Journal of Organometallic Chemistry, 335 (1987) 157–166
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Structural precursors of poly(diphenylsilylene)

II *. Crystal and molecular structure of $HO(SiPh_2)_4OH$ and $HO(SiPh_2)_7OH$

Yu.E. Ovchinnikov, V.E. Shklover, Yu.T. Struchkov, V.V. Dement'ev*, **T.M. Frunze and B.A. Antipova**

Institute of Organoelement Compounds of USSR Academy of Sciences, 28 Vavilov St., Moscow, 117813 (U.S.S.R.)

(Received April 23rd, 1987)

Abstract

An X-ray diffraction study was carried out on $HO(SiPh_2)_4OH$ (I) and $HO(SiPh_2)_7OH$ (II), which were prepared from phenylcyclopolysilanes. H bonds, found in both cases, strongly affect the conformation of polysilane chain. The intramolecular H bond in crystal I ($O \cdots O$ 2.81 Å) closes the six-membered pseudocycle OSi_4O to give "chair" conformation, with one of the OH groups participating in the intermolecular H bond ($O \cdots O$ 2.75 Å). Two of these bonds link the molecules into the centrosymmetric dimer. In crystal II there are intermolecular H bonds linking the molecules into head-to-tail type chains ($O \cdots O$ distance of 2.78 Å, Si–Si–Si–Si torsion angles of 149–160°), and in addition there is an $O\text{–}H \cdots \pi$ intramolecular H bond formed by one of the two terminal OH groups with the π-system of the Ph ring (the distances from the O and H atoms to the Ph plane are 3.2 and 2.52 Å respectively). The Si-chain conformation of molecule II is intermediate between *trans*-planar and *gauche*, the chain is twisted and the degree of twisting increases steadily in both directions from the middle towards each chain end. The Si–Si bond lengths in I and II are 2.361–2.412 Å, the terminal bonds in the molecule II (av. 2.368 Å) are somewhat shorter than the others (av. 2.400 Å). In I the Si–Si–Si bond angles are 108.6 and 113.3°, in II the bond angle at the central Si atom is 118.9°, significantly exceeding other angles (109.6–111.7°).

---

* For part I see ref. 1.

Introduction

In a previous communication [1] we reported the crystal and molecular structure of 1,4-dichlorooctaphenyltetrasilane (III), representing the smallest oligomeric model of the poly(diphenylsilylene) $\lbrace SiPh_2 \rbrace_n$ (PDPS) chain. On the basis of the structure III and X-ray data on the crystalline PDPS it was suggested that the Si-chain of PDPS has a *trans*-planar structure. To elucidate the flexibility of polysilane chain and, in particular, to investigate the influence of polar interactions (H bonds) between the terminal groups on the chain conformation we carried out an X-ray diffraction study on the two PDPS oligomers with terminal OH groups, viz. $HO(SiPh_2)_4OH$ (I) and $HO(SiPh_2)_7OH$ (II). The first compound was prepared by octaphenylcyclotetrasilane cleavage with tetrachloroethane followed by hydrolysis of the 1,4-dichloro derivative formed [2]. Tetradecaphenylheptasilane-1,7-diol (m.p. 248–250 °C) (II) was prepared from 1,7-dichloroheptasilane, which, in turn, had been obtained from 1,5-dilithio-decaphenylpentasilane:

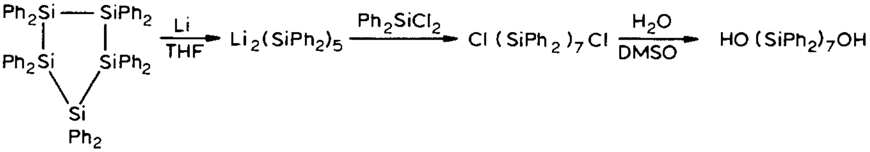

Table 1

Summary of crystal data for compounds I and II

	I	II
Diffractometer	Enraf–Nonius CAD-4	Hilger & Watts
Temp. (°C)	20	20
Irradiation	Mo-K_α	Mo-K_α
Monochromator	graphite	graphite
Scan, $2\theta_{max}$ (°)	θ/ω, 44	$\theta/2\theta$, 60
Cell parameters:		
a (Å)	13.346(3)	14.442(1)
b (Å)	20.930(4)	20.066(3)
c (Å)	15.663(2)	25.575(1)
β (°)	104.91(1)	95.573(4)
V (Å^3)	4228(1)	7376(1)
d_{calc} (g/cm^3)	1.20	1.18
Z	4	4
Space group	$P2_1/c$	$P2_1/c$
Number of reflections:		
measured	4946	9490
used in calculations	2862 ($I > 3\sigma$)	5005 ($I > 2.75\sigma$)
Solution method	direct (MULTAN)	direct (MULTAN)
Refinement method	Full-matrix least-squares	Block-diagonal least-squares
Number of refined parameters	655	1056
Final R-value	0.033	0.040
R_w-value	0.034	0.032
Computer	PDP-II/23	Eclipse S/200
Program	SDP-PLUS [9]	INEXTL [10]

