

Racemic and chiral 1-[*N*-(chloroacetyl)carbamoylamino]-2,3-dihydro-1*H*-inden-2-yl chloroacetate

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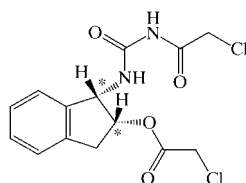
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In the racemic crystals of (1*S*,2*R*)- or (1*R*,2*S*)-1-[*N*-(chloroacetyl)carbamoylamino]-2,3-dihydro-1*H*-inden-2-yl chloroacetate, C₁₄H₁₄Cl₂N₂O₄, (I), the enantiomeric molecules form a dimeric structure *via* the N—H···O cyclic hydrogen bond of the carbamoyl moieties. In the chiral crystals of (–)-(1*S*,2*R*)-1-[*N*-(chloroacetyl)carbamoylamino]-2,3-dihydro-1*H*-inden-2-yl chloroacetate, C₁₄H₁₄Cl₂N₂O₄, (II), the N—H···O intermolecular hydrogen bond forms a zigzag chain around the twofold screw axis. The melting points and calculated densities of (I) and (II) are 446 and 396 K, and 1.481 and 1.445 Mg m^{−3}, respectively.

Comment

In a study of the kinetic resolution of the racemic title compound by lipase-mediated hydrolysis, a difference of 50 K in the melting point between the racemic and chiral crystals was recognized by Suzuki *et al.* (2000). Wallach's rule states that racemic crystals tend to be denser than their chiral counterparts (Wallach, 1895). However, Brock *et al.* (1991) tested this rule with the help of the January 1989 version of the Cambridge Structural Database (Allen & Kennard, 1993) to show that Wallach's rule is not so obvious and there are many



(I): racemic
(II): chiral, (1*S*,2*R*)

exceptions. In the present study, the crystal structures of racemic (I) and chiral (II) have been determined to compare the molecular packing.

As shown in Fig. 1, the molecular structures of (I) and (II) are essentially the same, except for the torsion angles at the junction of the *N*-(chloroacetyl)carbamoylamino moiety and the indene skeleton (Tables 1 and 3). This side chain partici-

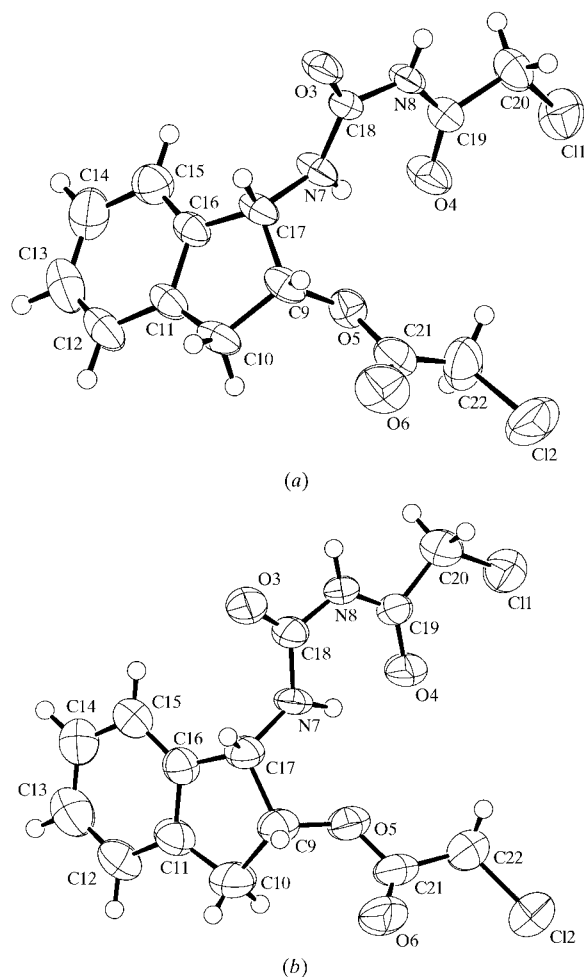


Figure 1

The molecular structures in the crystals of (a) (I) and (b) (II). Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as spheres of arbitrary size.

pates in an intramolecular N7—H7···O4 hydrogen bond, as well as an N8—H8···O3ⁱ intermolecular one in both structures (Tables 2 and 4). In (I), two neighbouring molecules related by a centre of symmetry form a dimeric structure *via* the cyclic hydrogen bond (Fig. 2a). In (II), the intermolecular hydrogen bond forms a zigzag chain around the twofold screw axis parallel to **b** (Fig. 2b).

The calculated densities of (I) and (II) are 1.481 and 1.445 Mg m^{−3}, respectively. The title compound is therefore a typical example of one which follows Wallach's rule. Since the strength of the intermolecular hydrogen bond in the two crystals is similar, the lower density of (II) is attributed to the low packing efficiency among the zigzag chains around the twofold screw axes.

