

Data collection

Rigaku AFC-5R diffractometer	$R_{\text{int}} = 0.009$
ω - 2θ scans	$\theta_{\text{max}} = 27.45^\circ$
Absorption correction: none	$h = 0 \rightarrow 16$
2456 measured reflections	$k = 0 \rightarrow 6$
2353 independent reflections	$l = -18 \rightarrow 18$
1561 reflections with $I > 1.5\sigma(I)$	3 standard reflections
	every 150 reflections
	intensity decay: none

Refinement

Refinement on F	$(\Delta/\sigma)_{\text{max}} = 0.001$
$R = 0.042$	$\Delta\rho_{\text{max}} = 0.15 \text{ e } \text{\AA}^{-3}$
$wR = 0.045$	$\Delta\rho_{\text{min}} = -0.27 \text{ e } \text{\AA}^{-3}$
$S = 1.63$	Extinction correction: none
1561 reflections	Scattering factors from International Tables for X-ray Crystallography (Vol. IV)
171 parameters	
H atoms refined isotropically	
$w = 4F_o^2/\sigma^2(F_o^2)$	

Table 1. Selected geometric parameters (\AA , $^\circ$)

O(1)—C(12)	1.291 (2)	C(3)—C(9)	1.438 (2)
O(2)—C(12)	1.243 (2)	C(3)—C(10)	1.494 (2)
N(1)—C(2)	1.380 (2)	C(10)—C(11)	1.517 (2)
N(1)—C(8)	1.375 (2)	C(11)—C(12)	1.493 (2)
C(2)—C(3)	1.358 (2)		
C(2)—N(1)—C(8)	108.9 (1)	C(3)—C(9)—C(4)	133.1 (2)
N(1)—C(2)—C(3)	110.2 (2)	C(3)—C(9)—C(8)	107.7 (1)
C(2)—C(3)—C(9)	106.1 (1)	C(3)—C(10)—C(11)	113.3 (1)
C(2)—C(3)—C(10)	129.1 (1)	C(10)—C(11)—C(12)	115.1 (1)
C(9)—C(3)—C(10)	124.8 (1)	O(1)—C(12)—O(2)	122.5 (1)
N(1)—C(8)—C(7)	130.7 (2)	O(1)—C(12)—C(11)	113.8 (1)
N(1)—C(8)—C(9)	107.0 (1)	O(2)—C(12)—C(11)	122.3 (1)

All H atoms were located from difference Fourier maps and included in the refinement calculations isotropically. The B_{eq} values of H atoms ranged from $3.4(4) \text{ \AA}^2$ for H(11B) to $9.0(7) \text{ \AA}^2$ for H(3), and the C—H bond distances from $0.88(2) \text{ \AA}$ for N(1)—H(1) to $1.02(2) \text{ \AA}$ for C(10)—H(10A).

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1985). Program(s) used to solve structure: *MITHRIL* (Gilmore, 1984) and *DIRDIF* (Beurskens, 1984). Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *ORTEPII* (Johnson, 1976).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FR1089). Services for accessing these data are described at the back of the journal. A packing diagram has also been deposited.

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The Absolute Configuration of *cis*-(α S,1S,2R)-2-Methyl-1-(α -methylbenzyl-amino)cyclohexanecarboxamide

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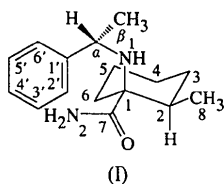
Abstract

The title compound, $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}$, was obtained during our investigations on the asymmetric Strecker synthesis of non-proteinogenous α -quarternary α -amino acids with vicinal chiral centres. The X-ray structure determination was carried out in order to verify the absolute configuration, which was determined *via* experimentally measured triplet phases.

Comment

During our systematic investigations on an asymmetric Strecker synthesis starting from (*RS*)-2-methylcyclohexanone, *S*-(–)- α -methylbenzylamine and trimethylsilyl cyanide, we obtained either kinetically or thermodynamically controlled diastereomeric mixtures of the four feasible 2-methyl-1-(α -methylbenzylamino)cyclohexanecarbonitriles as crucial intermediates (Volk & Frahm, 1996). These were hydrolysed to the corresponding α -amino amide mixtures containing 11–15% of the title compound (I), (Fig. 1), which was isolated by means of column chromatography, followed by Lobar chromatography and preparative HPLC. The complete NMR data set of (I) has been published elsewhere (Volk & Frahm, 1996). Its relative stereochemistry was derived from the heteronuclear ^{13}C - ^1H coupling between C7 and the protons H21, H61 and H62. Since

