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The Crystal and Molecular Structure of *meso*-2,4-Pentanediol Borate

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The crystals of *meso*-2,4-pentanediol borate are monoclinic with a space group of C2/c. There are eight molecules in the unit cell with dimensions of: $a=15.36$, $b=13.53$, $c=7.68$ Å, and $\beta=113.3°$. The crystal structure was determined by the X-ray method. The final discrepancy index is 0.121 for 1030 non-zero reflections. The molecule has a six-membered ring composed of one boron, three carbon, and two oxygen atoms. The borate group and the two carbon atoms of the pentane group are nearly co-planar. The five carbon atoms are also coplanar, and they are in *trans* positions. The molecule was proved to be of the *meso* type.

In the course of our investigation of model compounds of polymers, the molecular and crystal structure of 2,4-pentanediol seemed of great interest for us as a model compound for polyvinyl alcohol.

As has been reported earlier,[1,2] chemically-synthesized 2,4-pentanediols are composed of three components, of the *meso*, *d*, and *l* types. They are separated into two components by column chromatography; one of them is assumed to be of the *meso* form, and the other, of the racemic form.

When eluted by chromatography, the compounds are separated in a form of borate. The present paper will report the crystal and molecular structure of *meso*-2,4-pentanediol borate.

Experimental

The sample was prepared by a method reported earlier.[1] The crystals are monoclinic and colorless. They crystallize in the form of needles elongated along the *c*-axis or in a lozenge shape. The cell dimensions were determined by the method of least-squares for a *c*-axis oscillation photograph, using Si powder as the standard. The systematic

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[1] M. Shiraki and E. Nagai, *Nippon Kagaku Zasshi*, **81**, 976 (1960).

[2] E. Nagai, S. Kuribayashi, M. Shiraki, and M. Ukita, *J. Polym. Sci.*, **35**, 295 (1959).

TABLE 1. CRYSTAL DATA

$C_5O_3BH_{11}$
$a=15.36$ (6) Å
$b=13.53$ (2)
$c=7.68$ (6)
$\beta=113.3$ (4)°
Mol. wt. 129.
$Z=8$
Space group C2/c
V = 1465 Å^3

Systematic absences
of the reflections
$h+k=2n+1$ for $h\,k\,l$
$l=2n+1$ for $h\,0\,l$
$\rho_c=1.17\,\mathrm{g\cdot cm^{-3}}$
$\rho_0=1.17$—$1.19\,\mathrm{g.cm^{-3}}$
mp 87°C

absences showed that the space group was C2/c or Cc. The former was chosen on the basis of the Wilson statistics. The measured density was about 1.17—1.19, which is in good agreement with the density calculated assuming that the unit cell contains eight molecules. It was difficult to determine the accurate density of the crystal by the ordinary flotation method, as this compound is very hygroscopic and is easily dissolved in nearly all kinds of solvents. The crystal data are shown in Table 1.

Multiple-film equi-inclination Weissenberg photographs were taken about the *c*-axis, with Ni-filtered Cu*Kα* radiation from zero to the sixth layer. Oscillation and precession photographs were also taken about the *b*-axis using Zr-filtered Mo*Kα* radiation; they were used mainly for the scaling of the structure amplitudes obtained from the Weissenberg photographs. The intensities were estimated visually by comparison with a standard scale prepared by the same crystal. They were corrected for the Lorentz, polarization, and spot-shape factors. No absorption correction was made. 1030 non-zero structure factors were obtained by these procedures.

Structure Determination

A Patterson projection along the *c*-axis and a consideration of the packing offered us effective clues for analyzing the structure. Reflections with $l=2n$ are generally stronger than those with $l=2n+1$. Especially, the $\bar{3}12$ and $\bar{2}02$, reflections are extremely strong. From these facts, a trial structure was deduced; it was then refined by the Fourier method in the (001) projection. By these procedures, the discrepancy index, R, became 0.217 for $F(h\;k\;0)$. At this stage, the z parameters were introduced for every atom, on the assumption that the planar molecule lies nearly on the $(\bar{3}12)$ plane. The block-diagonal least-squares method with isotropic temperature factors was applied, using a program written by N. Yasuoka for the OKITAC 5090 C. After 6 cycles of iterations, the discrepancy index, *R*, for all the observed reflections decreased from 0.253 to 0.179. Then, a block-diagonal least-squares procedure with anisotropic temperature factors was applied on a TOSBAC 3400–41 using a program, HBLS IV, written by T. Ashida.[3] The function to be minimized was $\sum w\Delta^2$, where the weighting scheme used was:

$$w=(25.0/|F_0|)^2 \quad \text{for } |F_0|\geqq 25.0$$
$$w=1 \quad \text{for } 25.0>|F_0|\geqq 5.0, \text{ and}$$
$$w=0.2 \quad \text{for } |F_0|<5.0$$

After five cycles of interactions, the R factor decreased to 0.134.

