

trans*-1,4-Dibromocyclohexane-1,4-dicarboxylic acid*Gustavo A. Echeverría,^{a*} Andrés Goeta,^b Máximo Barón^c and Graciela Punte^a**^aIFLP and LANADI, Departamento de Física, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, La Plata, CC 67, Argentina, ^bDepartment of Chemistry, University of Durham, Durham DH1 3LE, England, and ^cFacultad de Ciencias Exactas y Naturales, Universidad de Belgrano, Villanueva 1324, 1426 Buenos Aires, Argentina

Correspondence e-mail: geche@fisica.unlp.edu.ar

Key indicators

Single-crystal X-ray study

T = 110 K

Mean $\sigma(\text{C}-\text{C}) = 0.003 \text{ \AA}$

R factor = 0.026

wR factor = 0.077

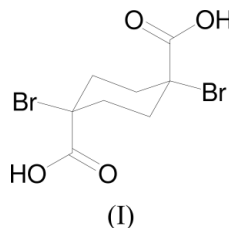
Data-to-parameter ratio = 14.6

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

Molecules of the title compound, $\text{C}_8\text{H}_{10}\text{Br}_2\text{O}_4$, 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-di- and tetrasubstituted symmetrical cyclohexanes (Echeverría *et al.*, 2000, 1995*a,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), $Q_T = 0.585$ (2) Å, $\theta = 0.0$ (1)° and φ undefined, is not distorted. The torsion angle C1—C2—C3ⁱ—C1ⁱ 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.*, 1995*a*), and 57.1 (3)° in *trans*-cyclohexane-1,4-dicarbonitrile (Echeverría *et al.*, 1995*b*). In contrast to observations in other studies, where flatter chairs were found as the size of substituents was increased (Juaristi, 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 $\text{H}_{\text{eq}}-\text{C}-\text{H}_{\text{ax}}$ 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 $R_{\text{eq}}-\text{C}-R_{\text{ax}}$ 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

Received 6 May 2003

Accepted 4 June 2003

Online 17 June 2003

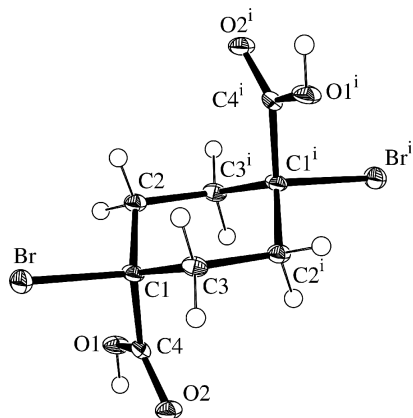


Figure 1
A view of (I), with displacement ellipsoids drawn at the 50% probability level. Symmetry code: (i) $1 - x, -y, 1 - z$.

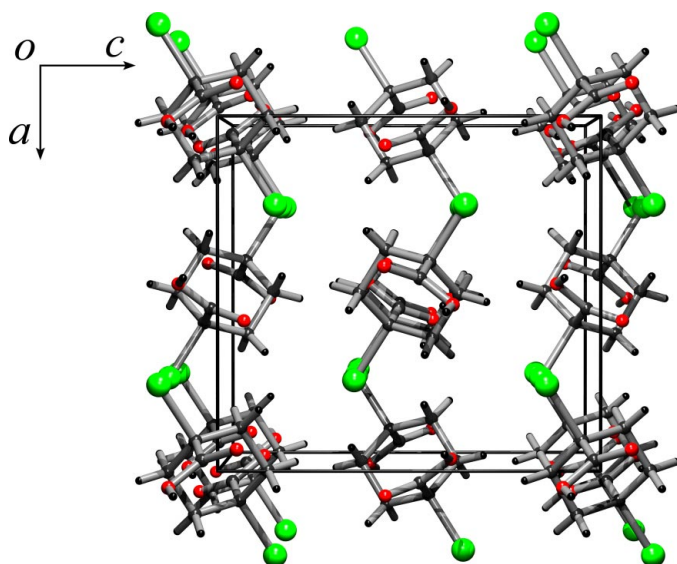


Figure 2
A view, along *b*, of the unit-cell contents for (I).