(I) was prepared using α S-configured α -methylbenzylamine as chiral auxiliary in an asymmetric Strecker synthesis, we were able to attribute unambiguously the α S,1S,2R configuration. The absolute configuration was determined by direct measurement of suitable triplet phases (Hümmer & Weckert, 1995). This method does not depend on anomalous-dispersion effects and works also, therefore, for organic light-atom structures with low oxygen and nitrogen contents. The three-beam interference experiments were carried out at the Swiss-Norwegian beamline at the ESRF (Grenoble, France).



The values of the dihedral angles C7—C1—C2—C8 [$-65.1(2)^\circ$], N1—C1—C2—C8 [$52.8(2)^\circ$], C7—C1—C2—H21 [$50.7(12)^\circ$] and N1—C1—C2—H21 [$168.6(11)^\circ$] prove the *cis*-substitution pattern at the C1 and C2 positions of the cyclohexane ring, which shows the expected chair conformation. The bulky α -methylbenzylamino substituent at C1 is in an axial position, whereas the carboxamide and methyl substituents take equatorial positions at C1 and C2, respectively. The structure shows an intermolecular N2—H3...O1ⁱ hydrogen bond with an N...O distance of 2.859(2) Å and a bond angle of 159(3)° [symmetry code: (i) $1-x, y+\frac{1}{2}, -z$], as well as a weak intramolecular bridge N2—H2...N1 [N...N 2.697(2) Å and N—H...N 108(2)°].

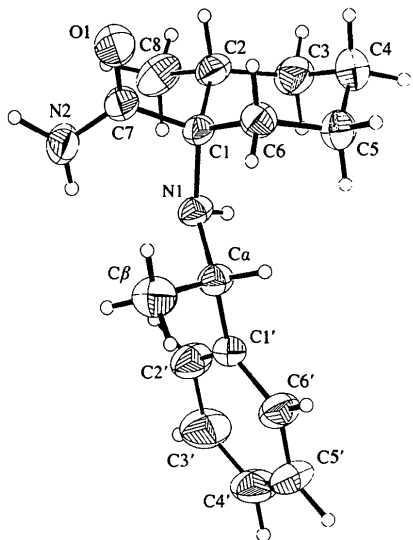


Fig. 1. The structure of (I) with 50% probability displacement ellipsoids for non-H atoms and arbitrarily small displacement spheres for H atoms.

Experimental

The title α -amino-amide, (I), was prepared by hydrolysis of diastereomeric mixtures of the four feasible 2-methyl-1-(α -methylbenzylamino)cyclohexanecarbonitriles followed by column chromatography on silica gel and preparative HPLC on RP-18 material. Colourless crystals were obtained from methanol–water (1:1) [m.p. 321–323 K; $[\alpha]_D^{25} = -3.7^\circ$ ($c = 1.15$, MeOH)].

Crystal data

C₁₆H₂₄N₂O
M_r = 260.38
 Monoclinic
*P*2₁
a = 6.973(1) Å
b = 7.678(1) Å
c = 14.472(1) Å
 β = 92.830(3)°
V = 773.9(2) Å³
Z = 2
D_x = 1.117 Mg m⁻³
D_m not measured

Mo *K* α radiation
 λ = 0.71073 Å
 Cell parameters from 6118 reflections
 θ = 11.6–25.6°
 μ = 0.0654 mm⁻¹
T = 293 K
 Prism
 0.3 × 0.25 × 0.2 mm
 Colourless

Data collection

MAR 180 mm image-plate scanner
 Area detector
 Absorption correction: none
 6998 measured reflections
 2762 independent reflections

2762 reflections with $F > 0$
 $R_{\text{int}} = 0.03$
 $\theta_{\text{max}} = 26^\circ$
 $h = -8 \rightarrow 8$
 $k = -8 \rightarrow 8$
 $l = -17 \rightarrow 17$

Refinement

Refinement on *F*
R = 0.0361
 wR = 0.0387
S = 1.16
 2762 reflections
 189 parameters
 H atoms: see below
 $w = 1/[\sigma^2(F) + 0.15]$
 $(\Delta/\sigma)_{\text{max}} = 0.01$

