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A new structural type of liquid crystal

Crystal structures and thermotropic mesophases of dihydroxytetraalkyldisiloxanes: columnar phases with hydrogen bonded assemblies

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Previous structural investigations of mesogenic organosilicon compounds (1,3-dihydroxytetraalkyldisiloxanes, $[R_2(OH)Si]_2O$, $R=C_nH_{2n+1}$) which form thermotropic phases are outlined. The crystal and molecular structure determination of a non-mesogenic member of this series $[Me_2(OH)Si]_2O$ is described. It is inferred that the mesophases formed by this family of compounds belong to a new structural type with columnar stacks of the molecules laced together with hydrogen bonds.

1. Introduction

Classical thermotropic mesogens are composed of rod-like or disc-like molecules. Recently, however, some novel mesophases have been found, for example, built of bowl-like mesogens molecules [1, 2]. Similarly, new chemical types of mesogens have also been identified such as Schiff's base complexes of transition metals [3–5].

One example of a mesogen with unconventional chemical and structural properties is di-isobutylsilanediol. This compound was first prepared and recognized as a mesogen as early as 1952 [6]. In a re-examination in 1982 [7] the mesophase was characterized as discotic and it was suggested that the structural units of the mesophase were hydrogen-bonded dimers stacked in columns. It is now thought that the mesophase consists of hydrogen-bonded trimers [8].

Recently, we have found a new series of organosilicon compounds (1,3-di-hydroxytetraalkyldisiloxanes $[R_2(OH)Si]_2O$, $R=C_nH_{2n+1}$, $n\geqslant 2$) which form thermotropic liquid-crystalline phases [9–11]. These compounds were studied by differential scanning calorimetry and polarizing microscopy [9, 11]. The transition temperatures and enthalpy changes are listed in table 1. The optical textures of compounds II–IV are similar to those of discotics. The X-ray diffraction patterns of mesophases II–IV show that they are built of hexagonally arranged molecular columns [9].

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Table 1. Transition temperatures T and enthalpies of transition ΔH (J mol^{-1}) in dihydroxytetraalkyldisiloxanes $[R_2(OH)Si]_2O$.

		C→LC		LC→I		C→I	
	R	*T*/°C	Δ*H*	*T*/°C	Δ*H*	*T*/°C	Δ*H*
I	Me	—	—	—	—	64·5–66·0	†
	Et	−36·0	8332·5	37·0	2599·7	—	—
III	*n*-Pr	35·0	8151·3	64·0	5814·4	—	—
IV	*n*-Bu	17·7‡	7151·9‡	53·5	5714·8	—	—

† Not measured.
‡ Transition solid mesophase (1)→mesophase (2).

Table 2. Crystal data for I.

Molecular formula	$C_4H_{14}O_3Si_2$
Crystal size/mm	0·2 × 0·2 × 0·4
Crystal system	Monoclinic
Space group	$P2_1/n$
Temperature/K for data collection	153 ± 2
Cell dimensions:	
a/Å	8·442(4)
b/Å	5·792(3)
c/Å	19·308(9)
β/°	91·67
Volume/Å^3	943·7(8)
Z	4
Data collection range	$2° < 2\theta < 50°$
Total reflections measured	1624 ($\pm h, k, l$)
Reflections used in refinement ($I > 2\sigma$)	1342
R	0·028
R_w	0·031

X-ray investigations of mesogneic crystals can provide very important information regarding the molecular conformation and packing. Since the dihydroxytetraalkyldisiloxanes are a new type of liquid crystal, the X-ray study of single crystals of mesogenic and non-mesogenic compounds of this series is valuable in the development of a model for mesophase structure as well as in the study of structural distinctions between mesogens and non-mesogens.

Previously we have investigated the crystal structures of compounds II and III [10, 12]. In the present paper the results of a structural investigation of compound I are reported.

2. Experimental

Crystals of I were grown from pentane solution to be used for X-ray analysis. A crystal was examined at 153 K on a Syntex $P2_1$ automatic diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0{\cdot}71069$ Å). The unit cell parameters were obtained by a least squares analysis of diffractometer angular settings of 24 well-centred reflections in the range $28° < 2\theta < 30°$. The structure was solved by the

Table 3. Coordinates (× 10^4) and isotropic thermal parameters ($Å^2$) of non-hydrogen atoms.

