Racemic 2-isopropyl-3-(2-nitrobenzyl)-1,3-thiazolidin-4-one crystallizes in the space group $P2_12_12_1$ with $Z' = 2$: two different interpenetrating three-dimensional frameworks formed by C—H⋯O hydrogen bonds

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rac-2-Isopropyl-3-(2-nitrobenzyl)-1,3-thiadiazolin-4-one, $C_{13}H_{16}N_2O_3S$, is a rare example of a racemate crystallizing in the space group $P2_12_12_1$, with one molecule each of S and R configurations, whose conformations are almost mirror images, within the asymmetric unit. The molecules of S configuration are linked by two C—H⋯O hydrogen bonds into a three-dimensional framework, and the molecules of R configuration are linked by two further C—H⋯O hydrogen bonds into a different type of three-dimensional framework; the two frameworks are linked by a fifth C—H⋯O hydrogen bond.

Comment

Thiazolidinones and their derivatives are an important group of heterocyclic compounds having valuable biological activities in the areas of medicine and agriculture (Singh *et al.*,

(I)

(II)
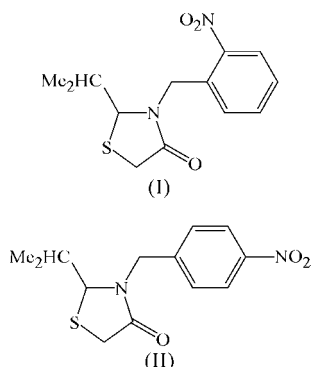
1981). We report here the molecular and supramolecular structure of the title compound, (I), which was obtained from

the reaction between 2-amino-3-methylbutanoic acid (valine), 2-nitrobenzaldehyde and mercaptoacetic acid; a mechanism for this reaction has recently been proposed (Cunico *et al.*, 2007).

Compound (I) crystallizes with $Z' = 2$ in the space group $P2_12_12_1$. The two independent molecules, denoted A and B (Fig. 1), have S and R configurations, respectively, at atom C2. Hence, (I) is a racemate with a chiral crystal structure (Flack, 2003). A recent study (Dalhus & Görbitz, 2000), based on the Cambridge Structural Database (Allen, 2002), of racemates crystallizing in noncentrosymmetric space groups found that these nearly always crystallize in space groups containing glide planes. Five space groups (Pc, Cc, $Pca2_1$, $Pna2_1$ and $Fdd2$) account for over 90% of all such racemates. By contrast, genuine racemates that crystallize in space groups having no symmetry operators of the second kind (inversion, reflection or roto-inversion) were found to be extremely rare, with only
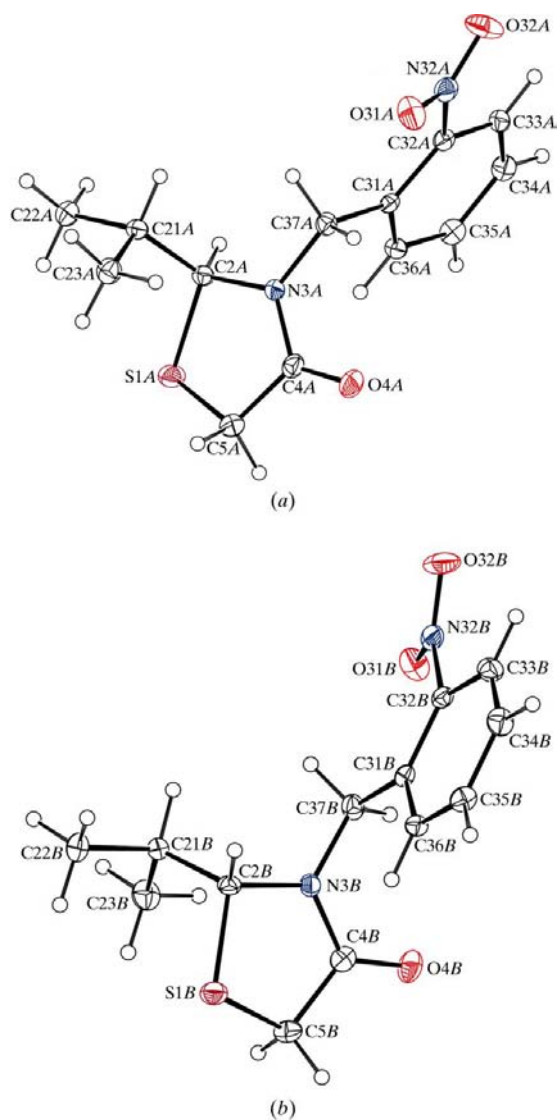
Figure 1
The two independent molecules in (I), showing the atom-labelling scheme for (*a*) a type A molecule of S configuration and (*b*) a type B molecule of R configuration.