1,4-bis(difluoromethyl)cyclohexane-1,4-dicarboxylate (Swenson *et al.*, 1996) and $106.7(2)^\circ$ in 1Ha:2He/4Ha:5He-octafluorocyclohexane (Goodhand & Hamor, 1978). In spite of the equatorial position of Br, the C—Br bond length, $1.988(2) \text{ \AA}$, is longer than the C—Br bond length, 1.834 \AA , 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

$\text{C}_8\text{H}_{10}\text{Br}_2\text{O}_4$
 $M_r = 329.98$
Orthorhombic, *Pbca*
 $a = 10.5125(8) \text{ \AA}$
 $b = 8.3836(5) \text{ \AA}$
 $c = 11.2817(9) \text{ \AA}$
 $V = 994.29(12) \text{ \AA}^3$
 $Z = 4$
 $D_x = 2.204 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation
Cell parameters from 914 reflections
 $\theta = 11.5\text{--}26.3^\circ$
 $\mu = 8.14 \text{ mm}^{-1}$
 $T = 110(2) \text{ K}$
Prism, colourless
 $0.20 \times 0.13 \times 0.10 \text{ mm}$

Data collection

Bruker SMART 1K CCD diffractometer
 ω scans
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)
 $T_{\min} = 0.244, T_{\max} = 0.443$
10 606 measured reflections

1224 independent reflections
975 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.041$
 $\theta_{\text{max}} = 28.2^\circ$
 $h = -13 \rightarrow 13$
 $k = -11 \rightarrow 11$
 $l = -13 \rightarrow 15$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.027$
 $wR(F^2) = 0.077$
 $S = 1.06$
1224 reflections
84 parameters
H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0491P)^2 + 0.3512P]$
where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 1.04 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.56 \text{ e \AA}^{-3}$

Table 1

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

Br1—C1	1.988 (2)	C3—C1	1.525 (3)
O1—C4	1.304 (3)	C3—C2 ⁱ	1.545 (3)
O1—H1	0.82	C2—C1	1.525 (3)
O2—C4	1.235 (3)	C1—C4	1.536 (3)
C1—C3—C2 ⁱ	109.97 (18)	C2—C1—Br1	107.70 (16)
C1—C2—C3 ⁱ	110.57 (18)	C4—C1—Br1	102.23 (13)
C3—C1—C2	111.75 (18)	O2—C4—O1	125.0 (2)
C3—C1—C4	111.99 (18)	O2—C4—C1	120.60 (19)
C2—C1—C4	113.69 (18)	O1—C4—C1	114.39 (19)
C3—C1—Br1	108.88 (15)	C1—C2—C3 ⁱ —C1 ⁱ	−56.1 (2)
C1—C2—C3 ⁱ —C1 ⁱ	−56.1 (2)	C2 ⁱ —C3—C1—C2	−56.8 (2)
C2 ⁱ —C3—C1—C4	72.1 (2)	C2 ⁱ —C3—C1—Br1	−175.6 (1)
C2 ⁱ —C3—C1—Br1	−175.6 (1)	C3 ⁱ —C2—C1—C3	57.1 (2)
C3 ⁱ —C2—C1—C3	57.1 (2)	C3 ⁱ —C2—C1—C4	−70.8 (2)
C3 ⁱ —C2—C1—C4	−70.8 (2)	C3 ⁱ —C2—C1—Br1	176.7 (1)
C3 ⁱ —C2—C1—Br1	176.7 (1)	C3—C1—C4—O2	25.0 (3)
C3—C1—C4—O2	25.0 (3)	C2—C1—C4—O2	152.8 (2)
C2—C1—C4—O2	152.8 (2)	Br1—C1—C4—O2	−91.4 (2)
Br1—C1—C4—O2	−91.4 (2)	C3—C1—C4—O1	−156.2 (2)
C3—C1—C4—O1	−156.2 (2)	C2—C1—C4—O1	−28.4 (3)
C2—C1—C4—O1	−28.4 (3)	Br1—C1—C4—O1	87.4 (2)
Br1—C1—C4—O1	87.4 (2)		