Atom	x/a	y/b	z/c	B_{iso}
Si(1)	168(1)	924(1)	2380(1)	1·84(2)
Si(2)	−2632(1)	3873(1)	3928(1)	1·96(2)
O(1)	−887(2)	−860(3)	2996(1)	2·79(5)
O(2)	−2702(2)	5397(3)	3212(1)	2·64(5)
O(3)	−991(2)	2401(3)	3975(1)	2·41(4)
C(1·1)	1460(3)	−897(5)	4036(1)	2·82(7)
C(1·2)	1266(4)	2939(5)	2931(2)	3·08(7)
C(2·1)	−4337(4)	1895(6)	3857(2)	3·65(9)
C(2·2)	−2684(4)	5785(6)	4691(1)	3·28(8)

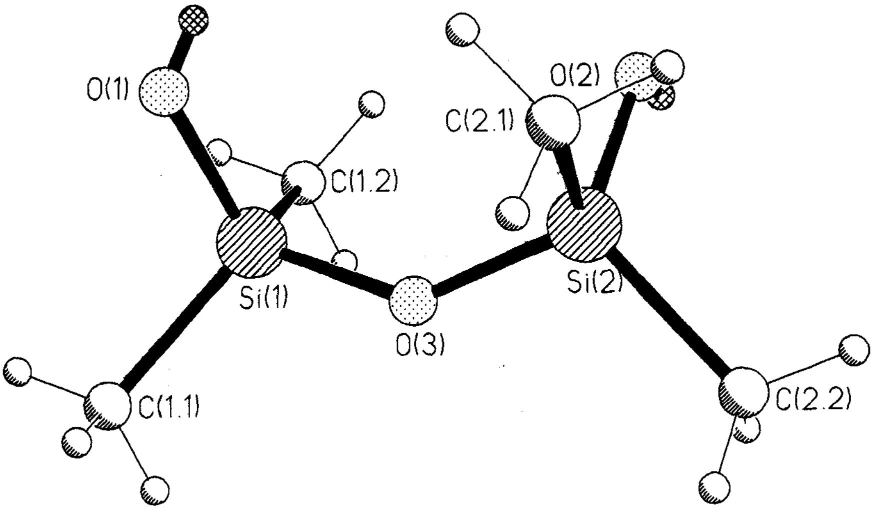


Figure 1. The X-ray structure of molecule I.

MULTAN method. The difference Fourier series revealed the positions of all the hydrogen atoms. The structure was refined by a full matrix least a squares method with anisotropic temperature factors for heavy atoms and isotropic temperature factors for the hydrogen atoms. Parameters relating to the data collection and refinement are summarized in table 2. The final atomic parameters are listed in table 3.

3. Results and discussion

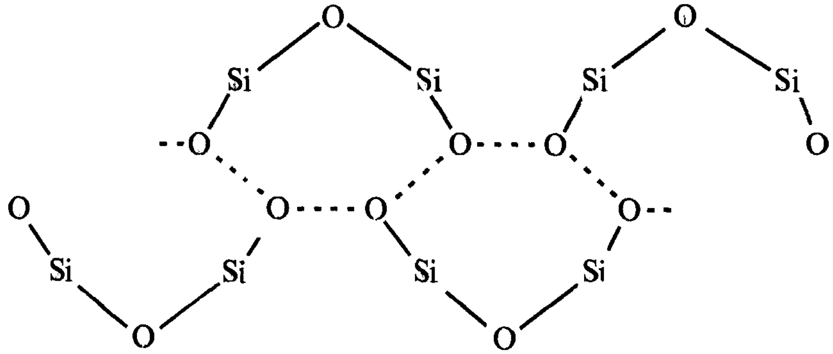
The structure of molecule I is shown in figure 1. Bond lengths and angles are presented in table 4, they are all typical of compounds of this type [13].

