*Crystal Structure and Lattice Energy of i-Erythritol. I. Crystal Structure of i-Erythritol**

By Akira SHIMADA

(Received August 13, 1958)

i-Erythritol ($CH_2OH \cdot C^*HOH \cdot C^*HOH \cdot CH_2OH$) is one of the polyalcohols, which has a close relationship with carbohydrates. Hence a knowledge of its stereochemical configuration would be of great interest and importance to the chemistry of carbohydrates. The molecule of this compound is built up of two and, in a sense, identical groups, each of which has an asymmetric carbon atom, C*, as indicated in the above chemical formula. It has already been reported that in the crystal of this substance these two identical groups are related to each other by a center of symmetry[1,2]. However, the detailed spatial configuration of this molecule still remains unexplored.

Interesting roles of the hydrogen bond have been elucidated for pentaerythritol in connection with its thermal and electrical properties[3-8]. Therefore, it seems highly promising to make an attempt to find out what types of hydrogen bond are linking molecules together in the crystal of *i*-erythritol, in order to understand some physical properties of this crystal.

Experimental

i-Erythritol crystallizes in the tetragonal bipyramidal class. Crystals were prepared by the slow evaporation of the solution in a mixture of ethyl alcohol and water. They were ground to cylindrical rods, elongated parallel to the [001] or [010] axis; their diameters are less than 0.4 mm. All photographs were taken with Cu K_α radiation. The crystal has been shown by the previous workers[1,2] to possess the space group symmetry $C_{4h}^6-I4_1/a$, with eight molecules in the unit cell. This assignment of the space group was verified by oscillation and Weissenberg photographs in the present experiment, and a redetermination of the unit cell dimensions gave the following values.

$$a=12.81\pm0.03\ \text{Å} \qquad c=6.81\pm0.02\ \text{Å}$$

The axial ratio $c/a=0.532\pm0.003$ as deduced from these lattice constants will give $c/\sqrt{2}\ a=0.376\pm0.002$ if we refer to the old choice of the crystallographic axes*, which is in excellent agreement with the goniometric value 0.3762[9]. Assuming eight molecules in the unit cell with the dimensions given above, the density is calculated to be 1.45±0.01 g./cc., which is in good harmony with the value, 1.450 g./cc., reported by Schröder[10].

The (*hk*0) and (*h*0*l*) intensity data were estimated visually from multiple-film Weissenberg photographs. They were corrected for the Lorentz and polarization factors, using Cochran's chart[11]. Correction was applied to the absorption in the usual way, although this was found to be very small (absorption coefficient $\mu=12.7\ \text{cm}^{-1}$). The observed structure ampliudes were first set on to an absolute scale using Wilson's method[12] which were further improved during the later stages of refinement.

Structure Determination

The unit cell contains only eight molecules, that is, sixteen C, sixteen C*, sixteen O_1 and sixteen O_2 atoms, suggesting that the center of gravity of each molecule must occupy a special position in the unit cell. In accord with the conclusion[1,2] already derived from a preliminary consideration of intensities of certain principal planes, it was confirmed that each molecule was situated at a center of symmetry. Hence each atom occupies the general positions given by,

---

* The major part of this paper was read at the 7th Annual Meeting of the Chemical Society of Japan, April, 1954. A short communication is now in press in Acta Crystallographica, and the present account describes the structure analysis in detail.

1) W. G. Burgers, *Phil. Mag.*, (7) **1**, 289 (1926).

2) N. Schönfeldt, K. Hermann und O. Hassel, *Z. physik. Chem.* (A) **124**, 305 (1926).

3) I. Nitta and T. Watanabé, *Nature*, **140**, 365 (1937); *Sci. Papers Inst. Phys. Chem. Research*, **34**, 1669 (1938).

4) F. J. Llewllyn, E. G. Cox and T. H. Goodwin, *J. Chem. Soc.*, **1937**, 883.

5) I. Nitta, S. Seki and M. Momotani, *Proc. Japan Acad.*, **26**, (9) 25 (1950).