Experimental

The main details of the X-ray diffraction experiment for I and II are given in Table 1. In both cases the H atoms of OH groups were located in the difference Fourier syntheses, the H atoms of Ph rings were placed in calculated positions and refined isotropically with the fixed thermal parameters $B_{iso} = 8$ Å^2 for I and 5 Å^2 for II. Though the electron density peaks identified as H atoms of OH groups were located at the normal distances of 0.75–1.0 Å from the respective O atoms, on refinement these distances decreased (particularly in structure I) to 0.4–0.5 Å. At the same time the thermal parameters of H atoms remained low enough ($B_{iso} = 6$–12 Å^2) and showed no tendency to increase. No other unrealistic geometry distortions were detected during refinement. The apparent shortening of O–H bonds is probably caused by an insufficient number of high-angle reflections, which is especially pronounced in the case of I. The atomic coordinates in structures I and II are given in Tables 2 and 3.

Table 2

Atomic coordinates ($\times 10^5$ for Si, $\times 10^4$ for C and O) in structure I [a]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Si(1)	59372(8)	3288(6)	16649(7)	C(22)	6935(5)	401(3)	5636(3)
Si(2)	66870(8)	−4017(6)	27983(7)	C(23)	7462(4)	−115(3)	5517(3)
Si(3)	83332(8)	−7156(6)	26249(7)	C(24)	7402(4)	−346(2)	4686(3)
Si(4)	82857(8)	−10516(6)	11648(7)	C(25)	9159(3)	27(2)	2843(2)
O(1)	5813(2)	−67(2)	737(2)	C(26)	9474(3)	289(2)	3681(3)
O(2)	7714(2)	−481(1)	478(2)	C(27)	10016(4)	865(3)	3819(3)
C(1)	6700(3)	1068(2)	1627(3)	C(28)	10223(4)	1184(2)	3131(4)
C(2)	7361(4)	1327(2)	2372(4)	C(29)	9944(4)	934(2)	2306(3)
C(3)	7889(4)	1896(3)	2335(5)	C(30)	9416(3)	360(2)	2163(3)
C(4)	7763(4)	2195(3)	1552(4)	C(31)	8948(3)	−1358(2)	3436(2)
C(5)	7138(5)	1963(3)	811(4)	C(32)	10003(3)	−1344(2)	3854(3)
C(6)	6587(4)	1392(3)	848(3)	C(33)	10461(4)	−1836(3)	4417(3)
C(7)	4626(3)	572(2)	1767(2)	C(34)	9887(5)	−2340(3)	4564(3)
C(8)	4459(3)	1185(2)	2034(3)	C(35)	8863(4)	−2363(3)	4170(4)
C(9)	3510(4)	1367(3)	2163(3)	C(36)	8389(4)	−1879(2)	3605(3)
C(10)	2716(3)	937(3)	2025(3)	C(37)	9643(3)	−1127(2)	1053(2)
C(11)	2855(3)	329(3)	1763(3)	C(38)	10397(3)	−1456(2)	1669(2)
C(12)	3798(3)	149(2)	1636(3)	C(39)	11408(3)	−1503(2)	1608(3)
C(13)	5736(3)	−1083(2)	2641(3)	C(40)	11685(3)	−1243(2)	917(3)
C(14)	5617(3)	−1505(3)	1949(3)	C(41)	10965(3)	−924(3)	289(3)
C(15)	4912(4)	−2003(4)	1826(4)	C(42)	9958(3)	−862(2)	360(3)
C(16)	4281(3)	−2067(2)	2379(4)	C(43)	7577(3)	−1818(2)	822(3)
C(17)	4353(4)	−1653(3)	3045(3)	C(44)	7864(3)	−2391(2)	1248(3)
C(18)	5067(3)	−1169(2)	3184(3)	C(45)	7327(4)	−2950(2)	961(3)
C(19)	6810(3)	−58(2)	3939(3)	C(46)	6493(4)	−2943(3)	251(4)
C(20)	6283(5)	474(3)	4077(3)	C(47)	6195(4)	−2386(3)	−179(4)
C(21)	6350(6)	708(4)	4920(4)	C(48)	6714(4)	−1826(2)	99(3)

[a] Tables of H atom coordinates and thermal parameters of the atoms are available from the authors on request.

