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Linear Si—O—Si Fragments: Structure of 1,1,3,3-Tetramethyl-1,3-bis[(2-oxo-1-pyrrolidinyl)methyl]disiloxane Dihydrochloride and Analysis of Displacement Parameters

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Abstract

An X-ray diffraction study of 1,1,3,3-tetramethyl-1,3-bis[(2-oxo-1-pyrrolidinyl)methyl]disiloxane di-
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hydrochloride, $C_{14}H_{30}N_2O_3Si_2^{2+}.2Cl^-$, $M_r = 357 \cdot 1$, has been carried out at 120 K. The crystal is monoclinic, space group $P2_1/n$, $Z = 2$; the cell dimensions at 120 K are $a = 11 \cdot 116\,(3)$, $b = 8 \cdot 176\,(3)$, $c = 12 \cdot 138\,(6)$ Å, $\beta = 114 \cdot 34\,(3)°$, $V = 1005 \cdot 1$ Å³.

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Weighted least-squares refinement based on 1885 reflections converged at $R = 0.031$. The crystal is built of linear centrosymmetric disiloxane dications and Cl$^-$ anions bonded to the dications by strong O—H···Cl hydrogen bonds. Some aspects of the atomic motion and small deviations from standard geometry in the dication may be interpreted as indicating a weak Si···O interaction. Analysis of the displacement parameters of eight linear disiloxane moieties suggests that disordered arrangements of bent Si—O—Si fragments lead to apparent linearity of the molecules.

Introduction

As part of a structural study on N-[(halogeno-dimethylsilyl)methyl]lactams, (1) (Macharashvili, Shklover, Struchkov, Oleneva, Kramarova, Shipov & Baukov, 1988) and their interconversions we carried out an X-ray analysis of 1,1,3,3-tetramethyl-1,3-bis[(2-oxo-1-pyrrolidinyl)methyl]disiloxane di-hydrochloride, (2), the product of hydrolysis of the corresponding lactam (3). The apparent linearity of the Si—O—Si fragment in (2) led us to analyze distances, angles and displacement parameters in other Si—O—Si fragments.

(CH$_2$)$_n$ structure (1) — X = F,Cl,Br,I; n = 1,2,3

(1)

structure (2) — ·2Cl$^-$

(2)

structure (3)

(3)
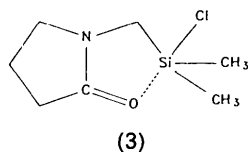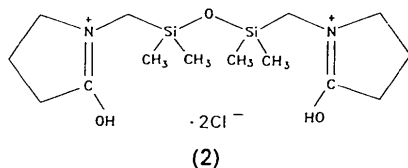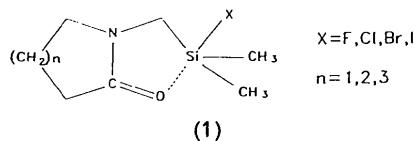
Experimental

A shapeless low-melting yellow crystal of (2) (diameter ~ 0.03 mm) was mounted on a quartz fiber with the help of a glass stage cooled by dry ice. After mounting, the crystal was transferred immediately into a cold nitrogen stream on an Enraf–Nonius CAD-4 diffractometer. The unit-cell dimensions were determined from a least-squares fit to 24 reflections $(25 < \theta < 28°)$. The crystal is monoclinic at 120 K with $a = 11.116$ (3), $b = 8.176$ (3), $c = 12.138$ (6) Å, $\beta = 114.34$ (3)°, $D_x = 1.321$ g cm^{-3}, $V = 1005.1$ Å^3, Z

