*The Crystal Structure of Diallylsilanediol**

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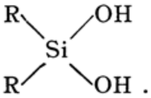
Introduction

The present study is the fourth in a series of organosilanol crystal structure determinations carried out in this laboratory, the previous three compounds examined having been diethylsilanediol[1,2,3], diphenylsilanediol[4], and bis-dimethylhydroxysilyl methane[5].

Diallylsilanediol, $(CH_2=CH\text{-}CH_2)_2Si(OH)_2$, was first prepared by Mr. R. Ōkawara and his coworkers[6].

This compound was selected for study as a typical one of the unsaturated dialkylsilanediols having the formula



It is of interest to compare the structure of this crystal, with the cases of the above-mentioned compounds especially, in respect to the molecular chain formation through hydrogen bondings or the layer structure.

Experimental

The crystals used in this experiment were recrystallized from their ethyl ether-petroleum ether solution. The crystals are colorless, flat prismatic in habit as shown in Fig. 1; the c-face is a remarkably complete cleavage plane. These properties are quite similar to those of diethylsilanediol. It is well dissolved in oxygen containing organic solvents.

Melting point: 81±0.5°C.

Density: 1.105 (by floatation method at 10°C)

For the structure determination, the oscillation and the rotation photographs were taken around both the b-axis and a-axis using nickel filtered CuK$_\alpha$ radiation.

Some physical constants and the dimensions of

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* Read before the 7th annual meeting of the Chemical Society of Japan held in Tokyo, April, 1954.

1) M. Kakudo and T. Watase, *Technol. Repts. Osaka Univ.*, **2**, 50 (1952).

2) M. Kakudo and T. Watase, *J. Chem. Phys.*, **21**, 167 (1953).

3) M. Kakudo, N. Kasai and T. Watase, *J. Chem. Phys.*, **21**, 1894 (1953).

4) T. Watase, M. Kakudo and N. Kasai *Ann. Repts. Textile Research Inst. Osaka Univ.*, **6**, 38 (1952) (in Japanese).

5) M. Kakudo and T. Watase, *Ann. Repts. Textile Research Inst. Osaka Univ.*, **7**, 17 (1953) (in Japanese).

6) R. Okawara, K. Hashitani, and T. Watase, This Bulletin, **26**, 279 (1953).

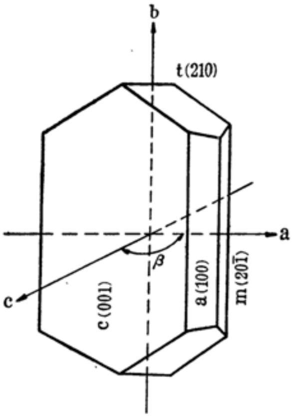

Fig. 1. The crystal form

the unit cell were listed in Table I in comparison with those of diethylsilanediol.

TABLE I

	Diallylsilanediol	Diethylsilanediol
m.p.	81±0.5°C	96±0.5°C
Density	1.105	1.134
System	Monoclinic	Monoclinic
Cleavage	(001)	(001)
Unit cell	a=14.59 kX.	a=14.55 kX.
	b= 4.94 kX.	b= 4.96 kX.
	c=13.37 kX.	c=10.25 kX.
	β=114°30′	β=110°50′
Space group	C^5_{2h}	C^5_{2h}

The physical and chemical properties of these two silanols suggest that they are much like each other not only in their chemical constitution but also in crystal structure.

The unit cell contains four molecules of $(CH_2=CH\text{-}CH_2)_2Si(OH)_2$ (calculated value $z=4.03$).

All the reflexions (hkl) were observed without any speciality, whereas no reflexions (h0l) with h odd or (0k0) with k odd were found. Consequently, the space group corresponds to C^5_{2h}—$P2_1/a$. All the atoms of this molecule are to be in the general positions of C^5_{2h},

$$(x,\ y,\ z)\ (\bar{x}, \frac{1}{2}+y, \frac{1}{2}-z)\ (x, \frac{1}{2}-y, \frac{1}{2}+z)\ (\bar{x},\ y,\ z).$$

The relative intensities of reflexions were estimated by visual method with the standard density scale. The observed structure factors, $|F_{obs.}|$'s, were derived from these values by the usual method.

