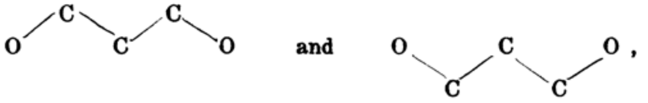
X-Ray Investigation of the Cubic Modification of Pentaerythritol, $C(CH_2OH)_4$.

By Isamu NITTA and Tokunosuké WATANABÉ.

(Received December 28, 1937.)

It has been reported by L. Ebert,⁽¹⁾ that pentaerythritol, $C(CH_2OH)_4$, shows in the temperature range between 179.5 and 260.5°C., its melting point, another crystalline modification, which is optically isotropic, and that the heat of transition is estimated from the cooling curve to be several times as large as the heat of fusion. Now that the structure of the ordinary tetragonal modification has been determined independently by the present authors⁽²⁾ and by Llewellyn, Cox, and Goodwin,⁽³⁾ it will be of interest to make an X-ray investigation of the cubic modification to see if there exist some close relationships between the two structures.

The important features of the determined tetragonal structure may be summarized as follows: If the hydrogen atoms of the OH groups are not taken into consideration, the molecule $C(CH_2OH)_4$ in the crystal possesses approximately the symmetry of D_{2d}–$\bar{4}2m$, precisely S_4–$\bar{4}$, with one pair of primary alcohol radicals puckered upwards and the other downwards, namely,



all the bond angles of these atoms being approximately tetrahedral (Fig. 1). The molecules are arranged flat in a sheet parallel to the crystallographic c-plane, and the whole crystal is made up of such molecular layers. The linkage between neighbouring molecules in a layer is more or less firm by the interaction of the hydroxyl groups. The geometrical aspect of this linkage is such that four hydroxyl oxygen atoms, one out of each adjoining molecule, constitute a square, of which every side is presumably bridged over by a hydrogen atom (Fig. 2).

---

(1) L. Ebert, *Ber.*, **64** (1931), 114. See also K. Weissenberg, *Naturwissenschaften*, **15** (1927), 996; W. M. Cohn, *Z. Physik*, **50** (1928), 134.

(2) I. Nitta and T. Watanabé, *Nature*, **140** (1937), 365.

(3) F. J. Llewellyn, E. G. Cox, and T. H. Goodwin, *J. Chem. Soc.*, **1937**, 883.

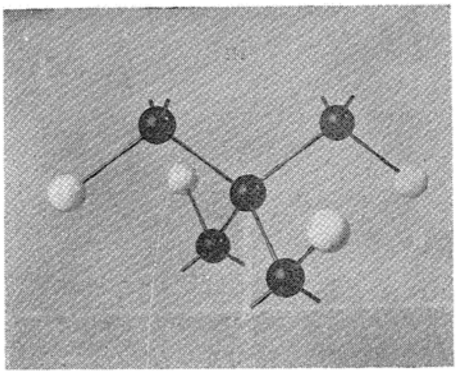


Fig. 1. Atomic configuration in tetragonal pentaerythritol, with C atoms shown as black and O atoms as white balls.

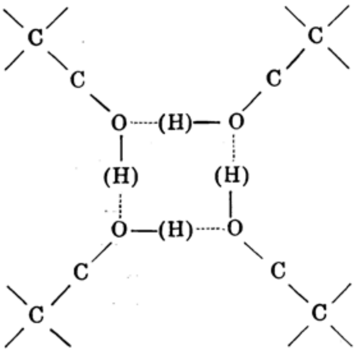


Fig. 2. Hydrogen bridges in tetragonal pentaerythritol.

In such closed hydrogen bridges, the "synchronized oscillations" may, according to Huggins,(4) cause an increased stability of the intermolecular linkage.

