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The twinned crystal structure of *rac*-(*R*,*R*)-*N*,*N*′-oxalyldivalinol

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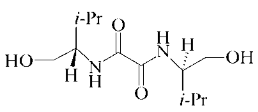
The title compound, *rac*-(*R*,*R*)-*N*,*N*′-bis(1-hydroxy-3-methyl-2-butyl)oxalamide, $C_{12}H_{24}N_2O_4$, crystallizes as a non-merohedral twin in the triclinic space group $P\overline{1}$. The twin is generated by a twofold rotation about c^*. The terminal hydroxy groups of molecules related by an inversion center form hydrogen-bonded dimers. This hydrogen-bonding pattern is further extended into a one-dimensional chain by N—H$\cdots$O hydrogen bonds.

Comment

The present structure determination forms part of a systematic study related to hydrogen bonding and gelation properties of bis(amino acid) (Makarević *et al.*, 2001; Perić *et al.*, 2001) and bis(amino alcohol) oxamide derivatives (Makarević *et al.*, 2003). Fig. 1 (Burnett & Johnson, 1996) shows the molecule of the title compound, (I), with the atom-numbering scheme.



(I)

The two isobutyl residues are bonded on the same side of the oxalamide bridge and have similar geometries (Table 1). Atoms O1 and O11 of the central oxalamide unit are in a *trans* conformation and are almost coplanar, with an O1—C1—C11—O11 torsion angle of 177.1 (4)°. The terminal hydroxy groups form a hydrogen-bonded dimer [O21—H21O$\cdots$O22($-x$, $-y$, $-z$)] with inversion symmetry (Table 2 and Fig. 2). Consequently, the two molecules of the dimer have opposite chirality. These dimers are further interconnected by N1—H1N$\cdots$O1($1 + x$, y, z) and N11—H11N$\cdots$O11($x - 1$, y, z) hydrogen bonds involving the oxalamide units. The molecules linked by the latter motif have the same chirality and form a one-dimensional ladder pattern (Fig. 3) typical of those found in the crystal structures of many retropeptides (Makarević *et al.*, 2001, 2003). This ladder pattern involves intra- and intermolecular interactions, which form bifurcated (three-centred) hydrogen bonds; oxalamide atoms O11 and O1 act as double acceptors, while atoms N11 and N1 are double donors (Fig. 3 and Table 2). In addition, there is an intermolecular hydrogen bond between the oxalamide group and a terminal hydroxy O atom of an adjacent molecule [O2—H2O$\cdots$O1($1 + x$, y, z); Table 2 and Fig. 3], and thus oxalamide atom O1 acts as a triple acceptor. The hydrogen-bonding pattern is a one-dimensional or α-network (Coe *et al.*, 1997), composed of tunnels running along the crystallographic a axis. The inside of the tunnel is hydrophilic, comprising hydroxy and amide groups. The outside of the tunnel is dominated by isobutyl groups and is thus hydrophobic (Fig. 2). The triclinic crystal is non-merohedrally twinned, with a twofold rotation about c^* (see *Experimental*). The corresponding twin supercell is approximately monoclinic [a = 5.0475 (9) Å, b = 40.895 (5) Å, c = 13.735 (3) Å, α = 90.74 (1)°, β = 93.71 (1)° and γ = 89.93 (2)°], with three times the volume of the triclinic cell. The twofold axis of the pseudo-monoclinic cell is coaxial

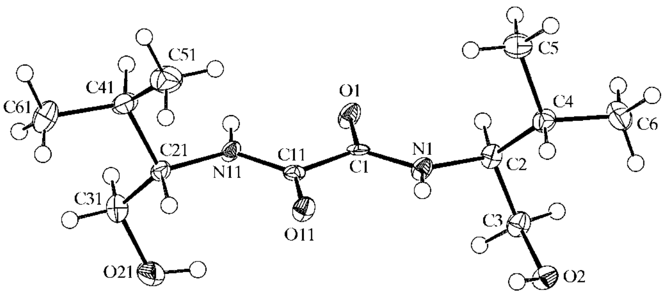


Figure 1
The molecular structure of (I), showing the (*S*,*S*) enantiomer, with displacement ellipsoids at the 50% probability level.

