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Key indicators

Single-crystal X-ray study

T = 120 K

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

R factor = 0.036

wR factor = 0.096

Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Methyl *exo*-bicyclo[3.1.0]hexane-6,6-dicarboxylate

The bicyclo[3.1.0]hexane fragment of the title molecule, $\text{C}_9\text{H}_{12}\text{O}_4$, adopts a boat-like conformation, with its methoxycarbonyl substituent in the *endo* position. In the crystal structure, molecules form centrosymmetric $\text{O}-\text{H}\cdots\text{O}$ hydrogen-bonded dimers, which are arranged in layers.

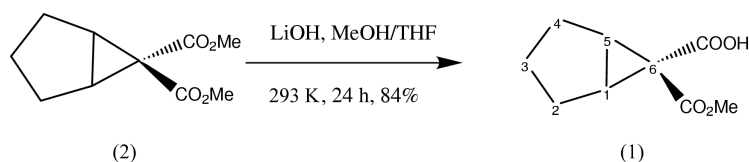
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Comment

According to several studies, bicyclo[3.1.0]hexane adopts a boat-like conformation rather than a chair-like one. These results were obtained experimentally by electron diffraction and microwave spectroscopy in the gas phase (Cook & Malloy, 1974; Mastryukov *et al.*, 1977; Shen *et al.*, 1995), as well as by computation, performed at different levels of theory ($\Delta\Delta H = 3.1\text{--}3.3 \text{ kcal mol}^{-1}$) (Shen *et al.*, 1995; Kang *et al.*, 2000; Okazaki *et al.*, 1988; Siam *et al.*, 1987; Skancke, 1982; Mjoberg & Almlof, 1978). However, much less is known about the conformational behaviour of substituted bicyclo[3.1.0]hexanes in the crystalline state, for example, a search for 3,6-disubstituted bicyclo[3.1.0]hexanes in version 5.24 of the Cambridge Structural Database (Allen, 2002) revealed only 14 such molecules. Depending on the position and the nature of the substituents, the bicyclo[3.1.0]hexane skeleton can adopt the whole range of conformations from chair-like to boat-like (Kozhushkov *et al.*, 2003). However, five out of six 6-substituted bicyclo[3.1.0]hexane derivatives have a boat-like conformation in their crystal structures. Probably, the eclipsing torsional strain caused by the substituents determines the shape of the molecule.



The title compound, (1) (Bagutskii, 2003), was prepared by regioselective saponification of the known (Troxler & Schefold, 1994) dimethyl bicyclo[3.1.0]hexane-6,6-dicarboxylate, (2), as an intermediate along the route to new vinylcyclopropane monomers for radical ring-opening polymerization (Moszner *et al.*, 2003; de Meijere *et al.*, 2003).

The structure of compound (1) has been determined by X-ray crystallography and we report here the results of the study. The bicyclo[3.1.0]hexane fragment adopts a boat-like conformation, which is the most common for 6,6-disubstituted derivatives, with the methoxycarbonyl group in an *endo* and carboxylic acid substituent in an *exo* position, respectively (Fig. 1). The dihedral angle between the planes C1/C2/C4/C5

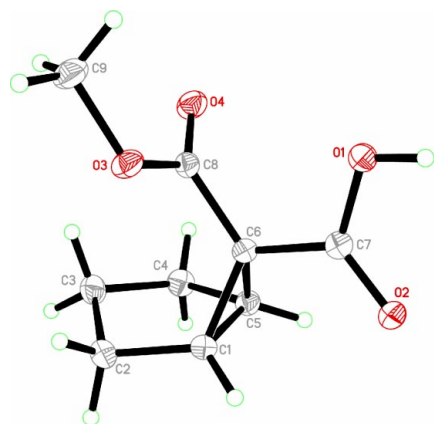


Figure 1
The molecular structure and labelling scheme of (1). Ellipsoids are drawn at the 50% probability level.

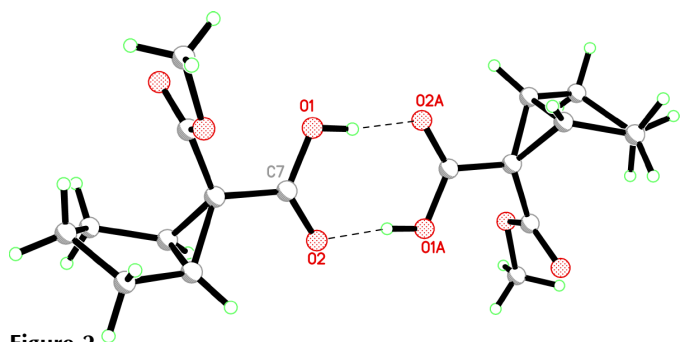


Figure 2
Hydrogen-bonded dimers in the structure of (1). Atoms labelled with A are related by the symmetry code $(1 - x, 2 - y, -z)$.