In the present experiment, material from Schering-Kahlbaum A. G. was fractionally crystallized from aqueous solution. The melting point of the sample was 257°C. Although the same sample was ascertained to melt, after sublimation, at a temperature higher than 260°C. as Ebert describes, such sublimate was not used.(5)

Since the old crystallographic choice of the principal axes of tetragonal pentaerythritol gives the value $c/a = 1.0236$ at a room temperature,(6) it was first examined by the Laue photographic method if the ratio c/a tends to unity as the temperature approaches to the transition point so that the transformation from tetragonal to cubic takes place rather continuously. Several Laue photographs were prepared at various temperatures up to 179.5°C. with the incident X-ray beam normal to the crystal slice cleaved along (001). The change of the ratio c/a was not found in the sense to decrease to unity. For example, the observed value was $c/a = 1.043$ at a temperature a little below the transition point. It was also found that the dissymmetrical intensity distribution of the Laue spots, (hkl) and (khl) in pairs, remains almost unaltered over the whole examined range of temperatures below 179.5°C. This implies that any torsional change of the atomic arrangement around a tetragonal axis does not sensibly occur. In other words, the molecular shape itself and the

---

(4) M. L. Huggins, *Nature*, **139** (1937), 550.

(5) For the ordinary and microscopic determination of the melting point our thanks are due to Mr. Z. Kochi at the Osaka Pharmaceutical College.

(6) P. Groth, "Chemische Krystallographie," Part III, 385.

relative orientation of the molecules in a (001) layer undergo practically no change up to the vicinity of the transition point. Thus it seems probable that the observed increase in the value of c/a is mainly due to the enlargement of the spacing $c/2$ between successive molecular layers. When the temperature of the crystal slice is raised above the transition point, the characteristic Laue pattern of the tetragonal modification is replaced by an assembly of a large number of smaller Laue spots distributed quite irregularly on the photograph, thus rendering our attempt unsuccessful to obtain Laue photographs of a single cubic crystal.

Debye-Scherrer photographs of the high temperature modification were made with the copper K radiation filtered through a nickel foil, the camera radius being 100 mm. and the angular range of the film ca. 70°. The temperature of the rotating sample was kept at 230°C. approximately. The films were protected by a paper screen in front of them from heat radiation of the electrical furnace, in which the sample was placed, and they were also water-cooled on the back side in order to prevent difficulties, such as their deformation and fogging, which will be caused by the elevation of the film temperature. It took about ten times as much time of exposure to obtain photographs with the appearance of the first seven lines as that necessary for good photographs of the tetragonal modification at ordinary temperatures. The obtained data are given in Table 1. It may be remarked here that Cohn(7) has already shown in his paper three powder photographs of pentaerythritol taken at 20, 140 and 230°C. respectively, of which he made no analysis of the obtained lines. Perhaps he regarded the third one of his photographs as solely due to the high temperature modification. However, it is now obvious from our present experiment that this is not a pure one but a mixed photograph due to both of the two modifications, indicating that his sample was not kept constantly at a temperature above the transition point.

As shown in Table 1, all the lines on the photographs are very well accounted for by a cubic face-centered lattice, the side of the unit cube being $a = 8.963$ A. at 230°C. Taking the number of molecules contained in the unit as four, the density of the crystal is computed to be $\rho = 1.255$ at 230°C., which is much lower than the value $\rho = 1.398$ at 25°C. for the tetragonal modification. As the volume increase of this tetragonal modification in the range from room temperatures to the transition point is estimated to be not much more than one per cent, the transformation should be accompanied by a considerable expansion of volume, and this is actually in accord with Ebert's and our observations. As for the re-

---

(7) W. M. Cohn, *Z. Physik*, **50** (1928), 134.

Table 1. Powder photographic data of cubic pentaerythritol.

l (mm.)	θ	$\sin\theta$	d (A.)	hkl	a (A.)
29.8	8°32′	0.1484	5.18_5	111	8.98_0
34.5	9°52′	0.1713	4.49_2	200	8.96_4
49.0	14° 4′	0.2431	3.16_5	220	8.95_1
60.4	17°18′	0.2974	2.58_7	222	8.96_1
70.1	20° 5′	0.3434	2.24_1	400	8.96_4
76.7	21°58′	0.3741	2.05_7	331	8.96_6
78.8	22°35′	0.3839	2.00_4	420	8.96_2
					mean 8.96_3

maining possible units for the crystal, it will be shown that either they contradict with the observed facts or they can be looked upon as improbable.

