

Crystal and Molecular Structures of (\pm)*trans*- and *cis*-1,2-Cyclohexanediols

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The crystal and molecular structures of (\pm)*trans*-1,2-cyclohexanediol (*1*) and *cis*-1,2-cyclohexanediol (*2*) have been determined by X-ray methods. The molecular formula of both compounds is C₆H₁₂O₂ and both crystallize in the orthorhombic space group *Pbca* with *Z*=8. The unit cell parameters are *a*=7.885(2) Å, *b*=19.301(6) Å, *c*=8.498(2) Å for (*1*) and *a*=7.687(1) Å, *b*=19.696(7) Å, *c*=8.611(3) Å for (*2*). The calculated densities are 1.193 g cm⁻³ for (*1*) and 1.183 g cm⁻³ for (*2*). Both structures are formed of hydrogen bonded 1,2-cyclohexanediol dimers held together by interdimeric hydrogen bonds. The cyclohexanediol rings have a chair conformation in both compounds. In (*1*) the two OH groups are equatorial, whereas in (*2*) one OH group is equatorial and the other axial.

During studies on the coordination chemistry of weak neutral oxygen-donor ligands with copper(II) ion¹ we have found that the coordination of neutral 1,2-cyclohexanediol to copper(II) greatly affects the diol molecule. In studies on the solvation of cellulose, (\pm)*trans*-1,2-cyclohexanediol (*1*) has been used as a model compound, and in the formed *N*-methylmorpholine *N*-oxide/ (\pm)*trans*-1,2-cyclohexanediol adduct² the values of bond lengths and angles of the diol likewise differ from the expected normal bond lengths and angles.

Brunel reported³ in 1903 that the crystals of (*1*) and *cis*-1,2-cyclohexanediol (*2*) are orthorhombic. In a later X-ray study White⁴ found the crystals of (*2*) to be orthorhombic and the crystals of (*1*) monoclinic. We obtained orthorhombic crystals for both diols, but possibly

(*1*) has two crystal forms. The aim of this study was to determine the bonding parameters and crystal packing of the orthorhombic forms of (*1*) and (*2*). We also attempted to prepare the other form of (*1*) and to identify it through IR- and X-ray powder measurements.

EXPERIMENTAL

Syntheses. The title compounds were prepared by methods described in the literature.^{5,6} The crude products were purified by sublimation, and crystals of (*1*) were grown slowly from tetrahydrofuran (THF) and crystals of (*2*) from ethylacetate.

Slow crystallization of (*1*) from different solvents (H₂O, EtOH, C₆H₆, EtAc and THF) in every case produced orthorhombic crystals. The IR spectra of these samples were identical with the IR spectra of the crystals from which the structure was determined.

When the crystallization was done quickly from the same solvents, however, the IR spectra indicated the material to be a mixture of two forms or possibly entirely another form. When the slowly grown crystals of (*1*) were pressed to KBr pellets, the measured IR spectra were similar to, though not identical with, the spectra of the quickly crystallized samples. The X-ray powder patterns of all measured samples could be indexed as orthorhombic and the unit cell dimensions were close to those found in single crystal measurements. In particular, the *b*-axis was only slightly (0.1 Å) longer in the pressed sample than in the non-pressed sample, both prepared from single crystals.

IR-spectra were recorded from KBr pellets and nujol mull suspensions with a Perkin Elmer 180

IR-spectrometer.

X-ray measurements. X-ray diffraction powder patterns of (1) were recorded from samples crystallized from different solvents and also from a sample crystallized from THF and pressed with

a pressure of 60 MPa to a pellet. The apparatus and method used in the measurement have been described earlier.⁷

The single crystal X-ray diffraction measurements were made with a SYNTEX P2₁ (Fortran

Table 1. Fractional atomic coordinates and isotropic temperature factors with their e.s.d.'s. The equivalent isotropic temperature factors for non-hydrogen atoms are of the form $U_{eq} = (U_{11} + U_{22} + U_{33})/3$.