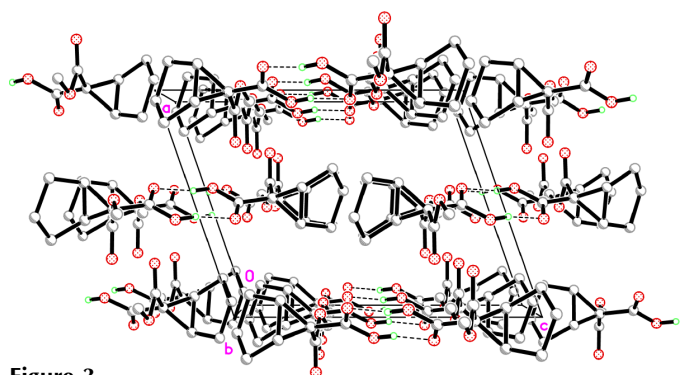


Figure 3
The packing of the molecules of (1) in the crystal structure, viewed along the b axis. H atoms have been omitted for clarity.

and C2/C3/C4 is $154.7(1)^\circ$ [*cf.* $154.8(28)^\circ$ (Mastryukov *et al.*, 1977)] and between the planes C1/C2/C4/C5 and C1/C2/C6 is $112.0(1)^\circ$. The methoxycarbonyl substituent in the *endo* position is orientated perpendicular to the bisecting plane of the three-membered ring, while the *exo*-carboxyl substituent adopts a bisected conformation, which is usually more favourable for interaction with a cyclopropane system. Similar orientations of carboxylic acid groups were found in other 1,1-disubstituted cyclopropane derivatives (*e.g.* Yang *et al.*, 2001; Shea *et al.*, 2000). Apparently, such an orientation of an *endo*-methoxycarbonyl substituent is favourable in order to reduce the number of short intramolecular contacts with the H atoms of the five-membered ring.

In the crystal structure, molecules of (1) form centrosymmetric hydrogen-bonded dimers (Fig. 2 and Table 1), as is usual for carboxylic acids. These dimers are arranged in loose layers, parallel to the bc plane (Fig. 3)

Experimental

The synthesis of (1) is described in detail elsewhere (de Meijere *et al.*, 2003). The crystals were obtained by slow evaporation of a hexane/ Et_2O solution.

Crystal data

$\text{C}_9\text{H}_{12}\text{O}_4$
 $M_r = 184.19$
Monoclinic, $P2_1/n$
 $a = 9.1290(2) \text{ \AA}$
 $b = 8.7002(2) \text{ \AA}$
 $c = 11.6958(3) \text{ \AA}$
 $\beta = 109.28(1)^\circ$
 $V = 876.82(5) \text{ \AA}^3$
 $Z = 4$

$D_x = 1.395 \text{ Mg m}^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 3387 reflections
 $\theta = 2.9\text{--}30.4^\circ$
 $\mu = 0.11 \text{ mm}^{-1}$
 $T = 120(2) \text{ K}$
Spheroid, colourless
 $0.20 \times 0.12 \times 0.10 \text{ mm}$

Data collection

Bruker APEX CCD diffractometer
 ω scans
Absorption correction: none
7793 measured reflections
2315 independent reflections
1972 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$
 $\theta_{\text{max}} = 29.0^\circ$
 $h = -12 \rightarrow 12$
 $k = -11 \rightarrow 11$
 $l = -15 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.036$
 $wR(F^2) = 0.096$
 $S = 1.06$
2315 reflections
166 parameters

All H-atom parameters refined
 $w = 1/[\sigma^2(F_o^2) + (0.06P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.22 \text{ e \AA}^{-3}$

Table 1

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

O1—C7	1.3149 (12)	C1—C6	1.5284 (13)
O2—C7	1.2291 (11)	C2—C3	1.5448 (15)
O3—C8	1.3434 (11)	C3—C4	1.5432 (14)
O3—C9	1.4531 (12)	C4—C5	1.5143 (14)
O4—C8	1.2032 (12)	C5—C6	1.5327 (14)
C1—C5	1.5032 (13)	C6—C7	1.4849 (14)
C1—C2	1.5165 (14)	C6—C8	1.5043 (13)
C8—O3—C9	114.41 (8)	C7—C6—C1	115.24 (8)
C5—C1—C2	108.11 (8)	C8—C6—C1	123.24 (8)
C5—C1—C6	60.73 (6)	C7—C6—C5	112.89 (8)
C2—C1—C6	117.93 (8)	C8—C6—C5	121.55 (8)
C1—C2—C3	105.54 (8)	C1—C6—C5	58.82 (6)
C4—C3—C2	105.58 (8)	O2—C7—O1	123.98 (9)
C5—C4—C3	105.48 (8)	O2—C7—C6	122.12 (9)
C1—C5—C4	108.67 (8)	O1—C7—C6	113.89 (8)
C1—C5—C6	60.45 (6)	O4—C8—O3	124.06 (9)
C4—C5—C6	117.42 (8)	O4—C8—C6	124.87 (9)
C7—C6—C8	114.02 (8)	O3—C8—C6	111.05 (8)

Table 2

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

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O1—H1O \cdots O2 ⁱ	0.885 (19)	1.74 (2)	2.6175 (11)	170.4 (16)

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

All H atoms were located in the difference Fourier maps and included in the refinement with isotropic displacement parameters. The C—H distances range from 0.944 (14) to 1.016 (12) Å, and the O—H distance is 0.885 (19) Å.

Data collection: *SMART-NT* (Bruker, 1998); cell refinement: *SMART-NT*; data reduction: *SAINT-NT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 1998); software used to prepare material for publication: *SHELXTL*.

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