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Key indicators

Single-crystal X-ray study

T = 150 K

Mean $\sigma(\text{C}-\text{C}) = 0.002 \text{ \AA}$

R factor = 0.029

wR factor = 0.071

Data-to-parameter ratio = 9.2

For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.**(2*S*,3*aR*,7*aR*)-Perhydro-1*H*-1,3-benzimidazol-1-ium-2-carboxylate**

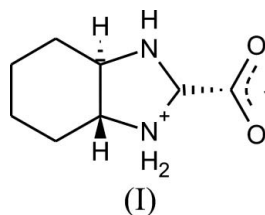
The title compound, $\text{C}_8\text{H}_{14}\text{N}_2\text{O}_2$, exists in the solid state in a zwitterionic form. The imidazolidinium fragment adopts an envelope conformation. The carboxylate group is involved in an intramolecular $\text{N}^+ - \text{H} \cdots \text{O}^-$ hydrogen bond.

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Comment

Imidazolidine-2-carboxylic acid belongs to the family of aliphatic α, α' -diamino acids. Its derivatives can be prepared in a well known condensation reaction of α -diamines with aldehydes (Hofmann, 1953; Fieser & Fieser, 1967) when glyoxalic acid is used as an aldehydic substrate. The products of this reaction are relatively unstable in aqueous solutions, where they hydrolyse to the substrates. Recently, we have reported the crystal structure of the (4*R*,5*R*)-4,5-diphenyl derivative of imidazolidine-2-carboxylic acid, which has found application as an organocatalyst in asymmetric synthesis (Halland *et al.*, 2002, 2003). Here, we report the crystal structure of its close analogue derived from *trans*-cyclohexane-1,2-diamine, the title octahydrobenzimidazole derivative, (I), which, due to a *trans* junction of the five- and six-membered rings, contains a conformationally strained bicyclic system. Both the *R,R*-isomer (m.p. 453 K) and the racemate of (I) (m.p. 451 K) were synthesized. The unit-cell parameters of the crystals taken from the racemic sample and those of optically active (I) were identical within experimental error, thus indicating the conglomerate nature of racemic (I).



The molecular structure of (I) is shown in Fig. 1. The main structural features are similar to those of (2*S*,4*R*,5*R*)-4,5-dimethylimidazolidin-1-ium-2-carboxylate (Biskupska & Gdaniec, 2006). Compound (I) crystallizes in a zwitterionic form, with an H atom transferred from the carboxylic acid group to the imidazolidine atom N1. It has the five-membered ring in an envelope conformation, with atom C4 as the flap (Table 1).

The carboxylate group is involved in an intramolecular $\text{N1}-\text{H1A} \cdots \text{O1}$ hydrogen bond, which is a part of a bifurcated hydrogen bond (Table 2). A new chiral centre at atom C2, which results from a difference in the protonation state of the imidazolidine N atoms, has an *S* configuration.

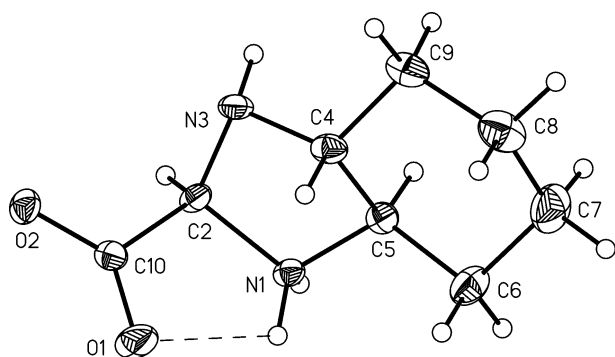


Figure 1

The molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates the intramolecular hydrogen bond.

The crystal packing in (I) is shown in Fig. 2. All N—H donors are involved in hydrogen bonding. The molecules are connected *via* N—H...O hydrogen bonds into a two-dimensional assembly which is parallel to the (001) plane (Table 2, Fig. 2*b*). The cyclohexane rings protrude from both sides of this assembly, leaving deep grooves on its surface, which are occupied by cyclohexane rings from adjacent assemblies (Fig. 2*a*).

Experimental

To a solution of (1*R*,2*R*)-cyclohexane-1,2-diamine (0.114 g, 1 mmol) in CH₂Cl₂ (5 ml) at 273 K was added glyoxalic acid monohydrate (0.092 g, 1 mmol) dissolved in MeOH (2.5 ml). The reaction mixture was stirred for 15 h at room temperature. Compound (I) precipitated as a white powder. Crystals of (I) suitable for X-ray analysis were obtained by recrystallization from a solution in water. A similar procedure was used for the preparation of racemic (I) from racemic *trans*-cyclohexane-1,2-diamine.