$= 2$, space group $P2_1/n$. Data collection up to $2\theta = 54°$ for $\lambda(Mo\ K\alpha) = 0.71069$ Å, ω scan, width $(2.20 + 0.34\tan\theta)°$; aperture width $(2.0 + 3.0\tan\theta)$ mm; maximum time spent on any reflection 300 s; three standards for orientation and intensity control every 200 reflections; variation in standard intensities less than 2.3%, reflections measured: $-14 \leq h \leq 14$, $0 \leq k \leq -10$, $0 \leq k \leq 15$; 2234 unique reflections with $I > 3\sigma(I)$; $R(I) = 0.04$ for equivalent reflections. For six of the systematically absent reflections $I > 3\sigma(I)$, no absorption correction. Multisolution direct methods using the program SHELXS86 (Sheldrick, 1985) revealed all non-H atoms. The refinement was carried out on all atoms (including H's) by full-matrix least squares (on F) using the SHELX76 program (Sheldrick, 1976); 166 parameters, 1885 reflections with $F > 6\sigma(F)$, anisotropic thermal displacement parameters for non-H atoms. All H atoms located on a difference map.* Weighted least-squares refinement, $w = [\sigma^2(F) + 0.00184F^2]^{-1}$, maximum value of shift/e.s.d. for non-H atoms 0.15, $R = 0.031$, $wR = 0.062$. The largest peak on the final difference map was 0.32 e Å^{-3} and is situated midway between Si and C(1). Scattering factors from International Tables for X-ray Crystallography (1974, Vol. IV). For the analysis of atomic displacement parameters the THMA11 program (Trueblood, 1985) was used.

The structure was also refined with a split anisotropic O(2) atom. The R values $(R = 0.032$ and $wR = 0.061)$ were not significantly improved compared to the standard refinement. The distance between the split positions was quite small [0.331 (2) Å], but the geometry around Si was chemically unacceptable [Si—O bond distances: 1.521, 1.717 (18) Å].

Results and discussion

Final positional and displacement parameters of (2) are listed in Tables 1 and 2, distances and bond angles in Table 3. Fig. 1 shows the structure of the dication with the atom-numbering scheme.

The ionic structure of (2), with two charged pyrrolidinium moieties in the dication, follows from the distribution of bond lengths at the planar N atom. The N—C(7) bond length [1.301 (2) Å] and the C(7)—O(1) distance [1.283 (2) Å] indicate that the O(1)—H(O) bond order is approximately 2/3 (Dunitz & Winkler, 1975). The dication occupies a centrosymmetrical position in the crystal and is bonded to two Cl$^-$ anions by strong O(1)—H···Cl hydrogen bonds [O(1)···Cl 2.820 (1), O(1)—H(O)

Table 1. Final atomic positional parameters and B_{eq} values

Anisotropically refined atoms are given in the form of the equivalent isotropic thermal parameter defined as $B_{eq} = \frac{8}{3}\pi^2 \Sigma_i \Sigma_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$. $\sigma(B_{eq})$'s were evaluated according to Schomaker & Marsh (1983).

	x	y	z	$B_{eq}(\text{Å}^2)$
Cl	0·12803 (4)	0·15504 (6)	0·96186 (4)	2·87 (1)
Si	0·40644 (4)	0·65608 (5)	0·94144 (4)	1·56 (1)
O(1)	0·5038 (1)	0·5785 (2)	1·2789 (1)	2·43 (2)
O(2)	¼	¼	1	3·07 (3)
N	0·3098 (1)	0·6339 (2)	1·1231 (1)	1·61 (2)
C(1)	0·4970 (2)	0·8128 (2)	0·8969 (2)	2·47 (3)
C(2)	0·2536 (2)	0·5917 (3)	0·8123 (2)	3·31 (4)
C(3)	0·3649 (1)	0·7496 (2)	1·0641 (1)	1·74 (2)
C(4)	0·1699 (1)	0·5813 (2)	1·0681 (1)	2·13 (3)
C(5)	0·1560 (2)	0·4829 (2)	1·1694 (2)	2·38 (3)
C(6)	0·2970 (2)	0·4356 (2)	1·2541 (1)	2·26 (3)
C(7)	0·3793 (1)	0·5540 (2)	1·2217 (1)	1·80 (2)

Table 2. Anisotropic displacement parameters (Å^2)