It is now required to arrange four molecules of $C(CH_2OH)_4$ in the face-centered cubic unit so as to furnish the crystal as a whole with the symmetry characteristic of the cubic system. However, such high symmetry cannot be afforded by the usual manner of arranging the four molecules of the symmetry S_4-$\bar{4}$, which is found in the case of tetragonal pentaerythritol. Thus it comes into question if the unit chosen above is wrong. In order, for the molecule of the symmetry S_4-$\bar{4}$, to yield a unit of cubic symmetry, their number in such unit must be some multiples of 3. After elimination on account of absurd values for the density of the crystal, there remains only one unit containing 12 molecules to be taken into consideration. In this case the side of such a unit becomes 12.67 A. and the underlying lattice simple or body-centered. However, the number of lines actually observed is too few to be accounted for in a natural way by such simple or body-centered lattice. Thus the unit of twelve molecules may also be eliminated. Returning to the original cubic face-centered unit containing four molecules, there arises a second question how it is possible to explain this peculiarity in the symmetry consideration. As in the cases of certain crystal structures,(8) a statistical explanation can be given to such phenomena; i.e. acquisition of higher molecular symmetry by some statistical means. In the present case of pentaerythritol, there will be three ways possible to realize such acquisi-

---

(8) See, for example, S. B. Hendricks and L. Pauling, *J. Am. Chem. Soc.*, **47** (1925), 2904; S. B. Hendricks, *Z. Krist.*, **74** (1930), 29; L. Pauling, *Phys. Rev.*, **36** (1930), 430; S. B. Hendricks, *Z. Krist.*, **84** (1932), 85; I. Nitta and T. Watanabé, *Sci. Papers Inst. Phys Chem. Research* (Tokyo), **26** (1935), 164.

tion. In the first one, the molecule is considered to keep the symmetry of S_4-$\bar{4}$; in the second, it is regarded to be non-rigid owing to the rotation about the single C–C bonds, of which the four directions from the central carbon atom are in angles of 109°28′; and in the third, both the molecular shape and the mutual orientation of the molecules are to be changed. All of these three possible ways will be taken into the following considerations to see which will give the best account for the observed intensities, the atomic separations in the molecule being assumed to be 1.54 A. for the C–C and 1.46 A. for the C–O bonds and the valency angles of the carbon atoms to be 109°28′.

On the assumption of the rigid molecule possessing the symmetry of S_4-$\bar{4}$, there are two extreme cases conceivable, in which the cubic symmetry of the statistical molecule is attained. The one case is that in which free spatial rotation of the molecule sets in so as to furnish it with the spherical symmetry (Case I). Then the corresponding space group is O_h^5-$Fm3m$ in the statistical sense. In the other case, which is rather statical, the whole crystal is constituted by a random distribution of three kinds of molecules, in equal concentration, the molecular $\bar{4}$-axis of each kind being parallel to each of the principal axes of the crystal (Case II). The space group is now statistically T_d^2-$F\bar{4}3m$. Intermediate of the above two, there is another important case, in which half of the molecules in Case II are rotated about the molecular axis through the angle of 90° (Case III). By the addition of these new orientations, the crystal acquires the cubic holohedral symmetry, the space group being again O_h^5-$Fm3m$. Among these three cases, it was found that Cases II and III account for the observed intensities fairly well, while Case I does not. The calculation of the intensities was made by assuming the molecular symmetry to be T_d-$43m$.