Crystal data

C ₈ H ₁₄ N ₂ O ₂	$Z = 4$
$M_r = 170.21$	$D_x = 1.366 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12_1$	Mo $K\alpha$ radiation
$a = 5.6176$ (4) Å	$\mu = 0.10 \text{ mm}^{-1}$
$b = 9.1414$ (5) Å	$T = 150$ (2) K
$c = 16.1195$ (7) Å	Plate, colourless
$V = 827.78$ (8) Å ³	$0.4 \times 0.25 \times 0.08 \text{ mm}$

Data collection

Kuma KM4 CCD κ geometry diffractometer	1005 independent reflections
ω scans	988 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{\text{int}} = 0.017$
5897 measured reflections	$\theta_{\text{max}} = 26.4^\circ$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0379P)^2 + 0.2085P]$
$R[F^2 > 2\sigma(F^2)] = 0.029$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.071$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.08$	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
1005 reflections	$\Delta\rho_{\text{min}} = -0.17 \text{ e \AA}^{-3}$
109 parameters	
H-atom parameters constrained	

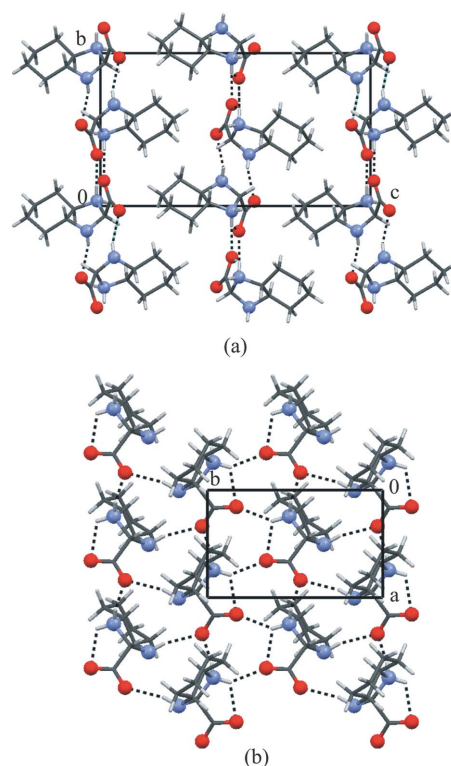


Figure 2

The crystal structure of (I). (a) The crystal packing viewed down the *a* axis. (b) The two-dimensional network of hydrogen-bonded (dashed lines) molecules parallel to (001).

Table 1

Selected geometric parameters (Å, °).

O1—C10	1.245 (2)	N1—C2	1.5301 (19)
O2—C10	1.2572 (18)	C2—N3	1.4601 (19)
N1—C5	1.4975 (19)	N3—C4	1.467 (2)
C5—N1—C2	105.18 (11)	O1—C10—O2	127.75 (15)
N3—C2—N1	107.04 (12)	O1—C10—C2	117.29 (14)
C2—N3—C4	103.65 (11)	O2—C10—C2	114.88 (12)
N1—C2—N3—C4	−24.89 (15)	C5—N1—C2—N3	−1.42 (14)
C2—N3—C4—C5	41.71 (14)	C9—C4—C5—C6	63.90 (17)
N3—C4—C5—N1	−42.04 (13)	N1—C2—C10—O1	10.69 (19)
C4—C5—N1—C2	25.92 (13)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 <i>N</i> A...O1	0.90	2.14	2.6425 (18)	114
N1—H1 <i>N</i> A...O1 ⁱ	0.90	2.03	2.8014 (17)	143
N1—H1 <i>N</i> B...O2 ⁱⁱ	0.90	1.83	2.7098 (17)	167
N3—H3 <i>N</i> ...O2 ⁱⁱⁱ	0.90	2.13	2.9760 (17)	157

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

The chirality of atoms C4 and C5 was assigned from the known chirality of the starting material. In the absence of significant anomalous scattering, Friedel pairs were merged before the final refinement. All H atoms were located in electron-density difference maps. However, for the structure refinement they were placed in calculated positions, with C—H = 0.97–0.98 Å and N—H = 0.90 Å,

and treated as riding on their parent atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2004); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *MERCURY* (Macrae *et al.*, 2006); software used to prepare material for publication: *SHELXL97*.

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