The Patterson function was first calculated using $F^2_{obs.}$'s. Approximate atomic arrangement was easily assumed from the b-plane projection of Patterson function by comparing with that of diethylsilanediol.

After several trials of structure factor and electron density computations, a good agreement between $F_{obs.}$ and $F_{calc.}$ was obtained for both of F(h0l)'s and F(0kl)'s. The final electron density map is shown in Fig. 2. The atomic parameters are given in Table II. The observed and calculated F-values are also listed in Table III. The

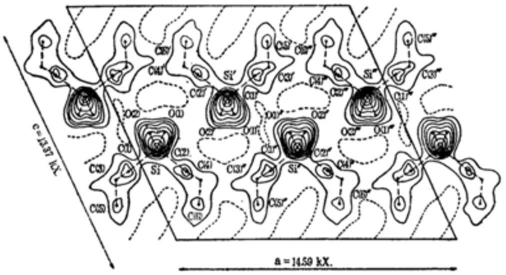

Fig. 2a. The Fourier projection map on the b-plane.

TABLE II

ATOMIC PARAMETERS

	x	y	z
0(1)	0.084	0.257	0.463
0(2)	0.138	$\overline{0.257}$	0.463
Si	0.082	0.000	0.386
C(1)	$\overline{0.054}$	0.091	0.296
C(2)	0.146	$\overline{0.091}$	0.296
C(3)	$\overline{0.115}$	0.171	0.259
C(4)	0.182	$\overline{0.171}$	0.259
C(5)	$\overline{0.152}$	0.244	0.153
C(6)	0.138	$\overline{0.244}$	0.153

TABLE III

A PART OF CALCULATED AND OBSERVED F-VALUES

(hkl)	$F_{obs.}$	$F_{calc.}$	(hkl)	$F_{obs.}$	$F_{calc.}$	(hkl)	$F_{obs.}$	$F_{calc.}$
001	86	−87	20$\bar{7}$	—	2.2	60$\bar{1}$	28	35
002	36	−27	20$\bar{8}$	11	−1.6	60$\bar{2}$	6	−15
003	30	−18	20$\bar{9}$	—	−11	60$\bar{3}$	30	−34
004	8.0	7.2	400	116	−108	60$\bar{4}$	19	29
005	29	−10	401	36	44	60$\bar{5}$	27	−38
006	25	8.3	402	22	17	60$\bar{6}$	38	40
007	—	11	403	46	−35	60$\bar{7}$	—	−10
008	41	28	404	37	28	60$\bar{8}$	31	−16
009	13	−46	405	20	25	60$\bar{9}$	40	25
0.0.10	25	−11	406	18	−33	800	25	−7.5
200	38	30	40$\bar{1}$	19	24	801	53	32

201	88	−74	$40\bar{2}$	20	−22	802	38	16
202	91	72	$40\bar{3}$	104	108	803	17	13
203	57	−40	$40\bar{4}$	52	−46	$80\bar{1}$	9	7
204	27	24	$40\bar{5}$	17	−22	$80\bar{2}$	9	27
205	18	− 7	$40\bar{6}$	41	38	$80\bar{3}$	51	−71
206	—	2.5	$40\bar{7}$	29	−34	$80\bar{4}$	15	31
207	—	4.5	$40\bar{8}$	15	−21	$80\bar{5}$	10	9
208	19	22	$40\bar{9}$	24	35	$80\bar{6}$	15	−17
$20\bar{1}$	8.3	8.2	600	25	−27	$80\bar{7}$	35	22
$20\bar{2}$	56	−53	601	57	51	$80\bar{8}$	21	−18
$20\bar{3}$	117	80	602	34	−27	$10.0.\bar{1}$	27	−34
$20\bar{4}$	77	53	603	33	− 8	$10.0.\bar{2}$	46	46
$20\bar{5}$	28	33	604	30	20	$10.0.\bar{3}$	—	1.3
$20\bar{6}$	20	−17						

