

1987). The pyrimidine ring is almost planar. The mean value of 1.380 (7) Å for the C—C bond length is in agreement with the average bond length [1.387 (18) Å] reported for C-substituted pyrimidines (Allen, Kennard, Watson, Brammer, Orpen & Taylor, 1987). The N—C bonds can be divided into two groups, those having a mean length of 1.336 (6) Å and those with a mean value of 1.316 (3) Å. Whereas the former length agrees with that given for H—C—N—C—H in N-containing aromatic rings, the latter differs significantly and corresponds to the N(3)—C(2) bond in imidazole (Allen *et al.*, 1987). From the molecular structure a straightforward explanation can be given for the observed ³¹P NMR spectrum: the chemical environments of C(1) and C(4) are different as a result of the asymmetry of the pyrimidine ring. This results in small differences in chemical shifts and coupling constants. From the number of bonds between P(1) and P(4) no coupling can be expected between these atoms.

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Structure of D,L-Iditol

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Abstract. C₆H₁₄O₆, *M_r* = 182.17, monoclinic, *P*2₁/*n*, *a* = 5.209 (1), *b* = 20.217 (1), *c* = 7.987 (1) Å, β = 103.45 (1)°, *V* = 818.0 (2) Å³, *Z* = 4, *D_x* = 1.479 g cm⁻³, λ(Cu Kα₁) = 1.54051 Å, μ = 11.1 cm⁻¹, *F*(000) = 392, *T* = 293 K, *R* = 0.047 for 1704 observed reflexions. The title compound crystallizes as a racemate. The molecules adopt a twisted conformation, thus avoiding 1,3-parallel interactions between O(2) and O(4) as well as O(3) and O(5). All

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six hydroxyl groups are involved as donors and acceptors in a complex pattern of intermolecular hydrogen bonds.

Introduction. Hexitols (sugar alcohols with a central chain of six C atoms) occur as six diastereomers, of which two are *meso* forms. Together with the most recently determined X-ray structure of D-altritol ('D-talitol') (Kopf, Bischoff & Köll, 1991) all the *meso* compounds and all the pure enantiomers of the four possible chiral isomers have been reported. The

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chiral diastereomers can be classified into two groups. In contrast to the asymmetrical altritol and glucitol, the sugar alcohols mannitol and iditol display C_2 symmetry.

So far, the X-ray structure of only one racemate of the four optically active isomers has been published, namely that of D,L-mannitol (Kanters, Roelofsen & Smits, 1977). We now report the structural determination of D,L-iditol as well as the structural comparison of this racemate with the pure enantiomer of D-iditol (Azarnia, Jeffrey & Shen, 1972).

Experimental. Crystals suitable for X-ray analysis were obtained from a mixture of equal amounts of D- and L-iditol dissolved in moist ethanol. L-Iditol was a commercial sample (Aldrich), while D-iditol was obtained by sodium borohydride reduction of penta-O-acetyl- α -D-idopyranose (Paulsen, 1972; Wolfrom & Thompson, 1963). The thus obtained racemic crystals of D,L-iditol melted at 361–362 K. Therefore, a conglomerate of pure D- and L-iditol crystals could be excluded (Jacques, Collet & Wilen, 1981), because the melting point of the pure enantiomers is considerably lower (347–348 K). A colorless transparent crystal of dimensions $0.9 \times 0.5 \times 0.5$ mm was used for data collection on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation. The cell parameters were determined by least-squares refinement of the setting angles of 25 reflexions within $40.6 \leq 2\theta \leq 50.5^\circ$. Intensity data were measured by $\theta/2\theta$ scans ($4.5 \leq 2\theta \leq 153^\circ$, $0 \leq h \leq 6$, $0 \leq k \leq 25$, $-10 \leq l \leq 10$). There was no significant decay in the intensities for three standards monitored every 2 h. 2009 data were measured of which 1725 were symmetry independent ($R_{int} = 0.052$). 1704 intensities were considered observed [$|F_o| > 3\sigma(F_o)$]. The data were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by direct methods. The solution with the highest figure of merit showed all non-H atoms. All aliphatic H atoms were localized in theoretical positions (sp^3 hybridization) with a C—H distance of 0.96 Å. The hydroxyl-group H atoms were all taken from a difference map. Full-matrix least-squares refinement on F of 165 parameters including scale-factor, positional and anisotropic thermal parameters for all non-H atoms, and positional and isotropic parameters for all H atoms resulted in $R = 0.047$ and $wR = 0.047$. The ratio of observations to number of variables was 10.3. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(|F_o|)$. Maximum shift/e.s.d. was 0.34 in the final cycle; maximum and minimum heights in the final $\Delta\rho$ map were 0.22 and $-0.25 \text{ e } \text{Å}^{-3}$, respectively. The complex neutral-atom scattering factors were taken from SHELX76. Programs used were SHELXS90 (Sheldrick, 1990),