$$T = \exp[-2\pi^2(U_{11}h^2a^{*2} + ...2U_{12}hka^*b^* + ...)].$$

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cl	0·0290 (3)	0·0406 (3)	0·0342 (3)	0·0035 (1)	0·0077 (2)	0·0099 (2)
Si	0·0205 (3)	0·0174 (3)	0·0221 (3)	0·0022 (1)	0·0095 (2)	0·0020 (1)
O(1)	0·0227 (5)	0·0363 (7)	0·0291 (6)	−0·0034 (5)	0·0065 (5)	0·0083 (5)
O(2)	0·054 (1)	0·0256 (9)	0·045 (1)	0·0206 (8)	0·0274 (9)	0·0114 (7)
N	0·0189 (6)	0·0198 (6)	0·0232 (6)	−0·0001 (4)	0·0096 (5)	−0·0010 (5)
C(1)	0·0332 (9)	0·0284 (8)	0·0360 (9)	−0·0004 (7)	0·0180 (8)	0·0070 (7)
C(2)	0·0297 (9)	0·063 (1)	0·0320 (9)	−0·0108 (9)	0·0116 (7)	−0·0185 (9)
C(3)	0·0254 (7)	0·0170 (7)	0·0248 (7)	0·0016 (5)	0·0115 (6)	0·0014 (5)
C(4)	0·0190 (7)	0·0294 (8)	0·0308 (8)	−0·0032 (6)	0·0084 (6)	−0·0047 (6)
C(5)	0·0264 (8)	0·0305 (8)	0·0384 (9)	−0·0055 (6)	0·0183 (7)	−0·0038 (7)
C(6)	0·0285 (8)	0·0333 (9)	0·0273 (8)	−0·0038 (6)	0·0149 (6)	0·0035 (6)
C(7)	0·0238 (7)	0·0225 (7)	0·0250 (7)	0·0014 (5)	0·0130 (6)	0·0002 (5)

Table 3. Bond distances (Å) and angles (°)

Si—O(2)	1·614 (1)	C(4)—C(5)	1·529 (2)
Si—C(1)	1·843 (2)	C(5)—C(6)	1·528 (2)
Si—C(2)	1·850 (2)	C(6)—C(1)	1·491 (2)
Si—C(3)	1·892 (2)	C(7)—O(1)	1·283 (2)
N—C(3)	1·464 (2)		
N—C(4)	1·481 (2)		
N—C(7)	1·301 (2)		
Si—O(2)—Si	180	C(3)—N—C(4)	122·7 (1)
O(2)—Si—C(1)	110·3 (1)	C(3)—N—C(7)	124·4 (1)
O(2)—Si—C(2)	110·4 (1)	C(4)—N—C(7)	112·6 (1)
O(2)—Si—C(3)	107·1 (1)	N—C(4)—C(5)	103·1 (1)
C(1)—Si—C(2)	111·8 (1)	C(4)—C(5)—C(6)	104·9 (1)
C(1)—Si—C(3)	106·9 (1)	C(5)—C(6)—C(7)	103·2 (1)
C(2)—Si—C(3)	110·1 (1)	C(6)—C(7)—N	111·8 (1)
Si—C(3)—N	114·3 (1)	C(6)—C(7)—O(1)	126·9 (1)
		N—C(7)—O(1)	121·2 (1)

0·98 (3), H(O)···Cl 1·86 (3) Å, C(7)—O(1)—H(O) 107 (2), O(1)—H(O)···Cl 168 (2)°].

There are several conformations possible for (2); in essence they differ in the torsional angles O(2)—Si—C(3)—N and Si—C(3)—N—C(7). Molecule (2) chooses a very specific conformation with nearly linear O(1)···Si—C(3) moieties [O(1)···Si—C(3) 172·7 (1)°] and Si—C(3)—N—C(7) torsional angles of 93·2°. The C(3)—N bond length seems slightly shortened [1·464 (2) versus 1·481 (2) Å for N—C(4)] and the Si—C(3) bond length slightly increased [1·892 (2) versus 1·843 (2) and 1·850 (2) Å for Si—C(1) and Si—C(2)]. This suggests that in the observed conformation the non-bonded orbital σ^*[Si—C(3)] acts as acceptor for the π-electron density of the N—C(7)—O(1) fragment and for the O(1)

lone-pair density which is 3·744 Å from Si. This Si···O(1) distance somewhat exceeds the sum of van der Waals radii of Si and O atoms (2·10 + 1·52 = 3·62 Å). Note, however, that the van der Waals radius of Si was not derived from observed contact distances but estimated from the densities of Si(s) and SiH₄(l) (Bondi, 1964). We do not want to discard the possibility that the Si···O(1) contact in (2) is indicative of incipient nucleophilic addition of O(1) to Si. It is certainly similar to contacts found in the octasilasesquioxane $H_8Si_8O_{12}$ (intermolecular Si···O contacts 3·623 and 3·644 Å, O···Si—O angles 163·6 and 158·7°; Auf der Heyde, Bürgi, Bürgy & Törnroos, 1991).

