Molecules of the title compound, C₈H₁₀Br₂O₄, located on symmetry centers, are in a rigid chair conformation, with the COOH and Br substituents axial and equatorial, respectively. The carboxylic acid groups form hydrogen bonds, in a cyclic motif, leading to infinite chains along the b axis.

Comment

This paper is part of a study of the molecular conformation and crystal polarity of trans-1,4-dit- and tetrasubstituted symmetrical cyclohexanes (Echeverría et al., 2000, 1995a,b).

The intramolecular bond lengths and the endocyclic bond angles that describe the molecular conformation of the title compound, (I), are given in Table 1. The mean C—C ring bond length and the mean endocyclic angle are 1.532 (3) Å and 110.7 (2)°, respectively; the latter value is close to the value for the ideal cyclohexane ring, C—C—C 111.1° (Bucourt & Hainaut, 1965) and to the observed mean value in the parent compound trans-1,4-cyclohexanedicarboxylic acid, (II) [111.4 (4)°; Dunitz & Strickler, 1966; Von Luger et al., 1972]. The cyclohexane ring, as described by the puckering parameters (Cremer & Pople, 1975), Qₚ = 0.585 (2) Å, θ = 0.0 (1)° and ϕ undefined, is not distorted. The torsion angle C₁—C₂—C₃—C₄ in (I), 56.2 (2)°, can be compared with 53.4 (3)° in (II), 54.8 (8)° in trans-1,4-dibromocyclohexane-1,4-dicarbonitrile (Echeverría et al., 1995a), and 57.1 (3)° in trans-cyclohexane-1,4-dicarbonitrile (Echeverría et al., 1995b). In contrast to observations in other studies, where flatter chairs were found as the size of substituents was increased (Juariisti, 1995; Echeverría et al., 2000), the molecule of (I) exhibits a more pronounced chair conformation. The exocyclic angle involving the substituents (C₄—C₁—Br₁) is 102.2 (1)°. This departs from the experimental Hₑq—C—Hₛₜ value, 106.6°, obtained from isotopomers of cyclohexane selectively substituted with deuterium and ¹³C, using pulsed microwave Fourier transform spectroscopy (Dommen et al., 1990). The Rₑq—C—Rₛₜ angle in (I) is also smaller than the values obtained in other heavily substituted cyclohexanes that include halogens and/or carboxymethyl groups, e.g. 105.7 (1)° in trans-dimethyl...
1,4-bis(difluoromethyl)cyclohexane-1,4-dicarboxylate (Swenson et al., 1996) and 106.7 (2)° in 1Ha2He/4Ha5He-octafluorocyclohexane (Goodhand & Hamor, 1978). In spite of the equatorial position of Br, the C—Br bond length, 1.988 (2) Å, is longer than the C—Br bond length, 1.834 Å, observed in trans-1,4-dibromocyclohexane (Hassel & Hadler Vihovde, 1953). This is consistent with the elongation predicted by HF calculations in overcrowded, perhalogenated cyclohexanes (Ciolowski et al., 1995).

The three-dimensional structure consists of infinite chains extending in the b direction. These chains result from hydrogen bonds, in a cyclic motif, formed by the carboxylic acid groups (Table 2). The chains are linked by weak C—H···O bonds (Steiner, 2002) and weak C—H···Br contacts.

**Experimental**

The title compound was synthesized according to Barón et al. (1975) and crystallized by slow evaporation from acetone.

**Crystal data**

C₈H₁₀Br₂O₄

Mo Kα radiation

Cell parameters from 914 reflections

θ = 11.5—26.3°

μ = 8.14 mm⁻¹

T = 110 (2) K

Prism, colourless

0.20 × 0.13 × 0.10 mm³

**Data collection**

Bruker SMART 1K CCD

Absorption correction: multi-scan

SADABS

1224 independent reflections

795 reflections with l > 2σ(I)

Refinement

R[1(l)] = 0.041

θ[max] = 28.2°

h = −13→13

k = −11→11

l = −13→15

Revised on F²

R(F²) = 0.027

wR(F²) = 0.077

S = 1.06

1224 reflections

84 parameters

H atoms treated by a mixture of independent and constrained refinement

**Table 1**

<table>
<thead>
<tr>
<th>Selected geometric parameters (Å, °)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Br1—C1</td>
</tr>
<tr>
<td>O1—C1</td>
</tr>
<tr>
<td>O1—H1</td>
</tr>
<tr>
<td>O2—C4</td>
</tr>
<tr>
<td>C1—C3</td>
</tr>
<tr>
<td>C3—C4</td>
</tr>
<tr>
<td>O1—C4</td>
</tr>
<tr>
<td>O2—C4</td>
</tr>
<tr>
<td>C4—C1</td>
</tr>
<tr>
<td>C3—C4</td>
</tr>
<tr>
<td>O1—C1</td>
</tr>
<tr>
<td>O2—C4</td>
</tr>
<tr>
<td>C4—C1</td>
</tr>
</tbody>
</table>

Symmetry code: (i) 1 − x, −y, 1 − z.

**Table 2**

<table>
<thead>
<tr>
<th>Hydrogen-bonding geometry (Å, °)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D—H···A</td>
</tr>
<tr>
<td>O1—H1···O2''</td>
</tr>
<tr>
<td>C2—H21···O1''</td>
</tr>
<tr>
<td>C2—H22···O2''</td>
</tr>
<tr>
<td>C3—H31···O2''</td>
</tr>
<tr>
<td>C3—H32···O1''</td>
</tr>
<tr>
<td>C2—H21···Br1''</td>
</tr>
<tr>
<td>C2—H22···Br1''</td>
</tr>
<tr>
<td>C3—H31···Br1''</td>
</tr>
</tbody>
</table>

Symmetry codes: (ii) −x, −y, −z; (iii) 1 − x, −y, 1 − z; (iv) x, 1 − y, −z; (v) 1 − x, y, 1 − z; (vi) x, 1 − y, z; (vii) 1 − x, −y, 1 − z; (viii) 1 − x, y, z; (ix) 1 − x, y, −z.
H atoms bound to C atom were located in difference Fourier syntheses and were refined freely in isotropic mode [C—H distances are in the range 0.96 (2)–1.01 (3) Å]. The H atom of the hydroxyl group was stereochemically positioned and allowed to ride on the bound O atom. The O—H bond was also allowed to rotate about the C—O bond. The largest difference electron-density peak is 0.94 Å from Br1.

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: PLATON (Spek, 1990), PARST (Nardelli, 1983, 1995) and ORTEP-3 (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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References