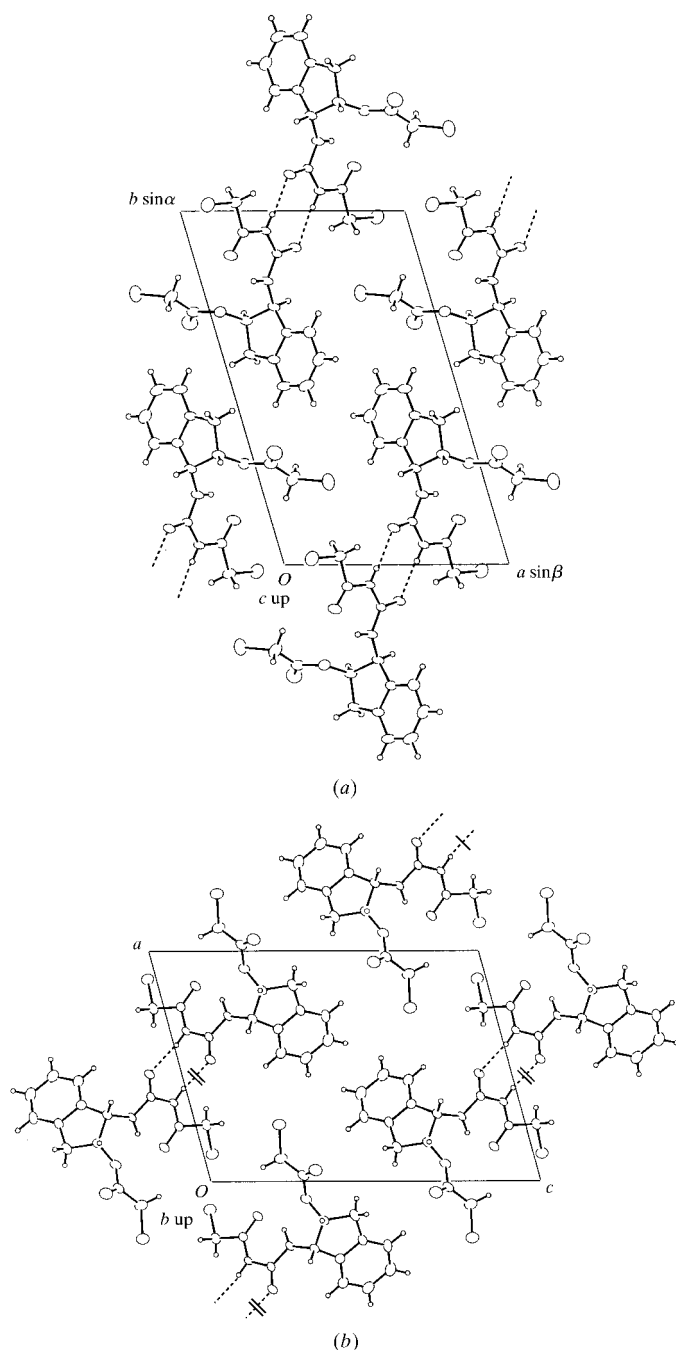


Figure 2
The projections of the crystal structures of (a) (I) along **c**, and (b) (II) along **b**. Displacement ellipsoids are plotted at the 25% probability level and broken lines indicate hydrogen bonds. The symbol - -| - - indicates that the two lines - -| and - -| are parallel, but their heights are different.

Experimental

The racemic (\pm) mixture, (I), and the enantiomerically pure ($-$) compound, (II), were prepared from (\pm)-*trans*-2-bromo-1-indanol and ($-$)-*cis*-aminoindanol, respectively. Crystals were grown separately from ethyl acetate solutions. The thin needle crystals of (II) elongated along **b** were very soft and curled easily even with careful treatment.

Compound (I)

Crystal data

$C_{14}H_{14}Cl_2N_2O_4$	$Z = 2$
$M_r = 345.18$	$D_x = 1.481 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 10.017 (3) \text{ \AA}$	Cell parameters from 25 reflections
$b = 16.575 (6) \text{ \AA}$	$\theta = 14.3\text{--}15.0^\circ$
$c = 4.883 (3) \text{ \AA}$	$\mu = 0.438 \text{ mm}^{-1}$
$\alpha = 95.63 (3)^\circ$	$T = 298 (1) \text{ K}$
$\beta = 90.84 (4)^\circ$	Needle, colourless
$\gamma = 106.28 (3)^\circ$	$0.60 \times 0.10 \times 0.05 \text{ mm}$
$V = 773.8 (6) \text{ \AA}^3$	