The second possibility of non-rigid molecule gives following important cases worth consideration, the four methylenic carbon atoms being assumed in all these cases as lying on the trigonal axes of the crystal. It is first conceivable that the hydroxyl groups rotate freely around the C–C bonds (Case IV, Fig. 3). Such arrangement corresponds to the space group T_d^2-$F\bar{4}3m$. However, this does not explain the observed intensity data. Next come two rather statical cases (Cases V and VI), in which each of the hydroxyl groups statistically take such three-fold positions, around the directions of the C–C bonds and at the same time in the planes defined by pairs of these C–C bonds, that the molecule may possess the symmetry of T_d-$\bar{4}3m$ (Fig. 4; black circles in Case V and open circles in Case VI). An atomic configuration of the molecule in Case V is closely related to Case II, followingly also to the original molecular shape, and the calculated intensities are the same for both cases. The space groups in Cases V and VI are T_d^2-$F\bar{4}3m$. Though not satisfactorily, Case V explains the observed intensities much better than Case VI. Besides these, there will be also another possible molecular symmetry of T-23. This seems, however, rather improbable in the present case of internal motions of non-rigid molecule.

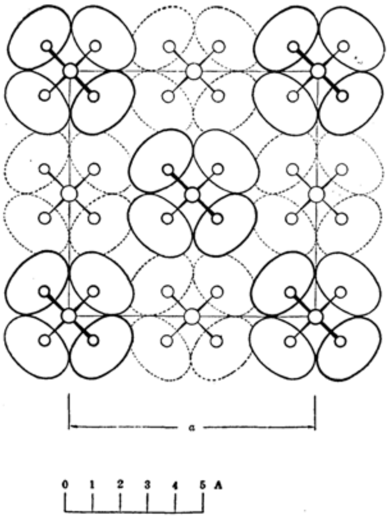


Fig. 3. Molecular arrangement of pentaerythritol in cubic form, corresponding to Case IV.

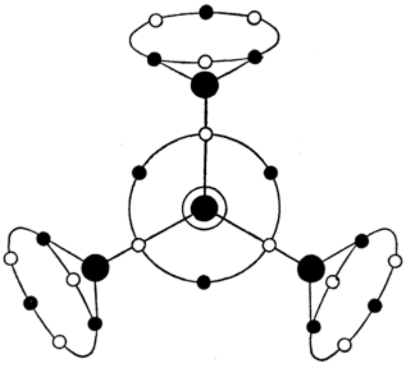


Fig. 4. Statistical atomic configurations of cubic pentaerythritol, $C(CH_2OH)_4$. The largest circle represents the central C, black circles the methylenic C atoms, and small circles the hydroxyl O atoms (black for Case V and white for Case VI).

The third possibility of non-fixed orientation of non-rigid molecules will now be discussed. In the first place, the spherical rotation of the molecule with freely rotating hydroxyl groups. This, however, does not seem to correspond to the observation. There comes next another case, in which half of the molecules of Case IV are rotated about the molecular axis through the angle of 90° as in Case III (Case VII). The mean molecular symmetry and the space group are O_h-$m3m$ and O_h^5-$Fm3m$ respectively. This case also does not explain the observed intensities. The same kind of change in the molecular orientations produces from Cases V and VI two new cases (Cases VIII and IX), to which the same molecular symmetry and the same space group as above can be given. The calculated intensities in Case VIII are the same as in Case III and explain the observed intensities fairly well, while Case IX fails. Perhaps it will be superfluous to note that the symmetry properties of Cases VII, VIII, and IX can be effected also by the rotations of molecular axes in azimuth.

After all these considerations, of which the resulting intensities are brought together in Table 2, following conclusions may be regarded as probable. Above the transition point, 179.5°C., pentaerythritol gives a cubic form, in which the central carbon atoms are arranged to build a cubic face-centered lattice, the distance between nearest molecular centers being calculated to be 6.338 A. from the side $a = 8.963$ A. of the unit. In this cubic modification, the layer structure of the tetragonal form is not retained any more, although fairly weakened hydrogen bonds seem to exist still. The molecule becomes non-rigid on account of rotation about the C–C bonds. This rotation, however, is not at all free, and the probability for the existence, accordingly the stability, of the atomic configuration, which corresponds to that observed in the molecule of the tetragonal modification, is outstandingly great among other possible configurations. By virtue of this rotation the orientation of the molecular $\bar{4}$-axis for such most stable atomic configuration can now and then be interchanged with each of the two directions, which are perpendicular to the original one. At the same time as the molecule becomes non-rigid, rotations of the molecule as a whole set in, but these are also not quite free. The most stable molecular orientations together with the most stable atomic configuration of the molecules are probably represented by what is described as Case VIII. Indeed, the actual motions in and of the molecules within the crystal will be very complicated and it will not be satisfactory to try to explain with any one of such models, rather statical in a certain sense, as above. Thus in order to make a better fit to the