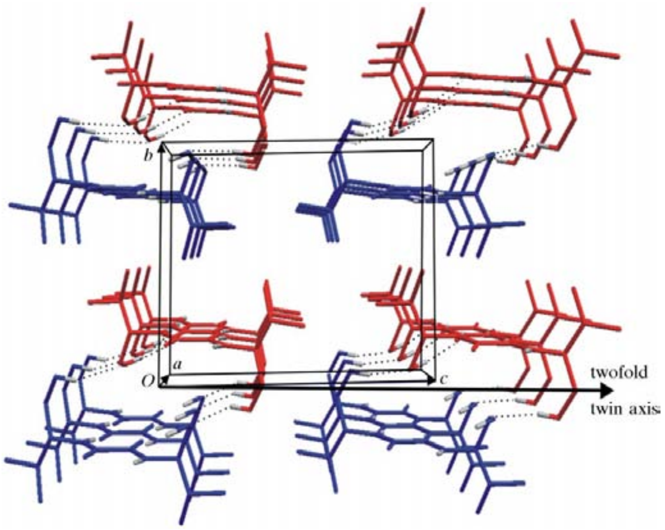


Figure 2
The crystal packing of (I), viewed along the crystallographic a axis. The terminal hydroxy groups connect molecules of opposite chirality *via* O—H$\cdots$O interactions into a centrosymmetric ring dimer. These ring dimers are connected by N—H$\cdots$O hydrogen bonds, forming *meso* bilayers. The darker molecules are of (*S*,*S*) chirality.

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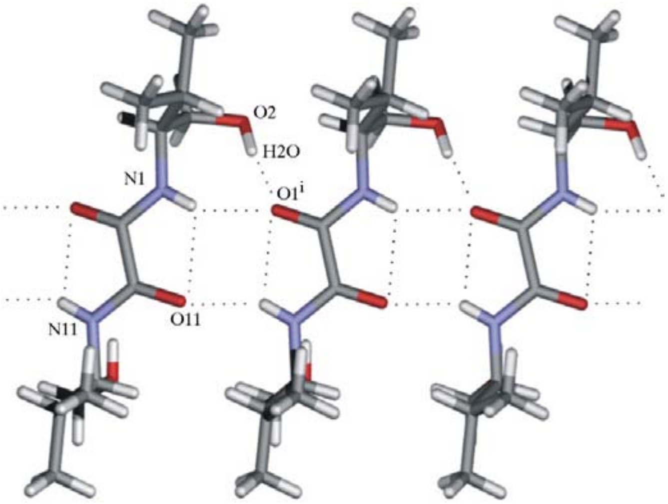

Figure 3
The intra- and intermolecular N—H···O hydrogen bonds that form the ladder motif running along *a*. Intermolecular hydrogen bonds between the oxalamide O atoms and the terminal hydroxy groups are shown. [Symmetry code: (i) $1 + x, y, z$.]

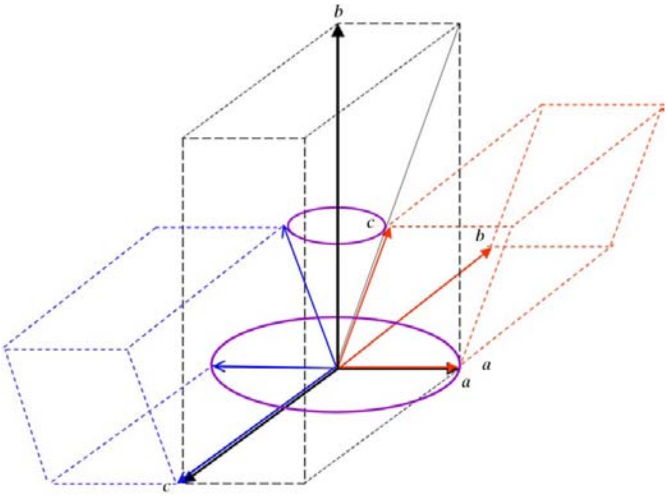

Figure 4
The relationship between the monoclinic supercell and triclinic cell: the twinning twofold axis coincides with the monoclinic *b* axis. The outermost outlines represent the two triclinic domains.