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17 authentic examples distributed amongst the space groups $P1$ (only one example identified), $P2_1$ (11 examples identified), $P2_12_12_1$ (four examples identified) and $P3_121$ (one example identified) (Dalhus & Görbitz, 2000). Compound (I) is thus an addition to this very rare class of crystalline racemates.

The two independent molecules in compound (I) are, in fact, almost enantiomeric, as shown by the leading torsion angles (Table 1) and by the puckering parameters for the heterocyclic rings. For racemates crystallizing in noncentrosymmetric space groups and having $Z' > 1$, it was found (Dalhus & Görbitz, 2000) that the independent molecules, in general, adopt closely similar conformations, as observed here for compound (I).

The value of the ring-puckering parameter φ for the atom sequence S1—C2—N3—C4—C5 is 177.1 (6)° for molecule A and 359.8 (6)° for molecule B, while the values of φ for true enantiomers differ by exactly 180°. In each independent molecule in (I), the heterocyclic ring thus adopts an envelope conformation, for which the ideal value of φ is $(36n)°$, where n is zero or an integer, and each ring is folded across the C2···C5 line. However, there is no additional crystallographic symmetry and the differences between the hydrogen bonds formed by the two independent molecules (Table 2) are sufficient to preclude any such additional symmetry.
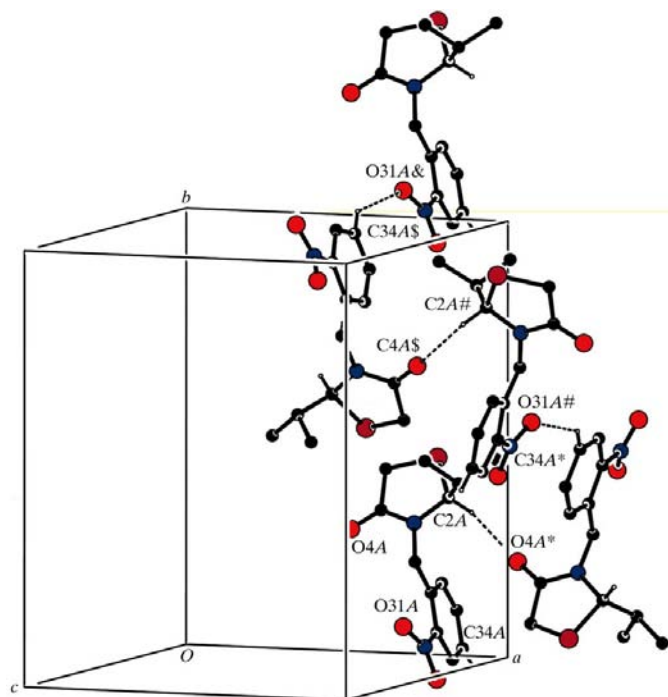
The hydrogen-bonded supramolecular structure is three-dimensional and it is convenient to consider in turn the supramolecular aggregation of the type A and B molecules. Atoms C2A and C34A in the type A molecule at (x, y, z) act, respectively, as hydrogen-bond donors to atoms O4A and O31A in the type A molecules at $(\frac{1}{2} + x, \frac{1}{2} - y, -z)$ and $(\frac{3}{2} - x, -y, -\frac{1}{2} + z)$. Propagation of each of these interactions alone produces a $C(5)$ (Bernstein et al., 1995) chain running parallel to the [100] direction and generated by the 2_1 screw axis along $(x, \frac{1}{4}, 0)$, and a $C(6)$ chain running parallel to [001] and generated by the screw axis along $(\frac{3}{4}, 0, z)$. The combination of these two hydrogen bonds generates a $C_2^2(17)$ chain running parallel to the [010] direction (Fig. 2) and the combination of chains along [100], [010] and [001] suffices to generate a three-dimensional framework built solely from type A molecules, all of S configuration.