values of $R=\sum||F_o|-|F_c||/\sum|F_o|$ is 0.27 for (h0l) and 0.33 for (0kl) respectively. Calculated structure factors have been corrected for atomic thermal motion by the factor $\exp\{-B(\sin\theta/\lambda)^2\}$ with $B=4.0\times10^{-16}$.

The (F_o-F_c) series map (Fig. 3) indicates, though it may not be said to be accurate, the positions of hydrogen atoms such as are assumed from its molecular structure.

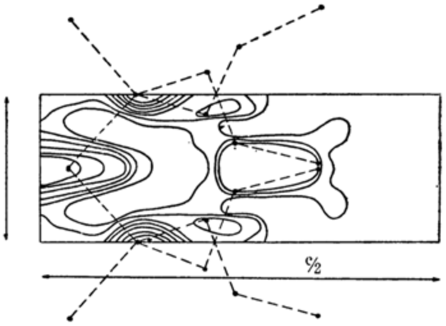

Fig. 2b. The Fourier projection map on the a-plane.

Interatomic distances and bond angles are given in Table IV.

TABLE IV
INTERATOMIC DISTANCES AND BOND ANGLES
(The suffix and number of each atom are the same as in Fig. 2 or Fig. 4.)

Si—0(1)=1.63 Å.,	∠0(1)–Si–0(2)=110°,
Si—C(1)=1.90 Å.,	∠C(1)–Si–C(2)=110°,
C(1)—C(3)=1.54 Å.,	∠Si–C(1)–C(3)=109°,
C(3)—C(5)=1.33 Å.,	∠C(1)–C(3)–C(5)=120°,
C(6)...C(5)″=3.93 Å.,	0(1)′*...0(2)′=2.53 Å.,
C(6)...C(5)‴*=4.16 Å.,	0(1)′*...0(2)=3.75 Å.,
C(6)...C)6)‴*=4.25 Å.,	0(1)′*...0(2)″=3.75 Å.,
C(5)″...C(5)‴*=4.53 Å.,	0(1)′*...0(1)″=3.65 Å.,
C(5)″...C(6)′*=4.16 Å.,	0(1)′*...0(1)″*=3.65 Å.

Discussion

The silicon-tetrahedron was recognized as retaining its ordinary shape and size.

The feature of the whole structure is considerably similar to that of diethylsilanediol as shown in Fig. 4.

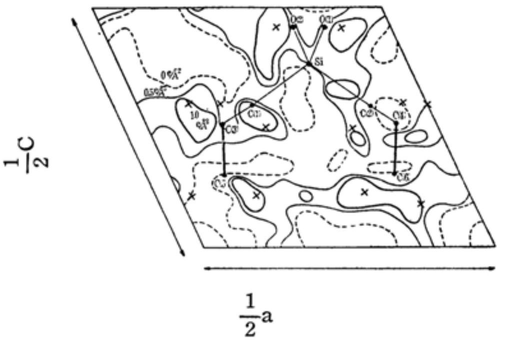

Fig. 3. (F_o-F_c) series map. (The projection on the b-plane)
×: the assumed position of the hydrogen atom.

The OH……OH distance in molecular chains $\left\{\cdots\cdots OH-\overset{|}{\underset{|}{Si}}-OH\cdots OH-\overset{|}{\underset{|}{Si}}-OH\cdots\right\}$ parallel to the b-axis is 2.53 Å (2.54 Å in diethylsilanediol). These OH...OH linkages by hydrogen bonds join the molecules to form infinite chains parallel to the b-axis just the same as in the case of diethylsilanediol.