The values of U(obs) were analyzed by rigid-body analysis (Schomaker & Trueblood, 1968). The residual atomic motion not explained by rigid-body libration and translation shows three principal features (Fig. 1):

(a) The largest components of U(obs) − U(rigid body) for C(2) and O(2) atoms are approximately in the plane C(2)–Si–O(2)–Si'–C(2').

(b) The difference surfaces [U(obs) − U(rigid body)]$^{1/2}$ for O(2), C(2) and C(1) all show an essential component nearly along the O(1)···Si—C(3) direction.

(c) The main oscillation of the O(1) atom is perpendicular to the plane of the five-membered ring and nearly in the direction of the Si atom.

We are tempted to postulate a connection between the lengthening of the Si—C(3) bond, the Si···O(1) non-bonded contact and the appearance of the residuals U(obs) − U(rigid body) [points (b) and (c) above]. The geometric and kinematic observations described here are consistent with an incipient nucleophilic substitution in which movement of O(1) towards Si pushes C(1), C(2) and O(2) along the O(1)···Si—C(3) direction towards C(3) [and lengthens the Si—C(3) bond].
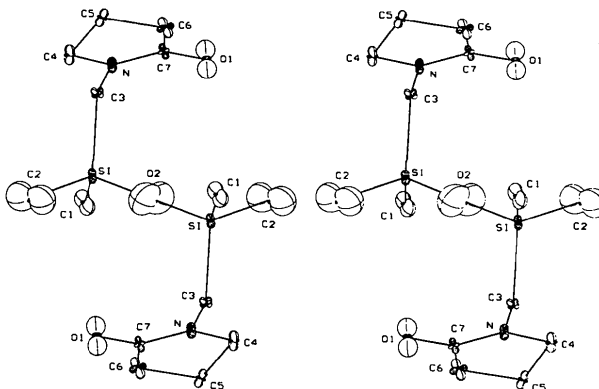

Fig. 1. Stereopair projection of the centrosymmetrical dication (2). The atoms are shown as difference surfaces [U(obs) − U(rigid body)]$^{1/2}$ (PEANUT program; Hummel, Hauser & Bürgi, 1990).

The large residual displacements on C(2) and O(2) [point (a) above] are probably related to a disorder which is observed frequently with linear Si—O—Si fragments and will be discussed in detail below.

First we give an overview of the structural parameters of Si—O—Si fragments. A connectivity search through the Cambridge Structural Database (CSD User Manual, 1989) for structures with a C_3Si—O—SiC$_3$ fragment yielded 23 structures with atomic coordinates. In 11 structures the C_3Si—O—SiC$_3$ moiety is not part of a ring system; in eight of these the Si—O—Si bond angle equals 180° (△ in Fig. 2). Two chemically symmetrical disiloxanes are non-linear in the crystal, 'BuPh$_2$SiOSiPh$_2$'Bu (14 in Fig. 2) and Me$_3$SiOSiMe$_3$ (15 in Fig. 2); the Si—O—Si angles are 152·5 and 148·8° respectively. The Si—O—Si bond angle in the related molecule MePh$_2$SiOSiPh$_3$ (13 in Fig. 2) with non-symmetrical substitution at Si is 158·8°. In the 12 remaining structures the disiloxane moieties are part of a ring and the Si—O—Si angles are constrained to 118·2–158·2° (+ in Fig. 2). The dependence of Si—O bond lengths on Si—O—Si bond angles for these structures (27 fragments) is shown in Fig. 2.

According to ab initio calculations the minimum energy configuration of (HO)$_3$SiOSi(OH)$_3$ is located at the bottom of a valley which is narrow in the d(Si—O) coordinate but elongated along the bond-angle coordinate (Si—O—Si). The calculated minimum shows an Si—O distance of ca 1·60 Å and an

Fig. 2. Average of the two Si—O bond lengths versus Si—O—Si bond angles in molecules with a C_3Si—O—SiC$_3$ fragment (+, in a ring; △, not in a ring). Point 2 refers to the structure reported here, points 4–6 refer to the compounds (4)–(6) with Cambridge refcodes OXBZSI, CECXAJ01, DOHDOT; points 9–30 refer to the following refcodes: 9 = CIWZUD (150 K), 10 = DUCVUS, 11 = OXTPSI10, 12 = FEZCES, 13 = BARBIF, 14 = DEPGOU, 15 = HMDSIX, 16 = DUWBOM, 17 = DUBZEF, 18 = BUZYEA, 19 = FIMBOS, 20 = BAGYAC, 21 = DUBZEF, 22 = CEFDAS, 23 = DUBZEF, 24 = NASINB, 25 = SIOCHX, 26 = BEPHAF, 27 = FIBJIJ, 28 = COTHIC, 29 = OMBOSI, 30 = CIWZUD (295 K). At the request of a referee one data point, an outlier [8 = FACKID, ⟨d(Si—O)⟩ = 1·57 Å, angle (Si—O—Si) = 180°] has been omitted.

