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## The Preferred Rotational Orientation of Equatorial and Axial Carboxyl Groups and Their Influence on the Cyclohexane Ring Geometry. Structures of Two Cyclohexanecarboxylic Acids: *cis*-1,3-Cyclohexanedicarboxylic Acid (I) and *trans*-1,3-Cyclohexanedicarboxylic Acid (II), C<sub>8</sub>H<sub>12</sub>O<sub>4</sub>

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**Abstract.** (I):  $M_r = 172.18$ , triclinic,  $P\bar{1}$ ,  $a = 5.340$  (2),  $b = 6.558$  (1),  $c = 13.834$  (1) Å,  $\alpha = 104.54$  (1),  $\beta = 96.36$  (2),  $\gamma = 69.64$  (2)°,  $V = 439.5$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.305$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.113$  mm<sup>-1</sup>,  $F(000) = 184$ ,  $T \approx 293$  K,  $R = 0.044$  for 1634 observed reflections [ $I > 2.5\sigma(I)$ ]. (II):  $M_r = 172.18$ , triclinic,  $P\bar{1}$ ,  $a = 5.301$  (1),  $b = 6.192$  (3),  $c = 13.311$  (2) Å,  $\alpha = 102.79$  (4),  $\beta = 97.20$  (1),  $\gamma = 90.50$  (4)°,  $V = 422.4$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 1.359$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.117$  mm<sup>-1</sup>,  $F(000) = 184$ ,  $T \approx 293$  K,  $R = 0.054$  for 1671 observed reflections [ $I > 2.5\sigma(I)$ ]. The crystal of (I) consists of infinite chains of molecules along [201]. In each chain the molecules are held together around centres of symmetry by approximately linear hydrogen bonds of 2.664 and 2.648 Å. The carbonyl O atoms of the equatorial carboxyl groups are twisted away from the C<sub>β</sub>-eclipsed position by 21.3 and 15.5°. The average C–C bond distance, C–C–C bond angle and C–C–C–C torsion angle in the ring are 1.525 Å, 110.9° and 56.4°, respectively. The cyclohexane ring is very regular: no single distance or angle deviates more than 3σ from its

average ring value. No significant local influence of an equatorial carboxyl group on the geometry of the cyclohexane ring can be established. The crystal of (II) consists of infinite chains of molecules along  $[\bar{1}11]$ . In each chain the molecules are held together around centres of symmetry by approximately linear hydrogen bonds of 2.666 and 2.686 Å. The carbonyl O atom of the equatorial and axial carboxyl group is twisted away from the C<sub>β</sub>-eclipsed position by 5.2 and 5.4°, respectively. The average C–C bond distance, C–C–C bond angle and C–C–C–C torsion angle in the ring are 1.524 Å, 111.4° and 55.0°, respectively. Flattening of the cyclohexane ring at the axial carboxyl side of the ring, enlarging of the C<sub>α</sub>–C<sub>β</sub>–C<sub>γ</sub> angle, elongation of the C<sub>α</sub>–C<sub>β</sub> bonds and shortening of the C<sub>β</sub>–C<sub>γ</sub> bonds is observed. These effects on the ring parameters have been observed as well in several other structures containing an axial carboxyl group. The analysis (again) illustrates that there is no difference between the rotational orientation of an axial and an equatorial carboxyl group in cyclohexanecarboxylic acids: both prefer the synperiplanar C<sub>β</sub>–C<sub>α</sub>–C=O arrangement.

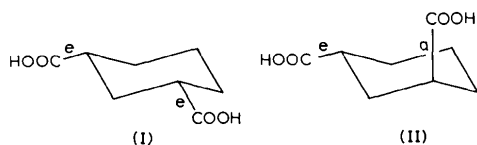
Table 1. Fractional atomic coordinates ( $\times 10^4$ ), with their e.s.d.'s, and isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ )
$$U_{\text{eq}} = \frac{1}{3}(U_{11} + U_{22} + U_{33}).$$

	Compound (I)				Compound (II)			
	x	y	z	$U_{\text{eq}}$	x	y	z	$U_{\text{eq}}$
C(1)	3947 (4)	2605 (3)	1591 (1)	42	3238 (4)	4262 (3)	1877 (2)	40
C(2)	5239 (4)	1396 (3)	2422 (1)	40	5245 (5)	4835 (4)	2816 (2)	44
C(3)	6931 (4)	2619 (3)	3125 (1)	40	4491 (5)	6751 (4)	3658 (2)	45
C(4)	5272 (5)	5037 (3)	3559 (2)	52	3725 (6)	8763 (4)	3201 (2)	54
C(5)	3980 (5)	6237 (4)	2730 (2)	56	1713 (6)	8149 (4)	2283 (2)	59
C(6)	2273 (4)	5037 (3)	2020 (2)	52	2549 (7)	6311 (4)	1434 (2)	58
C(7)	2237 (4)	1433 (3)	896 (1)	44	4065 (5)	2415 (3)	1051 (2)	43
C(8)	8248 (4)	1442 (3)	3942 (1)	43	2468 (5)	6026 (4)	4218 (2)	46
O(1)	1337 (3)	159 (3)	1126 (1)	69	6163 (4)	1643 (3)	1124 (1)	65
O(2)	1783 (4)	1935 (3)	22 (1)	76	2339 (4)	1732 (3)	266 (2)	65
O(3)	7575 (3)	13 (3)	4148 (1)	78	1664 (4)	4110 (3)	4078 (1)	65
O(4)	10179 (3)	2106 (3)	4417 (1)	70	1638 (4)	7622 (3)	4913 (2)	68

