov, Simova, Mladenova & Linden (1995). Suitable crystals were grown by slow evaporation of $CHCl_3$ solutions.

Compound (I)

Crystal data

$C_{19}H_{29}NO_3S$
$M_r = 351.50$
Monoclinic
$P2_1$
$a = 8.684\ (3)$ Å
$b = 12.239\ (4)$ Å
$c = 8.974\ (2)$ Å
$\beta = 93.91\ (2)°$
$V = 951.6\ (5)$ Å^3
$Z = 2$
$D_x = 1.227$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 19.0–20.0°$
$\mu = 0.186$ mm^{-1}
$T = 173\ (1)$ K
Prism
0.38 × 0.35 × 0.23 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
4946 measured reflections
4474 independent reflections
4000 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.034$

$\theta_{\rm max} = 30°$
$h = -10 \rightarrow 12$
$k = -14 \rightarrow 17$
$l = -12 \rightarrow 12$
3 standard reflections monitored every 150 reflections intensity decay: insignificant

Refinement

Refinement on *F*
$R = 0.0368$
$wR = 0.0353$
$S = 1.754$
4000 reflections
332 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$

$(\Delta/\sigma)_{\rm max} = 0.0005$
$\Delta\rho_{\rm max} = 0.49$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.36$ 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)

Compound (II)

Crystal data

$C_{19}H_{29}NO_3S$
$M_r = 351.50$
Trigonal
$P3_2$
$a = 12.457\ (1)$ Å
$c = 10.505\ (2)$ Å
$V = 1411.7\ (3)$ Å^3
$Z = 3$
$D_x = 1.240$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å
Cell parameters from 25 reflections
$\theta = 19.0–20.0°$
$\mu = 0.188$ mm^{-1}
$T = 173\ (1)$ K
Prism
0.50 × 0.43 × 0.32 mm
Colourless

Data collection

Rigaku AFC-5*R* diffractometer
$\omega/2\theta$ scans
Absorption correction: none
5515 measured reflections
4932 independent reflections
4651 observed reflections $[I > 2\sigma(I)]$
$R_{\rm int} = 0.014$

$\theta_{\rm max} = 30°$
$h = -15 \rightarrow 15$
$k = -14 \rightarrow 15$
$l = -13 \rightarrow 14$
3 standard reflections monitored every 150 reflections intensity decay: insignificant

Refinement

Refinement on *F*
$R = 0.0295$
$wR = 0.0292$
$S = 1.768$
4651 reflections
333 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + (0.005F_o)^2]$
$(\Delta/\sigma)_{\rm max} = 0.0003$

$\Delta\rho_{\rm max} = 0.27$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.25$ e Å^{-3}
Extinction correction: Zachariasen (1963)
Extinction coefficient: $g = 6\ (1) \times 10^{-7}$
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) *for* (I)

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

	x	y	z	$U_{\rm eq}$
S(12)	0.13408 (6)	0.37270	0.34765 (5)	0.0210 (1)
O(1)	−0.2792 (2)	0.4830 (1)	0.2922 (2)	0.0281 (5)
O(2)	0.0674 (2)	0.4322 (1)	0.4665 (2)	0.0302 (5)
O(3)	0.2317 (2)	0.2802 (1)	0.3867 (2)	0.0335 (5)
N(13)	0.2383 (2)	0.4600 (2)	0.2612 (2)	0.0272 (6)
C(1)	−0.2632 (2)	0.4331 (2)	0.4090 (3)	0.0213 (6)
C(2)	−0.2195 (3)	0.3109 (2)	0.4180 (2)	0.0199 (6)
C(3)	−0.3652 (3)	0.2539 (2)	0.4728 (3)	0.0274 (7)
C(4)	−0.4076 (3)	0.3004 (2)	0.6230 (3)	0.0306 (8)
C(5)	−0.4387 (3)	0.4242 (2)	0.6160 (3)	0.0306 (8)
C(6)	−0.3003 (3)	0.4816 (2)	0.5557 (3)	0.0284 (7)
C(7)	−0.4730 (4)	0.4679 (3)	0.7689 (4)	0.047 (1)
C(8)	−0.1542 (2)	0.2599 (2)	0.2756 (2)	0.0210 (6)
C(9)	−0.2793 (3)	0.2501 (2)	0.1470 (3)	0.0283 (7)
C(10)	−0.0933 (3)	0.1447 (2)	0.3172 (3)	0.0320 (8)
C(11)	−0.0234 (2)	0.3337 (2)	0.2156 (2)	0.0188 (6)
C(14)	0.1657 (4)	0.5657 (2)	0.2211 (4)	0.041 (1)
C(15)	0.3555 (3)	0.4250 (3)	0.1638 (3)	0.042 (1)
C(16)	0.0438 (3)	0.2958 (2)	0.0722 (2)	0.0215 (6)
C(17)	0.0076 (3)	0.3550 (2)	−0.0589 (2)	0.0268 (7)
C(18)	0.0709 (3)	0.3278 (2)	−0.1923 (3)	0.0351 (8)
C(19)	0.1699 (3)	0.2397 (3)	−0.1974 (3)	0.0392 (9)
C(20)	0.2057 (3)	0.1794 (2)	−0.0694 (3)	0.0376 (8)
C(21)	0.1434 (3)	0.2063 (2)	0.0645 (3)	0.0288 (7)