With these positional parameters and temperature factors, a difference Fourier map was synthesized, but hydrogen atoms were not found clearly in this map. Therefore, the co-ordinates of hydrogen atoms were assumed to have C–H bond lengths of 1.09 Å and bond angles of 109.5°. They were included in the structure-factor calculation, and the R value was reduced to 0.121. The final atomic co-ordinates and temperature factors, with their estimated standard deviations, are shown in Tables 2 and 3. A list of

TABLE 2. POSITIONAL PARAMETERS IN FRACTIONAL CO-ORDINATES AND ESTIMATED STANDARD DEVIATIONS (in Å)

Atom	x/a	$\sigma(x)$	y/b	$\sigma(y)$	z/c	$\sigma(z)$
C (1)	0.0941	0.009	0.2525	0.007	0.0319	0.009
C (2)	0.1378	0.008	0.1772	0.007	0.1904	0.009
C (3)	0.2439	0.007	0.1671	0.006	0.2632	0.007
C (4)	0.2805	0.008	0.0833	0.008	0.4047	0.008
C (5)	0.3854	0.008	0.0633	0.008	0.4802	0.009
O (1)	0.0934	0.004	0.0811	0.003	0.1222	0.004
O (2)	0.2319	0.004	−0.0081	0.004	0.3235	0.004
O (3)	0.0976	0.004	−0.0930	0.003	0.1285	0.004
B	0.1414	0.006	−0.0047	0.007	0.1932	0.006

TABLE 3. ANISOTROPIC TEMPERATURE FACTORS OF NONHYDROGEN ATOMS IN THE FORM $\exp\{-10^{-4}\times(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\}$.
Their estimated standard deviations are given in parenthesis.

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C (1)	128 (6)	63 (4)	383 (24)	−5 (4)	36 (10)	35 (8)
C (2)	86 (5)	73 (5)	466 (26)	−14 (4)	45 (9)	−26 (9)
C (3)	74 (4)	81 (4)	291 (18)	−15 (3)	64 (7)	5 (7)
C (4)	82 (5)	100 (6)	391 (23)	−12 (4)	20 (8)	7 (10)
C (5)	71 (4)	131 (7)	423 (25)	−21 (5)	43 (8)	−20 (11)
O (1)	62 (2)	49 (2)	229 (10)	−9 (2)	31 (3)	−2 (3)
O (2)	64 (2)	66 (2)	234 (9)	−10 (2)	18 (3)	−0 (4)
O (3)	62 (2)	50 (2)	260 (11)	−5 (2)	33 (4)	6 (4)
B	55 (3)	58 (3)	158 (13)	−2 (3)	41 (5)	6 (7)

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[3] "Universal Crystallographic Computation Program System," ed. by Tosio Sakurai, Crystallographic Society of Japan, Tokyo (1967).

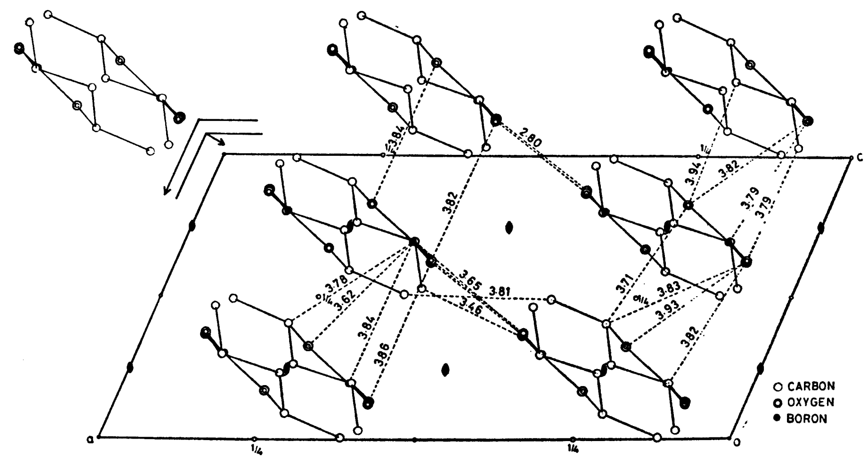

Fig. 1. The crystal structure projected onto the ac plane, with some distances shorter than 4.0 Å.