to the c^* axis of the triclinic cell (Fig. 4). A preliminary study with a Nonius CAD-4 point detector found the monoclinic cell. Only reflections with $h + k = 3n$ for any l were present, and scan profiles were split, indicating a possible twin supercell (Fig. 4). After transformation to the triclinic subcell, the twin relation was revealed using *ROTAX* (Cooper *et al.*, 2002). However, since data processing with *EVALCCD* (Duisenberg *et al.*, 2003; see *Experimental*) is much more appropriate than treatment with *ROTAX*, we have chosen to use the *EVALCCD* data. *EVALCCD* uses physically relevant parameters, such as detector set-up and crystal dimensions, to predict reflection shapes and consequently treats overlapping reflections correctly. This physical information is not available in the *ROTAX* approach.

Experimental

Compound (I) was synthesized according to the method described by Makarević *et al.* (2003).

Crystal data

$C_{12}H_{24}N_2O_4$
$M_r = 260.33$
Triclinic, $P\overline{1}$
$a = 5.0475$ (9) Å
$b = 10.0957$ (9) Å
$c = 13.735$ (3) Å
$\alpha = 88.674$ (12)°
$\beta = 83.414$ (19)°
$\gamma = 85.922$ (10)°
$V = 693.5$ (2) Å^3
$Z = 2$
$D_x = 1.247$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 212 reflections
$\theta = 4.1$–$20.5°$
$\mu = 0.09$ mm^{-1}
$T = 150$ (2) K
Prism, colorless
$0.10 \times 0.05 \times 0.01$ mm

Data collection

Nonius KappaCCD diffractometer
ω scans
3065 measured reflections
3065 independent reflections
2017 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.097$
$\theta_{\rm max} = 27.5°$
$h = -6 \rightarrow 6$
$k = -13 \rightarrow 13$
$l = -16 \rightarrow 17$

Refinement

Refinement on F^2
$R(F) = 0.063$
$wR(F^2) = 0.126$
$S = 1.21$
1690 reflections
164 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0193P)^2 + 0.8157P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.24$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.23$ e Å^{-3}

Table 1
Selected torsion angles (°).

C11—C1—N1—C2	177.0 (4)	C1—C11—N11—C21	175.1 (4)
C1—N1—C2—C3	−101.3 (5)	C11—N11—C21—C31	−121.3 (4)
C1—N1—C2—C4	129.4 (4)	C11—N11—C21—C41	112.9 (4)
N1—C2—C3—O2	−73.9 (5)	N11—C21—C31—O21	61.5 (5)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2O···O1^{i}	0.82	1.97	2.780 (4)	169
N1—H1N···O1^{i}	0.86	2.14	2.896 (5)	147
O21—H21O···O2^{ii}	0.88	2.03	2.880 (4)	162
N11—H11N···O11^{iii}	0.86	2.07	2.870 (4)	156
N1—H1N···O11	0.86	2.32	2.704 (5)	108
N11—H11N···O1	0.86	2.33	2.713 (5)	108

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

Reflections for indexing were obtained by a locally written peak-search program on the first 40 frames. These reflections were indexed using *DIRAX* (Duisenberg, 1992), resulting in two triclinic lattices related by a twofold rotation about *hkl* (001). Cell parameters and orientation were refined with *PEAKREF* (Schreurs, 2003). Reflection intensities for both domains were integrated using the *EVALCCD* program suite (Duisenberg *et al.*, 2003). Single reflections of the first domain and overlapping reflections of both domains were merged with *MERGEHKLF5* (Schreurs, 2003). The twin refinement was performed with *SHELXL97* (Sheldrick, 1997) using the data in *HKLF5* format and refinement of batch scale factors (Herbst-Irmer & Sheldrick, 1998). The refinement resulted in a ratio of 80.6 (2):19.4 (2) for the two twin domains. H-atom coordinates were calculated geometrically and refined using a riding model. *PLATON* (Spek, 2003) was used for the preparation of material for publication.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SX1143). Services for accessing these data are described at the back of the journal.

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