**Introduction.** Recently, a paper on the preferred rotational position of the carboxyl group in (substituted) cyclohexanecarboxylic acids appeared (van Koningsveld & Jansen, 1984). The authors concluded that the synperiplanar  $C_\beta-C_\alpha-C=O$  arrangement seems to be a general feature, as in a whole series of straight-chain acids.

Force-field calculations and electron-diffraction experiments on equatorial and axial methylcyclohexane have shown (Altona & Sundaralingam, 1970; Geise, Mijlhoff & Altona, 1972; Burkert & Allinger, 1982) that the influence of the equatorial substituent on the ring geometry is negligible and that the axial substituent causes flattening at the substituted side of the ring.

The aim of this investigation is to study these aspects by determining the molecular structure of *cis*-1,3-cyclohexanedicarboxylic acid (I) and *trans*-1,3-cyclohexanedicarboxylic acid (II)



and by comparing the results with data extracted from literature.

**Experimental.** [Data for compound (II) within brackets.] Title compounds synthesized by M. van Minnen-Pathuis in the Laboratory of Organic Chemistry, Delft. Crystals grown by evaporation from acetone solution,  $D_m$  not measured, approximate dimensions  $0.50 \times 0.40 \times 0.10$  [ $0.25 \times 0.60 \times 0.15$ ] mm, Enraf-Nonius CAD-4F diffractometer with graphite-monochromated  $\text{Mo K}\alpha$  radiation. Cell parameters from the diffractometer angular settings of 25 centred reflections ( $10^\circ < \theta < 18^\circ$ ), 2562 [2460] independent reflections measured,  $\theta_{\text{max}} = 30$ ,  $h = -7$  to 7,  $k = 0$  to 9,  $l = -19$  to 19 [ $h = -7$  to 7,  $k = 0$  to 8,  $l = -18$  to 18],  $\omega/2\theta$  scan, width =  $1.20^\circ + 0.35^\circ \tan \theta$ , max. recording time 120 s,  $\sigma_{\text{count}}(I)/I < 0.02$  requested in

scan, intensity variation of three standard reflections within 4% [3%], no decay; 1636 [1673] reflections with  $I > 2.5\sigma(I)$  used in structure determination. No absorption and extinction corrections. Structures solved by direct methods (*MULTAN*, Germain, Main & Woolfson, 1971) and refined on  $F$  by full-matrix least squares, anisotropic for non-hydrogen atoms. H atoms located from difference Fourier map and refined with fixed isotropic  $U$  value. Two reflections ( $11\bar{1}$  and  $10\bar{2}$ ) [ $101$  and  $010$ ] were excluded because they apparently suffered from extinction. Final  $wR = 0.044$  [0.054] for 1634 [1671] observed reflections,  $w = 1$ ,  $(\Delta/\sigma)_{\text{max}} = 0.10$  [0.25] for H(20) [H(40)],  $S = 0.73$  [1.13],  $|\Delta\rho|$  in final difference Fourier map  $0.27$  [0.25]  $\text{e \AA}^{-3}$ . All calculations performed with *XRAY72* (Stewart, Kruger, Ammon, Dickinson & Hall, 1972).

**Discussion.** Fig. 1 shows the molecular structures of (I) and (II). Atomic parameters are in Table 1. Bond distances, bond angles and selected torsion angles are given in Table 2.\*

#### The carboxyl groups

All three equatorial carboxyl groups are planar within experimental error. The deviation of any atom from the corresponding mean plane is  $< 0.004 \text{ \AA}$ . In the axial C(3)C(8)O(3)O(4) group, the deviations of the atoms from the mean plane are 0.003,  $-0.010$ , 0.004 and  $0.004 \text{ \AA}$ , respectively. Each of the four carboxyl groups is hydrogen bonded to another, leading to the well-known eight-membered rings around centres of symmetry. The hydrogen-bonding scheme is included in Table 2.

The rotational orientation of the carboxyl groups is given by the values of the  $\text{O}=\text{C}-\text{C}_\alpha-\text{C}_\beta$  torsion angles

\* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, and bond lengths and angles have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39565 (24 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

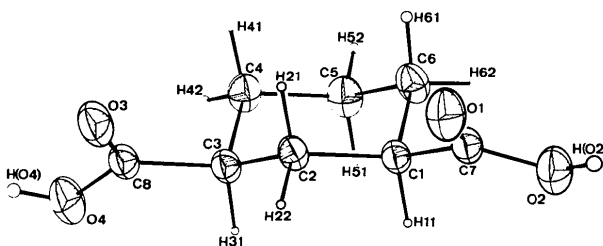
(Table 2). There is no difference in rotational preference between an axial and an equatorial carboxyl group: all four are synperiplanar with a  $C_\alpha-C_\beta$  ring bond. This observation is in agreement with the experimental data reported recently (van Koningsveld & Jansen, 1984, and references cited therein).

