The crystal structure of $(HOMe_2Si)_2O$

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Abstract

X-Ray crystallography shows that in the solid state, molecules of $(HOMe_2Si)_2O$ are extensively hydrogen bonded together to form zig-zag double chains with no bonding between the chains.

1. Introduction

The disiloxane diol $(HOMe_2Si)_2O$ (1) is an important precursor of polysiloxanes and has been prepared by numerous methods but its solid state structure is not known in detail. The crystal structures of a variety of other disiloxanediols (2–6) have been reported and found to exhibit an interesting range of hydrogen bonded networks, and it was thus thought of interest to determine that of $(HOMe_2Si)_2O$.
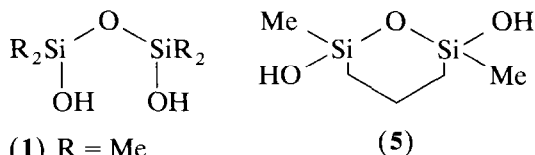
(1) R = Me
(2) R = ⁿPr
(3) R = ⁱPr
(4) R = Ph

(5)

(6)
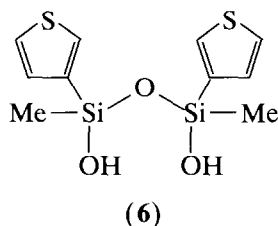
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2. Experimental details

2.1. Preparation of $(HOMe_2Si)_2O$

1,3-Dichlorotetramethyldisiloxane (101.5 g, 0.5 mol) was added dropwise during 1.5 h to a vigorously stirred mixture of diethyl ether (800 cm³), distilled water (800 cm³), ammonium carbonate (67.25 g, 0.7 mol) and dimethylaminopyridine (1 g) at 0°C in a three-necked flask. The mixture was stirred for a further 60 min then saturated with sodium chloride, and the ethereal layer separated then dried over $CaCl_2$. The ether was then removed by evaporation and the resulting solid was crystallized from Et_2O/hexane to give $(HOMe_2Si)_2O$ as a colourless solid (54.4 g, 63%), m.p. 67–67.5°C, ^{29}Si NMR (C_6D_6) −12,56 ppm. Crystals suitable for X-ray crystallography were obtained from an Et_2O/toluene solution. A crystal of dimensions 0.3 × 0.2 × 0.1 mm, sealed in a thin-walled capillary was used for the structure determination.

2.2. Crystal data

$C_4H_{14}O_3Si_2$, M 166.3, monoclinic, space group $P2_1/n$, $a = 8.512(3)$, $b = 5.821(2)$, $c = 19.407(6)$ Å, $\beta = 91.95(2)°$, $U = 961.0(6)$ Å³, $D_c = 1.150$ g cm⁻³ for $Z = 4$, $F(000) = 360$, monochromated Mo-Kα radiation, μ(Mo-Kα) 0.313 mm⁻¹, λ(Mo-Kα) = 0.71073 Å, $T = 234$ K, crystal size 0.3 × 0.2 × 0.1 mm³.

Data were collected using a Siemens R3m/V diffractometer with graphite monochromator. Cell di-

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\mathring{A}^2 \times 10^3$) for (HOMe₂Si)₂O with estimated standard deviations in parentheses

	x	y	z	U_{eq} [a]
Si(1)	5151(2)	926(4)	8473(1)	42(1)
Si(2)	2389(2)	3898(4)	8927(1)	45(1)
O(3)	4099(5)	−799(8)	7974(2)	57(2)
O(2)	2303(6)	5420(9)	8213(2)	57(2)
O(1)	4004(5)	2410(9)	8961(2)	51(2)
C(4)	6438(8)	−886(13)	9027(3)	60(3)
C(2)	2370(9)	5780(13)	9682(3)	71(3)
C(3)	6239(8)	2873(14)	7919(3)	61(3)
C(1)	683(8)	1939(15)	8870(4)	70(3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