	x	y	z	U_{eq}/U_{iso}
a. (\pm)trans-1,2-Cyclohexanediol				
O(1)	0.0856(3)	0.4371(1)	0.3204(2)	0.0463(8)
O(2)	0.2091(4)	0.4977(1)	0.5997(3)	0.0583(9)
C(1)	0.1652(4)	0.3980(2)	0.4417(4)	0.0399(11)
C(2)	0.2947(4)	0.4405(1)	0.5285(4)	0.0389(11)
C(3)	0.3899(5)	0.3974(2)	0.6493(4)	0.0534(14)
C(4)	0.4733(6)	0.3351(2)	0.5724(6)	0.0624(16)
C(5)	0.3423(6)	0.2917(2)	0.4873(6)	0.0648(15)
C(6)	0.2476(5)	0.3352(2)	0.3667(4)	0.0503(13)
H(O1)	-0.009(5)	0.465(2)	0.364(4)	0.058(10)
H(O2)	0.268(6)	0.515(2)	0.669(5)	0.105(18)
H(C1)	0.077(4)	0.384(1)	0.519(3)	0.052(9)
H(C2)	0.376(4)	0.458(1)	0.449(3)	0.053(10)
H(1C3)	0.475(4)	0.429(1)	0.703(3)	0.058(10)
H(2C3)	0.306(4)	0.382(1)	0.728(4)	0.054(10)
H(1C4)	0.530(5)	0.308(2)	0.655(4)	0.070(11)
H(2C4)	0.560(6)	0.351(2)	0.502(5)	0.108(17)
H(1C5)	0.252(5)	0.271(2)	0.565(4)	0.073(12)
H(2C5)	0.400(5)	0.255(2)	0.438(4)	0.075(12)
H(1C6)	0.317(5)	0.352(1)	0.284(3)	0.058(10)
H(2C6)	0.160(4)	0.305(1)	0.312(3)	0.057(10)
b. cis-1,2-Cyclohexanediol				
O(1)	0.2444(1)	0.0313(1)	0.3726(1)	0.0466(3)
O(2)	0.0637(1)	0.0411(1)	0.6586(1)	0.0457(4)
C(1)	0.3200(2)	0.0637(1)	0.5048(2)	0.0375(5)
C(2)	0.1810(2)	0.0930(1)	0.6097(2)	0.0379(4)
C(3)	0.0797(2)	0.1486(1)	0.5313(2)	0.0514(6)
C(4)	0.2005(3)	0.2041(1)	0.4726(2)	0.0641(7)
C(5)	0.3398(3)	0.1752(1)	0.3667(2)	0.0557(6)
C(6)	0.4402(2)	0.1187(1)	0.4454(2)	0.0483(5)
H(O1)	0.153(3)	0.006(1)	0.400(2)	0.079(6)
H(O2)	0.119(2)	0.019(1)	0.727(2)	0.061(6)
H(C1)	0.383(2)	0.029(1)	0.563(2)	0.030(3)
H(C2)	0.239(2)	0.111(1)	0.701(2)	0.042(4)
H(1C3)	0.017(2)	0.128(1)	0.446(2)	0.054(5)
H(2C3)	-0.003(2)	0.166(1)	0.602(2)	0.058(5)
H(1C4)	0.262(2)	0.226(1)	0.567(2)	0.078(6)
H(2C4)	0.130(3)	0.239(1)	0.417(2)	0.083(6)
H(1C5)	0.288(2)	0.157(1)	0.271(2)	0.062(5)
H(2C5)	0.421(2)	0.210(1)	0.334(2)	0.066(5)
H(1C6)	0.526(2)	0.098(1)	0.377(2)	0.056(5)
H(2C6)	0.501(2)	0.137(1)	0.539(2)	0.056(4)

version) automatic four-circle diffractometer employing graphite monochromatized $\text{MoK}\alpha$ -radiation. The unit cell parameters were calculated by least-squares refinements of 24 reflections. The intensities were recorded using the θ - 2θ scan technique with varying scan speed (1.5 – $29.3^\circ \text{ min}^{-1}$) depending on the peak intensity of the reflection. The systematic absences in the hkl -indices indicated the space group $Pbca$ for both crystals.

Crystal data. (\pm)*trans*- $\text{C}_6\text{H}_{12}\text{O}_2$ (1); F.W. 116.16. Space group: $Pbca$; $a=7.885(2)$ Å, $b=19.301(6)$ Å, $c=8.498(2)$ Å; $V=1293.3$ Å³; $D_c=1.193$ g cm⁻³; $Z=8$; $\mu=0.52$ cm⁻¹ ($\text{MoK}\alpha$). *cis*- $\text{C}_6\text{H}_{12}\text{O}_2$ (2); F.W. 116.16. Space group: $Pbca$; $a=7.687(1)$ Å, $b=19.696(7)$ Å, $c=8.611(3)$ Å; $V=1303.7$ Å³; $D_c=1.183$ g cm⁻³; $Z=8$; $\mu=0.52$ cm⁻¹ ($\text{MoK}\alpha$).