the observed and calculated structure factors is given in Table 6.[4)]

Results and Discussion

The crystal structure projected along the b- and c-axes is shown in Figs. 1 and 2. The molecular structure is shown in Figs. 3 and 4. In Table 4, the bond lengths and angles are listed. As was assumed in the earlier report,[5)] the five carbon atoms are in a *trans* position and the molecule is of the *meso* type.[1,2)]

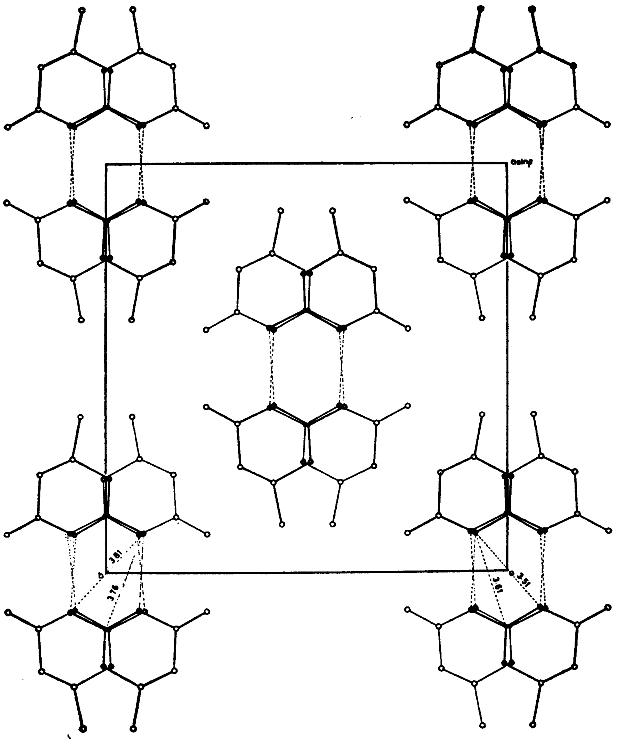

Fig. 2. The crystal structure projected onto ab plane, with some distances shorter than 4.0 Å. The broken lines which connect two oxygen atoms indicate the hydrogen bonds.

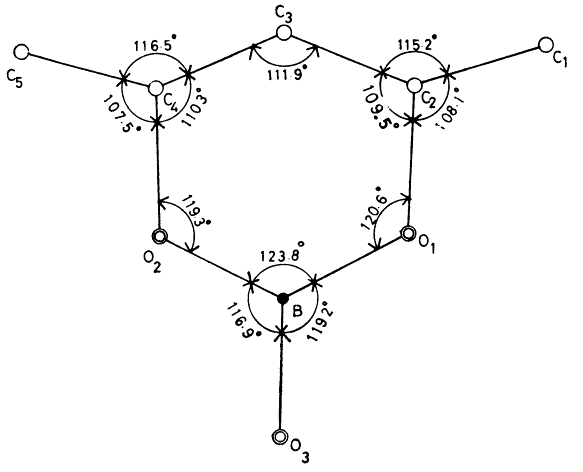

Fig. 3. The molecular shape looking along the direction normal to the molecular plane. The bond angles are also shown.

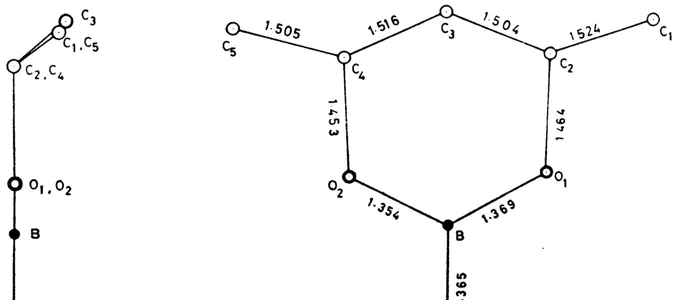

Fig. 4. The molecular shape looking along the direction normal to the molecular plane and the side view, with bond lengths.