A second three-dimensional framework is formed by the type B molecules. Atoms C2B and C35B in the type B molecule at (x, y, z) act as hydrogen-bond donors, respectively, to atoms O4B and O32B in the molecules at $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$ and $(1 - x, -\frac{1}{2} + y, \frac{1}{2} - z)$, so forming, respectively, a $C(5)$ chain parallel to [100] generated by the screw axis along $(x, \frac{1}{4}, \frac{1}{2})$, and a $C(7)$ chain parallel to [010] generated by the screw axis along $(\frac{1}{2}, y, \frac{1}{4})$. The combination of the two hydrogen bonds generates a $C_2^2(16)$ chain running parallel to the [001] direction (Fig. 3), and the combination of the [100], [010] and [001]
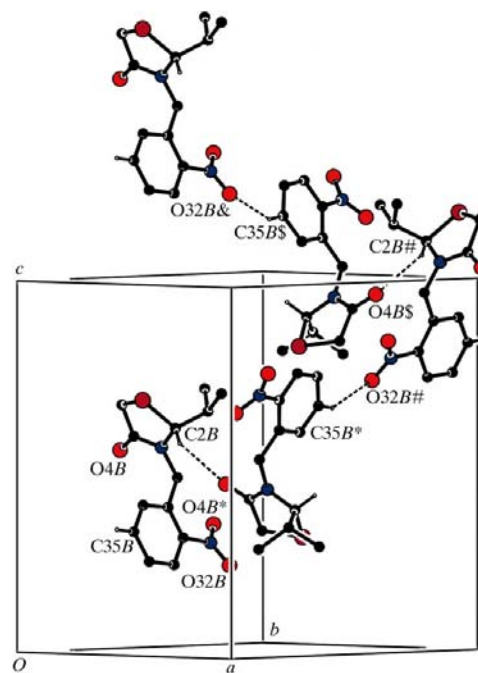

Figure 2
Part of the crystal structure of (I), showing the formation of a $C_2^2(17)$ chain of type A molecules along [010], built from the alternating action of two C—H···O hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign ($) or an ampersand (&) are at the symmetry positions $(\frac{1}{2} + x, \frac{1}{2} - y, -z)$, $(2 - x, \frac{1}{2} + y, \frac{1}{2} - z)$, $(\frac{3}{2} - x, 1 - y, \frac{1}{2} + z)$ and $(x, 1 + y, z)$, respectively.

Figure 3
Part of the crystal structure of (I), showing the formation of a $C_2^2(16)$ chain of type B molecules along [001], built from the alternating action of two C—H···O hydrogen bonds. For the sake of clarity, H atoms not involved in the motif shown have been omitted. Atoms marked with an asterisk (*), a hash (#), a dollar sign ($) or an ampersand (&) are at the symmetry positions $(\frac{1}{2} + x, \frac{1}{2} - y, 1 - z)$, $(\frac{3}{2} - x, 1 - y, \frac{1}{2} + z)$, $(1 - x, \frac{1}{2} + y, \frac{3}{2} - z)$ and $(x, y, 1 + z)$, respectively.
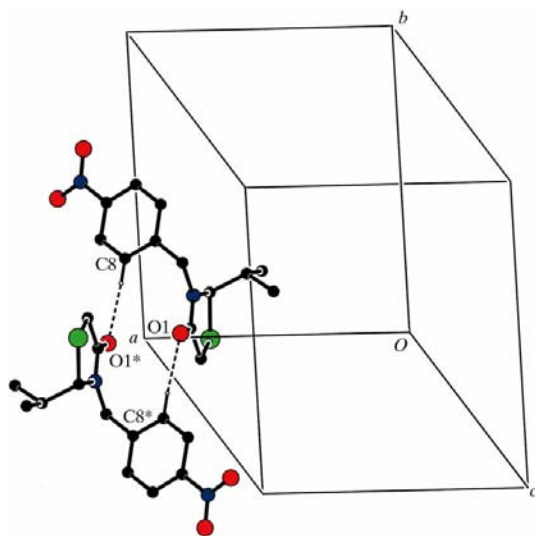
Figure 4
Part of the crystal structure of (II), showing the formation of a centrosymmetric $R_2^2(14)$ dimer. The atom coordinates and atom labelling are those in the original publication (Cunico *et al.*, 2007) and, for the sake of clarity, H atoms not involved in the motif shown have been omitted. The atoms marked with an asterisk (*) are at the symmetry position ($2 - x$, $-y$, $-z$).

chains generates a three-dimensional framework built solely from type *B* molecules, all of *R* configuration.

The two frameworks, of type *A* and type *B* molecules, are necessarily continuously interwoven, and they are linked by the single hydrogen bond between the two molecular types. Within the selected asymmetric unit, atom C33*B* acts as a hydrogen-bond donor to atom O4*A* and propagation of this interaction links the two interpenetrating networks into a single continuous structure. The type *A* framework, which contains only molecules of *S* configuration, has component chains of $C(5)$, $C(6)$ and $C_2^2(17)$ types, while the type *B* framework, which contains only molecules of *R* configuration, has component chains of $C(5)$, $C(7)$ and $C_2^2(16)$ types. Hence, although each framework is enantiomerically pure, in that it contains just one stereoisomer, the two frameworks thus formed are not, in fact, enantiomers of one another.

