The Molecular and Crystal Structure of DL-3-Chloro-2,4-pentanediol

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The crystal structure of DL-3-chloro-2,4-pentanediol has been determined by X-ray analysis. The crystal is triclinic, with dimensions of $a=6.573$, $b=8.991$, $c=6.243$ Å, $\alpha=80.18°$, $\beta=94.25°$, and $\gamma=102.87°$. The five carbon atoms have a TT conformation, and the two OH groups have intermolecular hydrogen bondings, whose distances are 2.75 Å and 2.80 Å respectively.

As in the case of 2,4-pentanediol,[1,2] 3-chloro-2,4-pentanediol is separated into two parts by elution chromatograph; one of the parts seems to be racemic, and the other, the *meso* form. However in the case of 3-chloro-2,4-pentanediol, synthesized by the hydrogenation of 3-chloro-2,4-pentanedione, the *meso* form is eluted faster than the racemic form when separated by an ion-exchanger chromatograph. The conformation, configuration, and hydrogen bonding of these compounds have been investigated by NMR and IR spectra.[3,4] The structure determination was undertaken by means of the X-ray method for the racemic form, which crystallizes at room temperature, in order to elucidate the conformation, configuration, and hydrogen bonding of the molecule, and to compare the results with those obtained by NMR and IR spectroscopy.

Experimental

The colorless prismatic crystals or platelets were obtained by the distillation of this substance under a pressure of 22 mmHg. The crystal used for the X-ray diffraction was a needle elongated along the c-axis; the crystal was cut into the cubic form to make its shape suitable for X-ray diffractometry. The crystallographic data are shown in Table 1. The cell dimensions were determined by the least-squares method using 15 reflections. The intensity data were collected by using a Rigaku four-circle diffractometer with Mo$K\alpha$ radiation, in the region from 2.5° to 55° for 2θ. The experiment was carried out by the ω-2θ technique. Out of 1637 possible independent reflections, 1329 non-zero data were collected. No absorption or extinction correction was made. The crystal density was measured by the flotation method.

TABLE 1. CRYSTAL DATA

$C_5H_{11}O_2Cl$	mol wt 138.6
$a=6.573(1)$ Å	mp 56—56.5 °C
$b=8.991(1)$ Å	$D_m=1.294$ g·cm^{-3}
$c=6.243(1)$ Å	$D_x=1.299$ g·cm^{-3}
$\alpha=80.18(1)°$	$Z=2$
$\beta=94.25(1)°$	Space group $P\bar{1}$
$\gamma=102.87(1)°$	
$V=354.22(7)$ Å^3	

Structure Determination

A sharpened Patterson map was synthesized, from which the co-ordinate of the Cl atom was then deduced. Successive structure factor calculations and Fourier syntheses revealed all of the remaining non-hydrogen atoms. On the basis of these atomic locations, least-squares refinements using isotropic temperature factors were carried out. After 5 cycles of refinements, the R factor was found to be 0.198 for the non-zero reflections. Anisotropic temperature factors were then introduced for all of the non-hydrogen atoms. After 6 cycles of refinements, the R factor was reduced to 0.079 for the non-zero reflections. At this stage of analysis, the difference Fourier map was computed; all of the hydrogen atoms were located in it, but the peaks thus obtained were not very sharp, so their locations, except for those which were attached to oxygen atoms, were replaced by the calculated values, assuming that the CH bond lengths are 1.09 Å and that the bond angles of the carbon atoms are kept tetrahedral. With these positional parameters, 6 more cycles of least-squares refinements were carried out. In these procedures, the positional and thermal parameters of the hydrogen atoms which are attached to carbon atoms were not varied, and the thermal parameters of all of the hydrogen atoms were assumed to be the same as the isotropic parameters of those of the atoms to which they are bonded. By these procedures, the R factor was reduced to 0.053. The weighting scheme used here was:

$$|F_0|<F_{\min}:\quad w=0.2$$

$$F_{\min}\leq|F_0|\leq F_{\max}:\quad w=1.0$$

$$F_{\max}<|F_0|:\quad w=F_{\max}/|F_0|$$

where $F_{\max}=20.0$ and $F_{\min}=10.0$. The numerical calculations were carried out on a TOSBAC 3400-41 computer, using the program written by Tamaichi Ashida which is included in the UNICS program system.[5] The final atomic co-ordinates and temperature factors are shown in Tables 2 and 3. The