Table 1. Final fractional coordinates of C and O atoms with equivalent isotropic thermal parameters (Å^2) and of H atoms with isotropic thermal parameters (Å^2)

E.s.d.'s are given in parentheses.

$$U_{eq} = \frac{1}{3} \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}(\text{Å}^2)$
O(1)	0.1342 (3)	0.2653 (1)	0.1756 (2)	0.0419 (4)
O(2)	0.5435 (2)	0.1167 (1)	0.2111 (2)	0.0290 (3)
O(3)	0.0093 (2)	0.0824 (1)	0.1508 (2)	0.0277 (3)
O(4)	-0.0845 (2)	0.0483 (1)	-0.2013 (2)	0.0282 (3)
O(5)	0.1622 (3)	0.1708 (1)	-0.2982 (2)	0.0325 (4)
O(6)	0.5187 (3)	0.0887 (1)	-0.4641 (2)	0.0352 (4)
C(1)	0.2740 (4)	0.2093 (1)	0.2581 (2)	0.0295 (5)
C(2)	0.3422 (3)	0.1615 (1)	0.1277 (2)	0.0219 (4)
C(3)	0.1012 (3)	0.1229 (1)	0.0300 (2)	0.0202 (4)
C(4)	0.1593 (3)	0.0774 (1)	-0.1092 (2)	0.0205 (4)
C(5)	0.2969 (3)	0.1109 (1)	-0.2341 (2)	0.0223 (4)
C(6)	0.3209 (4)	0.0657 (1)	-0.3808 (2)	0.0294 (5)
H(11)	0.160 (1)	0.1843 (9)	0.327 (1)	0.034 (1)
H(12)	0.444 (1)	0.2276 (9)	0.342 (1)	0.053 (1)
H(2)	0.417 (1)	0.1871 (8)	0.044 (1)	0.031 (1)
H(3)	-0.034 (1)	0.1589 (9)	-0.025 (1)	0.036 (1)
H(4)	0.280 (1)	0.0408 (8)	-0.050 (1)	0.020 (1)
H(5)	0.474 (1)	0.1223 (9)	-0.161 (1)	0.033 (1)
H(61)	0.149 (1)	0.0643 (9)	-0.471 (1)	0.050 (1)
H(62)	0.357 (1)	0.0207 (9)	-0.341 (1)	0.038 (1)
H(10)	0.257 (1)	0.2944 (9)	0.157 (1)	0.054 (1)
H(20)	0.506 (1)	0.1064 (9)	0.306 (1)	0.046 (1)
H(30)	-0.136 (1)	0.0979 (9)	0.175 (1)	0.052 (1)
H(40)	-0.080 (1)	0.0049 (9)	-0.190 (1)	0.049 (1)
H(50)	0.262 (1)	0.1991 (9)	-0.323 (1)	0.058 (1)
H(60)	0.663 (1)	0.0840 (9)	-0.398 (1)	0.053 (1)

Table 2. Bond lengths (Å) and bond angles ($^\circ$) between C and O atoms and selected torsion angles ($^\circ$)