$\Delta\rho_{\text{max}} = 0.22 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\text{min}} = -0.20 \text{ e } \text{Å}^{-3}$
 Extinction correction: Larson (1970)
 Extinction coefficient: 514(1)
 Scattering factors from *International Tables for X-ray Crystallography* (Vol. IV)

Table 1. Selected geometric parameters (Å, °)

O1—C7	1.228(2)	N2—C7	1.323(2)
N1—C α	1.476(2)	C1'—C α	1.521(2)
N1—C1	1.479(2)	C α —C β	1.530(3)
C1—N1—C α	120.0(1)	C β —C α —N1	112.1(1)
C1'—C α —N1	109.4(1)	C β —C α —C1'	110.0(1)

The structure was solved by direct methods. Atoms H1 to H4 were refined isotropically. The positions of the remaining H atoms were calculated, each with an isotropic displacement parameter of 1.05 times that of the attached C atom. All other atoms were refined anisotropically. The absolute configuration was determined by means of measured triplet phases by three-beam interferences. The experimental procedure is described elsewhere (Hümmer & Weckert, 1995; Weckert & Hümmer, 1997). The signs of the three triplet phases with moduli close to 90° were determined. All of them indicate unambiguously the same absolute structure.

Data collection: *MARxds* (Kabsch, 1988). Cell refinement: *MARxds*. Data reduction: *CRYSTALS* (Watkin *et al.*, 1985). Program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994). Program(s) used to refine structure: *CRYSTALS*. Molecular graphics: *CRYSTAN* (Buzzlaff & Rothammel, 1988). Software used to prepare material for publication: *CRYSTALS* and local software.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1153). Services for accessing these data are described at the back of the journal.

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A Cyclic Sulfate with a Seven-Membered Ring: 1,3,2-Dioxathiepane 2,2-Dioxide

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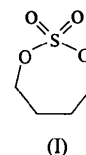
Abstract

We report the first structure of a seven-membered cyclic organosulfate, $C_4H_8O_4S$. The molecule has almost a local C_2 symmetry (r.m.s. deviation within molecule 1 is 0.018 Å). The two molecules in the asymmetric unit show the same conformation [r.m.s. deviation of all non-

H atoms is 0.017 (7) Å]. Although the seven-membered ring is flexible in solution, the conformations of the two independent molecules are apparently not influenced by crystal-packing effects.

Comment

Epoxides play a unique role in organic synthesis. They simultaneously activate and protect adjacent functionalized C atoms for nucleophilic attack (Gao & Sharpless, 1988). The same favorable properties are shared by cyclic sulfates, which have recently found useful applications as ring-closing reagents for the synthesis of saturated phosphorus-containing heterocycles (Field & Thomas, 1996) and as substrates for selective substitution reactions involving fluoride or phenoxide ions as nucleophiles (Berridge *et al.*, 1990). The title compound, (I), was prepared in a two-step synthesis according to the method described by Sharpless (Gao & Sharpless, 1988).



Compound (I) crystallizes in space group $P\bar{1}$ with two molecules in the asymmetric unit. Both molecules have a local C_2 symmetry (r.m.s. deviation within molecule 1 is 0.018 Å), which does not coincide with any crystallographic symmetry element. The S—O and O—C bond lengths are as expected from other cyclic sulfates. In both independent molecules, the α -C—C (*e.g.* C1—C2) bond lengths (average 1.488 Å) are shorter than the β -C—C (*e.g.* C2—C3) bond lengths (average 1.504 Å), but agree within both molecules in spite of their different environments [r.m.s. deviation of all non-H atoms is 0.017 (7) Å]. The relatively short C_{sp^3} — C_{sp^3} bonds lengths and the correspondingly large

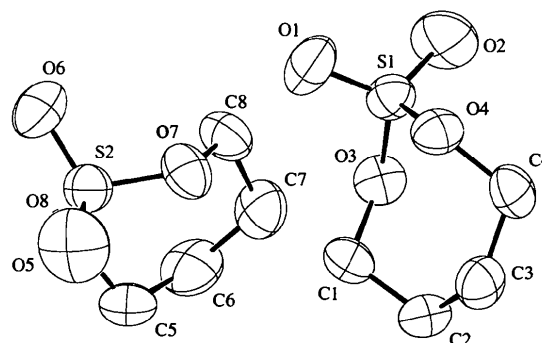


Fig. 1. View of the two molecules in the asymmetric unit of (I) showing the labeling of the non-H atoms. Atomic displacement ellipsoids are shown at the 50% probability level.