6) I. Nitta, S. Seki, M. Momotani, K. Suzuki and S. Nakagawa, ibid., **26**, (10) 11 (1950).

7) I. Nitta, T. Watanabé, S. Seki and M. Momotani, ibid., **26**, (10) 19 (1950).

8) R. Kiriyama, S. Yabumoto and I. Nitta, This Bulletin, **27**, 115 (1954).

9) P. Groth, "Chemische Krystallographie", Engelmann, Leipzig (1906), part III, p. 240.

* The old axes are such that the *z* axis is unchanged and the *x* axis is the diagonal of the basal plane of the new unit cell.

10) Schröder, *Ber.*, **12**, 562 (1879).

11) W. Cochran, *J. Sci. Instr.*, **25**, 253 (1948).

12) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

$$(0,0,0;\ 1/2,1/2,1/2)+$$
$$x,y,z;\ \bar{x},1/2-y,z;\ 3/4-y,1/4+x,1/4+z;$$
$$1/4+y,1/4-x,1/4+z;$$
$$\bar{x},\bar{y},\bar{z};\ x,1/2+y,\bar{z};\ 1/4+y,3/4-x,3/4-z;$$
$$3/4-y,3/4+x,3/4-z$$

Because of the short c axis, it was expected that an approximate structure might appear in an electron density projection on the (001) plane, without complication due to overlappings of atoms. Since a molecule contains only lighter atoms, a Patterson projection $P(uv)$ on the (100) plane, shown in Fig. 1, did not give any useful information about the location of each atom. Hence, an attempt was made to solve the structure with a minimum function[13] derived from this Patterson projection. In order to get a minimum function, a location of rotation peaks must be determined and various minimum functions were tried, regarding acceptable peaks in the Patterson function as the possible image-seeking vectors. The location of rotation peaks, marked by a cross in the Patterson function, gave the most promising minimum function $M_4(xy)$ as shown in Fig. 2. Another approach to the clue to an approximate structure was obtained by the inequality method[14] using Sakurai's chart[15], and the signs of five out of fifty-two observed reflections could be determined. The first Fourier map prepared with these terms, given in Fig. 3, shows a good resemblance to the minimum function $M_4(xy)$.

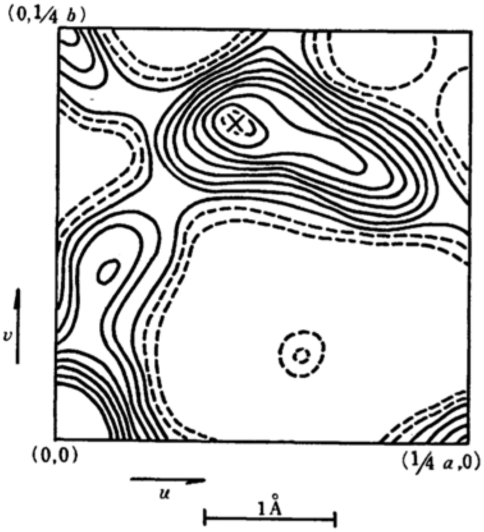

Fig. 1. Patterson projection $P(uv)$ onto (001) with contours at arbitrary intervals.

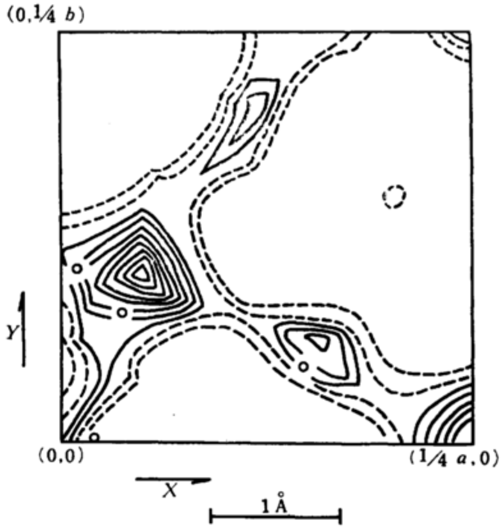

Fig. 2. Minimum function $M_4(xy)$ with contours at arbitrary intervals. Circles indicate the location of atoms corresponding to Fig. 4.