The shortening of the  $C_\alpha-C(OOH)$  bonds (to 1.508, 1.501, 1.511 and 1.499 Å) is observed in several other compounds (whether the carboxyl group is axial or equatorial) and can be attributed to the  $sp^2-sp^3$  character of the bond.

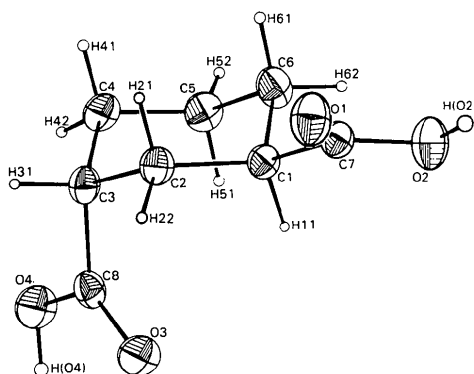
### The cyclohexane ring

The cyclohexane ring in (I) is very regular: no single bond length or angle deviates more than  $3\sigma$  from the corresponding average ring value. In (II) the cyclohexane ring is flattened at the axial carboxyl side of the ring. The corresponding\*  $C_\alpha-C_\beta$  bonds are elongated and the  $C_\beta-C_\gamma$  bonds are shortened compared to the average C-C ring bond.

\* The ring atom bearing a COOH group is  $C_\alpha$ ; the first ring-neighbour atoms are  $C_\beta$ , etc.; this means that in the 1,3-cyclohexanedicarboxylic acids the ring C atom which is  $C_\alpha$  with respect to the first COOH group is  $C_\gamma$  with respect to the second COOH group.



(a)



(b)

Fig. 1. The molecular structure and atom numbering of (a) compound (I) and (b) compound (II).

To see whether these effects can be generally attributed to axial carboxyl groups we first consider the influence of the substituents and packing forces on the average ring geometry. Table 3 summarizes the weighted-average geometry of the cyclohexane rings in several (substituted) cyclohexane (mono/di)carboxylic acids. The data, retrieved from the Cambridge Structural Database (CSD; Allen *et al.*, 1979), are divided into two groups. Table 3(a) contains the average ring parameters in molecules with equatorial substituents

Table 2. Molecular geometry in (I) and (II)

#### (a) Bond lengths (Å)

	(I)	(II)
C(1)-C(2)	1.525 (3)	1.511 (3)
C(1)-C(7)	1.507 (3)	1.511 (3)
C(2)-C(3)	1.525 (3)	1.535 (3)
C(3)-C(4)	1.524 (3)	1.539 (4)
C(3)-C(8)	1.501 (3)	1.499 (4)
C(4)-C(5)	1.520 (3)	1.495 (4)
C(5)-C(6)	1.526 (4)	1.528 (4)
C(6)-C(1)	1.532 (3)	1.541 (4)
C(7)-O(1)	1.215 (3)	1.216 (3)
C(7)-O(2)	1.307 (3)	1.291 (3)
C(8)-O(3)	1.216 (3)	1.223 (3)
C(8)-O(4)	1.305 (3)	1.316 (3)

#### (b) Bond angles (°)

	(I)	(II)
C(2)-C(1)-C(6)	111.1 (1)	111.5 (2)
C(2)-C(1)-C(7)	111.4 (2)	111.1 (2)
C(6)-C(1)-C(7)	109.8 (2)	110.9 (2)
C(1)-C(2)-C(3)	110.7 (2)	112.4 (2)
C(2)-C(3)-C(4)	111.0 (2)	111.0 (2)
C(2)-C(3)-C(8)	111.6 (2)	111.5 (2)
C(4)-C(3)-C(8)	110.8 (1)	112.4 (2)
C(3)-C(4)-C(5)	110.7 (2)	111.8 (2)
C(4)-C(5)-C(6)	111.5 (2)	111.7 (2)
C(5)-C(6)-C(1)	110.3 (2)	109.8 (2)
C(1)-C(7)-O(1)	123.4 (2)	122.9 (2)
C(1)-C(7)-O(2)	113.6 (2)	113.8 (2)
O(1)-C(7)-O(2)	122.9 (2)	123.3 (2)
C(3)-C(8)-O(3)	123.4 (2)	124.2 (2)
C(3)-C(8)-O(4)	113.6 (2)	114.5 (2)
O(3)-C(8)-O(4)	123.0 (2)	121.2 (2)