Table 3

Atomic coordinates ($\times 10^5$ for Si, $\times 10^4$ for C and O, $\times 10^3$ for H) in structure II [a]

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Si(1)	19137(8)	22533(6)	52922(5)	C(40)	6964(3)	855(2)	4911(2)
Si(2)	35050(8)	19820(6)	52729(5)	C(41)	7123(3)	748(2)	5437(2)
Si(3)	44694(8)	28616(6)	56709(4)	C(42)	6784(3)	1183(2)	5788(2)
Si(4)	58868(7)	23978(6)	60823(4)	C(43)	5669(2)	2029(2)	6735(1)
Si(5)	72025(7)	31119(5)	62704(4)	C(44)	5401(3)	1368(2)	6795(2)
Si(6)	83154(7)	26413(6)	69254(4)	C(45)	5293(3)	1112(2)	7286(2)
Si(7)	98297(8)	30418(6)	68207(5)	C(46)	5422(4)	1496(3)	7725(2)
O(1)	1721(2)	2264(2)	5912(1)	C(47)	5684(3)	2149(2)	7679(2)
O(2)	10142(2)	2876(1)	6229(1)	C(48)	5796(3)	2405(2)	7187(2)
C(1)	1122(3)	1618(2)	4950(2)	C(49)	7870(2)	3191(2)	5676(1)
C(2)	475(3)	1289(2)	5226(2)	C(50)	8267(3)	2633(2)	5460(2)
C(3)	−178(4)	870(3)	4969(3)	C(51)	8818(3)	2680(2)	5047(2)
C(4)	−208(4)	755(3)	4447(3)	C(52)	8977(3)	3288(3)	4836(2)
C(5)	408(4)	1061(3)	4173(2)	C(53)	8583(4)	3842(3)	5029(2)
C(6)	1071(3)	1482(3)	4418(2)	C(54)	8026(3)	3794(2)	5438(2)
C(7)	1621(3)	3092(2)	4989(2)	C(55)	6876(2)	3969(2)	6501(1)
C(8)	1533(3)	3209(2)	4456(2)	C(56)	7551(3)	4468(2)	6591(2)
C(9)	1313(4)	3832(3)	4243(2)	C(57)	7336(3)	5069(2)	6813(2)
C(10)	1186(4)	4338(2)	4576(2)	C(58)	6468(3)	5183(2)	6954(2)
C(11)	1270(4)	4253(2)	5100(2)	C(59)	5783(3)	4711(2)	6868(2)
C(12)	1491(3)	3628(2)	5309(2)	C(60)	5995(3)	4108(2)	6640(2)
C(13)	3693(3)	1807(2)	4567(2)	C(61)	8150(3)	2850(2)	7628(1)
C(14)	3456(3)	1183(2)	4348(2)	C(62)	8637(3)	2485(3)	8020(2)
C(15)	3564(4)	1034(3)	3834(2)	C(63)	8597(4)	2640(3)	8543(2)
C(16)	3896(4)	1490(3)	3505(2)	C(64)	8075(4)	3153(3)	8689(2)
C(17)	4123(3)	2109(3)	3705(2)	C(65)	7594(3)	3528(3)	8315(2)
C(18)	4016(3)	2268(2)	4222(2)	C(66)	7636(3)	3382(2)	7789(2)
C(19)	3708(3)	1179(2)	5656(2)	C(67)	8355(3)	1693(2)	6875(2)
C(20)	3210(3)	1026(2)	6080(2)	C(68)	7814(3)	1298(2)	7168(2)
C(21)	3391(3)	436(2)	6366(2)	C(69)	7822(3)	605(2)	7110(2)
C(22)	4061(3)	8(2)	6231(2)	C(70)	8364(3)	312(2)	6778(2)
C(23)	4555(3)	147(2)	5818(2)	C(71)	8915(3)	684(2)	6483(2)
C(24)	4388(3)	726(2)	5527(2)	C(72)	8913(3)	1378(2)	6533(2)
C(25)	3819(3)	3265(2)	6187(2)	C(73)	10716(2)	2604(2)	7277(2)
C(26)	3528(3)	2906(2)	6602(2)	C(74)	11049(3)	2867(2)	7760(2)
C(27)	3051(3)	3196(3)	6989(2)	C(75)	11729(3)	2547(3)	8088(2)
C(28)	2849(3)	3862(3)	6961(2)	C(76)	12078(3)	1955(3)	7945(2)
C(29)	3116(3)	4233(2)	6567(2)	C(77)	11767(3)	1673(2)	7471(2)
C(30)	3594(3)	3948(2)	6176(2)	C(78)	11092(3)	1996(2)	7145(2)
C(31)	4696(3)	3509(2)	5162(2)	C(79)	9929(3)	3968(2)	6930(2)
C(32)	5577(3)	3657(2)	5032(2)	C(80)	9621(3)	4278(2)	7374(2)
C(33)	5726(3)	4115(3)	4648(2)	C(81)	9676(3)	4966(3)	7441(2)
C(34)	4983(4)	4436(3)	4386(2)	C(82)	10035(4)	5333(2)	7064(3)
C(35)	4109(3)	4310(3)	4502(2)	C(83)	10347(4)	5052(3)	6629(2)
C(36)	3964(3)	3847(2)	4887(2)	C(84)	10289(3)	4367(2)	6563(2)
C(37)	6285(2)	1755(2)	5618(1)	H(O1)	124(2)	243(2)	601(1)
C(38)	6134(3)	1847(2)	5080(2)	H(O2)	981(2)	289(2)	600(1)
C(39)	6460(3)	1400(2)	4729(2)				