Data collection

Rigaku AFC-7R diffractometer	$R_{\text{int}} = 0.021$
ω scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: by integration (Coppens <i>et al.</i> , 1965)	$h = -13 \rightarrow 13$
$T_{\text{min}} = 0.916$, $T_{\text{max}} = 0.979$	$k = -22 \rightarrow 22$
3951 measured reflections	$l = 0 \rightarrow 6$
3536 independent reflections	3 standard reflections
2066 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0588P)^2 + 0.3077P]$
$R(F) = 0.051$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.141$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.51 \text{ e \AA}^{-3}$
3536 reflections	$\Delta\rho_{\text{min}} = -0.31 \text{ e \AA}^{-3}$
208 parameters	
H atoms treated by a mixture of independent and constrained refinement	

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

C11—C20	1.754 (4)	Cl2—C22	1.747 (5)
C9—O5—C21—C22	-169.5 (2)	C17—N7—C18—N8	173.7 (3)
C9—C17—N7—C18	-115.3 (3)	C17—C9—O5—C21	157.2 (2)

Table 2

Hydrogen-bonding geometry (\AA , $^\circ$) for (I).

$D\text{--}H\cdots A$	$D\text{--}H$	$H\cdots A$	$D\cdots A$	$D\text{--}H\cdots A$
N7—H7 \cdots O4	0.79 (3)	2.02 (3)	2.694 (3)	143 (3)
N8—H8 \cdots O3 ⁱ	0.81 (3)	2.01 (3)	2.823 (3)	179 (3)

Symmetry code: (i) $1 - x, 2 - y, -z$.

Compound (II)

Crystal data

$C_{14}H_{14}Cl_2N_2O_4$	$D_x = 1.445 \text{ Mg m}^{-3}$
$M_r = 345.18$	Mo $K\alpha$ radiation
Monoclinic, $P2_1$	Cell parameters from 22 reflections
$a = 11.409 (2) \text{ \AA}$	$\theta = 10.4\text{--}14.5^\circ$
$b = 4.595 (2) \text{ \AA}$	$\mu = 0.427 \text{ mm}^{-1}$
$c = 15.667 (1) \text{ \AA}$	$T = 298 (1) \text{ K}$
$\beta = 105.079 (9)^\circ$	Needle, colourless
$V = 793.1 (3) \text{ \AA}^3$	$0.70 \times 0.02 \times 0.01 \text{ mm}$
$Z = 2$	

Data collection

Rigaku AFC-7R diffractometer	$R_{\text{int}} = 0.029$
ω scans	$\theta_{\text{max}} = 27.5^\circ$
Absorption correction: by integration (Coppens <i>et al.</i> , 1965)	$h = 0 \rightarrow 15$
$T_{\text{min}} = 0.956$, $T_{\text{max}} = 0.991$	$k = -6 \rightarrow 0$
2130 measured reflections	$l = -20 \rightarrow 20$
2031 independent reflections	3 standard reflections
831 reflections with $I > 2\sigma(I)$	every 150 reflections
	intensity decay: none

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0468P)^2]$
$R(F) = 0.057$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.126$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 0.97$	$\Delta\rho_{\text{max}} = 0.24 \text{ e } \text{\AA}^{-3}$
2031 reflections	$\Delta\rho_{\text{min}} = -0.24 \text{ e } \text{\AA}^{-3}$
208 parameters	Absolute structure: Flack (1983)
H atoms treated by a mixture of independent and constrained refinement	Flack parameter = 0.2 (2)

Table 3

Selected geometric parameters (\AA , $^\circ$) for (II).

C11—C20	1.741 (8)	C12—C22	1.726 (8)
C9—O5—C21—C22	-171.7 (6)	C17—N7—C18—N8	180.0 (7)
C9—C17—N7—C18	-149.4 (7)	C17—C9—O5—C21	156.6 (6)

Table 4

Hydrogen-bonding geometry (\AA , $^\circ$) for (II).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
N7—H7 \cdots O4	1.05 (7)	1.75 (7)	2.688 (8)	146 (4)
N8—H8 \cdots O3 ⁱ	0.82 (5)	2.05 (6)	2.837 (6)	159 (8)

Symmetry code: (i) $1 - x, y - \frac{1}{2}, -z$.

The H atoms bonded to N were located from a difference map and were refined isotropically; other H atoms were allowed for as riding atoms. The absolute structure of (II) was assigned based on the known absolute configurations around the C7 and C9 atoms, which came from (–)-(1*S*,2*R*)-*cis*-aminoindanol; refinement of (II) (with no Friedel reflections) led to a Flack parameter (Flack, 1983) of 0.2 (2).

For both compounds, data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1993); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1999); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1022). Services for accessing these data are described at the back of the journal.

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