#### (c) Hydrogen-bonding scheme

$X-H\cdots Y$	$X\cdots Y$ (Å)	$H\cdots Y$ (Å)	$X-H\cdots Y$ (°)
Compound (I)			
O(2)-H(O2) $\cdots$ O(1 <sup>i</sup> )	2.664 (3)	1.87 (3)	168 (2)
O(4)-H(O4) $\cdots$ O(3 <sup>ii</sup> )	2.648 (3)	1.78 (3)	174 (3)
Compound (II)			
O(2)-H(O2) $\cdots$ O(1 <sup>iii</sup> )	2.666 (3)	1.97 (3)	161 (2)
O(4)-H(O4) $\cdots$ O(3 <sup>iv</sup> )	2.686 (3)	1.79 (3)	178 (3)

Symmetry code: (i)  $-x, -y, -z$ ; (ii)  $-x + 2, -y, -z + 1$ ; (iii)  $-x + 1, -y, -z$ ; (iv)  $-x, -y + 1, -z + 1$ .

#### (d) Selected torsion angles (°) (e.s.d.'s $\sim 0.2^\circ$ )

	(I)	(II)
C(6)-C(1)-C(2)-C(3)	56.5	54.1
C(1)-C(2)-C(3)-C(4)	56.6	52.3
C(2)-C(3)-C(4)-C(5)	56.4	53.4
C(3)-C(4)-C(5)-C(6)	56.5	56.9
C(4)-C(5)-C(6)-C(1)	56.1	57.4
C(5)-C(6)-C(1)-C(2)	56.0	55.7
O(1)-C(7)-C(1)-C(2)	21.3	5.2
O(3)-C(3)-C(8)-C(2)	15.5	5.4

only. Table 3(b) gives the same information for molecules containing, besides equatorial substituents, an axial carboxyl group. The values of  $n_j$  in Table 3 show that environmental effects (e.g. crystal packing) are negligible for the average  $\overline{C-C}$  ring distance: no single  $\bar{x}_j$  deviates more than  $2.7\sigma(\Delta)$  from  $\bar{X}$ , whether

the carboxyl group is equatorial or axial. Within each group of structures the mean average  $\overline{CCC}$  angle is hardly affected. However, there is a significant difference between  $\bar{X}(\text{eq})$  and  $\bar{X}(\text{ax})$ :  $\delta = 6.7\sigma(\delta)$ . Finally, Table 3 shows that the easiest way in which strain is relieved and environmental conditions are fulfilled is by

Table 3. Average endocyclic C—C bond length (Å), C—C—C bond angle (°) and C—C—C—C torsion angle (°) in (substituted) cyclohexane (mono/di)carboxylic acids

Data for ( $\pm$ )-trans-1,2-cyclohexanedicarboxylic acid (Benedetti, Corradini, Pedone & Post, 1969) are omitted because of (large) discrepancies between published and calculated values of the internal coordinates. The table includes data for structures with  $R$  factors  $< 7.3\%$ , except for the two structures described in reference (b) which have  $R = 13.6$  and  $15.2\%$ , respectively.

(a) Structures containing only equatorial substituents

Ref.	$\overline{C-C}$			$\overline{C-C-C}$			$\overline{C-C-C-C}$		
	$\bar{x}_j^{(1)}$	$10^4 \times \Delta_j^{(3)}$	$n_j^{(4)}$	$\bar{x}_j$	$10^2 \times \Delta_j$	$n_j$	$\bar{x}_j$	$10^2 \times \Delta_j$	$n_j$
(a)	1.5283 (15)	5 (16)	0.3	110.93 (8)	7 (9)	0.8	56.13 (16)	18 (18)	1.0
(b)	1.5520 (122)	232 (122)	1.9	110.40 (82)	60 (82)	0.7	57.33 (164)	138 (164)	0.8
(f)	1.5303 (8)	15 (10)	1.5	110.98 (6)	2 (7)	0.3	55.93 (12)	2 (14)	0.1
(h)	1.5345 (33)	57 (33)	1.7	111.15 (20)	15 (20)	0.8	55.47 (40)	48 (41)	0.9
(i)	1.5253 (12)	35 (13)	2.7	110.88 (8)	12 (9)	1.3	56.35 (16)	40 (18)	2.2
(k)	1.5257 (40)	31 (40)	0.8	112.00 (29)	100 (29)	3.4	53.23 (58)	272 (58)	4.7
(l)	1.5233 (35)	55 (35)	1.6	111.70 (17)	70 (18)	3.9	54.03 (34)	192 (35)	5.4
(m)	1.5303 (29)	15 (30)	0.5	111.08 (21)	8 (21)	0.4	56.17 (42)	22 (43)	0.5
(m)	1.5287 (29)	1 (30)	0.0	110.83 (17)	17 (18)	1.0	56.47 (34)	52 (35)	1.5
$\bar{X}(\text{eq})^{(2)}$	1.52877 (56)			110.999 (37)			55.949 (75)		
$\overline{\sigma^2(\bar{x}_j)} \times 2.25^{(5)}$	$52.3 \times 10^{-6}$			$22.9 \times 10^{-6}$			$91.4 \times 10^{-6}$		
$\sigma^2(\text{sample})^{(6)}$	$73.3 \times 10^{-6}$			$22.8 \times 10^{-6}$			$163.4 \times 10^{-6}$		

