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5-*cis*-Bromo-2,2,6,6-tetramethyltetrahydropyran-3-carboxylic acid

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Key indicators

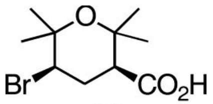
Single-crystal X-ray study
T = 299 K
Mean σ(C–C) = 0.005 Å
R factor = 0.043
wR factor = 0.135
Data-to-parameter ratio = 17.4

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

Enantiomers of the title compound, $C_{10}H_{17}BrO_3$, form hydrogen-bonded centrosymmetric dimers, where the carboxy H atom serves as donor and the C=O group of a neighbouring molecule acts as acceptor. The proximity of two axial methyl substituents causes distortions of the tetrahydropyran chair conformation, which are evident from the magnitude of the endocyclic bond angle at the O atom and the values of the endocyclic torsion angles.

Comment

The title compound, (I), was prepared from its ethyl ester, which in turn is the minor cyclization product formed upon treatment of ethyl [2-(1-hydroxy-1-methylethyl)-5-methyl]-hex-4-enoate with electrophilic bromination reagents (Hartung *et al.*, 2006). In order to explore structural aspects that might explain the low selectivity of 2,2,3,5,6,6-substituted tetrahydropyran formation in electrophile-induced ring closures, the title compound, (I), was crystallized and investigated by X-ray diffraction.


(I)

Compound (I) crystallizes in monoclinic space group *C*2/*c* (*Z* = 8). The tetrahydropyran nucleus adopts an $^1C_4$ conformation, with atoms O1 [0.531 (4) Å] and C4 [−0.668 (6) Å] offset in opposite directions from the C2/C3/C5/C6 plane (Fig. 1). The angle between the C2/O1/C6 plane and the C2/C3/C5/C6 mean plane [50.2 (4)°] is approximately similar to the tilt between the latter and segment C3/C4/C5 [49.9 (4)°]. A chair-like arrangement, with Br1, the carboxy substituent, and methyl groups $C8H_3$ and $C10H_3$ in equatorial positions, has been suggested as the predominant conformation of (I) in $CDCl_3$ solution (298 K) on the basis of vicinal H,H coupling constants (^{1}H NMR). The distance C7···C9 = 3.167 (6) Å falls below the sum of the van der Waals radii (1.70 Å for C; Bondi, 1964). The repulsion that occurs between $C7H_3$ and $C9H_3$ (Fig. 1) causes a widening of the bond angle at O1 [123.0 (3)°] and probably the flattening of the tetrahydropyran chair conformation that is evident by summing the absolute values of the endocyclic torsion angles. A value of 320° for this sum is less than expected for the undistorted chair conformation of tetrahydropyran (Hartung & Bergsträsser, 2006).

Enantiomers of (I) form hydrogen-bonded centrosymmetric dimers in the solid state. The carboxy H atom serves as hydrogen-bond donor and the C=O group of a neighbouring molecule as acceptor (Fig. 2 and Table 2).

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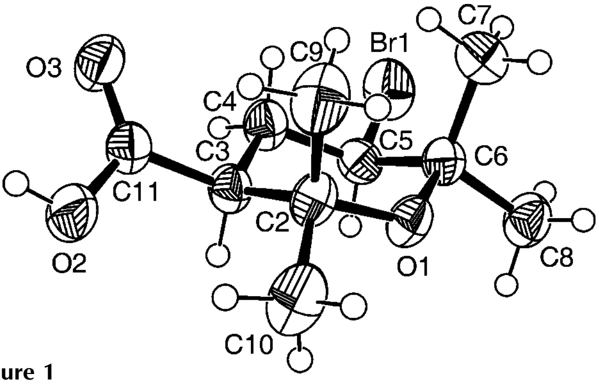

Figure 1
The molecular structure of (I) in the solid state. Displacement ellipsoids are drawn at the 50% probability level.