TABLE 2. ATOMIC CO-ORDINATES ALONG WITH THEIR ESTIMATED STANDARD DEVIATIONS

Atom	x/a	y/b	z/c
C (1)	−0.0833(5)	0.2952(4)	−0.2966(5)
C (2)	0.1208(4)	0.3494(2)	−0.1756(3)
C (3)	0.1702(3)	0.2272(2)	0.0100(3)
C (4)	0.3699(3)	0.2776(2)	0.1410(3)
C (5)	0.4229(5)	0.1493(4)	0.3136(5)
O (1)	0.2808(3)	0.3790(2)	−0.3263(2)
O (2)	0.3637(3)	0.4109(2)	0.2328(2)
Cl	−0.0439(1)	0.1708(1)	0.1895(1)
H(O$_1$)	0.392(6)	0.434(4)	−0.291(7)
H(O$_2$)	0.305(7)	0.389(4)	0.347(6)

Table 3. Temperature factors for every atom

The anisotropic parameters are represented by the form $\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\times 10^{-4}\}$. Estimated standard deviations are shown in parentheses by cell edge for non-hydrogen atoms and in Å^2 for hydrogen atoms.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C (1)	317 (8)	227 (5)	282 (7)	15 (5)	−61 (6)	−44 (5)
C (2)	283 (6)	138 (3)	208 (5)	12 (3)	−5 (4)	−48 (3)
C (3)	242 (5)	122 (2)	198 (5)	−3 (3)	41 (4)	−38 (2)
C (4)	234 (5)	151 (3)	222 (5)	2 (3)	12 (4)	−29 (3)
C (5)	354 (9)	218 (5)	372 (10)	65 (5)	−19 (7)	21 (5)
O (1)	325 (5)	196 (3)	187 (3)	−60 (3)	26 (3)	−50 (2)
O (2)	313 (5)	153 (2)	197 (4)	−43 (2)	25 (3)	−50 (2)
Cl	278 (1)	210 (1)	273 (1)	−38 (1)	80 (1)	−49 (1)
H(O$_1$)	4.5 (8)					
H(O$_2$)	4.2 (8)					

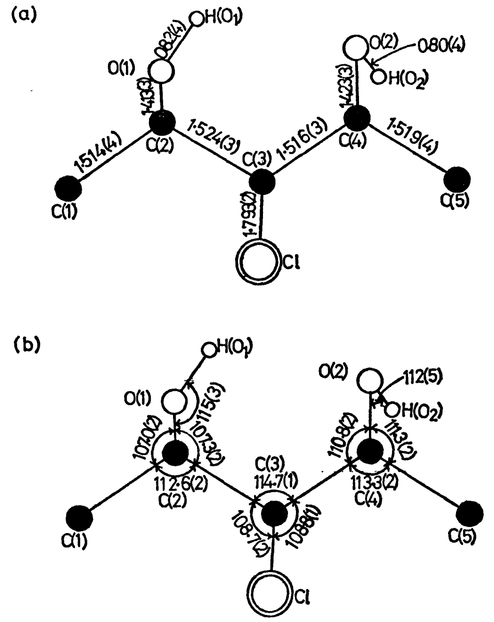

Fig. 1. The molecular shape, bond lengths (a), and angles (b), looking down through the direction perpendicular to the least square plane.

observed and calculated structure factors are listed in Table 4.*)

Results and Discussion

The bond lengths, bond angles, and the molecular shape are shown in Fig. 1. The bond lengths, ranging from 1.514 to 1.524 Å for C–C and from 1.413 to 1.423 Å for C–O, are not significantly different from the respective mean values of 1.519 and 1.418 Å. The OH bond lengths are 0.80 and 0.82 Å, a little shorter than the ordinary OH bond lengths. The C–C–C bond angles are systematically about 6° greater than the C–C–O bond angles. This fact has also been pointed out for other polyols.[6–10)] The five carbon atoms are nearly on a plane, and they take a TT sequence. The equation of the least-squares plane through five carbon atoms is given by:

$$-0.6454x + 0.5489y + 0.7445z = 0.4262$$

with respect to the crystallographic axes. The deviations of five carbon atoms from the plane are shown in Table 5. The calculations were carried out using the program written by Tosio Sakurai.[5)] The torsional angles, listed in Table 6 were calculated by means of the program written by Reikichi Iwamoto of our laboratory. In Figs. 2 and 3, the packing of the molecules looking down the c- and a-axes in the unit cell are shown. As is shown in these figures, the two oxygen atoms are hydrogen-bonded to each other. Each hydroxyl group forms two hydrogen bonds intermolecularly, one as donor and the other as acceptor. These two hydrogen-bond distances are 2.800 and 2.752 Å respectively. As is commonly observed, the spread of C–O–H angles at the donor oxygen atom of