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

Table 2

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

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1...O2 ⁱⁱ	0.82	1.82	2.639 (2)	176
C2—H21...O1 ⁱⁱⁱ	0.97 (3)	2.73 (2)	3.274 (3)	116 (2)
C2—H22...O2 ^{iv}	0.96 (2)	2.93 (2)	3.719 (3)	140 (2)
C3—H31...O2 ^v	1.01 (3)	2.71 (3)	3.431 (3)	129 (2)
C3—H32...O1 ^{vi}	0.96 (3)	3.18 (3)	3.889 (3)	132 (2)
C2—H21...Br1 ^{vii}	0.96 (3)	3.17 (3)	4.081 (2)	158 (2)
C2—H22...Br1 ^{viii}	0.96 (2)	3.03 (2)	3.813 (2)	139 (2)
C3—H31...Br1 ^{vii}	1.01 (3)	3.22 (2)	4.137 (2)	152 (2)

Symmetry codes: (ii) $-x, -y, -z$; (iii) $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$; (iv) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (v) $\frac{1}{2} - x, y - \frac{1}{2}, z$; (vi) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$; (vii) $x - \frac{1}{2}, y, \frac{1}{2} - z$.

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: *SAINTE-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).

We thank CONICET (Argentina), UNLP, UB, the EPSRC (UK) and CSIC (Spain), for financial support. GP and GE are members of the CONICET.

References

- Barón, M., de Zenobi, E. L. & Davidson, M. (1975). *J. Mol. Struct.* **124**, 432–438.
- Bucourt, R. & Hainaut, D. (1965). *Bull. Soc. Chim. Fr.* **5**, 1366–1378.
- Bruker (1998). *SMART-NT* (Version 5.0) and *SAINTE-NT* (Version 5.0). Bruker AXS Inc., Madison, Wisconsin, USA.
- Ciolowski, J., Edgington, L. & Stefanov, B. B. (1995). *J. Am. Chem. Soc.* **117**, 10381–10384.
- Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.
- Dommen, J., Brupbacher, Th., Grassi, G. & Bauder, A. (1990). *J. Am. Chem. Soc.* **112**, 953–957.
- Dunitz, J. D. & Strickler, P. (1966). *Helv. Chim. Acta*, **49**, 290–291.
- Echeverría, G., Barón, M. & Punte, G. (2000). *Struct. Chem.* **11**, 35–40.
- Echeverría, G., Punte, G., Rivero, B. E. & Barón, M. (1995a). *Acta Cryst. C51*, 1020–1023.
- Echeverría, G., Punte, G., Rivero, B. E. & Barón, M. (1995b). *Acta Cryst. C51*, 1023–1026.
- Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
- Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.
- Goodhand, N. & Hamor, T. A. (1978). *Acta Cryst.* **B34**, 513–516.
- Hassel, G. & Hadler Vihovde, E. (1953). *Acta Chem. Scand.* **7**, 1164–1169.
- Juaristi, E. (1995). Editor. *Conformational Behavior of Six-Membered Rings: Analysis, Dynamics, and Stereoelectronic Effects*. New York: VCH Publishers.
- Nardelli, M. (1983). *Comput. Chem.* **7**, 95–97.
- Nardelli, M. (1995). *J. Appl. Cryst.* **28**, 659.
- Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.
- Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Spek, A. L. (1990). *Acta Cryst.* **A46**, C-34.
- Steiner, Th. (2002). *Angew. Chem. Int. Ed. Engl.* **41**, 48–76.
- Swenson, D. C., Davis, C. R. & Burton, D. J. (1996). *Acta Cryst.* **C52**, 2844–2847.
- Von Luger, P., Plieth, K. & Ruban, G. (1972). *Acta Cryst.* **B28**, 706–710.