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Racemic 6-*exo*-hydroxybicyclo[2.2.1]heptane-2-*exo*-carboxylic acid

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The crystal structure of the title cage hydroxy acid, $C_8H_{12}O_3$, has confirmed the *exo* configuration for both the carboxylic acid and hydroxy substituents, as previously determined from chemical and ^{13}C NMR evidence. Both the carboxylic acid and the hydroxy O atoms are involved in intermolecular hydrogen-bonding interactions, giving a centrosymmetric 12-membered cyclic ring system which extends *via* hydrogen bonding into an infinite two-dimensional network.

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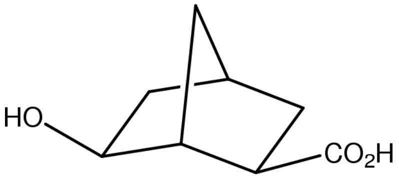
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.132
Data-to-parameter ratio = 12.1

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

Comment

Racemic 6-*exo*-hydroxybicyclo[2.2.1]heptane-2-*exo*-carboxylic acid, (I), was first reported in 1969 together with the isomeric 5-*exo*-hydroxy isomer (Beckmann *et al.*, 1969) with which it forms in the normal synthetic route. The hydroboration procedure used here in the preparation (Fischer *et al.*, 1980) gives predominantly the 6-*exo*-hydroxy isomer, whereas the oxymercuration/demercuration procedure of Beckmann *et al.* (1969) gives predominantly the 5-*exo*-hydroxy isomer.



(I)

The crystal structure determination of (I) shows the relatively inflexible norbornane cage which is similar to other norbornane carboxylic acids (Apgar & Ludwig, 1972; Albinati *et al.*, 1973), with both the carboxylic acid and hydroxy groups *exo*-related (Fig. 1). The torsion angles C1—C2—C21—O212 and C2—C1—C6—O6 are 80.9 (2) and 173.6 (1)°, respectively. The carboxylic acid O atoms associate with the hydroxy groups of two different acids [O212—H212···O6^{i} 2.665 (2) Å and O—H···O 167 (2)°; O6—H6···O211^{ii}, 2.752 (2) Å, O—H···O, 170 (2)°; symmetry codes: (i) $\frac{1}{2}+x$, $\frac{1}{2}-y$, $1+z$; (ii) $\frac{1}{2}-x$, $-\frac{1}{2}+y$, $1-z$], forming cyclic centrosymmetric 12-membered $R_4^4(12)$ rings (Etter *et al.*, 1990) (Fig. 2). These then form into an infinite two-dimensional structure. This association is different from the common $R_2^2(8)$ cyclic *A*–*A* dimers or the more unusual catemer structures found among the monofunctional carboxylic acids (Leiserowitz, 1976).

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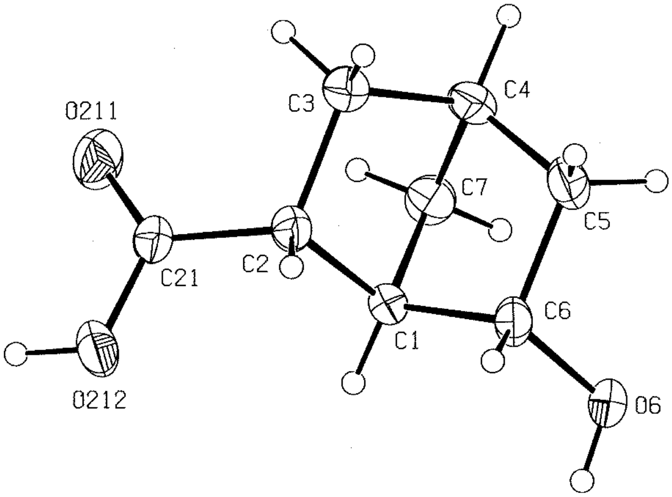

Figure 1
The molecular configuration and atom-numbering scheme for the title compound. Atoms are shown as 30% probability ellipsoids (Spek, 1999).

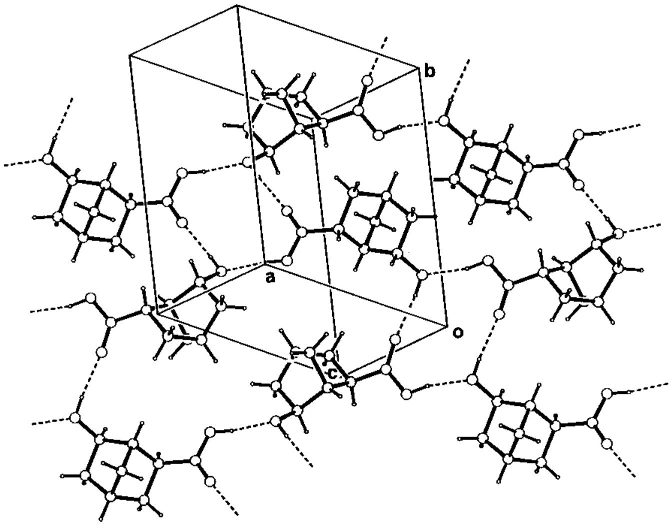

Figure 2
Perspective view of the two-dimensional polymer structure. Hydrogen bonds are shown as broken lines (Spek, 1999).

Experimental

The title compound was synthesized using a modification of the method of Fischer *et al.* (1980) by the hydroboration of the unsaturated ester precursor followed by hydrolysis with sodium hydroxide. The modification (Vogel, 1989) involved the generation of diborane *in situ* by addition of the boron trifluoride–dietherate to a mixture of sodium borohydride and the ester precursor under a nitrogen atmosphere (Wermuth, 1995). Fractional crystallization of the isomeric mixture from acetone gave the 5-hydroxy and 6-hydroxy isomers. Crystals of the 6-hydroxy isomer (the title compound) suitable for X-ray analysis were obtained by slow evaporation from acetone.

Crystal data

$C_8H_{12}O_3$
$M_r = 156.18$
Monoclinic, $P2_1/a$
$a = 11.821\ (2)$ Å
$b = 10.7618\ (18)$ Å
$c = 6.3146\ (11)$ Å
$\beta = 101.860\ (14)^\circ$
$V = 786.2\ (2)$ Å^3
$Z = 4$

$D_x = 1.320$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 13.1$–16.3°
$\mu = 0.10$ mm^{-1}
$T = 295\ (2)$ K
Prism, colourless
0.50 × 0.35 × 0.20 mm

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
2170 measured reflections
1805 independent reflections
1216 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.033$
$\theta_{\rm max} = 27.5^\circ$

$h = -8 \rightarrow 15$
$k = 0 \rightarrow 13$
$l = -8 \rightarrow 8$
3 standard reflections every 150 reflections intensity decay: 1.2%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.132$
$S = 1.04$
1805 reflections
149 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0615P)^2 + 0.1309P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.17$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.023 (5)

All H atoms were refined; the range of C—H distances was 0.95 (2)–1.03 (2) Å.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1999*a*); cell refinement: *MSC/AFC Diffractometer Control Software*; data reduction: *TEXSAN for Windows* (Molecular Structure Corporation, 1999*b*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *PLATON for Windows* (Spek, 1999); software used to prepare material for publication: *TEXSAN* for Windows.

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