---

[a] Tables of H atom coordinates of Ph rings and thermal parameters of the atoms are available from the authors on request.

Results and discussion

The results of the present study turned out to be somewhat unexpected. Generally, good flexibility of the polysilane chain even with bulky Ph substituents is not surprising. As the Si–Si–Si bond angle is close to the tetrahedral value of 109.5° and the normal Si–Si bond length is ca. 2.38 Å, the resulting shortest nonbonded Si · · · Si distance of ca. 4.0 Å allows such substituents as Me and Ph to be arranged along the planar transoid Si-chain without mutual Van der Waals contacts. Certainly such contacts can occur in other chain conformations but in the known structures of perphenylcyclopolysilanes $(Ph_2Si)_n$ ($n = 4, 5, 6$) beginning with $n = 6$ the cycle [3] (designated below as IV) is almost unstrained because the Si–Si–Si bond angles of 113.8° (av.) exceed the tetrahedral value and approach the value of 115.8° observed in the linear molecule III [1]. Steric overcrowding does not arise because the cycle conformation (centrosymmetric chair) provides a possibility of a staggered arrangement of Ph rings at the adjacent Si atoms.

In structure I such conformation is observed in the acyclic molecule (Fig. 1). In fact the $(SiPh_2)_4$ chain in I has the structure of a Si_4 "half-cycle" observed in structure IV [3]. Indeed, the Si(1)–Si(2)–Si(3)–Si(4) torsion angle of 53° in I (Table 4) is close to the corresponding angle of 47.5° in IV; even comparison of drawings of the molecules I and IV confirms a similarity in Ph substituent orientations. One of the two Si–Si–Si bond angles in I (at Si(3)) is close to the corresponding angle in IV (113.3 vs. 114.5°), another angle (at Si(2)) is slightly smaller (108.6 vs. 113.2°). The pseudocyclic conformation of the molecule I is evidently governed by the

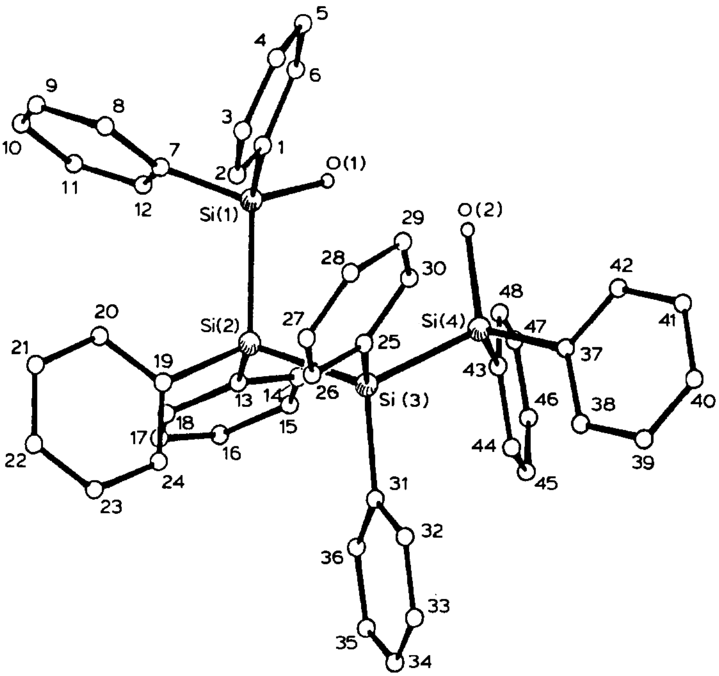

Fig. 1. General view of molecule I, H atoms have been omitted for clarity.