(Si—O—Si) angle of ca 140° (Gibbs, 1982). The distribution of points in Fig. 2 maps the general appearance of this valley. However, there is a conspicuous lack of observed disiloxane structures with Si—O—Si bond angles in the range 160–180°. At the same time the existence of many structures with a linear disiloxane bridge is somewhat surprising since a linear Si—O—Si fragment corresponds to a local maximum in energy of ca 8 kJ mol^{-1} (Gibbs, 1982).

How can the apparent accumulation of linear Si—O—Si fragments be understood? As can be seen from Fig. 1, the largest components of the differences $[U(\text{obs}) - U(\text{rigid body})]^{1/2}$ of the dication (2) are in the C(2)–Si–O(2)–Si'–C(2') plane [point (a) above]. This indicates large amplitude motion or some kind of disorder for these atoms consistent with an equilibrium Si—O—Si bond angle smaller than 180°. We have therefore analyzed eight linear Si—O—Si fragments for which mean-square-displacement amplitudes (MSDA's) were available to us. Two different models were used to estimate the degree of deviation from linear geometry.

One is the riding model (Johnson, 1970) leading to Si—O distances corrected for the riding motion of O on Si:

$$d(\text{Si—O})_{\text{corr}} = [d^2(\text{Si—O}) + \langle u^2 \rangle_O - \langle u^2 \rangle_{Si}]^{1/2}.$$

The quantities $\langle u^2 \rangle$ are MSDA's perpendicular to the Si—O bond and in the plane defined by the Si—O bond and the eigenvector belonging to the largest eigenvalue of $U[O(2)]$, λ_{max}. Assuming that the Si···Si distances is not affected by the large amplitude motion of O(2), a corrected angle $\alpha(\text{Si—O—Si})_{\text{corr}}$ may be calculated as

$$\alpha(\text{Si—O—Si})_{\text{corr}} = 2\sin^{-1}[d(\text{Si—O})/d(\text{Si—O})_{\text{corr}}].$$

The other model assumes independent motion of O and Si (Johnson, 1970) and leads to

$$d'(\text{Si—O})_{\text{corr}} = [d^2(\text{Si—O}) + \langle u^2 \rangle_O + \langle u^2 \rangle_{Si}]^{1/2}$$

$$\alpha'(\text{Si—O—Si})_{\text{corr}} = 2\sin^{-1}[d(\text{Si—O})/d'(\text{Si—O})_{\text{corr}}].$$

The analysis was applied to the molecule described in this communication, (2), to (Ph$_3$Si)$_2$O, (4) (Glidewell & Liles, 1978), to its benzene and piperidine solvates, (5) and (6) (Suwinska, Palenik & Gerdil, 1986), to [(CO)$_3$CpFe(CH$_3$)(F)Si]$_2$O, (7) (Ries, Albright, Silvestre, Bernal, Malisch & Burschka, 1986) all of which occupy a centrosymmetrical position in the crystal, and to Ph$_3$SiO-Si(C$_2$H$_3$)$_3$, (9) (Gusev, Los, Vlasenko, Zhun & Sheludyakev; 1984; Gusev, 1991) with crystallographic C_3 symmetry. All these structures were determined with reasonable accuracy.