Out of 854 independent reflections for (1), 499 having $I > 2.5\sigma(I)$ were used in the refinements. Two check reflections, (334) and (002), were recorded after every 100 measurements. Their intensities were decreased by 35 and 38%, respectively. Corrections for crystal decay and Lorentz and polarization factors were applied, but no absorption correction was made.

Out of 1151 independent reflections for (2), 827 intensities with $I > 2.5\sigma(I)$ were used in the refinements. One check reflection showed no crystal decay. The intensities were corrected for Lorentz and polarization factors.

The structures were solved by direct methods, which gave positional parameters for heavy atoms. The atomic scattering factors and anomalous dispersion correction factors for non-hydrogen atoms were taken from *International Tables*.⁸ The structures were refined with anisotropic temperature factors for non-H atoms and isotropic temperature factors for hydrogen atoms.

Omission of 3 poorly agreeing weak reflections of (1) and application of an empirical extinction correction [$F_c^* = f_c(1 - xF_c^2/\sin\theta)$, $x = 5.6 \cdot 10^{-7}$] led to final $R=0.036$ and $R_w=0.035$, where $R = \Sigma\Delta/\Sigma F_o$, $R_w = \Sigma\sqrt{w}\Delta/\Sigma\sqrt{w}F_o$, $\Delta = |F_o - F_c|$ and $w = 0.8767/(\sigma^2(F_o) + 7 \cdot 10^{-4}F_o^2)$.

Omission of 23 poorly agreeing weak reflections of (2) and application of an extinction correction ($x = 3.4 \cdot 10^{-7}$) gave $R=0.034$ and $R_w=0.033$ with $w = 3.889/(\sigma^2(F_o) + 2 \cdot 10^{-4}F_o^2)$. All crystallographic computations were performed with the program SHELX-76⁹ and the figures of molecules were drawn with ORTEP-II.¹⁰

RESULTS AND DISCUSSION

The final positional parameters for (1) and (2) are presented in Table 1. The unit cells of both

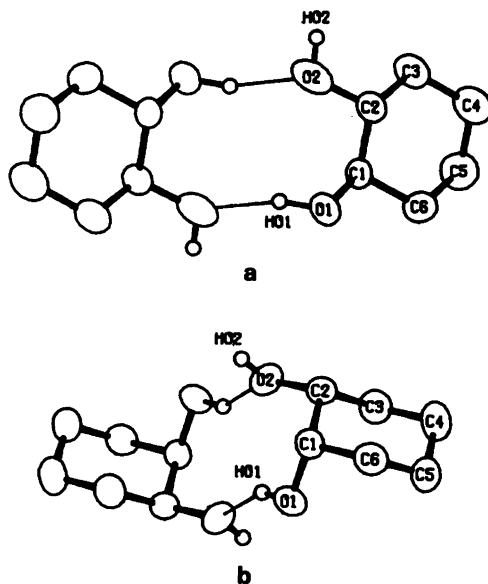


Fig. 1. The dimeric centrosymmetric structure of 1,2-cyclohexanediols showing the atom numbering scheme. (a) (\pm)*trans*-1,2-Cyclohexanediol, (b) *cis*-1,2-cyclohexanediol. Thin lines represent hydrogen bonds, ring hydrogen atoms are not shown.

compounds are formed of 8 diol molecules, which are joined into dimeric pairs through two hydrogen bonds. Each dimer is formed of two different diol enantiomers. In (1) these enantiomers are

Table 2. Bond distances (Å) of 1,2-cyclohexanediols.

Exocyclic	(\pm) <i>trans</i>	<i>cis</i>
C(1)–O(1)	1.422(4)	1.428(2)
C(2)–O(2)	1.429(4)	1.426(2)
O(1)–H(O1)	0.99(4)	0.89(2)
O(2)–H(O2)	0.83(4)	0.85(2)
Non-bonded	(\pm) <i>trans</i>	<i>cis</i>
O(1) ... O(2)	2.820(3)	2.834(1)
Endocyclic	(\pm) <i>trans</i>	<i>cis</i>
C(1)–C(2)	1.503(4)	1.514(2)
C(2)–C(3)	1.519(4)	1.504(2)
C(3)–C(4)	1.519(5)	1.521(2)
C(4)–C(5)	1.514(5)	1.518(2)
C(5)–C(6)	1.521(5)	1.513(2)
C(6)–C(1)	1.517(4)	1.513(2)

Table 3. Bond angles ($^{\circ}$) of 1,2-cyclohexanediols.