Table 5. Deviations of five carbon atoms from the least-square plane

Atom	Deviations (Å)
C (1)	0.005
C (2)	−0.030
C (3)	0.020
C (4)	0.030
C (5)	−0.025

Table 6. Torsional angles

	Torsional angles
C (1)-C (2)-C (3)-C (4)	−178.19
C (2)-C (3)-C (4)-C (5)	−175.64
C (4)-C (3)-C (2)-O (1)	64.20
C (2)-C (3)-C (4)-O (2)	58.31
C (1)-C (2)-C (3)-Cl	−56.04
C (5)-C (4)-C (3)-Cl	62.30

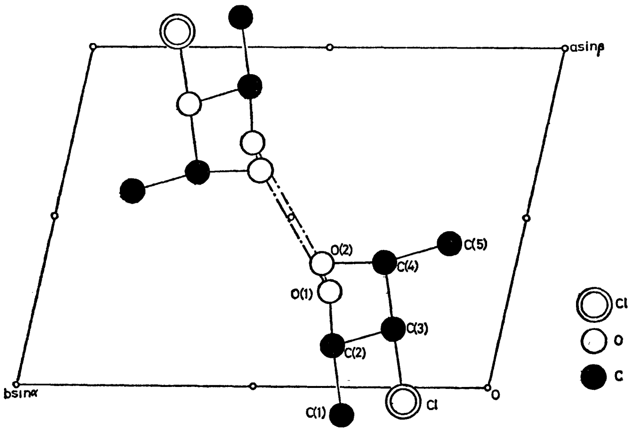

Fig. 2. The crystal structure of DL-3-chloro-2,4-pentanediol viewed down along the c-axis. Hydrogen bonds are shown by the chain lines.

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* Table 4, which gives a complete list of the observed and the calculated structure factors, has been submitted to, and is kept by, the office of the Bulletin of the Chemical Society of Japan. (Document No. 7518).

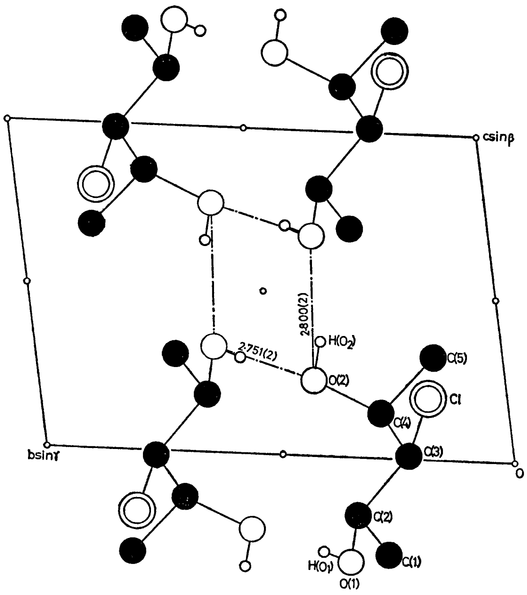

Fig. 3. The crystal structure of DL-3-chloro-2,4-pentanediol viewed down along the *a*-axis.

the hydrogen bond is less than those of H···O–C at the acceptor oxygen. The angles of the former are 112.5° and 115.4°, and of the latter, 124.0° and 137.9°. Surrounding the center of symmetry, four molecules are linked together by the hydrogen bonds. The shortest van der Waals contacts of C–C, C–O, C–Cl, O–O, and O–Cl are 3.52, 3.54, 3.60, 3.48, and 3.95 Å respectively.

As has been pointed out on the basis of NMR observation, the configuration of the molecule is proved to be the racemic form. From the IR spectra, measured in two concentrations, the conformations of racemic chloro-diol are thought to be mixtures of TT and TG, but in the crystalline state the conformations are TT only and all of the OH groups are linked together by intermolecular hydrogen bonds.

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