Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical *via* ψ scan (Fair, 1990)
T_{min} = 0.924, T_{max} = 0.999
4502 measured reflections
4502 independent reflections
2917 reflections with $I > 2\sigma(I)$
θ_{max} = 26.29°
$h = 0 \rightarrow 11$
$k = -12 \rightarrow 12$
$l = -15 \rightarrow 15$
3 standard reflections
frequency: 120 min
intensity decay: 2.3%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.062
$wR(F^2)$ = 0.129
S = 1.481
4502 reflections
404 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0237P)^2 + 0.5769P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.182 e Å^{-3}
$\Delta\rho_{min}$ = −0.172 e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.008 (1)
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å,°)*

	Molecule 1	Molecule 2†
O1—C1	1.217 (3)	1.218 (3)
O2—C4	1.221 (3)	1.223 (3)
C12—C13	1.319 (4)	1.327 (5)
O1—C1—C2	119.6 (3)	120.3 (3)
O1—C1—C6	120.2 (3)	119.5 (3)
O2—C4—C3	121.0 (3)	119.6 (3)
O2—C4—C5	118.7 (3)	120.0 (3)
C3—C4—C5	120.3 (2)	120.4 (2)
C6—C1—C2	120.2 (2)	120.3 (2)
C14—C15—C11	93.6 (2)	93.1 (3)
C11—C12—C13—C14	0.3 (3)	−0.1 (4)
C13—C12—C11—C15	32.5 (3)	−33.3 (3)
C15—C14—C13—C12	−33.3 (3)	33.6 (3)

† The atomic labels are each appended by *A*.

H atoms were located from difference Fourier maps and refined isotropically. The needle-shaped fragile crystals were difficult to cut so, eventually, a specimen of length 0.64 mm had to be used.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *ORTEP*II (Johnson, 1976). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AB1411). Services for accessing these data are described at the back of the journal.

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(±)-*tert*-Butyl 3-Hydroxy-4-phenyl-2-(*p*-toluenesulfonylamino)pentanoate–Dichloromethane (1/1): a Pseudo Centre of Symmetry in an Enantiomeric Pair

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Abstract

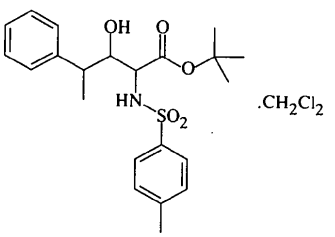
The title compound, $C_{22}H_{29}NO_5S.CH_2Cl_2$, was investigated in order to study the stereochemistry of the β-hydroxy-α-amino acid derivatives formed by the aldol reaction of an ester enolate with an aldehyde. The racemate crystallizes with two independent formula units in the non-centrosymmetric space group *Pn* as hydrogen-bonded dimers in which the two enantiomers are related by a pseudo centre of symmetry.

Comment

Among non-proteinogenic unnatural α-amino acids, β-hydroxy-α-amino acids are of special interest, especially in view of their activity as enzyme inhibitors (Rando, 1975; Walsh, Metzler, Powell & Jacobsen, 1980; Abeles,

1981; Walsh, 1982; Ramalingam & Woodward, 1985; Tendler, Threadgill & Tisdale, 1987). A number of methods are known for the synthesis of these important compounds, the aldol reaction of aldehydes with α-amino acid equivalents being one of the best studied (Williams, 1989; Duthaler, 1994). The relative configuration of the aldol product depends strongly on the configuration of the enolate reacting with the aldehyde. An efficient method of controlling the configuration of an α-amino acid ester enolate is offered *via* a chelated metal complex, the reaction of which with aldehydes should lead to diastereomeric *anti* and *syn* aldol products with noticeable selectivity due to the fixed enolate geometry (Kazmaier & Grandel, 1995; Grandel, Kazmaier & Nuber, 1996). From a synthetic point of view, reactions with chiral α-substituted aldehydes are of great interest. In addition to the possibility of the formation of complex structures, the asymmetric centre of the aldehyde allows control of the absolute configuration of the newly generated centres of asymmetry. As a simple model, the aldol reaction of the tin-chelated enolate of *N*-tosyl *tert*-butylglycinate (obtained by deprotonation of the latter with two equivalents of LDA and subsequent addition of $SnCl_2$) with racemic 2-phenylpropionaldehyde was investigated. The aldol product consisted of an 87:10:3 mixture of isomers. To determine the relative configuration of the main diastereomer, an X-ray structure investigation was performed.