Table 4

Main bond lengths (Å), bond angles and torsion angles (°) in molecule I [a]

Si(1)–Si(2)	2.361(2)	O(1)–Si(1)–Si(2)	105.4(1)
Si(2)–Si(3)	2.375(2)	Si(1)–Si(2)–Si(3)	108.59(6)
Si(3)–Si(4)	2.378(2)	Si(2)–Si(3)–Si(4)	113.29(5)
Si(1)–O(1)	1.643(3)	Si(3)–Si(4)–O(2)	107.8(1)
Si(4)–O(2)	1.656(3)		
Si(1)–C(1)	1.860(5)	O(1)–Si(1)–Si(2)–Si(3)	−50 [b]
Si(1)–C(7)	1.869(4)	Si(1)–Si(2)–Si(3)–Si(4)	+53
Si(2)–C(13)	1.882(4)	Si(2)–Si(3)–Si(4)–O(2)	−50
Si(2)–C(19)	1.893(4)	Si(3)–Si(4)–O(2) ··· O(1)	+69
Si(3)–C(25)	1.884(4)	Si(4)–O(2) ··· O(1)–Si(1)	−62
Si(3)–C(31)	1.887(4)	O(2) ··· O(1)–Si(1)–Si(2)	+61
Si(4)–C(37)	1.870(4)		
Si(4)–C(43)	1.868(4)		

[a] C–C bond lengths of 1.328–1.412, e.s.d.'s of 0.005–0.009 Å, other bond angles at Si atoms are 104.5–115.6°, the Si–Si–C angles have maximum deviations from tetrahedral. [b] E.s.d.'s of torsion and pseudotorsion angles are less than 1°.

intramolecular H bond O(1) ··· H(O2)–O(2), as in the analogous compound III with terminal Cl substituents, the *trans*-planar chain conformation is realized and replacement of the Cl atoms by the OH groups probably cannot significantly influence the energy ratio of different conformations if the H bonds are not taken into account. The intramolecular H bond in I is of average strength, judging from its geometrical parameters, viz. the O(1) ··· O(2) distance of 2.808(4) Å and linearity of the O–H ··· O grouping (the latter may be assumed in spite of the low accuracy of the H(O2) atom localization, as no shortened contacts prevent its disposition on the O(1) ··· O(2) line, with the Si(4)–O(2)–H(O2) bond angle has a normal value of 116°). Assuming the bond distance O(2)–H(O2) to be equal to 0.96 Å which according to the correlation proposed in [4] corresponds approximately to the observed O(1) ··· O(2) distance and employing the empirical potential given in [5], the energy of the discussed H bond would be estimated as ca. 5 kcal/mol. This value markedly exceeds the energy difference between the *trans* and *gauche* conformations of the acyclic molecule $Me(SiMe_2)_5Me$ of 0.9 kcal/mol, from empirical force field calculations [6]. It is possible that the perphenylated Si-chain is still more flexible than the permethylated one owing to the possibility of different Ph ring rotations around the Si–Ph bonds, i.e. because of their different orientations relative to the Si atoms coordination planes.

A significant energy gain (no less than ca. 4 kcal/mol) is as yet not enough for formation of the intramolecular H bond proposed. This bond closes the six-membered pseudocycle and its length has to correspond to the conditions of cycle closure without significantly changing the usual molecular geometry. It has been shown that the "silicon" part of the pseudocycle apparently assumes the most favourable conformation with minimum strain. The pseudocycles geometrical parameters (Fig. 2) correspond to the "chair" conformation with the approximately equal bending of the Si(1)O(1)O(2) and Si(2)Si(3)Si(4) moieties from the central planar part of the pseudocycle. The mean value of the endocyclic torsion angles is 57.5°, i.e. 10° greater than in the symmetrical Si_6 cycle of molecule IV.

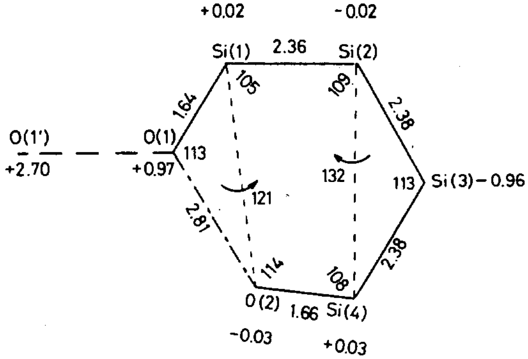

Fig. 2. Geometrical parameters of the pseudocycle in I (distances in Å, angles in °). The deviations of atoms from the mean plane fragment Si(1)Si(2)Si(4)O(2) and the dihedral angles between this plane and the Si(1)O(1)O(2) and Si(2)Si(3)Si(4) moieties are shown. The O(1) and O(1′) atoms are linked by the H bond across the symmetry centre.