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

S(12)—O(2)	1.445 (2)	C(1)—C(6)	1.499 (3)
S(12)—O(3)	1.444 (2)	C(2)—C(3)	1.554 (3)
S(12)—N(13)	1.630 (2)	C(2)—C(8)	1.563 (3)

S(12)—C(11)	1.811 (2)	C(3)—C(4)	1.531 (4)
O(1)—C(1)	1.213 (3)	C(4)—C(5)	1.539 (3)
N(13)—C(14)	1.474 (4)	C(5)—C(6)	1.523 (3)
N(13)—C(15)	1.450 (3)	C(8)—C(11)	1.574 (3)
C(1)—C(2)	1.544 (3)	C(11)—C(16)	1.522 (3)
O(2)—S(12)—O(3)	118.3 (1)	C(1)—C(2)—C(3)	104.4 (2)
O(2)—S(12)—N(13)	106.5 (1)	C(1)—C(2)—C(8)	116.5 (2)
O(2)—S(12)—C(11)	107.02 (9)	C(3)—C(2)—C(8)	115.4 (2)
O(3)—S(12)—N(13)	107.1 (1)	C(2)—C(3)—C(4)	111.2 (2)
O(3)—S(12)—C(11)	110.9 (1)	C(3)—C(4)—C(5)	112.5 (2)
N(13)—S(12)—C(11)	106.3 (1)	C(4)—C(5)—C(6)	109.2 (2)
S(12)—N(13)—C(14)	116.7 (2)	C(1)—C(6)—C(5)	110.6 (2)
S(12)—N(13)—C(15)	121.9 (2)	C(2)—C(8)—C(11)	111.1 (2)
C(14)—N(13)—C(15)	114.7 (2)	S(12)—C(11)—C(8)	117.2 (1)
O(1)—C(1)—C(2)	123.1 (2)	S(12)—C(11)—C(16)	108.5 (1)
O(1)—C(1)—C(6)	122.7 (2)	C(8)—C(11)—C(16)	116.2 (2)
C(2)—C(1)—C(6)	113.9 (2)		

S(12)—C(11)—C(8)—C(2)	52.5 (2)
C(1)—C(2)—C(3)—C(4)	−58.1 (3)
C(1)—C(2)—C(8)—C(11)	48.4 (2)
C(1)—C(6)—C(5)—C(4)	54.2 (3)
C(2)—C(1)—C(6)—C(5)	−61.3 (3)
C(2)—C(3)—C(4)—C(5)	58.6 (3)
C(2)—C(8)—C(11)—C(16)	−176.9 (2)
C(3)—C(2)—C(1)—C(6)	61.0 (2)
C(3)—C(2)—C(8)—C(11)	171.3 (2)
C(3)—C(4)—C(5)—C(6)	−54.2 (3)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