(b) Structures with, at least, an axial carboxyl group

Ref.	$\overline{C-C}$			$\overline{C-C-C}$			$\overline{C-C-C-C}$		
	$\bar{x}_j$	$10^4 \times \Delta_j$	$n_j$	$\bar{x}_j$	$10^2 \times \Delta_j$	$n_j$	$\bar{x}_j$	$10^2 \times \Delta_j$	$n_j$
(b)	1.5400 (82)	115 (82)	1.4	110.95 (41)	44 (41)	1.1	55.98 (82)	123 (85)	1.5
(c)	1.5228 (61)	57 (61)	0.9	110.93 (41)	46 (41)	1.1	55.85 (82)	110 (83)	1.3
(d)	1.5307 (16)	22 (18)	1.2	111.68 (11)	29 (12)	2.4	53.20 (22)	155 (24)	6.5
(e)	1.5290 (16)	5 (18)	0.3	111.43 (8)	4 (9)	0.4	54.82 (16)	7 (18)	0.4
(g)	1.5307 (16)	22 (18)	1.2	111.10 (12)	29 (13)	2.2	55.73 (24)	98 (26)	3.8
(j)	1.5241 (15)	44 (17)	2.6	111.37 (8)	2 (9)	0.2	54.97 (16)	22 (18)	1.2
$\bar{X}(\text{ax})^{(2)}$	1.52848 (78)			111.393 (46)			54.748 (92)		
$\overline{\sigma^2(\bar{x}_j)} \times 2.25$	$42.9 \times 10^{-6}$			$14.1 \times 10^{-6}$			$56.3 \times 10^{-6}$		
$\sigma^2(\text{sample})$	$37.5 \times 10^{-6}$			$8.9 \times 10^{-6}$			$108.8 \times 10^{-6}$		
$\delta^{(7)}$	0.00029 (96)			0.394 (59)			1.20 (12)		

Notes

- (1)  $\bar{x}_j$  = average in structure  $j = \sum_i w_i x_i / \sum_i w_i$  with  $w_i = 1/\sigma^2(x_i)$ ;  $\sigma(x_i) = 1.0 \times \text{e.s.d. (published)}$ ;  $\sigma(\bar{x}_j) = (1/\sum_i w_i)^{1/2}$ ;  $\sigma(\overline{C-C-C-C}) \simeq 2\sigma(\overline{C-C-C})$ .
- (2)  $\bar{X}$  = mean average of  $j$  structures, calculated analogously to  $\bar{x}_j$  with  $x_i = \bar{x}_j$ ; (eq) or (ax): equatorially or axially substituted structures.
- (3)  $\Delta_j = \bar{X} - \bar{x}_j$  with  $\sigma(\Delta_j) = [\sigma^2(\bar{x}_j) + \sigma^2(\bar{X})]^{1/2}$ .
- (4)  $n_j = \Delta_j/\sigma(\Delta_j)$ .
- (5)  $\overline{\sigma^2(\bar{x}_j)} = \sum_{j=1}^k \sigma^2(\bar{x}_j)/k$ ; the factor 2.25 originates from  $(1.5)^2$ : the 'true' e.s.d. is taken as  $1.5 \times \text{e.s.d.}$  from least-squares refinement (see discussion in Taylor & Kennard, 1983);  $k$  = number of structures considered.
- (6)  $\sigma^2(\text{sample}) = \sum_{j=1}^k (\bar{x}_j - \bar{X}_u)^2/(k-1)$ , where  $\bar{X}_u$  is the unweighted mean average of the observations:  $\bar{X}_u = \sum_{j=1}^k \bar{x}_j/k$ .
- (7)  $\delta = \bar{X}(\text{eq}) - \bar{X}(\text{ax})$  with  $\sigma(\delta) = \{\sigma^2[\bar{X}(\text{eq})] + \sigma^2[\bar{X}(\text{ax})]\}^{1/2}$ .

References: (a) trans-4-(aminomethyl)cyclohexanedicarboxylic acid (Groth, 1968); (b) trans-4-(aminomethyl)cyclohexanedicarboxylic acid.HBr and cis-4-(aminomethyl)cyclohexanedicarboxylic acid.HCl (Kadoya, Hanazaki & Iitaka, 1966); (c) cis-4-(aminomethyl)cyclohexanedicarboxylic acid.HBr (Groth & Hassel, 1965); (d) cis-4-(aminomethyl)cyclohexanedicarboxylic acid. $\frac{1}{2}$ H<sub>2</sub>O (Yamazaki, Watanabe, Moroi & Sano, 1981); (e) cis-4-tert-butylcyclohexanedicarboxylic acid (van Koningsveld, 1972); (f) trans-4-tert-butylcyclohexanedicarboxylic acid (van Koningsveld & Jansen, 1984); (g) cis-1,2-cyclohexanedicarboxylic acid (Benedetti, Pedone & Allegra, 1970); (h) (+)-trans-1,2-cyclohexanedicarboxylic acid (Benedetti, Corradini & Pedone, 1969); (i) cis-1,3-cyclohexanedicarboxylic acid (this report); (j) trans-1,3-cyclohexanedicarboxylic acid (this report); (k) trans-1,4-cyclohexanedicarboxylic acid (Dunitz & Strickler, 1966); (l) trans-1,4-cyclohexanedicarboxylic acid (Luger, Plieth & Ruban, 1972a); (m) trans-1,4-cyclohexanedicarboxylic acid (Luger, Plieth & Ruban, 1972b).