O(1)—C(1)	1.422 (3)	O(2)—C(2)	1.428 (2)
O(3)—C(3)	1.430 (2)	O(4)—C(4)	1.437 (2)
O(5)—C(5)	1.432 (2)	O(6)—C(6)	1.428 (3)
C(1)—C(2)	1.522 (3)	C(2)—C(3)	1.529 (2)
C(3)—C(4)	1.527 (2)	C(4)—C(5)	1.517 (2)
C(5)—C(6)	1.514 (2)		
O(1)—C(1)—C(2)	111.3 (1)	O(2)—C(2)—C(1)	110.3 (1)
O(2)—C(2)—C(3)	109.9 (1)	C(1)—C(2)—C(3)	112.2 (1)
O(3)—C(3)—C(2)	108.2 (1)	O(3)—C(3)—C(4)	107.4 (1)
C(2)—C(3)—C(4)	113.7 (1)	O(4)—C(4)—C(3)	108.5 (1)
O(4)—C(4)—C(5)	110.0 (1)	C(3)—C(4)—C(5)	114.4 (1)
O(5)—C(5)—C(4)	110.2 (1)	O(5)—C(5)—C(6)	110.8 (1)
C(4)—C(5)—C(6)	112.1 (1)	O(6)—C(6)—C(5)	111.2 (1)
Angles in the chain			
O(1)—C(1)—C(2)—C(3)	-73.9 (2)	C(1)—C(2)—C(3)—C(4)	176.7 (1)
C(2)—C(3)—C(4)—C(5)	-51.8 (2)	C(3)—C(4)—C(5)—C(6)	-173.4 (1)
C(4)—C(5)—C(6)—O(6)	-161.3 (1)		
Angles between vicinal O atoms			
O(1)—C(1)—C(2)—O(2)	163.2 (1)	O(2)—C(2)—C(3)—O(3)	59.0 (2)
O(3)—C(3)—C(4)—O(4)	65.3 (2)	O(4)—C(4)—C(5)—O(5)	73.0 (2)
O(5)—C(5)—C(6)—O(6)	75.1 (2)		
Angles between vicinal H atoms			
H(11)—C(1)—C(2)—H(2)	167.4 (8)	H(12)—C(1)—C(2)—H(2)	-72.0 (9)
H(2)—C(2)—C(3)—H(3)	-63.7 (9)	H(3)—C(3)—C(4)—H(4)	-175.6 (9)
H(4)—C(4)—C(5)—H(5)	-52.7 (9)	H(5)—C(5)—C(6)—H(61)	-164.7 (9)
H(5)—C(5)—C(6)—H(62)	77.7 (9)		

SHELX76 (Sheldrick, 1976), PLATON88 (Spek, 1982) and SCHAKAL88 (Keller, 1986) on Micro-VAX II and VAX 3200 computers.

Discussion. The final fractional coordinates and isotropic or equivalent isotropic thermal parameters of C, O and H atoms are listed in Table 1.* Bond distances and angles between C and O atoms as well as some selected torsion angles within the title compound are given in Table 2. A perspective view of the molecule is shown in Fig. 1 which also contains the atom-numbering scheme. By definition, the displayed molecule is the *D*-enantiomer. The *L*-enantiomer is related by a center of symmetry ($\bar{1}$).

The molecules adopt ('bent') conformations which correspond to that found in enantiomerically pure *D*-iditol (Azarnia, Jeffrey & Shen, 1972). The observed twisted geometry is obtained by rotation of 120° around the central C(3)—C(4) bond starting from a planar extended ('zigzag') arrangement of the carbon chain. Such a conformation avoids the two repulsive 1,3-parallel interactions between O(2) and O(4) and between O(3) and O(5). Nevertheless, in a few exceptional cases such unfavorable 1,3-parallel interactions (designated O//O) are tolerated; for example, in the derivative 1-deoxy-1-nitro-*D*-iditol (Kopf, Brandenburg, Seelhorst & Köll, 1990).

The actual conformation found in the crystals of iditol also dominates in solution, but two alternatives devoid of any O//O interactions coexist. These alternative conformations are derived either from a single twist around the C(2)—C(3) bond or a double twist around the C(2)—C(3) and C(4)—C(5) bonds (Hawkes & Lewis, 1984). To the best of our knowledge, these alternative conformations have not yet been observed in crystalline derivatives of iditol.