From the systematic absences, two space groups were possible: the centrosymmetric *P*2/*n* and the non-centrosymmetric *Pn*. The former appeared to be more probable for the racemate, but no structure solution was obtained by direct methods. The intensity statistics strongly suggested a non-centrosymmetric space group with $|E^2 - 1| = 0.767$ (expected 0.968 for centrosymmetric and 0.736 for non-centrosymmetric). The structure was solved immediately in *Pn*, with the enantiomeric pair and two co-crystallized dichloromethane solvent molecules constituting the asymmetric unit of the structure, (I), displayed in Fig. 1.



(I)

Despite the lack of 0*k*0 systematic absences, the structure can be solved in the centrosymmetric space group $P2_1/n$. A subsequent anisotropic refinement, incorporating disorder for the solvent molecule, converged at a very high *R* factor of around 0.22 [$wR(F^2)$ = 0.52]. Further splitting of some amino acid atoms with

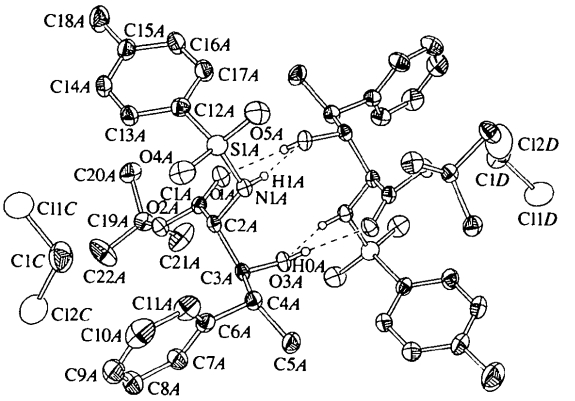


Fig. 1. The asymmetric unit with atomic numbering (*ORTEP*II, Johnson, 1976) (*B*, not explicitly labelled, is equivalent to *A*). Displacement ellipsoids are shown at 50% probability levels. H atoms of the hydroxyl groups and amide groups involved in hydrogen bonds are shown as spheres of arbitrary size; other H atoms have been omitted for clarity. O and N atoms are drawn without shading, S and Cl atoms as plain ellipsoids. Only one position of the disordered solvent molecule is shown.

elongated displacement ellipsoids did not improve these values.

The D-enantiomer (*A*) and the L-enantiomer (*B*) form a hydrogen-bonded dimer in the crystal and are related by a pseudo centre of symmetry located at approximately $x = \frac{1}{2}$, $y = \frac{3}{4}$ and $z = \frac{1}{2}$. The *x* and *z* coordinates result from our choice of origin on these axes (free floating in *Pn*), but the *y* coordinate is important since there are mirror glide planes at $y = 0$ and $y = \frac{1}{2}$. This means that pseudo centres of symmetry are located outside the glide planes, in contrast to *P*2/*n* which has true centres of symmetry located on the glide planes.

The differences between the two molecules as far as bond lengths and angles are concerned are insignificant, and all parameters have normal values. Differences between corresponding torsion angles (with opposite signs) are generally small, but with significant deviations of up to 7.5° (>30σ) (Table 1). A closer inspection of Fig. 1 reveals these differences most clearly for the phenyl groups. After inversion of molecule *B*, the r.m.s. deviation for superimposing non-H atoms in the two amino acid structures is 0.170 Å.

The two solvent molecules also occupy positions related by the pseudo centre of symmetry, but have different orientations. Two slightly different positions, with populations 0.55 (1) and 0.45 (1), were refined for each Cl atom in molecule *D*, but the disorder is probably even more complex. Difference Fourier electron density maps indicate some disorder also for molecule *C*, but no refinement model was found that yielded better results than usual anisotropy.

The four hydrogen bonds in the dimer, two with hydroxyl donors and ester C=O acceptors, and two with amide donors and hydroxyl acceptors, are listed in

Table 2. There are no short C—H···O contacts in the crystal; dimers and solvent molecules are held together by van der Waals contacts only.