Exocyclic	(\pm) <i>trans</i>	<i>cis</i>
C(2)–C(1)–O(1)	111.5(2)	111.0(1)
C(6)–C(1)–O(1)	108.0(2)	107.4(1)
C(1)–C(2)–O(2)	108.0(3)	110.4(1)
C(3)–C(2)–O(2)	111.7(3)	109.1(1)
Endocyclic	(\pm) <i>trans</i>	<i>cis</i>
C(1)–C(2)–C(3)	111.7(3)	112.0(1)
C(2)–C(3)–C(4)	110.9(3)	110.9(1)
C(3)–C(4)–C(5)	110.4(4)	111.1(1)
C(4)–C(5)–C(6)	110.6(3)	111.5(2)
C(5)–C(6)–C(1)	111.6(3)	111.5(1)
C(6)–C(1)–C(2)	110.6(3)	111.1(1)

separable, but in (2) ring inversion makes them equal. A view of the dimeric molecules of (1) and (2) with the numbering of the atoms is presented in Figs. 1a and 1b.

The interatomic distances, bond angles and torsion angles are presented in Tables 2, 3 and 4.

Table 4. Torsion angles ($^{\circ}$) of 1,2-cyclohexanediols.

Exocyclic	(\pm) <i>trans</i>	<i>cis</i>
O(1)–C(1)–C(2)–O(2)	61.4(3)	57.7(1)
O(1)–C(1)–C(2)–C(3)	–175.4(3)	–64.1(2)
O(1)–C(1)–C(6)–C(5)	177.7(3)	67.0(2)
O(2)–C(2)–C(1)–C(6)	–178.5(3)	177.1(1)
O(2)–C(2)–C(3)–C(4)	177.4(3)	–178.2(1)
Endocyclic	(\pm) <i>trans</i>	<i>cis</i>
C(1)–C(2)–C(3)–C(4)	56.4(4)	–56.6(2)
C(2)–C(3)–C(4)–C(5)	–56.7(4)	55.2(2)
C(3)–C(4)–C(5)–C(6)	56.7(5)	–55.0(2)
C(4)–C(5)–C(6)–C(1)	–56.5(4)	54.8(2)
C(5)–C(6)–C(1)–C(2)	55.5(4)	–54.5(2)
C(6)–C(1)–C(2)–C(3)	–55.3(4)	55.3(2)
mean	± 56.2	± 55.2

The C–O bond lengths are normal, with a mean value of 1.426 Å. The average of the C–C bond lengths is 1.515 Å, which falls in the range 1.51–1.52 Å found in cyclohexanes.^{11,12} The