The structure of *rac*-2-isopropyl-3-(4-nitrobenzyl)-1,3-thia-zolidin-4-one, (II), isomeric with (I), has recently been reported (Cunico *et al.*, 2007) as a proof of the constitution of this class of product, but no discussion of the supramolecular aggregation was given. In fact, the molecules of (II), which crystallizes in space group $P2_1/c$ with $Z' = 1$, are linked by pairs of nearly linear C—H···O hydrogen bonds into a cyclic centrosymmetric dimer characterized by an $R_2^2(14)$ motif (Fig. 4). The supramolecular aggregation of compound (II) is thus very much simpler than that of compound (I).

Experimental

A sample of compound (I) was prepared as described recently (Cunico *et al.*, 2007); crystals of (I) suitable for single-crystal X-ray diffraction were obtained by slow evaporation of a solution in a mixture of methanol and heptane (1:1 *v/v*).

Crystal data

$C_{13}H_{16}N_2O_3S$	$V = 2675.9\ (2)$ Å^3
$M_r = 280.34$	$Z = 8$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 11.7604\ (4)$ Å	$\mu = 0.25$ mm^{-1}
$b = 14.9847\ (7)$ Å	$T = 120\ (2)$ K
$c = 15.1844\ (8)$ Å	$0.28 \times 0.14 \times 0.03$ mm

Data collection

Bruker–Nonius KappaCCD diffractometer	21265 measured reflections
	6032 independent reflections
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)	4005 reflections with $I > 2\sigma(I)$
$T_{min} = 0.944$, $T_{max} = 0.993$	$R_{int} = 0.074$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	$\Delta\rho_{max} = 0.26$ e Å^{-3}
$wR(F^2) = 0.083$	$\Delta\rho_{min} = -0.27$ e Å^{-3}
$S = 0.99$	Absolute structure: Flack (1983), 2596 Friedel pairs
6032 reflections	Flack parameter: -0.02 (6)
347 parameters	
H-atom parameters constrained	

Table 1
Selected torsion angles (°).

N3*A*—C2*A*—C21*A*—C22*A*	176.94 (19)	N3*B*—C2*B*—C21*B*—C22*B*	−177.3 (2)
N3*A*—C2*A*—C21*A*—C23*A*	−58.2 (3)	N3*B*—C2*B*—C21*B*—C23*B*	58.3 (3)
C2*A*—N3*A*—C37*A*—C31*A*	−86.4 (3)	C2*B*—N3*B*—C37*B*—C31*B*	84.4 (3)
N3*A*—C37*A*—C31*A*—C32*A*	176.7 (2)	N3*B*—C37*B*—C31*B*—C32*B*	−171.1 (2)
C31*A*—C32*A*—N32*A*—O31*A*	13.9 (3)	C31*B*—C32*B*—N32*B*—O31*B*	−23.1 (3)

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

D—H···A	D—H	H···A	D···A	D—H···A
C2*A*—H2*A*···O4*A*[i]	1.00	2.54	3.295 (3)	132
C2*B*—H2*B*···O4*B*[ii]	1.00	2.56	3.337 (4)	134
C34*A*—H34*A*···O31*A*[iii]	0.95	2.60	3.355 (4)	137
C35*B*—H35*B*···O32*B*[iv]	0.95	2.38	3.196 (4)	144
C33*B*—H33*B*···O4*A*	0.95	2.59	3.512 (4)	165

Symmetry codes: (i) $x + \frac{1}{2}, -y + \frac{1}{2}, -z$; (ii) $x + \frac{1}{2}, -y + \frac{1}{2}, -z + 1$; (iii) $-x + \frac{3}{2}, -y, z - \frac{1}{2}$; (iv) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$.

The space group $P2_12_12_1$ was uniquely assigned from the systematic absences. All H atoms were located in difference maps and then treated as riding atoms, with C—H distances of 0.95 (aromatic), 0.98 (CH$_3$), 0.99 (CH$_2$) or 1.00 Å (aliphatic CH), and with $U_{iso}(H) = kU_{eq}(C)$, where $k = 1.5$ for the methyl groups and 1.2 for all other H atoms. The correct absolute structure, which establishes that the type *A* and *B* molecules have *S* and *R* configurations, respectively, was determined by means of the Flack (1983) parameter. A search for possible additional symmetry revealed none.

Data collection: *COLLECT* (Hooft, 1999); cell refinement: *DENZO* (Otwinowski & Minor, 1997) and *COLLECT*; data reduction: *DENZO* and *COLLECT*; program(s) used to solve structure: *OSCAIL* (McArdle, 2003) and *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *OSCAIL* and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *SHELXL97* and *PRPKAPPA* (Ferguson, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK3126). Services for accessing these data are described at the back of the journal.

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