* Tables of structure amplitudes, anisotropic thermal parameters, and bond distances and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54583 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

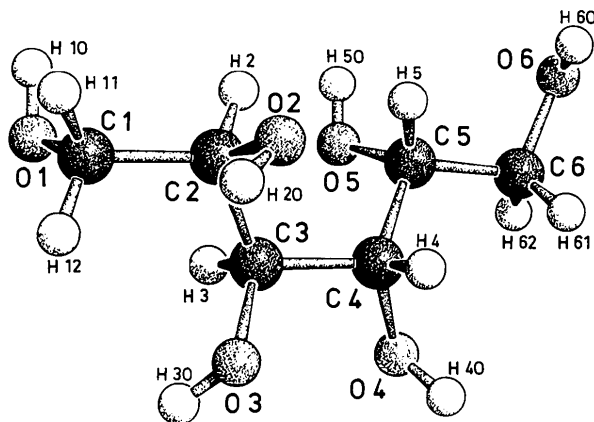


Fig. 1. SCHAKAL88 drawing (Keller, 1986) of the molecular conformation and atomic numbering scheme of the *D*-enantiomer in *D,L*-iditol.

Table 3. Geometry of the hydrogen bonds (\AA , $^\circ$)

E.s.d.'s are given in parentheses.

<i>D</i> —H... <i>A</i>	<i>D</i> —H	<i>D</i> ... <i>A</i>	H... <i>A</i>	<i>D</i> —H... <i>A</i>	Symmetry operation*
O(1)—H(10)...O(5)	0.90 (1)	3.002 (2)	2.18 (1)	151 (1)	$\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$
O(2)—H(20)...O(6)	0.85 (1)	2.688 (2)	1.86 (1)	165 (1)	$x, y, z+1$
O(3)—H(30)...O(2)	0.88 (1)	2.673 (2)	1.80 (1)	170 (2)	$x-1, y, z$
O(4)—H(40)...O(3)	0.88 (2)	2.688 (2)	1.82 (1)	170 (1)	$-x, -y, -z$
O(5)—H(50)...O(1)	0.83 (1)	2.829 (2)	2.07 (1)	152 (1)	$\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$
O(6)—H(60)...O(4)	0.82 (1)	2.707 (2)	1.94 (1)	156 (1)	$x+1, y, z$

* The symmetry operation is performed on the acceptor atoms. *D* denotes donor and *A* denotes acceptor.

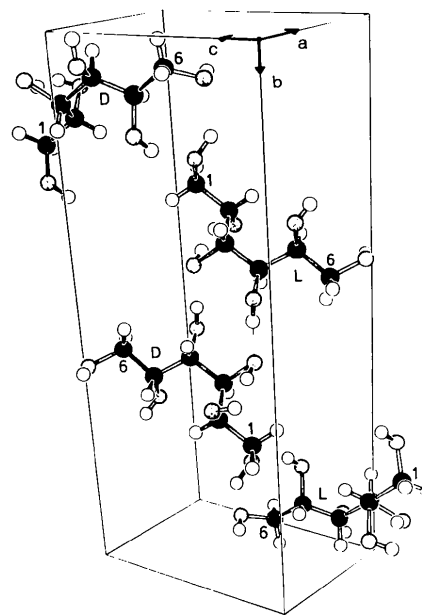


Fig. 2. Perspective view of the contents of the unit cell, showing some intermolecular hydrogen bonds.

While a very similar carbon-chain geometry is observed in the pure enantiomer as well as in the racemate, the conformations of the terminal O atoms display some differences. In *D*-iditol both O(1) and O(6) are in a *g,t* position resulting in a pseudo-twofold symmetry axis vertical to the midpoint of the C(3)—C(4) bond (Azarnia, Jeffrey & Shen, 1972). In *D,L*-iditol only O(6) adopts the above-mentioned position, while O(1) is oriented *t,-g* yielding an overall asymmetric conformation.