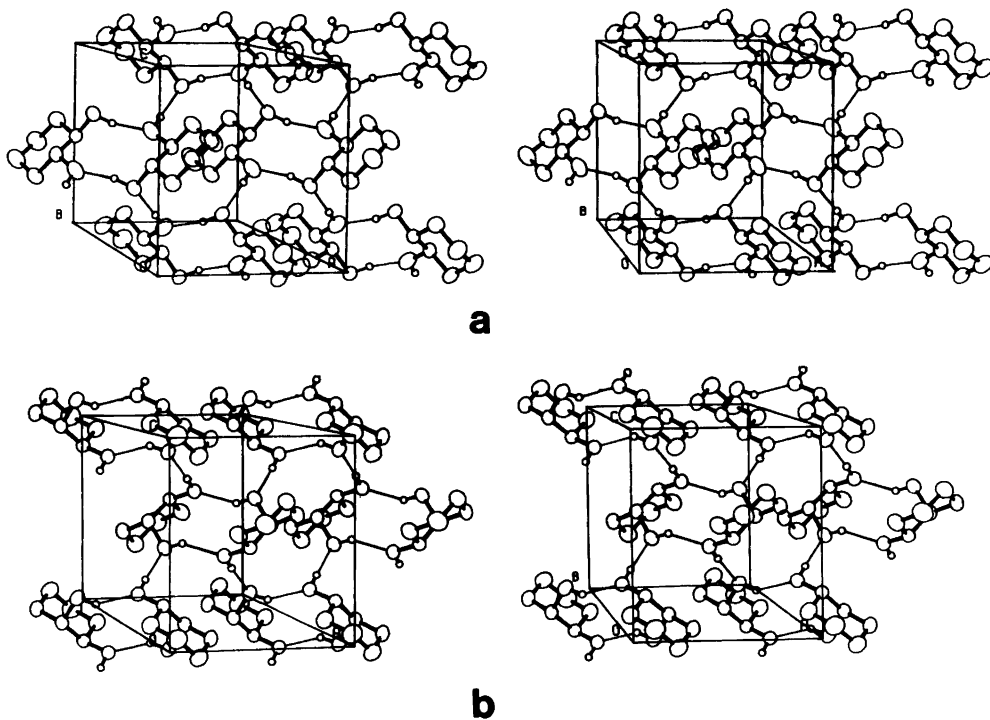


Fig. 2. Stereoscopic drawing of the packing of 1,2-cyclohexanediol molecules showing one layer in the *ac*-plane. (a) (\pm)*trans*-1,2-Cyclohexanediol, (b) *cis*-1,2-cyclohexanediol.

Table 5. Parameters for possible hydrogen bonds in 1,2-cyclohexanediols.^a

O—H...O	H...O (Å)	O...O (Å)	∠O—H...O(°)
a. (±) <i>trans</i> -1,2-Cyclohexanediol			
O(1)—H(O1)...O(2)	2.71(3)	2.820(3)	86(2)
O(1)—H(O1)...O(2 ⁱ)	1.78(4)	2.728(4)	164(2)
O(2)—H(O2)...O(1 ⁱⁱ)	1.81(4)	2.779(3)	175(3)
b. <i>cis</i> -1,2-Cyclohexanediol			
O(1)—H(O1)...O(2)	2.41(2)	2.834(1)	106(2)
O(1)—H(O1)...O(2 ⁱⁱⁱ)	1.91(2)	2.778(2)	148(2)
O(2)—H(O2)...O(1 ^{iv})	1.79(2)	2.758(1)	177(1)
Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1/2-x, 1-y, 1/2+z$; (iii) $-x, -y, 1-z$; (iv) $1/2-x, -y, 1/2+z$			

^a The H...O distances and O—H...O angles are calculated by assuming the O—H bonds to be 0.97 Å. The e.s.d.'s are the actual ones obtained in the refinements.

greatest deviations from the mean value are for the bond lengths C(1)—C(2) and C(2)—C(3) in (1) and (2), respectively. The former value is 1.503 Å and the latter 1.504 Å. The values of C—C—C bond angles and ring torsion angles show that in both compounds the cyclohexane ring has the *chair* form, where the angle C—C—C is 111° and the ring torsion angle 56°. ¹³

In (1) the OH groups are equatorial, while in (2) one OH group is equatorial and the other axial. The distances between the oxygen atoms in the two diols are almost equal, however, for the distance O(1)...O(2) in (1) is 2.820 Å and in (2) the corresponding distance is 2.832 Å. The torsion angles O(1)—C(1)—C(2)—O(2) are 61.4° for (1) and 57.7° for (2). The distance O(1)...O(2) and the torsion angle O(1)—C(1)—C(2)—O(2) are 2.802 Å and 60.8° in (±)*trans*-1,2-cyclohexanediol when it forms an adduct with *N*-methylmorpholine *N*-oxide.² However, the C—C distances of this adduct are distorted from the C—C distances of the free diol.

Both structures are formed of layers of hydrogen bonded dimers. A stereoview of one layer for each compound is shown in Fig. 2. The parameters for possible hydrogen bonds are presented in Table 5. There could be a bifurcated hydrogen bond from H(O1). However, according to the parameters presented in Table 5, the existence of an intramolecular hydrogen bond is unlikely at least in (1). In (2) the parameter values are near to those presented for the

bifurcated hydrogen bond.¹⁴

The solution IR-spectra of the compounds indicate an intramolecular hydrogen bond for both diols.¹⁵ In crystalline state, however, intermolecular hydrogen bonding generally takes precedence over intramolecular.¹⁶ Interdimeric hydrogen bonds are formed via H(O2) to O(1) and these hydrogen bonds are almost at right angles to each other.

The slight elongation of the *b*-axis found in the pressed sample of (1) is presumably due to a reorganization of the hydrogen bond system within layers. This reorganization, and thus the existence of two forms of (1), is suggested also by the IR-studies.

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