Table 2. Calculated intensities for various possible cases.

hkl	I	II, V	III, VIII	IV	VI	VII	IX	X	$I_{obs.}$
111	206	327	306	262	280	260	220	287	v.v.s.
200	97.5	11.2	11.2	31	57.3	31	57.3	19.7	v.s.
220	62 3	1.8	1.8	1.8	1.2	1.8	1.2	1.8	—
311	49.5	3.1	2.2	5.0	11.0	0.7	1.2	1.3	v.v.w.
222	13.0	20.0	20.0	2.7	3.3	1.4	3.4	7.9	m.
400	4.0	0.0	0.0	0.3	2.2	0.3	2.2	0.0	v.v.w.
331	9.8	4.8	1.9	4.3	3.0	1.2	0.8	1.6	v.w.
420	8.2	2.2	2.2	0.0	1.5	0.0	1.5	0.7	v.w.
422	5.5	2.5	0.8	3.0	2.7	1.9	1.5	1.3	—
333	4.8	3.8	3.1	0.6	1.1	0.6	0.1	1.6	—
511		0.3	0.1	1.1	1.3	0.5	0.6	0.4	

observed intensities, it is necessary to take into account more cases in addition to Case VIII; for example, a weighted mean of Cases VIII and VII (Case X in Table 2). It will be added that, from the physical point of view, Case III does not probably represent the actual state of matter, though this can explain the intensities as well as Case VIII.

Perhaps it is interesting to notice that the molecular state in the cubic modification already approaches very much to that of the liquid state. This is fairly obvious from the very small heat of fusion.⁽¹⁾ The thermal vibrations of the molecular centers in the cubic crystal must be considerable chiefly because of the non-rigidity of the molecules. This is shown in the strong decrease of the intensity distribution with increasing angle on the powder photographs. In fact, a temperature factor $\exp(-B\sin^2\theta)$ with so large a constant B as 6.7 was used in the calculation of the intensities (Table 2).

It is well-known that the molecule of pentaerythritol was found in the molecular beam experiment of Estermann⁽⁹⁾ to possess a dipole moment of approximately 2×10^{-18} E.S.U. Since a molecule of the symmetry of S_4-$\bar{4}$ cannot have a dipole moment, some intramolecular motions should be assumed in the molecule of pentaerythritol.⁽¹⁰⁾ In this respect the non-rigidity of the molecule found in the present experiment may be looked upon as giving a concrete ground for this assumption, if in the molecular beam investigation above mentioned the temperature, not given in the paper of Estermann, is supposed to be enough high. On the other hand, no moment of pentaerythritol tetrabromide, of which the molecular structure in the gaseous state was determined by the electron diffraction study of de Laszlo⁽¹¹⁾ to be similar to that of the tetragonal pentaerythritol, will be interpreted by the non-rotation of the C–C bonds owing to the large volume and mass of the bromine atoms.

In conclusion, we wish to express our thanks to the Hattori Hôkôkwai for a grant.

Laboratory of Physical Chemistry, Faculty of Science,
Osaka Imperial University.

---

(9) J. Estermann, *Z. physik. Chem.*, B, **2**(1929), 287.

(10) Refer, for example, to L. Ebert, "Leipziger Vorträge," **1929**, p. 44.

(11) H. de Laszlo, *Compt. rend.*, **198** (1934), 2235.