As part of an ongoing project (Dalhus & Görbitz, 1997), we carried out an investigation of racemates which are present as such in each crystal, *i.e.* no spontaneous separation of enantiomers takes place upon crystallization. The structures were retrieved from the Cambridge Structural Database (Allen & Kennard, 1993) and identified by combining bit screen 98 (space group is non-centrosymmetric) with a search for various L/D, *R/S* and +/− combinations or keywords such as 'racemate' or 'racemic' in the title. The accepted entries were subjected to subsequent manual scrutiny with checking of *Z* values, *etc.* (This method is not foolproof; if there are no indications in the title that the published coordinates are actually those of a racemic pair, we have no way of finding the structure in the database.) The results show that about 7% of the racemates grow crystals in non-centrosymmetric space groups. Within this subgroup there were no observations of structures with three or more molecules in the asymmetric unit ($Z' \geq 3$), but about one in five (29 structures, 1.5%) has $Z' = 2$ (disregarding solvent molecules, *etc.*). As in the title compound, the two independent molecules in these structures are always related by a pseudo centre of symmetry.

Experimental

The crystals were grown by slowly evaporating a solution in dichloromethane.

Crystal data

$C_{22}H_{29}NO_5S.CH_2Cl_2$
$M_r = 504.45$
Monoclinic
Pn
$a = 14.4318\ (14)$ Å
$b = 10.2646\ (10)$ Å
$c = 17.997\ (2)$ Å
$\beta = 103.689\ (1)°$
$V = 2590.2\ (4)$ Å^3
$Z = 4$
$D_x = 1.294$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 6132 reflections
$\mu = 0.364$ mm^{-1}
$T = 123\ (2)$ K
Plate
0.85 × 0.45 × 0.15 mm
Colourless

Data collection

Siemens SMART CCD diffractometer
Sets of exposures each taken over 0.6° ω rotation
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.846$, $T_{max} = 0.961$

30 962 measured reflections
12 162 independent reflections
11 248 reflections with $I > 2\sigma(I)$
$R_{int} = 0.022$
$\theta_{max} = 28.97°$
$h = -19 \rightarrow 19$
$k = -13 \rightarrow 13$
$l = -23 \rightarrow 23$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.098$
$S = 1.086$
12 161 reflections
613 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.036P)^2 + 1.4P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = -0.031$
$\Delta\rho_{max} = 0.450$ e Å^{-3}
$\Delta\rho_{min} = -0.525$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute configuration: Flack (1983)
Flack parameter = 0.47 (4)

Table 1. *Selected torsion angles (°)*

C12*A*—S1*A*—N1*A*—C2*A*	−64.3 (2)
C12*B*—S1*B*—N1*B*—C2*B*	64.0 (2)
C19*A*—O2*A*—C1*A*—C2*A*	−169.4 (2)
C19*B*—O2*B*—C1*B*—C2*B*	176.9 (2)
S1*A*—N1*A*—C2*A*—C1*A*	89.1 (2)
S1*B*—N1*B*—C2*B*—C1*B*	−89.4 (2)
O2*A*—C1*A*—C2*A*—N1*A*	−155.1 (2)
O2*B*—C1*B*—C2*B*—N1*B*	161.4 (2)
N1*A*—C2*A*—C3*A*—C4*A*	65.4 (2)
N1*B*—C2*B*—C3*B*—C4*B*	−60.4 (2)
C2*A*—C3*A*—C4*A*—C6*A*	68.5 (2)
C2*B*—C3*B*—C4*B*—C6*B*	−68.3 (2)
C3*A*—C4*A*—C6*A*—C7*A*	63.4 (3)
C3*B*—C4*B*—C6*B*—C7*B*	−61.0 (3)
N1*A*—S1*A*—C12*A*—C13*A*	99.4 (2)
N1*B*—S1*B*—C12*B*—C13*B*	−100.3 (2)
C1*A*—O2*A*—C19*A*—C20*A*	−65.6 (3)
C1*B*—O2*B*—C19*B*—C20*B*	64.4 (2)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O3*A*—H0*A*···O1*B*	0.86 (3)	1.93 (3)	2.721 (2)	152 (3)
O3*B*—H0*B*···O1*A*	0.76 (4)	2.04 (4)	2.747 (2)	157 (3)
N1*A*—H1*A*···O3*B*	0.75 (3)	2.18 (3)	2.905 (2)	166 (3)
N1*B*—H1*B*···O3*A*	0.88 (3)	2.08 (3)	2.932 (2)	163 (2)