Based on these two promising figures, an effort was made to locate each atom at each peak by trial and error method. Starting from the approximate structure projected on the (001) plane, the structure was refined by successive Fourier syntheses with the aid of difference syntheses at later stages. The final Fourier

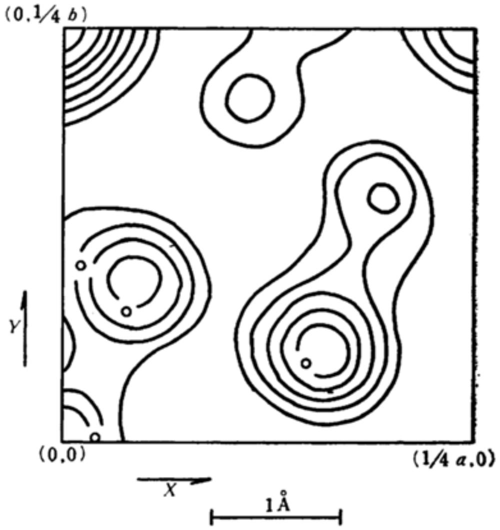

Fig. 3. First Fourier projection onto (001) prepared by inequality method with contours at arbitrary intervals. Circles indicate the location of atoms corresponding to Fig. 4.

---

13) M. J. Burger, *Acta Cryst.*, **4**, 531 (1951).
14) D. Harker and J. S. Kasper, ibid., **1**, 70 (1948).
15) K. Sakurai, ibid., **5**, 546 (1952).

projection on the (001) plane is shown in Fig. 4. The reliability index $R=(\sum||F_o|-|F_c||)/\sum|F_o|$ for (*hk*0) spectra is reduced to 16.5%, the contributions from hydrogen atoms being excluded. Several plausible configurations of the molecule were derived from the Fourier projection on the (001) plane with the aid of the Patterson projection $P(uw)$ on the (010) plane, which is shown in Fig. 5. They were put to the test by the comparison of observed and calculated structure factors for (*h*0*l*) spectra. One of these configurations led to an approximately good agreement between the observed and the calculated structure factors, so as to give an approximate value of z for each atom. Since the symmetry of the crystal is high, there are considerable overlappings of atoms in the (010) projection which make it difficult to refine x, y and z values by successive Fourier syntheses alone. We were able to overcome this difficulty by preparing difference syntheses with the coefficients F_o-F_c', where F_c' stands for the structure factor calculated by means of the coordinates of the atoms, the peaks of which were well resolved but equivalent peaks were overlapped by other atoms by the symmetry operations. The usual difference syntheses were also tried at later stages to refine the structure. The electron density projection on the (010) plane is shown in Fig. 6. The reliability index R for (*h*0*l*) spectra is found to be 13.3%*, the contributions from

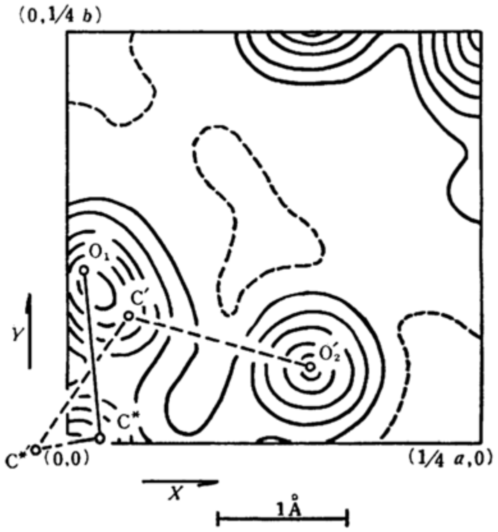

Fig. 4. Final electron density projection onto (001). Contours at intervals of 2 e.Å^{-2} with the lowest solid contour at 3 e.Å^{-2}.

