ON THE CRYSTAL STRUCTURE OF PENTA-ERYTHRITOL.

By Isamu NITTA.

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The presence of a non-tetrahedral carbon atom in the crystal of penta-erythritol, $C(CH_2OH)_4$, has been reported by H. Mark and K. Weissenberg[1] and recently by M. L. Huggins and S. B. Hendricks[2]. Now that there is no other X-ray investigation yet imparted which confirms the presence of such carbon atom in organic crystals, while the theory of the tetrahedral carbon atom has actually offered a great deal of applications to organic chemistry, it seems not insignificant to reexamine if there can never be a possibility of attributing the tetrahedral nature to the central carbon atom of penta-erythritol in crystalline state. Thus the reexamination was carried out using the Laue photographic and X-ray spectrometric methods. Mark and Weissenberg used the rotating crystal method, and their results will be summarized as follows. The unit cell, containing two chemical molecules, has the dimensions $a=6.16$ Å. and $c=8.76$ Å., and the corresponding space group is C_{4v}^9, the underlying translation lattice being tetragonal body centred. The symmetry of the molecule and of the central carbon atom is that of the point group C_4^v, the four substitution radicals CH_2OH are structurally equivalent and lie on the hemimorphic reflection planes. Huggins and Hendricks reported that they came also at the same results.

Penta-erythritol from Kahlbaum was recrystallized from aqueous solution and used in the investigation. The symmetrical Laue photograph, obtained with the incident X-ray beam normal to the cleavage plane (001), showed a simple tetragonal pattern indicating the absence of the planes of symmetry parallel to the tetragonal axis, quite similar to the case of iodoform[3], Thus it is evident that the space group C_{4v}^9 already reported is not a correct one for the crystal of penta-erythritol, for the symmetry class C_4^v possesses the planes of symmetry parallel to the tetragonal axis. The space groups conformable to the Laue photographic indications should be those which belong to the point groups S_4, C_4 and C_4^h. Besides the Laue photograph, several reflections from various atomic planes were investigated with an X-ray spectrometer. The dimensions of the unit cell and the kind of the underlying translations agree altogether with those determined by Mark and Weissenberg.

(1) H. Mark and K. Weissenberg, *Z. Physik.* **17** (1923), 301.
(2) M. L. Huggins and S. B. Hendricks, *J. Am. Chem. Soc.*, **48** (1926), 164.
(3) I. Nitta, *Scientific Papers of the Institute of Physical and Chemical Research*, **4** (1926), 49.

From these Laue photographic and X-ray spectrometric data the possible space groups are limited to S_4^2, C_4^5, C_4^6, C_{4h}^5 and C_{4h}^6. In order to sort out the corresponding space group, it is necessary to take into consideration the arrangement of the atoms in the unit cell; i.e. the arrangement of 10 carbon atoms, 24 hydrogen atoms and 8 oxygen atoms. From the space groups C_{4h}^5 and C_{4h}^6 there can be deduced no arrangement that accounts for the observed reflections from (001) plane, and in the case of C_4^6 we cannot arrange 10 carbon atoms conformably in the unit. Only two space groups S_4^2 and C_4^5 remain as the possible ones. Theoretically these two can be distinguished by the observation of the reflections from (001) plane, and the obtained data are somewhat favourable to S_4^2. As the problem hangs upon this point, these data may not be sufficient to decide S_4^2 as the correct one and the trial survey upon the atomic arrangements will be needed for each of the two groups. It is tedious indeed to carry this work through, for, although the parameters governing 24 hydrogen atoms are neglected, there are still six parameters to be determined. In this note it will, therefore, be discussed only what inference can be made for each of the alternatives.

In either case of S_4^2 and C_4^5 we can arrange four structurally equivalent alcohol radicals CH_2OH around the central carbon atom. The minimum possible symmetry of the molecule is that of the point group S_4 in the case of S_4^2, while it is C_4 in C_4^5. It implies that we are dealing with the tetrahedral central carbon atom in the former case and the non-tetrahedral one in the latter. This possibility of the tetrahedral nature of the cental carbon atom, which the observed reflections from (001) plane seem to favour, is what the above mentioned authors have not adverted to, and what will be of some importance from the chemical point of view. The determination of the parameters is now going on; and the full account will be published later as one of the Scientific Papers of the Institute of Physical and Chemical Research.

The Institute of Physical and Chemical Research,
Hongo, Tokyo.