The molecular chains are arranged parallel to each other in a plane (c-plane), and these sheets construct the layer structure, allyl groups of neighbouring molecules contacting back to back as in Fig. 4a. The remarkable

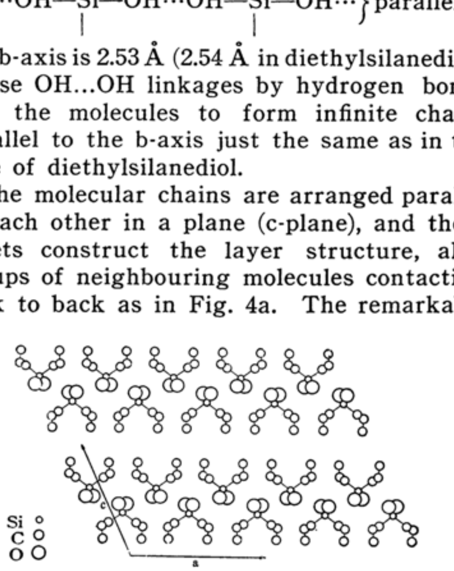

Fig. 4a. The atomic arrangement projected on the b-plane.

cleavage of (001) will be sufficiently understood from such a layer structure.

The feature of approach of OH-groups around an OH-group (Fig. 4b), and interaction of allyl groups will be explained by the same argument as presented on diethylsilanediol. This structural similarity is to be recognized as an example of isomorphism for the chemical homologues of diorganosilanediols.

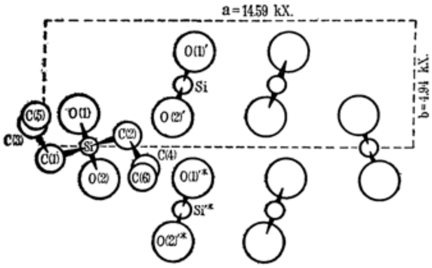

Fig. 4b. The arrangement of hydroxyl groups. (The projection on the plane $Z=\frac{1}{2}$, allyl groups are omitted except two.)

The most remarkable result is the fact that the molecular cohesion in the crystal of diorganosilanediol is mainly due to the hydroxyl bond which was formed along the b-axis by strongly polarized OH-groups, and such a way of molecular association characterizes the whole feature of crystal structure of each diorganosilanediol, which we have dealt with.

From the spreading of peaks about carbon atoms in the electron density maps and about hydrogen atoms in the (F_o-F_c) series, it is reasonably supposed that the thermal motion of allyl groups in the crystal may be in a considerable degree. This thermal libration is a noticeable property of the organoradicals directly combined to silicon atom as indicated in many other works. The low interaction of allyl groups, plus the long distance of Si-C bond should bring about a weak barrier to their thermal motion.

It is interesting to note that the peaks for all atoms in the electron-density map of Fig. 2b are elongated in such a manner as to suggest that one of the principal thermal motions is a vibration of the entire molecule along the direction perpendicular to the c-plane. This fact is also in agreement with our consideration that the intermolecular cohesive force of this crystal may be comparatively weak in this direction.

However, the anomaly of (001) reflexions expected to be sensitively influenced by such motion was not observed appreciably, though there were observed a few diffuse Laue spots. The qualitative relation of these diffuse reflexions and the molecular motion will be explained in comparison with diethylsilanediol before long.

Conclusion

The morphology and the crystal structure of diallylsilanediol were presented.

The whole feature of this structure is nearly the same as that of diethylsilanediol previously studied by one of the authors.

Many of the chemical and physical properties of diorganosilanediols can be interpreted in terms of obtained structural principles.

It was verified that the chemical homologues of diorganosilanediols give rise to a structural isomorphism.

The OH...OH distance (2.53 Å) with hydrogen bond is the same as in the case of diethylsilanediol (2.54 Å) within the range of error.

The thermal motion of allyl groups combined to silicon atom is considered as more vigorous than that in the corresponding organic compounds even at room temperature.

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