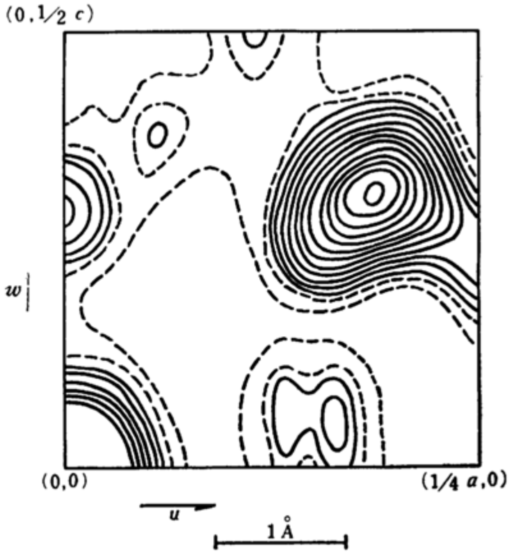

Fig. 5. Patterson projection onto (010) with contours at arbitrary intervals.

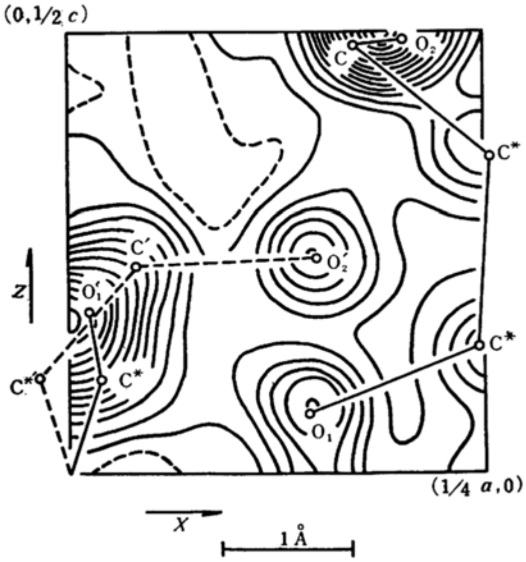

Fig. 6. Final electron density projection onto (010). Contours at intervals of 2 e.Å^{-2} with the lowest solid contour at 3 e.Å^{-2}.

TABLE I

ATOMIC COORDINATES

	x/a	y/b	z/c
C*	0.019	0.001	0.108
C	−0.039	−0.080	0.236
O_1	0.011	0.108	0.185
O_2	−0.148	−0.049	0.243

---

* The reliability indices for (*hk*0) and (*h*0*l*) spectra were reduced mainly because of the more careful measurement of intensity after the short communication was sent to Acta Crystallographica. The author hopes at some more favorable time to refine the structure by the use of I. B. M. computor which will be provided at his university in the near future.

TABLE II

VALUES OF CALCULATED AND OBSERVED STRUCTURE FACTORS

($hk0$)

h	k	$1/8(F_o)$	$1/8(F_c)$	h	k	$1/8(F_o)$	$1/8(F_c)$	h	k	$1/8(F_o)$	$1/8(F_c)$	h	k	$1/8(F_o)$	$1/8(F_c)$
2	0	1.0	−0.8	2	4	11.8	−14.8	2	8	5.7	−4.5	2	12	2.5	2.1
4	0	6.8	5.6	4	4	8.2	−7.5	4	8	10.0	10.5	4	12	1.4	0.6
6	0	12.8	14.2	6	4	2.1	2.1	6	8	1.8	2.3	6	12	0.9	0.3
8	0	4.6	5.3	8	4	3.5	−3.1	8	8	2.1	2.7	8	12	0	−0.7
10	0	2.7	−2.6	10	4	6.3	−6.3	10	8	2.4	2.8	10	12	0.5	−0.5
12	0	1.2	0.7	12	4	2.3	2.9	12	8	1.9	1.6				
14	0	0	0.7	14	4	1.5	−1.9	14	8	0.8	1.0	2	14	2.3	2.3
16	0	0.4	−0.3									4	14	0.7	−1.0
				2	6	3.2	2.2	2	10	5.2	5.0	6	14	1.3	−1.6
2	2	15.4	13.9	4	6	0.8	2.0	4	10	4.4	4.9	8	14	0	−0.4
4	2	4.3	−4.4	6	6	2.6	−2.1	6	10	2.6	2.1				
6	2	5.1	5.2	8	6	1.2	0.3	8	10	0	−0.3	2	16	1.2	1.1
8	2	5.8	−6.8	10	6	1.5	1.5	10	10	4.1	3.6				
10	2	0.9	0.1	12	6	1.4	1.7	12	10	0	−0.5				
12	2	1.4	−1.7	14	6	0	0.8								
14	2	0.7	−0.8												
16	2	1.6	−1.3												