changing the torsion angles. The difference between the mean average torsion angles exceeds significantly [ $\delta = 10 \cdot 0 \sigma(\delta)$ ] the differences between  $\bar{x}$  and  $\bar{X}$  in each group. Following Taylor & Kennard (1983), environmental effects are small when  $\sigma^2(\bar{x}_j)$  and  $\sigma^2(\text{sample})$  are similar in magnitude. These values have been added in Table 3 and confirm the conclusions drawn.

In the next step we try to establish the influence of equatorial and axial carboxyl groups on the 'local' geometry of the cyclohexane ring. To that end Table 4 contains the value of the  $C_\beta-C_\alpha-C_\beta$  angle, the average value of the two  $C_\alpha-C_\beta-C_\gamma$  angles, of the two

$C_\gamma-C_\beta-C_\alpha-C_\beta$  torsion angles, of the two  $C_\alpha-C_\beta$  bonds and of the two  $C_\beta-C_\gamma$  bonds. The division in sub-groups from Table 3 is used.

The  $\delta(\text{eq})$  values [Table 4(a)] show that the local influence of an equatorial carboxyl group on the ring parameters, except perhaps on the  $C_\beta-C_\alpha-C_\beta$  angle, is negligible.

The results of Table 4(b), on the other hand, show a significant local influence of an axial carboxyl group on the ring parameters. All  $\delta(\text{ax})$  values, except perhaps for the  $C_\beta-C_\alpha-C_\beta$  angle, are much larger than can be expected from environmental effects alone. The local

Table 4. Local (averaged) geometry (Å and deg) of the cyclohexane ring

$\bar{X}$  is the local analogon of  $\bar{X}$  defined in Table 3.

(a) Structures containing only equatorial substituents					
Ref.	$C_\beta-C_\alpha-C_\beta$	$C_\alpha-C_\beta-C_\gamma$	$C_\gamma-C_\beta-C_\alpha-C_\beta$	$C_\alpha-C_\beta$	$C_\beta-C_\gamma$
(a)	110.4 (2)	112.25 (14)	52.60 (28)	1.5325 (28)	1.5296 (24)
(b)	111.2 (20)	108.35 (140)	61.45 (283)	1.5605 (210)	1.5495 (210)
(f)	109.70 (13)	110.40 (9)	58.10 (18)	1.5295 (14)	1.5280 (14)
(h)	112.2 (5)	111.50 (35)	51.80 (71)	1.5400 (57)	1.5400 (57)
(h)	111.4 (5)	111.65 (35)	51.50 (71)	1.5485 (57)	1.5325 (57)
(i)	111.1 (2)	110.50 (14)	56.25 (28)	1.5285 (21)	1.5254 (24)
(j)	111.0 (2)	110.70 (14)	56.50 (28)	1.5245 (21)	1.5225 (21)
(k)	113.3 (5)	111.35 (35)	53.60 (71)	1.5240 (49)	1.5290 (70)
(l)	112.3 (3)	111.29 (24)	54.20 (48)	1.5180 (42)	1.5340 (70)
(m)	110.2 (4)	111.35 (28)	55.95 (57)	1.5290 (35)	1.5330 (50)
(m)	110.4 (3)	110.05 (21)	56.35 (42)	1.5245 (35)	1.5370 (50)
$\bar{X}$ (eq; local)	110.595 (76)	110.916 (53)	56.04 (11)	1.52846 (82)	1.52797 (88)
$\delta$ (eq) <sup>(1)</sup>	0.404 (85)	0.083 (65)	0.09 (13)	0.00031 (99)	0.0008 (10)
$n$ <sup>(2)</sup>	4.7	1.3	0.7	0.3	0.8
(b) Structures containing, at least, an axial carboxyl group					
Ref.	$C_\beta-C_\alpha-C_\beta$	$C_\alpha-C_\beta-C_\gamma$	$C_\gamma-C_\beta-C_\alpha-C_\beta$	$C_\alpha-C_\beta$	$C_\beta-C_\gamma$
(b)	112.3 (10)	111.55 (70)	53.00 (141)	1.5390 (140)	1.5510 (140)
(c)	111.6 (10)	113.20 (70)	50.40 (141)	1.4965 (110)	1.5455 (110)
(d)	109.7 (3)	113.50 (21)	51.70 (42)	1.5411 (31)	1.5190 (28)
(e)	111.0 (2)	112.05 (14)	52.15 (28)	1.5325 (28)	1.5210 (28)
(g)	109.8 (3)	112.20 (21)	55.10 (42)	1.5415 (28)	1.5200 (28)
(j)	111.0 (2)	112.10 (14)	52.85 (28)	1.5364 (24)	1.5052 (24)
$\bar{X}$ (ax; local)	110.65 (12)	112.315 (81)	52.75 (16)	1.5370 (14)	1.5161 (13)
$\delta$ (ax) <sup>(3)</sup>	0.74 (13)	0.922 (93)	2.00 (19)	0.0085 (15)	0.0123 (15)
$n$ <sup>(4)</sup>	5.7	9.9	10.5	5.6	8.2
(c) Structures mentioned in the text					
Ref.	$C_\beta-C_\alpha-C_\beta$	$C_\alpha-C_\beta-C_\gamma$	$C_\gamma-C_\beta-C_\alpha-C_\beta$	$C_\alpha-C_\beta$	$C_\beta-C_\gamma$
(A)	110.6 (3)	113.26 (17)	50.60 (42)	1.5416 (24)	1.5155 (35)
(B)	109.2 (3)	110.79 (24)	56.85 (48)	1.5638 (35)	1.5197 (38)
	110.1 (4)	113.06 (24)	53.25 (48)	1.5344 (35)	1.5197 (38)
(C)	111.05 (9)	112.65 (7)	51.05 (14)	1.5380 (14)	1.5295 (14)
	110.97 (9)	112.74 (6)	51.05 (12)	1.5375 (14)	1.5295 (14)