The data collection covered over a full sphere of reciprocal space by a combination of four sets of exposures with the detector set at $2\theta = 29°$. Each set had a different φ angle for the crystal and each exposure covered 0.6° in ω. The crystal-to-detector distance was 5.01 cm. Coverage of all data is 98.7 and 91.6% complete to 55 and 60° in 2θ, respectively, while the unique set is 100 and 98.9% complete at these two 2θ angles. H atoms bonded to O or N atoms were refined isotropically; other H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds for methyl groups). U_{iso} values were constrained to be $1.2U_{eq}$ of the carrier atom, or $1.5U_{eq}$ for methyl groups. Refinement parameters included the *SHELXTL BASF* parameter for racemic twinning, which is used for the Flack parameter (Flack, 1983).

Data collection: *SMART* (Siemens, 1995). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *SHELXTL* (Sheldrick, 1994). Molecular graphics: *SHELXTL*. Software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: JZ1189). Services for accessing these data are described at the back of the journal.

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Polysulfonylamines. LXXXV. *N*-Chlorodimesylamine†

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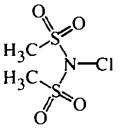
Abstract

In the molecule of the title compound, $C_2H_6ClNO_4S_2$, the N atom has a slightly pyramidal geometry characterized by the angles Cl—N—S 115.71 (7), 114.34 (6) and S—N—S 120.24 (6)°, and the distances S—N 1.7260 (11), 1.6992 (12) and Cl—N 1.7138 (11) Å. The crystal is stabilized by five intermolecular C—H···O hydrogen bonds and an intermolecular Cl···O interaction of 2.797 (1) Å, the latter linking the molecules to form infinite chains.

Comment

Although a number of *N*-fluorodisulfonylamines, *i.e.* $(RSO_2)_2N$—F, have emerged in recent years as electrophilic fluorinating agents (Lal, Pez & Syvret, 1996, and references therein), a search of the Cambridge Structural Database (Allen & Kennard, 1993) located no structural information for such a compound or any other *N*-halogenodisulfonylamine, $(RSO_2)_2N$—*X* (*X* = Cl, Br, I). As part of a wider study of N-substituted dimesylamines, we report here the first structure of a representative *N*-chlorodisulfonylamine, (1).



(1)

The molecule of the title compound shows no crystallographic symmetry (Fig. 1). The N atom lies 0.312 (1) Å out of the plane defined by S1, S2 and Cl, whereas the related molecule $(MeSO_2)_2N$—Me, (2), is essentially planar at the N atom (Blaschette, Näveke & Jones, 1991). In both structures, the S—N—S angle is *ca* 120°, and the slight pyramidality of (1) arises from the relatively small Cl—N—S angles, 115.71 (7) and 114.34 (6)°, as compared with the C—N—S angles of 119.9 (1) and 119.4 (1)° in (2). An interesting trend of increasing pyramidality is seen in the series (1), $MeSO_2$-NCl_2 (Minkwitz, Garzarek, Neikes, Kornath & Preut, 1997) and NCl_3 (Hartl, Schöner, Jander & Schulz, 1975), the angles at the N atom amounting to 108.61 (13)–110.87 (9)° for the dichloro compound (X-ray diffraction at 173 K) and to 105.1 (9)–108.5 (9)° for nitrogen trichloride (X-ray diffraction at 148 K).

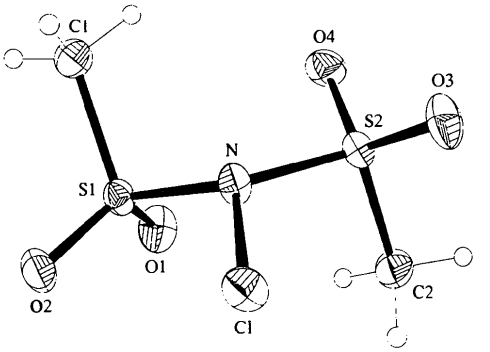


Fig. 1. The molecule of the title compound, (1), in the crystal. Ellipsoids represent 50% probability levels. H-atom radii are arbitrary.

† Part LXXXIV: Linoh *et al.* (1997).