This difference in the orientation of the O atoms can be explained by the tendency of all hydroxyl groups to form an optimal hydrogen-bonding pattern involving all hydroxyl-group O atoms as donors and acceptors. For the title compound these bonds are given in Table 3. The analysis of the hydrogen-bonding characteristics (Kuleshova & Zorky, 1980) shows that the molecules form an infinite three-dimensional framework. 12 hydrogen bonds (donors and acceptors) are formed by one molecule which is

hydrogen bonded to nine adjacent molecules. Along the base vector [100] an infinite one-dimensional chain is formed. Fig. 2 shows the unit cell with two sets of D- and L-enantiomers. Part of the pattern of hydrogen bonds can be discerned in this figure.

In violation of the 'Wallach rule' the density D_x of the racemate is considerably smaller than that of the pure enantiomer (1.510 g cm^{-3}). This could be an artefact of the different temperatures of the measurements or of the overall inferior crystal quality of the investigated D-iditol. The final R value is 0.09 for only 697 reflexions (Azarnia, Jeffrey & Shen, 1972). However, similar deviations from the rule have been observed in the past, indicating some problems of the general applicability of the 'rule' (Jacques, Collet & Wilen, 1981, pp. 28–31).

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Structure of 3-(4-Chlorophenyl)-4-[2-(3,4-dimethoxyphenyl)ethyl]-4,5-dihydro-5-(2-methoxyphenyl)-1-phenyl-1,2,4-triazole

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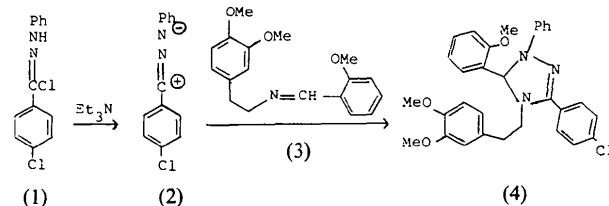
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Abstract. $\text{C}_{31}\text{H}_{30}\text{ClN}_3\text{O}_3$, $M_r = 528.06$, monoclinic, $P2_1/c$, $a = 10.793$ (3), $b = 19.317$ (3), $c = 14.038$ (5) Å, $\beta = 110.99$ (3)°, $V = 2733$ (3) Å³, $Z = 4$, $D_x = 1.283 \text{ g cm}^{-3}$, $\lambda(\text{Mo K}\alpha) = 0.71073$ Å, $\mu = 1.729 \text{ cm}^{-1}$, $F(000) = 1112$, $T = 295 \text{ K}$, $R = 0.043$ for 2403 independent observed reflections. The structure features a tetrasubstituted 1,2,4-triazole derivative.

Introduction. The nitrilimine (2) formed from α ,4-dichlorobenzaldehyde phenylhydrazine (1) and triethylamine, reacts as a 1,3-dipole and adds to the imine (3) formed from 2-methoxybenzaldehyde and 2-(3,4-dimethoxyphenyl)ethylamine, to give a new crystalline triazole *A*. As the cycloaddition may occur in two ways, *A* is either a 1,2,4- or a 1,2,3-triazole. In the first reported example of this type of reaction (Huisgen, Grashey, Knupfer, Kunz & Seidel, 1964), a 1,2,4-triazole structure was reported for the adduct obtained from diphenylnitrilimine and benzalaniline, as the adduct was found to be identi-

cal with the product from (α -anilinobenzal)phenylhydrazine and benzaldehyde (Busch & Ruppenthal, 1910), which was considered to be a 1,2,4-triazole. Since it is conceivable that the reactive (α -anilinobenzal)phenylhydrazine could rearrange *via* a triazetidene and form a 1,2,3-triazole, a more convincing proof seems necessary for triazoles formed from imine–nitrilimine cycloadditions. Furthermore, other imines and nitrilimines could cyclize in different ways. The 1,2,4-triazole structure (4) has now been confirmed for *A* in this X-ray crystallographic study. To the best of our knowledge no crystallographic structural investigations have been carried out on substituted 4,5-dihydro-1,2,4-triazoles.



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