All the C–C bond lengths (mean value, 1.51 Å) are a little shorter than the ordinary single bond, and the corresponding length in *dl*-2,4-pentanediol diacetate is 1.52 Å.[6)] The C–O bond distances are very close to the values found in various compounds. The B–O bond lengths are the same as those observed

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[4)] Table 6 has been submitted to, and is kept by the office of the Chemical Society of Japan, 1-5 Kanda Surugadai, Chiyoda-ku, Tokyo. (Document No. 7310).

[5)] S. Kuribayashi, This Bulletin, **39**, 2784 (1966).

[6)] K. Tichý, *Acta Crystallogr.*, **20**, 865 (1966).

TABLE 4. COVALENT BOND LENGTHS (Å) AND ANGLES (°)
Estimated standard deviations are given in parenthesis.

Bond	Length	Bond angles	
C (1) - C (2)	1.524 (10)	C (1) - C (2) - C (3)	115.2 (0.7)
C (2) - C (3)	1.504 (10)	C (2) - C (3) - C (4)	111.9 (0.6)
C (3) - C (4)	1.516 (10)	C (3) - C (4) - C (5)	116.5 (0.7)
C (4) - C (5)	1.505 (11)	C (1) - C (2) - O (1)	108.1 (0.5)
C (2) - O (1)	1.464 (7)	C (3) - C (2) - O (1)	109.5 (0.5)
C (4) - O (2)	1.453 (8)	C (5) - C (4) - O (2)	107.5 (0.6)
O (1) - B	1.369 (7)	C (3) - C (4) - O (2)	110.3 (0.5)
O (2) - B	1.354 (6)	C (2) - O (1) - B	120.6 (0.4)
C (3) - B	1.365 (7)	C (4) - O (2) - B	119.3 (0.5)
		O (1) - B - O - (2)	123.8 (0.5)
		O (1) - B - O (3)	119.2 (0.4)
		O (2) - B - O (3)	116.9 (0.5)

for H_3BO_3 and HBO_2.[7,8] The C(1)–C(2)–C(3) and C(3)–C(4)–C(5) bond angles are remarkably larger than those found for ordinary aliphatic compounds. Similar results have been also reported for *dl*-2,4-pentanediol diacetate.[6] The five carbon atoms are nearly co-planar, but C(3) is a little apart from this plane in the direction opposite of that for C(1) and C(5). This plane is expressed by the equation:

$$-0.1549x + 0.6848y + 0.7151z = 2.3405,$$

where x, y, and z are in Å units with repect to the crystallographic axes. The C(2), C(4), O(1), O(2), O(3), and B atoms are also co-planar. The equation of this plane is:

$$-0.6959x - 0.0085y + 0.9349z = -0.1248.$$

As can easily be realized from the co-efficients of the equation, this plane is nearly parallel to the b-axis. The deviations of atoms from these planes are listed in Table 5. The boron atom is surrounded by three oxygen atoms, which form an almost equilateral triangle about the boron.

TABLE 5. DEVIATION OF EACH ATOM FROM PLANES
Plane (I) (five carbon atoms)
Plane (II) (C(2), C(4), O(1), O(2), O(3) and B)

Atom	Deviation (Å)	Atom	Deviation (Å)
C (1)	−0.0488	C (2)	−0.0016
C (2)	0.0198	C (4)	0.0228
C (3)	0.0741	O (1)	−0.0056
C (4)	−0.0121	O (2)	−0.0312
C (5)	−0.0329	O (3)	0.0151
		B	0.0006

Surrounding the center of symmetry, two molecules are linked together by hydrogen bonds. The hydrogen-bond distances are 2.80 Å. The van der Waals distances shorter than 4.0 Å are shown in Figs. 1 and 2. The nearest intermolecular B–B and B–O distances are 3.84 and 3.61 Å respectively. These values are a little longer than the shortest distances found for H_3BO_3 and HBO_2.[7,8] The bond lengths, bond angles, van der Waals distances, and coefficients of the best planes were computed by means of a program written by T. Sakurai for the UNICS.[3]

The author wishes to express his thanks to Dr. T. Ashida, Dr. T. Sakurai, and Dr. N. Yasuoka for providing him with computing facilities. The author is also indebted to Dr. M. Shiraki for supplying the sample.

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7) W. H. Zachariasen, *Acta Crystallogr.*, **16**, 385 (1963).
8) W. H. Zachariasen, *ibid.*, **7**, 305 (1954).