#### Notes

(1)  $\delta(\text{eq}) = \bar{X}(\text{eq}) - \bar{X}(\text{eq; local})$  with  $\sigma[\delta(\text{eq})] = \{\sigma^2[\bar{X}(\text{eq})] + \sigma^2[\bar{X}(\text{eq; local})]\}^{1/2}$ .

(2)  $n = \delta(\text{eq})/\sigma[\delta(\text{eq})]$ .

(3) and (4): equal to (1) and (2) with (eq) replaced by (ax).

Ref.: see Table 3 and text.

flattening by axial substituents was predicted by force-field calculations (Burkert & Allinger, 1982) and was attributed to *syn*-axial interactions (Fig. 2). This might provide a possible explanation: if the line connecting the  $C_\beta$  atoms acts like a hinge, the  $C_\gamma-C_\beta-C_\alpha-C_\beta$  torsion angles decrease and the  $C_\alpha-C_\beta-C_\gamma$  angles increase. The increase in *s* character of  $C_\beta$  will cause shortening of the  $C_\beta-C_\gamma$  as well as the  $C_\alpha-C_\beta$  bonds. This shortening of the  $C_\alpha-C_\beta$  bonds, in turn, would lead to a larger  $C_\beta-C_\alpha-C_\beta$  angle and *syn*-axial interactions would become important again. Apparently, these interactions are further minimized by pushing  $C_\alpha$  out of the centre of the ring resulting in a decrease of the  $C_\beta-C_\alpha-C_\beta$  angle to a value a little less than the mean average ring value and in an elongation of the  $C_\alpha-C_\beta$  bonds at the same time. The elongation (shortening) of the  $C_\alpha-C_\beta$  ( $C_\beta-C_\gamma$ ) bonds is not predicted by force-field calculations.

Finally, Table 4(c) lists the relevant data observed in (A): 2-benzoylcyclohexanecarboxylic acid (axial benzoyl group; Choney, Holt, Pourahmady & Eisenbraun, 1983), in (B): methyl 3-(4-chlorobenzoyl)-4-(4-chlorophenyl)-1-cyano-4-hydroxyl-2,6-diphenylcyclohexanecarboxylate (axial -CN and -OH group; Kirfel, El

Kordy & Troschütz, 1983) and in (C): *cis-cisoid-cis*-perhydroanthracene (van Koningsveld, Baas & van de Graaf, 1984); a profound literature search for axially substituted structures, in which the cyclohexane ring can 'freely' relax, has not been made. From the examples listed, it seems that the same (average) local ring deformations are caused by any axial substituent.

The averaging procedure used has the disadvantage of masking possible 'asymmetric' ring deformations (*e.g.* twisting,  $C_\alpha-C_\beta$  bonds unequal, *etc.*). However, these asymmetric distortions of the parameters from their averaged values may be achieved by a much smaller amount of energy and may strongly depend on environmental (*e.g.* crystal packing) effects.

### Packing

The packing of the molecules is illustrated in Fig. 3. The crystal of (I) consists of molecules arranged, *via* H-bridges, in infinite chains along [201]. In (II) analogous chains run along [111]. The hydrogen-bonding scheme is given in Table 2.

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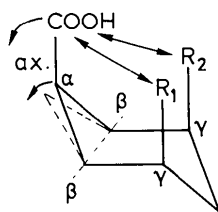


Fig. 2. *syn*-axial interactions in axially substituted derivatives.