($h0l$)

h	l	$1/8(F_o)$	$1/8(F_c)$	h	l	$1/8(F_0)$	$1/8(F_c)$	h	l	$1/8(F_o)$	$1/8(F_c)$	h	l	$1/8(F_o)$	$1/8(F_c)$
2	2	13.1	−12.2	2	6	2.4	−2.1	1	1	7.1	7.3	1	5	1.3	−0.4
4	2	3.3	−3.6	4	6	3.0	3.2	3	1	9.7	9.9	3	5	4.6	4.8
6	2	0.4	0.0	6	6	0	−0.6	5	1	4.9	−4.1	5	5	1.5	−1.6
8	2	4.2	−4.2	8	6	1.2	−1.1	7	1	8.0	8.3	7	5	0.8	1.1
10	2	2.9	2.6	10	6	2.2	3.3	9	1	0.9	1.4	9	5	0.8	0.6
12	2	0	−0.6	12	6	1.0	1.2	11	1	2.7	−2.2	11	5	0	−0.3
14	2	0	0.1					13	1	2.2	1.7	13	5	0.8	0.5
				0	8	2.0	2.0	15	1	0.5	0.3				
0	4	5.3	6.8	2	8	1.0	−1.4					1	7	2.1	−2.5
2	4	3.3	−3.2	4	8	0.4	0.5	1	3	10.8	−9.0	3	7	2.3	2.3
4	4	4.2	−4.6	6	8	0	0.0	3	3	0.9	−0.5	5	7	1.5	−1.5
6	4	4.3	4.1					5	3	8.2	−9.3	7	7	0.4	−0.8
8	4	4.4	−3.8					7	3	0	−0.3	9	7	0.6	0.6
10	4	0	−0.4					9	3	1.4	−1.2				
12	4	1.4	−1.6					11	3	2.4	−2.1				
14	4	0.6	0.6					13	3	0.9	0.2				
								15	3	0	−0.1				

hydrogen atoms being excluded. The atomic coordinates detemined in this way are listed in Table I. The observed and the calculated structure factors for ($hk0$) and ($h0l$) spectra are given in Table II. In the above calculation of structure factors, McWeeny's[16] scattering curves of "valence states" for carbon atom and of $f=1/3(f^{\parallel}+2f^{\perp})$ for oxygen atom were used with the isotropic temperature factor $B=2.17$ Å^2.

Discussion of the Structure

Since the molecule lies at the center of symmetry, two identical $CH_2OH \cdot C^*HOH$ groups constituting each half of the molecule are in the *trans*-position to each other, and the zig-zag chain of the four carbon atoms lies exactly in a plane, one of the C* atoms being of the nature *d* and the other *l*. All the valency angles for the carbon atoms are found to be approximately tetrahedral. Hence the configuration of the molecule as a whole can be described, only if we refer to the relative orientation of the outer $C–O_2$ bond with regard to the outer C*–C bond in each half of the molecule. The configuration of the molecule can be easily understood from Fig. 7, which shows the perspective view of a molecule in the C*–C bond direction. Intramolecular bond distances and bond angles are also listed in Table III. The plane of the $C^*–C–O_2$

---

[16] R. McWeeny, ibid., 4, 513 (1951).

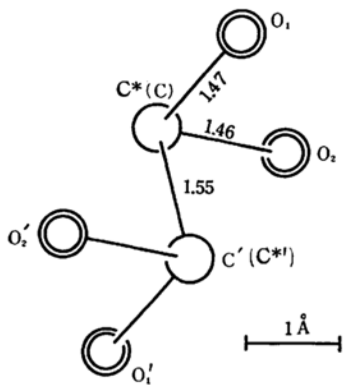

Fig. 7. *i*-Erythritol molecule projected on a plane at right angles to the C*-C bond. Intramolecular bond distances are given in Ångstrom units.