In the crystal structure I there are also intermolecular H-bond pairs linking the molecules into dimers at the inversion centres of the type $\frac{1}{2}$ 0 0 (Fig. 3a). The intermolecular distance O(1) ··· O(1′) of 2.745(4) Å is shorter than the intramolecular O(1) ··· O(2) distance, but to estimate the H-bond strength correctly it is important to know the O ··· H interaction distance. As was pointed out in Experimental the H atoms that participate in H bonds were located with low accuracy, in particular the O(1)–H(O1) bond distance of 0.42(3) Å is too short. However, assuming the bond length O(1)–H(O1) to be equal to the more realistic experimental value of the O(2)–H(O2) bond length of 0.96 Å, and the H(O1) ··· H(O1′) contact distance to be equal to ca. 2.0 Å, we obtain r(O(1) ··· H(O1)) 2.2 Å. According to [6], this value corresponds to a H-bond energy of ca. 1 kcal/mol and to a H-bonds pair energy of ca. 2 kcal/mol. Apparently, this is a reasonable upper limit, because shortening the O(1) ··· H(O1) distance to 2.0 Å, i.e. increasing of the energy of H-bond pair to ca. 4 kcal/mol would result in an unrealistically short H(O1) ··· H(O1′) contact of ca. 1.5. Å.

As can be seen from Fig. 2 the dimeric associates of the molecules I, which are formed by H-bond pairs, have a transoid structure, viz. the pseudocycles are turned to each other by their Si(1)–O(1)–O(2) angles. The relatively weak intermolecular H

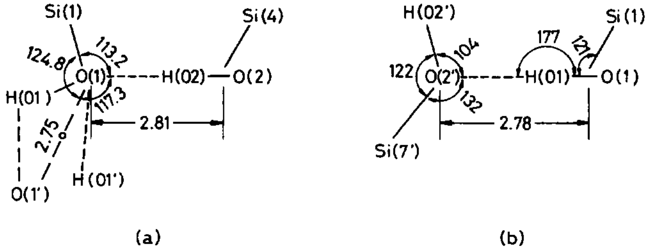

Fig. 3. Geometric parameters of H bonds in the structures I(a) and II(b). Primed atoms are related to corresponding atoms of the reference molecule by the transformations $1-x$, $-y$, $-z$ (a) and $-1+x$, y, z (b).

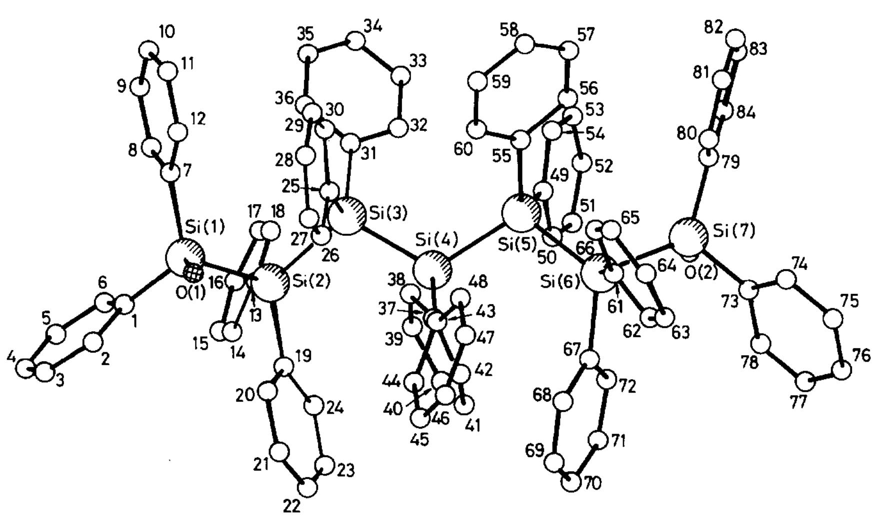

Fig. 4. General view of the molecule II (projection onto the Si(3)Si(4)Si(5) plane). The H atoms have been omitted for clarity.

bond cannot influence significantly the molecular geometry of I but the mutual arrangement of molecules in the dimer can be governed to some extent by the tendency of O(1) to acquire planar coordination. Indeed, O(1) deviation from the Si(1)O(2)O(1′) plane is not large (0.28 Å) and its deviation from the Si(1)H(O1)H(O2) plane is even smaller (0.03 Å, though this value is not reliable enough).

The Si-chain conformation of molecule II (Fig. 4) is in between *trans*-planar (in III) and *gauche* (in I). The chain is twisted symmetrically in one direction relative to the central Si(4) atom and the degree of twist increases steadily in both directions from the middle towards each chain end: the torsion angles around the central Si–Si bonds are 160° vs. 153–149° around the bonds that are more distant from the middle of the chain (Table 5). The Si(1)Si(2) ··· Si(6)Si(7) pseudotorsion angle, which defines an integral twist, is equal to −127°. In the case of *trans*-planar conformation this angle should be zero (the odd number of atoms in the chain). As a whole the molecule has an approximate two-fold symmetry axis, lying on the mean Si-chain plane and passing through Si(4) normal to the molecular long axis.