The crystal packing of I is shown in figures 2 (*a*), (*b*). The crystal is built of molecular chains in which the molecules are laced together with hydrogen bonds. Comparison of hydrogen bonding in the mesogenic crystals with R = Et (II) and *n*-Pr (III) [9, 11] and

Table 4. Bond lengths and bond angles for molecule I.

Bond lengths/Å		Bond angles/°	
Si(1)–O(1)	1·639(2)	O(1)Si(1)O(3)	109·0(1)
Si(1)–O(3)	1·630(2)	O(1)Si(1)O(1·1)	106·0(1)
Si(1)–C(1·1)	1·840(3)	O(1)Si(1)C(1·2)	110·2(1)
Si(1)–C(1·2)	1·845(3)	O(3)Si(1)C(1·1)	108·3(1)
Si(2)–O(2)	1·640(2)	O(3)Si(1)O(1·2)	109·0(1)
Si(2)–O(3)	1·627(2)	C(1·1)Si(1)O(1·2)	113·5(1)
Si(2)–O(2·1)	1·842(3)	O(2)Si(2)O(3)	109·8(1)
Si(2)–C(2·2)	1·844(3)	O(2)Si(2)C(2·1)	105·3(1)
		O(2)Si(2)C(2·2)	110·4(1)
		O(3)Si(2)C(2·1)	109·9(1)
		O(3)Si(2)C(2·2)	108·1(1)
		C(2·1)Si(2)C(2·2)	113·3(1)
		Si(1)O(3)Si(2)	140·1(1)

the non-mesogenic crystals with R = Me (I), Ph (V) [14] and *i*-Pr (VI) [15] shows that in I–III and V the hydrogen bonding schemes are similar



Although the crystal structures do not all have the same space group (I, $P2_1/n$, $Z=4$; II, $P2_1/n$, $Z=8$; III, $P\bar{1}$, $Z=12$; V, $P\bar{1}$, $Z=6$), they can all be regarded as distorted hexagonal arrangements of molecular columns in which the molecules are linked by hydrogen bonds. The cores of the aggregates are formed by polar oxygen containing groups and the external surfaces by non-polar hydrocarbon chains. The cylindrical assemblies in crystals I–III and V lie in pseudo-hexagonal arrays (see figure 2 (*b*)). The parameters of the hexagonal pseudo-cell of the mesogenic crystals II and III (which were grown directly from the mesophases (and of the hexagonal mesophases of II and III are similar ($a_{\mathrm{cryst}}(\mathrm{II}) = 10{\cdot}69$ Å, $a_{\mathrm{mes}}(\mathrm{II}) = 11{\cdot}10$ Å, $a_{\mathrm{cryst}}(\mathrm{III}) = 12{\cdot}66$ Å, $a_{\mathrm{mes}}(\mathrm{III}) = 12{\cdot}58$ Å [9–11]. The IR spectra of the mesophases and crystals of II and III are also similar [11] suggesting that the molecular arrangements in the mesophases and the crystals are virtually identical. This is a new type of mesophase structure and we propose the name columnar phases with hydrogen-bonded assemblies.

The possession of mesomorphic properties by compounds II and III is related to the liquid-like structure of the aliphatic external surface of the molecular columns. This liquid-like structure also manifests itself in the crystals by the presence of molecules in non-symmetry equivalent sites and in terms of the different conformationally and