mensions were obtained from centred reflections in the range $2\theta = 14–30°$. A total of 2014 reflections were measured to $2\theta = 50°$ using $\theta–2\theta$ scans in the ranges $-1 \leqslant h \leqslant 10$, $-6 \leqslant k \leqslant 6$, $-23 \leqslant l \leqslant 22$. There were 1696 independent reflections, $R_{int} = 0.09$, of which 800 satisfying the criterion $I > 3\sigma(I)$ were used in the refinement process. Three standard reflections were measured every 100 reflections and the crystal showed no significant decay during the data collection. The structure was solved by direct methods and refined by full matrix least squares on F using SHELXTL PLUS88 [1]. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were placed in calculated positions and allowed to ride on their respective parent atoms with fixed isotropic thermal parameters. A weighting scheme of the form $w^{-1} = \sigma^2(F) + 0.0018F^2$ was used in the refinement. At convergence, $R = 0.063$, $wR = 0.078$ ($R = 0.13$, $wR = 0.10$ for all data), $S = 1.34$ for 82 parameters (data parameter ratio 9.8:1), largest $\Delta/\rho = 0.001$. The maximum and minimum peaks observed in the final difference were 0.43 e $\mathring{A}^{-3}$ and -0.36 e $\mathring{A}^{-3}$, respectively.

Final atom coordinates, bond lengths and angles, together with details of the hydrogen-bonding in

TABLE 2. Intramolecular distances ($\mathring{A}$) and angles (°) in (HOMe₂Si)₂O with estimated standard deviations in parentheses

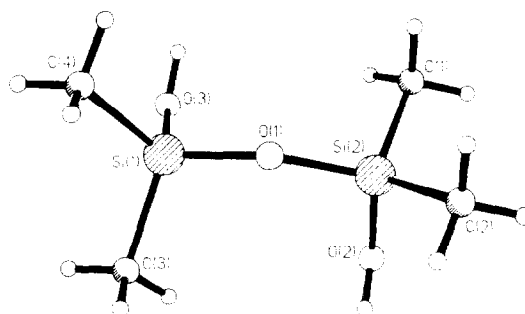| Si(1)–O(3)	1.640(5)	Si(1)–O(1)	1.631(5)
Si(1)–C(4)	1.841(7)	Si(1)–C(3)	1.835(8)
Si(2)–O(2)	1.643(5)	Si(2)–O(1)	1.624(5)
Si(2)–C(2)	1.831(7)	Si(2)–C(1)	1.847(8)
O(3)–Si(1)–O(1)	110.0(2)	O(3)–Si(1)–C(4)	107.2(3)
O(1)–Si(1)–C(4)	108.7(3)	O(3)–Si(1)–C(3)	108.0(3)
O(1)–Si(1)–C(3)	109.7(3)	C(4)–Si(1)–C(3)	113.2(3)
O(2)–Si(2)–O(1)	109.6(2)	O(2)–Si(2)–C(2)	110.5(3)
O(1)–Si(2)–C(2)	108.5(3)	O(2)–Si(2)–C(1)	105.7(3)
O(1)–Si(2)–C(1)	109.6(3)	C(2)–Si(2)–C(1)	112.9(4)
Si(1)–O(1)–Si(2)	141.4(3)		

Fig. 1. The molecular structure of (HOMe₂Si)₂O, together with the atom numbering scheme.

(HOMe₂Si)₂O are given in Tables 1 and 2. Lists of temperature factors and structure factors are available from the authors.

3. Results and discussion

The molecular structure of 1 together with the atom numbering scheme is shown in Fig. 1 and the hydrogen bonded chain formation is shown in Figs. 2 and 3.. The structure comprises siloxane molecules hydrogen bonded together to form chains which are further linked by hydrogen bonds to form double chains. There are two different hydrogen bonds present (see Fig. 2), one type, e.g. O(2a) ··· O(3b), that joins the molecules into long chains and a second type, e.g. O(3a) ··· O(2f), that connects pairs of chains to form double chains, the O ··· O distances being 2.728 and 2.656 $\mathring{A}$, respectively. There are no hydrogen bonds between the double chains. The hydrogen bonded O ··· O distances are similar to those found in other disiloxane diols; 2.66–2.77 $\mathring{A}$ in 2 [2], 2.719–2.849 in 3 [3], 2.651–2.795 [4] and 2.641–2.798 $\mathring{A}$ [5] (two separate structural determinations) in 4, 2.72–2.78 $\mathring{A}$ in 5 [6] and 2.702–7.741 $\mathring{A}$ in 6 [7]. The Si–O–Si angle in 1 is 141.5(3)°, which is within the range commonly found in siloxanes [8] but is smaller than those in 2, 3, 4 and 6, which average between about 155–164°, and is also smaller than that (149.6°) in the pyridinium chloride adduct of 4 in which both OH groups are hydrogen bonded to the chloride ion [9]. The cyclic compound 5, however, has Si–O–Si angles of 129.8° and 132.3° (two crystallographically
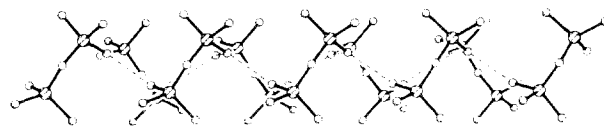