In crystal II as well as in crystal I both intra- and inter-molecular H bonds were found. The H(O2) atom is involved in the O(2)–H(O2) ··· π intramolecular H bond with the π-system of the C(49) ··· C(54) Ph ring, the H(O2) ··· C(Ph) distances varying from 2.90 Å (H(O2) ··· C(49) to 3.36 Å (H(O2) ··· C(54)). The distances from O(2) and H(O2) atoms to the Ph plane are equal to 3.2 and 2.52 Å, respectively. The Si(7)–O(2) and O(2) ··· H(O2) vectors are inclined to the Ph plane by 20.2 and 74.7° respectively.

Molecules II in crystal are linked by intermolecular head-to-tail type H bonds O(1)–H(O1) ··· O(2), thus forming infinitely long chains along the *a*-axis.

In view of the geometrical parameters of these bonds (Fig. 3b) it can be concluded that their energy is not less than the energy of the intramolecular H-bond in I, i.e. ca. 5 kcal/mol (according to ref. 5). Taking into account the great flexibility

Table 5

Main bond lengths (Å), bond angles and torsion angles (°) in molecule II [a]

Si(1)–Si(2)	2.367(2)	Si(1)–Si(2)–Si(3)	110.18(6)
Si(2)–Si(3)	2.412(2)	Si(2)–Si(3)–Si(4)	109.55(6)
Si(3)–Si(4)	2.397(2)	Si(3)–Si(4)–Si(5)	118.93(6)
Si(4)–Si(5)	2.391(2)	Si(4)–Si(5)–Si(6)	111.71(6)
Si(5)–Si(6)	2.400(2)	Si(5)–Si(6)–Si(7)	110.53(6)
Si(6)–Si(7)	2.369(2)	O(1)–Si(1)–Si(2)	106.3(1)
Si(1)–O(1)	1.635(3)	Si(6)–Si(7)–O(2)	111.9(1)
Si(7)–O(2)	1.654(3)		
O(1)–H(O1)	0.82(3)	O(1)–Si(1)–Si(2)–Si(3)	−66 [b]
O(2)–H(O2)	0.72(3)	Si(1)–Si(2)–Si(3)–Si(4)	+149
		Si(2)–Si(3)–Si(4)–Si(5)	+160
		Si(3)–Si(4)–Si(5)–Si(6)	+160
		Si(4)–Si(5)–Si(6)–Si(7)	+153
		Si(5)–Si(6)–Si(7)–O(2)	−58
		Si(1)–Si(2) ··· Si(6)–Si(7)	−127
		O(1)Si(1) ··· Si(7)–O(2)	+169

[a] Si–C bond lengths of 1.867–1.909 Å, e.s.d.'s of 0.004 Å, C–C 1.335–1.407 Å, e.s.d.'s 0.005–0.008 Å; the other bond angles at Si atoms are 103.6–116.1°, the Si–Si–C angles have maximum deviations from tetrahedral value. [b] E.s.d.'s of the torsion and pseudotorsion angles are less than 1°.

of the $(SiPh_2)_n$ chain such bonds can certainly cause the observed deviation of its conformation from the *trans*-planar geometry. The increasing of the degree of molecular twist towards the Si-chain ends together with a generally favourable arrangement of the molecules II related by the *a*-translation (in Fig. 3b the mean Si-chain plane is approximately normal to the paper) account for the distortion of planarity the nonequivalence of the O atoms (O(1) is a proton donor, O(2) is a proton acceptor) and other packing effects make the molecule somewhat asymmetrical, whereas with terminal substituents such as Cl the molecule should acquire the more precise C_2 symmetry.

The Si–Si bond lengths in the molecules I and II (2.361–2.412(2) Å, Tables 4 and 5) are usual for perphenylated polysilanes [3]. It should be noted that the two terminal Si–Si bonds in II are noticeably shorter than the other four, the mean values being 2.368 and 2.400 Å. This effect is not observed in shorter chains of molecules I and III, where the Si–Si distances vary by only 0.02 Å. The Si–O(H) bond lengths of 1.635–1.656 (3) Å in I and II are not unusual, e.g. in $Ph_2Si(OH)_2$ [7] their average value is 1.633(1) Å. As was mentioned before, in I the O–H bond lengths are unrealistically shortened, whereas in II their observed values of 0.72 and 0.82(3) Å as well as the Si–O–H bond angles of 121(2)° are more realistic and closer to the values typical of silanol groups in the structures determined from X-ray diffraction data [8].