Table 4 summarizes the results and shows that most of the corrected angles are ca 155–175° in better agreement with values observed in open-chain
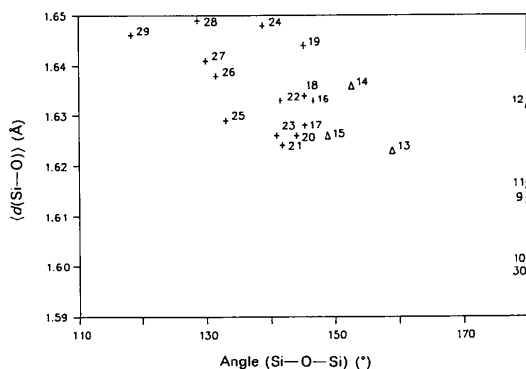
Table 4. *Corrected geometries of disiloxane fragments in structures* (2), (4)–(7) *and* (9) (*see text*)

	(2) 120 K	(4)	(5)	(6)	(7) 120 K	(7) 300 K	(9) 150 K	
$\lambda_O^{max,a}$ (Å²)	0.0660	0.0865	0.0262	0.0328	0.1131	0.1679	0.0393^g	0.0393^h
$\lambda_{Si}^{max,a}$ (Å²)	0.0231	0.0561	0.0209	0.0226	0.0411	0.0628	0.0195	0.0228
$\langle u^2\rangle_O^b$ (Å²)	0.0637	0.0856	0.0262	0.0328	0.1061	0.1604	0.0393	0.0393
$\langle u^2\rangle_{Si}^b$ (Å²)	0.0221	0.0529	0.0209	0.0226	0.0372	0.0580	0.0195	0.0228
φ^c (°)	79.1	82.4	90	90	73.7	75.8	90	90
d(Si—O)^d (Å)	1.614	1.616	1.617	1.616	1.611	1.603	1.620	1.611
α(SiOSi)^d (°)	180	180	180	180	180	180	180	—
d(SiO)$_{corr}^e$ (Å)	1.627	1.626	1.619	1.619	1.633	1.637	1.626	1.617
α(SiOSi)$_{corr}^e$ (°)	165.6	167.2	174.8	172.8	161.5	157.5	170.2	—
d'(Si—O)$_{corr}^f$ (Å)	1.640	1.658	1.632	1.633	1.656	1.673	1.638	1.629
α'(SiOSi)$_{corr}^f$ (°)	159.4	154.1	164.7	163.4	153.6	147.5	163.0	—

Notes: (*a*) λ_O^{max} and λ_{Si}^{max} are maximum eigenvalues of MSDA tensors of O and Si; (*b*) $\langle u^2\rangle_O$ and $\langle u^2\rangle_{Si}$ are MSDA's perpendicular to Si—O bonds in the plane with λ_O^{max}; (*c*) φ is the angle between d(Si—O) and λ_O^{max}; (*d*) uncorrected; (*e*) riding model; (*f*) independent motion model; (*g*) O—Si(C₆H₅)₃; (*h*) O—Si(C₂H₃)₃.

disiloxanes and calculated by *ab initio* methods. Most of the corrected Si—O distances are within the interval of Si—O distances observed in bent disiloxanes. Exceptions are (4) and (7) (120 and 300 K). For these the model of uncorrelated motion produces corrected Si—O distances which seem too large, whereas the riding model produces corrected distances more in line with those of bent disiloxanes.

The large MSDA's of the siloxane O atom are probably due to disorder as may be seen from a comparison of the data on (7) measured at 120 and 300 K. Both $\langle u^2\rangle_{Si}$ and $\langle u^2\rangle_O$ decrease substantially with decreasing temperature but not as much as would be expected from a classical or quantum-mechanical harmonic oscillator model (reduction approximately proportional to $120/300$ K $= 0.4$). From the available data it remains unclear whether the mean potential for oxygen in compounds (2), (4)–(7) and (9) shows a small local energy maximum for a linear Si—O—Si fragment or a minimum with a very flat (anharmonical) bottom. A more detailed study over a range of temperatures would be necessary to clarify these points further.

The orientation of the eigenvector corresponding to the maximum MSDA's of the siloxane O atoms in (2), (4) and (7) (λ_O^{max}, Table 4) deviates by $90° - \varphi \approx 10-15°$ from the plane perpendicular to the Si—O bond (Table 4); it is approximately eclipsed to the Si—F bond in (7) and approximately staggered to the Si—C(3) bond in (2). Ries *et al.* (1986) have argued that, for (7), this inclination is related to the electronegativities of the substituents at Si and that it is a consequence of the valence-electron distribution. In order to test this hypothesis, we have performed a refinement on (2) using 1015 data for which $\theta > 20°$. The inclination φ is found to be $80.5°$ (Table 4).

Since the contribution of valence-electron density to high-angle scattering should be significantly smaller than the contribution of the inner shells, it seems unlikely that the observed inclination is due to the contribution of valence electrons, at least for (2).

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