Fig. 2. View of the hydrogen bonded chains formed by (HOMe₂Si)₂O. Hydrogen bonds are represented by dashed lines and hydrogen atoms are omitted for clarity.
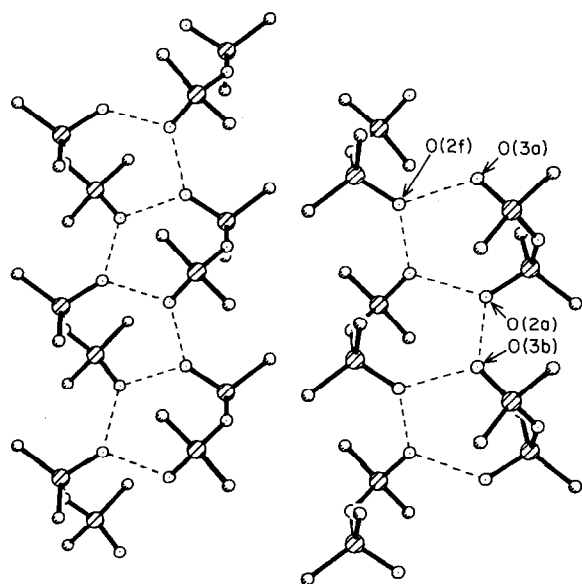
Fig. 3. View of the hydrogen bonded chains formed by (HOMe$_2$Si)$_2$O. Hydrogen bonds are represented by dashed lines and hydrogen atoms are omitted for clarity.

independent molecules are present in the lattice) which is presumably due to the constraints imposed by the ring structure [6].

The hydrogen bonded networks for the dihydroxy-disiloxanes 1–6 are shown in schematic form in I–IV (where only the OH oxygen atoms are shown for clarity). Network I is adopted by compounds 1, 2 and 4, network II by 3, network III by 5, and network IV (drawn after analysis of data in ref. 6) by 6. Networks I–III are all chains but differ in the relative positions of the two sides within each chain with respect to each other, whereas IV forms a sheet structure with alternating seven- and seventeen-membered rings.
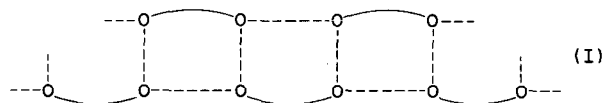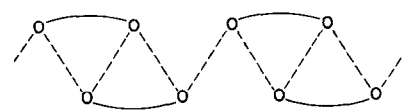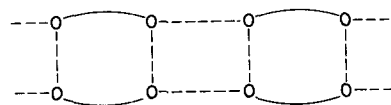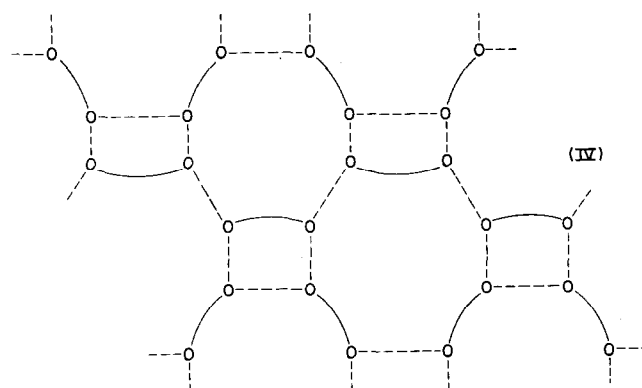

The solid state structure of 1 has been investigated previously by both X-ray and IR spectroscopic methods. Powder X-ray diffraction data [10] and unit cell data [11] for 1 were reported 30 years ago, the unit cell data being in good agreement with those reported here. The needle-like nature of 1 was also noted [11,12]. A detailed IR spectroscopic study of 1 in the solid state [12] assumed an Si–O–Si angle of 145° and indicated that the configuration of the molecules could be defined by the angle between one of the Si–OH bonds and the plane occupied by the other OH oxygen atom and the two silicon atoms. This angle was estimated to be "about 70°", which is in good agreement with the corresponding value of 75.2° found in this work. The corresponding angles in 4 and 6 are 68.6° and 86.9°, respectively, which suggests that this orientation of OH groups in disiloxanediols is a common feature.

Acknowledgements

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