The Si–Si–Si bond angles vary still more in II than in I, viz. the angle at the central Si(4) atom of 118.9° considerably exceeds the others which remain within the limits (109.6–111.7° (Table 5)) and this difference is not caused by steric interactions, as carbon atoms of the Ph substituents at Si(3) and Si(5) have no contacts shorter than 3.5 Å. Thus, the great variety of Si–Si–Si angles is the result of a general energetic favourability of the observed molecular geometry and indicates a rather small force constant for these angles.

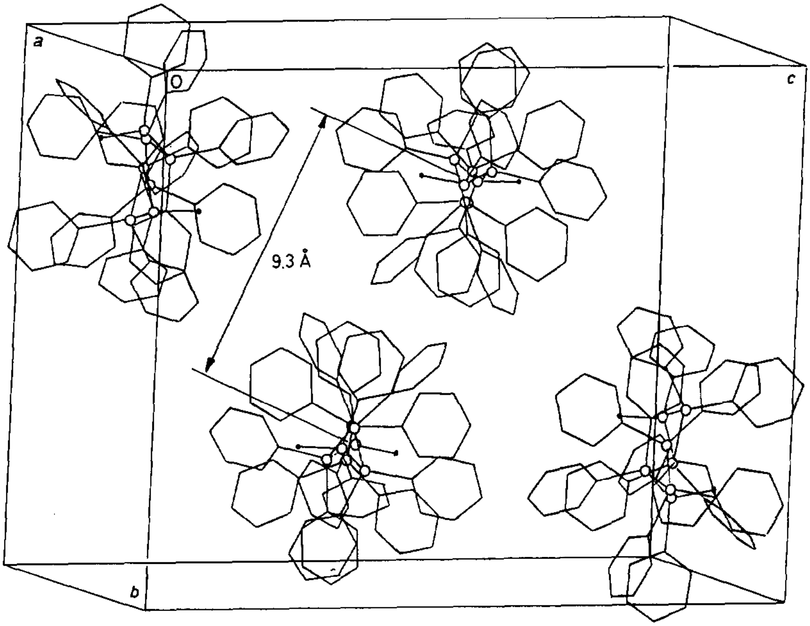

Fig. 5. Arrangement of the molecules II in the unit cell in the projection along the axes of the molecules forming the closest contact. The angle between this direction and the axes of two other molecules is ca. 15°. The Si atoms are light circles, the O atoms are black circles.

Because of the great twist of the Si-chain molecule II cannot be considered to be a fully adequate model of the PDPS fragment. Nevertheless it is clear that this twist only weakly influences the general form of the molecule contact surface which is made up of Van der Waals atomic spheres and is represented as a cylinder with comparatively shallow dents and ridges. A cross section of the molecule shows it to be almost round (Fig. 5) where arrangement of the molecules II in the unit cell is shown. The molecules, related by the inversion centre $\frac{1}{2}\frac{1}{2}\frac{1}{2}$ and having parallel axes with the closest contact on the side surfaces, are separated by an interaxial distance of ca. 9.3 Å. It is to be expected that approximately the same interchain distances exist also in crystalline PDPS and that these distances cannot be much shorter than the value given.

References

1 V.V. Korshak, Yu.E. Ovchinnikov, V.V. Dement'ev, V.E. Shklover, Yu.T. Struchkov and T.M. Frunze. Dokl. Acad. Nauk, USSR, 293 (1987) 140.
2 G.R. Chainani, S. Cooper and H. Gilman, J. Org. Chem., 28 (1963) 2146.
3 M. Drager and K.G. Walter, Z. Anorg. Allg. Chem., 479 (1981) 65.
4 G. Chiari and G. Ferraris, Acta Cryst., B, 38 (1982) 2331.
5 G.N. Sarkisov and V.G. Dashevski, J. Struct. Chim., 13 (1972) 199.
6 J.R. Damewood, Jr. and R. West, Macromolecules, 18 (1985) 159.
7 J.K. Fawcett, N. Camerman and A. Camerman, Can. J. Chem., 55 (1977) 3631.
8 V.E. Shklover, I.L. Dubchak and Yu.T. Struchkov, J. Struct. Chim., 22 (1981) 104.
9 B.A. Frenz, in H. Schenk, R. Olthof-Hazelkamp, H. van Konigsveld and G.C. Bassi (Eds.), Computing in Crystallography. Delft University Press, Delft, Holland, 1978, p. 64.
10 R.G. Gerr, A.I. Janovski and Yu.T. Struchkov, Kristallographia, 28 (1983) 1029.