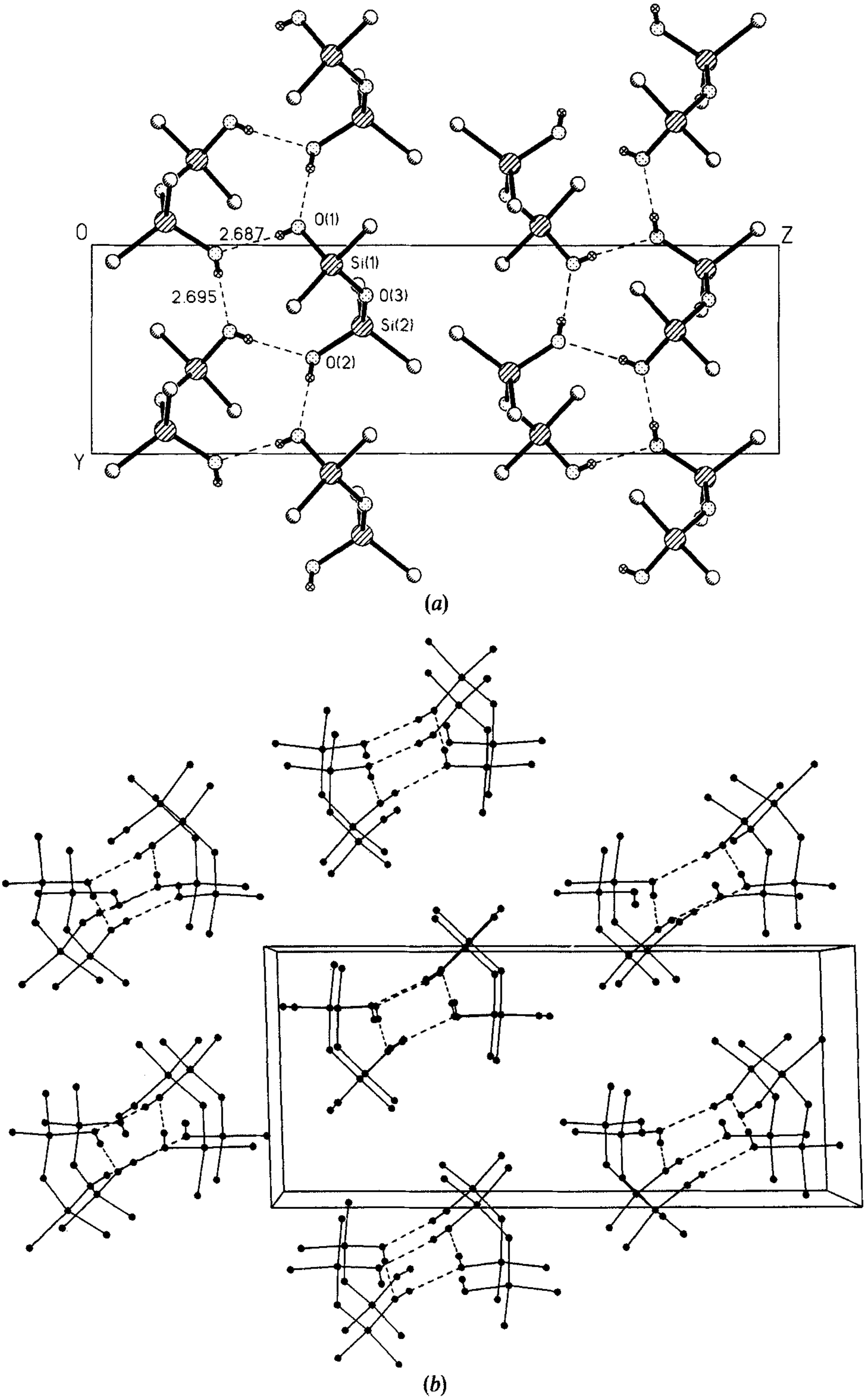


Figure 2. Packing diagrams of I showing molecular chains (columns) along the y axis. Hydrogen bonds are shown by broken lines.