TABLE III
INTRAMOLECULAR BOND DISTANCES AND BOND ANGLES

C*-C	1.54 Å	∠C*′-C*-C	110°
C*-C*′	1.55 Å	∠C*′-C*-O_1	110°
C*-O_1	1.47 Å	∠C-C*-O_1	113°
C-O_2	1.46 Å	∠C*-C-O_2	108°

group forms a dihedral angle of 59° with the plane of the C-C*-O_1 group and an angle of 65° with that of the zig-zag chain of carbon atoms. In other words, the directions of the outer C-O_2 bond and the C*-C*′ bond make the *gauche*-configuration with respect to the C*-C bond, and the two hydroxyl oxygen atoms in each half of the molecule are also in the *gauche*-positions around the C*-C bond. It is interesting to note that this relative configuration of the two hydroxyl groups with respect to the C*-C bond agrees with that found in tartaric acid and tartrate ion[17-21]. This mode of linkage is known to exist in carbohydrates. It must also be added that this configuration should be compared with the molecular configurations reported on ethylene glycol and glycerol on the basis of an electron diffraction study[22].

Fig. 8 gives the view of the crystal structure along the *c* axis. In this structure, important roles of two types of hydrogen bonds in the cohesion of the crystal can not be overlooked. The outer hydroxyl oxygen atom is linked to two oxygen atoms of the outer hydroxyl groups of the neighboring molecules, above and below, with a distance 2.66 Å forming a spiral chain arrangement of hydrogen bonds along the *c* axis. The inner hydroxyl oxygen atom, on the other hand, is linked to two oxygen atoms of the inner hydroxyl groups of the neighboring molecules. They form a distorted square of the side length 2.77 Å around the position given by the symmetry $\bar{4}$. They are making a lateral linkage, in a way, but at the same time they are uniting molecules within the same chain mentioned above. Thus, the crystal structure is held together by a three-dimensional net work of these hydrogen bonds, in which all the available hydrogen atoms and all the oxygen atoms also are joining, in agreement with the fact that this crystal has no cleavage.

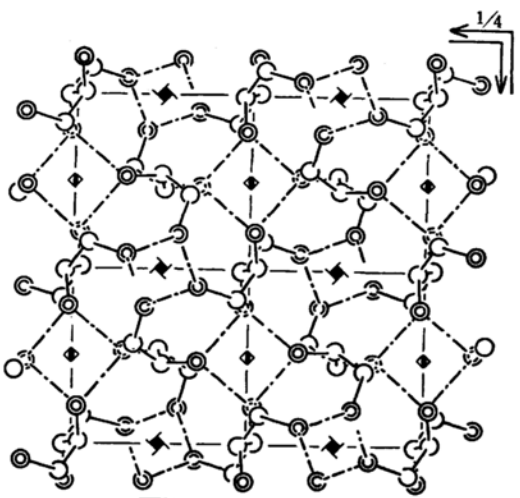

Fig. 8. A projection of the structure along the *c* axis of the crystal.

The author is indebted to Professor I. Nitta, and Professor T. Watanabé for their helpful advice.

Department of Chemistry
Faculty of Science
Konan University
Higashinada-ku, Kobe

---

[17] C. A. Beevers and W. Hughes, *Nature*, **146**, 96 (1940); *Proc. Roy. Soc.* A177, 251 (1941).
[18] F. Stern and C. A. Beevers, *Acta Cryst.*, **3**, 341 (1950).
[19] R. Sadanaga, ibid., **3**, 416 (1950).
[20] G. S. Parry, ibid., **4**, 131 (1951).
[21] A. J. van Bommel and J. M. Bijvoet, ibid., **11**, 61 (1958).
[22] O. Bastiansen, *Acta chem. scand.*, **3**. 415 (1949).