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

	x	y	z	U_{eq}
S(12)	0.41738 (3)	0.01902 (3)	−0.04420	0.0255 (1)
O(1)	0.7361 (1)	0.20791 (9)	0.2162 (1)	0.0293 (4)
O(2)	0.3752 (1)	0.0927 (1)	0.0205 (1)	0.0386 (6)
O(3)	0.3281 (1)	−0.1055 (1)	−0.0809 (1)	0.0389 (5)
N(13)	0.4860 (1)	0.0940 (1)	−0.1744 (1)	0.0270 (5)
C(1)	0.7376 (1)	0.1160 (1)	0.2529 (1)	0.0219 (5)
C(2)	0.6237 (1)	−0.0143 (1)	0.2560 (1)	0.0208 (5)
C(3)	0.6082 (2)	−0.0580 (2)	0.3964 (2)	0.0286 (6)
C(4)	0.7242 (2)	−0.0564 (2)	0.4467 (2)	0.0308 (7)
C(5)	0.8360 (2)	0.0734 (2)	0.4414 (2)	0.0288 (6)
C(6)	0.8543 (2)	0.1237 (2)	0.3047 (2)	0.0287 (6)
C(7)	0.9548 (2)	0.0807 (2)	0.4905 (2)	0.0415 (9)
C(8)	0.5034 (1)	−0.0298 (1)	0.1933 (1)	0.0219 (5)
C(9)	0.4536 (2)	0.0429 (2)	0.2681 (2)	0.0305 (7)
C(10)	0.4035 (2)	−0.1684 (2)	0.1956 (2)	0.0315 (6)
C(11)	0.5394 (1)	0.0213 (1)	0.0530 (1)	0.0198 (5)
C(14)	0.5781 (2)	0.2252 (2)	−0.1642 (2)	0.0364 (7)
C(15)	0.5013 (2)	0.0294 (2)	−0.2834 (2)	0.0375 (9)
C(16)	0.6073 (1)	−0.0284 (1)	−0.0256 (1)	0.0237 (6)
C(17)	0.7298 (2)	0.0526 (2)	−0.0606 (2)	0.0303 (7)
C(18)	0.7948 (2)	0.0138 (2)	−0.1377 (2)	0.043 (1)
C(19)	0.7390 (2)	−0.1063 (2)	−0.1794 (2)	0.048 (1)
C(20)	0.6180 (2)	−0.1888 (2)	−0.1451 (2)	0.045 (1)
C(21)	0.5514 (2)	−0.1509 (2)	−0.0693 (2)	0.0337 (7)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

S(12)—O(2)	1.436 (1)	C(1)—C(6)	1.509 (2)
S(12)—O(3)	1.438 (1)	C(2)—C(3)	1.551 (2)
S(12)—N(13)	1.636 (1)	C(2)—C(8)	1.558 (2)
S(12)—C(11)	1.819 (1)	C(3)—C(4)	1.529 (2)
O(1)—C(1)	1.218 (2)	C(4)—C(5)	1.518 (2)
N(13)—C(14)	1.458 (2)	C(5)—C(6)	1.538 (2)
N(13)—C(15)	1.465 (2)	C(8)—C(11)	1.579 (2)
C(1)—C(2)	1.532 (2)	C(11)—C(16)	1.518 (2)
O(2)—S(12)—O(3)	118.89 (8)	C(1)—C(2)—C(3)	106.2 (1)
O(2)—S(12)—N(13)	106.52 (7)	C(1)—C(2)—C(8)	116.5 (1)
O(2)—S(12)—C(11)	107.13 (7)	C(3)—C(2)—C(8)	114.6 (1)
O(3)—S(12)—N(13)	107.06 (7)	C(2)—C(3)—C(4)	111.9 (1)
O(3)—S(12)—C(11)	110.91 (7)	C(3)—C(4)—C(5)	111.1 (1)
N(13)—S(12)—C(11)	105.47 (6)	C(4)—C(5)—C(6)	109.8 (1)
S(12)—N(13)—C(14)	118.2 (1)	C(1)—C(6)—C(5)	111.7 (1)
S(12)—N(13)—C(15)	121.0 (1)	C(2)—C(8)—C(11)	106.5 (1)
C(14)—N(13)—C(15)	115.3 (1)	S(12)—C(11)—C(8)	116.83 (9)
O(1)—C(1)—C(2)	124.1 (1)	S(12)—C(11)—C(16)	108.64 (9)
O(1)—C(1)—C(6)	121.5 (1)	C(8)—C(11)—C(16)	116.6 (1)
C(2)—C(1)—C(6)	114.4 (1)		

S(12)—C(11)—C(8)—C(2)	−178.52 (9)
C(1)—C(2)—C(3)—C(4)	−57.4 (2)
C(1)—C(2)—C(8)—C(11)	54.4 (1)
C(1)—C(6)—C(5)—C(4)	53.4 (2)
C(2)—C(1)—C(6)—C(5)	−55.9 (2)
C(2)—C(3)—C(4)—C(5)	60.2 (2)
C(2)—C(8)—C(11)—C(16)	50.7 (1)
C(3)—C(2)—C(1)—C(6)	56.0 (2)
C(3)—C(2)—C(8)—C(11)	179.3 (1)
C(3)—C(4)—C(5)—C(6)	−55.9 (2)

The data collections were extended to include the measurement of the intensities of the Friedel opposites of all unique reflections with $2\theta < 50°$ for (I) and $2\theta < 55°$ for (II). 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 values of the enantiopole parameter were 0.07 (7) for (I) and −0.02 (5) for (II), thus confirming that the atomic coordinates for each structure represented the correct enantiomorph.

For both compounds, 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 structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *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: BM1003). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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