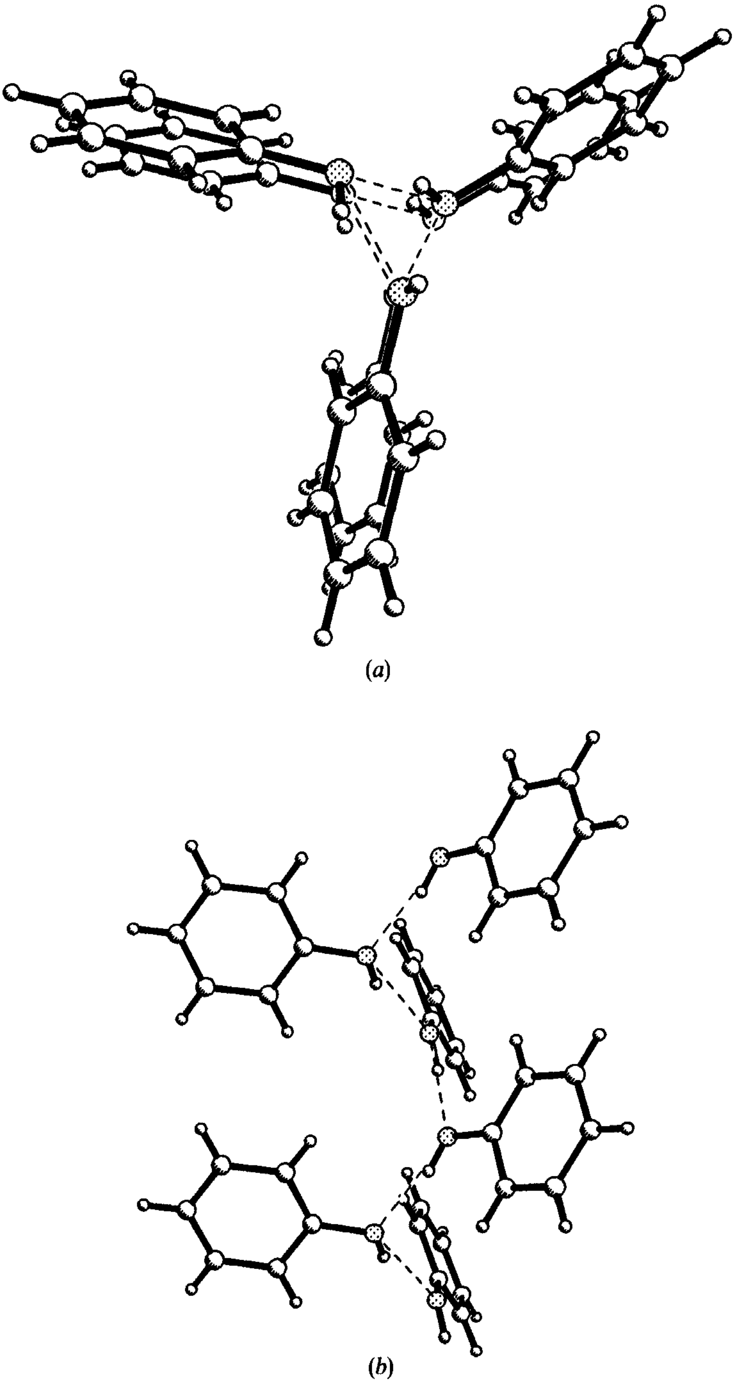
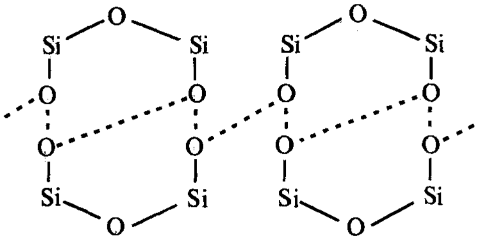


Figure 3. The crystal structure of a phenol derivative showing columns of molecules linked by hydrogen bonding (*a*) viewed down the column and (*b*) viewed normal to the molecular chains. Hydrogen bonds are shown by broken lines. (We predict that compounds of this type will prove to have similar mesogenic properties to the dihydroxytetraalkyldisiloxanes.)

orientationally disordered aliphatic substituents. The absence of mesomorphic properties in compounds I and V is, in our opinion, probably due to the rigidity of the surfaces of the molecular columns.

It seems that the absence of mesophase formation by compound VI is due to an alternative pattern of hydrogen bonding distinct from that found in compounds I–III, VI:



On the basis of our structural investigations of dihydroxytetraalkyldisiloxanes we suggest that other compounds which form extended hydrogen-bonded assemblies may form similar mesophases. Thus we predict that the 3-mono- or 3,4,5-trialkyl- or alkoxysubstituted phenols [16] which often form crystals with molecular chains of the type shown in figure 3 will exhibit similar mesogenic properties.

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