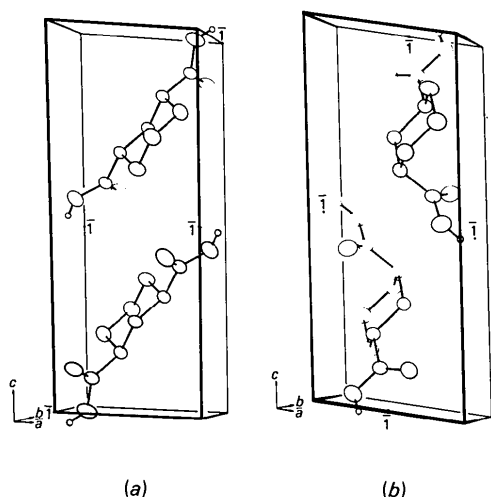


Fig. 3. Packing in (a) compound (I) and (b) compound (II). Hydrogen bonds are around the I sites indicated.

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## Structure of $\beta$ -D-Allose, $C_6H_{12}O_6$

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**Abstract.**  $M_r = 180.09$ , orthorhombic,  $P2_12_1$ ,  $a = 4.918$  (1),  $b = 11.925$  (2),  $c = 12.805$  (2) Å,  $V = 751.0$  (2) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.593$  (1) g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 0.96$  cm<sup>-1</sup>,  $F(000) = 384$ ,  $T = 294$  K. Final  $R = 0.029$  for 662 unique observed reflexions. The molecule has the  ${}^4C_1$  pyranose chair conformation. The hydroxymethyl group has the *gauche-gauche* conformation. Each  $\beta$ -D-allose molecule is surrounded by eight symmetry-related molecules through hydrogen bonding. All five hydroxyl groups serve as proton donors. Four of the hydroxyl groups and the ring oxygen act as proton acceptors. The anomeric O atom is twice an acceptor which is a very unusual observation.

**Introduction.**  $\beta$ -D-Allose is a member of the class of common D-aldoheptoses of which, presumably owing to its poor crystallization habit, no crystallographic structural data are available. Up to now only derivatives of D-allose, 1,6-anhydro- $\beta$ -D-allose (Norrestam, Bock & Pedersen, 1981) and 2,6-dideoxy- $\beta$ -D-allose (Kanters, Batenburg, Gaykema & Roelofsen, 1978) have been studied. According to the literature (Ferrier, 1983) D-allose occurs in the leaves of plants as substituted aryl glycosides. We have undertaken the structure determination as part of our research project on the conformation of saccharides.

**Experimental.** Crystals grown from a sample obtained from the Bio-Organic Chemistry Group of the Rijksuniversiteit Utrecht. As conventional crystallization techniques failed, a newly developed procedure based on a method described by McPherson (1976) was applied. 25  $\mu$ l of a solution containing 250 mg D-allose per ml water-ethanol (50:50) was equilibrated against water-

ethanol (10:90) using the sitting-drop vapour-phase diffusion method. After four weeks small needle-shaped crystals ( $\varnothing < 0.01$  mm) appeared, which were used as seeds in the next step. First 50  $\mu$ l of a solution containing 250 mg D-allose per ml water-ethanol (50:50) was equilibrated against water-ethanol (25:75). After two weeks no crystals could be observed and the seeds were added. Successive equilibration against water-ethanol (20:80) and water-ethanol (15:85), for two weeks each, yielded crystals of sufficient size.

Crystal dimensions 0.24  $\times$  0.62  $\times$  0.07 mm. Enraf-Nonius CAD-4 automatic diffractometer. Lattice dimensions determined by least squares on 14 reflexions. Systematic absences,  $h00$  with  $h = 2n+1$ ,  $0k0$  with  $k = 2n+1$  and  $00l$  with  $l = 2n+1$ , indicating  $P2_12_1$ . Reflexions measured up to  $\theta = 25^\circ$ , Mo  $K\alpha$  radiation,  $\omega$ - $2\theta$  scan mode,  $\Delta\omega = (1.0 + 0.35 \tan\theta)^\circ$ , in one half of the reflexion sphere,  $h \pm k \pm l$  (max. 5, 14, 15), 2983 reflexions, 803 unique reflexions,  $R_{\text{int}} = 0.052$ , 662 with  $I \geq 2.5\sigma(I)$  used for structure determination, four standard reflexions: mean deviations less than 1%,  $L_p$  correction applied, no correction for absorption. Structure solved by direct methods with *MULTAN80* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Final structure obtained by minimizing  $\sum w(\Delta F)^2$  with *SHELX76* (Sheldrick, 1976). Scattering factors for C and O from Cromer & Mann (1968), for H from Stewart, Davidson & Simpson (1965). All H atoms located by difference Fourier synthesis. C- and O-atom positions refined using anisotropic thermal parameters. Full-matrix least-squares refinement gave final  $R = 0.029$ ,  $R_w = 0.033$  with  $w = 1/[\sigma^2(F_o) + 0.002335 F_o^2]$ ,  $S = 0.69$ . Final difference Fourier map showed no peaks above the level  $\pm 0.21$  e Å<sup>-3</sup>. Max.  $\Delta/\sigma$  for C and O parameters 0.007, for H 0.022.