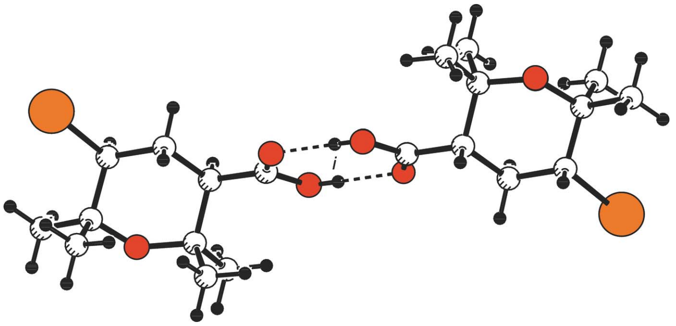

Figure 2
the hydrogen-bonding (dashed lines) of (I) in the solid state. O atoms are depicted in red and Br atoms in orange. The letter *i* marks a centre of inversion.

Experimental

A solution of ethyl 5-*cis*-bromo-2,2,6,6-tetramethyltetrahydropyran-3-carboxylate (Hartung *et al.*, 2006) (400 mg, 1.36 mmol) and LiOH·H_2O (916 mg, 21.8 mmol) in dimethoxyethane (18 ml) and water (27 ml) was stirred for 2 d at 293 K. The solution was then acidified with HCl (pH 2) and extracted with CH_2Cl_2 (4 × 80 ml). The organic washings were combined, dried ($MgSO_4$), and concentrated under reduced pressure to furnish (I) as a yellow solid (357 mg, 98%). Colorless crystals suitable for X-ray diffraction were grown by slowly concentrating a saturated solution of (I) in CH_2Cl_2–diethyl ether (3:1 *v*/*v*) at 298 K (m.p. 407 K). Analysis calculated for $C_{10}H_{17}BrO_3$: C 45.30, H 6.46%; found C 46.08, H 6.40%.

Crystal data

$C_{10}H_{17}BrO_3$
$M_r = 265.15$
Monoclinic, $C2/c$
$a = 30.539\ (1)$ Å
$b = 10.051\ (1)$ Å
$c = 7.748\ (1)$ Å
$\beta = 95.74\ (1)^\circ$
$V = 2366.3\ (4)$ Å^3
$Z = 8$
$D_x = 1.489$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 3.46$ mm^{-1}
$T = 299\ (2)$ K
Flat needle, colourless
0.80 × 0.33 × 0.08 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.169$, $T_{\max} = 0.782$
2604 measured reflections
2328 independent reflections
1596 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 26.0^\circ$
3 standard reflections
frequency: 120 min
intensity decay: 0.1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.135$
$S = 1.02$
2328 reflections
134 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0793P)^2 + 3.5651P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.005$
$\Delta\rho_{\max} = 0.94$ e Å^{-3}
$\Delta\rho_{\min} = -0.90$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C2—O1	1.441 (4)	C5—C6	1.531 (5)
C2—C3	1.551 (5)	C5—Br1	1.966 (3)
C3—C11	1.510 (5)	C6—O1	1.455 (4)
C3—C4	1.533 (5)	C11—O3	1.216 (5)
C4—C5	1.515 (5)	C11—O2	1.310 (5)
O1—C2—C3	108.8 (3)	O1—C6—C5	105.0 (3)
C4—C3—C2	112.0 (3)	O3—C11—O2	122.8 (3)
C5—C4—C3	110.0 (3)	C2—O1—C6	123.0 (3)
C4—C5—C6	112.9 (3)		
O1—C2—C3—C4	−46.7 (4)	C4—C5—C6—O1	55.1 (4)
C2—C3—C4—C5	53.0 (4)	C3—C2—O1—C6	51.8 (4)
C3—C4—C5—C6	−58.8 (4)	C5—C6—O1—C2	−55.0 (4)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O2—H2···O3$^{\rm i}$	0.81 (1)	1.83 (1)	2.645 (4)	176 (6)

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

Atom H2 was located in a difference Fourier map and its atomic coordinates were refined, with $U_{\rm iso}$(H) set at $1.2U_{\rm eq}$(O2). All other H atoms were positioned geometrically and treated as riding atoms, with C—H distances in the range 0.95–1.00 Å and with $U_{\rm iso}$(H) set at $1.2U_{\rm eq}$ of the parent atom. A free rotating-group refinement was used for the CH_3 groups.

Data collection, cell refinement and data reduction: *CAD-4 Diffractometer Control Software* (Enraf–Nonius, 1993); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON2002* (Spek, 2003) and *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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