The gas-phase structure of the hexasilsesquioxane Si₆O₉(OSiMe₃)₆

Citation for published version:
Wann, DA, Reilly, AM, Rataboul, F, Lickiss, PD & Rankin, DWH 2009, 'The gas-phase structure of the hexasilsesquioxane Si6O9(OSiMe3)6' Zeitschrift fur naturforschung section b-A journal of chemical sciences, vol 64, pp. 1269-1275.

Link:
Link to publication record in Edinburgh Research Explorer

Document Version:
Preprint (usually an early version)

Published In:
Zeitschrift fur naturforschung section b-A journal of chemical sciences

The Gas-phase Structure of the Hexasilsesquioxane $Si_6O_9(OSiMe_3)_6$

Derek A. Wann[a], Anthony M. Reilly[a], Franck Rataboul[b], Paul D. Lickiss[b],
and David W. H. Rankin[a]

[a] School of Chemistry, University of Edinburgh, West Mains Road, Edinburgh, UK EH9 3JJ
[b] Department of Chemistry, Imperial College London, South Kensington, London, UK SW7 2AZ

Reprint requests to Prof. D. W. H. Rankin. E-mail: d.w.h.rankin@ed.ac.uk

Z. Naturforsch. **2009**, *64b,* 1269 – 1275; received August 14, 2009

Dedicated to Professor Hubert Schmidbaur on the occasion of his 75th birthday

The equilibrium molecular structure of the hexasilsesquioxane, $Si_6O_9(OSiMe_3)_6$, has been determined in the gas phase by electron diffraction. With OSi-containing substituents on the cage silicon atoms, this molecule closely resembles the moiety that if reproduced in a periodic manner would yield a zeolite-type structure. Semi-empirical molecular-dynamics (SE-MD) calculations were used to give amplitudes of vibration, vibrational distance corrections (differences between interatomic distances in the equilibrium structure and the vibrationally averaged distances that are given directly by the diffraction data) and anharmonic constants. A number of different SE-MD methods were tested, and their results are compared. The inclusion of d-type orbitals in the SE-MD method is crucial for obtaining accurate vibrational quantities for $Si_6O_9(OSiMe_3)_6$, with the PM6 and MNDO/D methods both giving acceptable values.

Key words: Silsesquioxane, Gas Electron Diffraction, Molecular Dynamics

Introduction

The chemistry of polyhedral silsesquioxanes has been the subject of increasing interest in recent years, with particular focus on the cubic octasilsesquioxanes of general formula $Si_8O_{12}R_8$, which have found many applications [1]. Much less widely studied are the closely related hexasilsesquioxanes, $Si_6O_9R_6$, which are usually prepared in low yields by hydrolysis of alkyltrichlorosilane or alkyl(trisalkoxy)silane precursors, routes that tend to give the octasilsesquioxanes in preference [1]. It is these low-yield syntheses and the relative inaccessibility of the $Si_6O_9R_6$ compounds compared to the $Si_8O_{12}R_8$ analogues that has hampered studies on these compounds. However, the related silicate anion $[Si_6O_{15}]^{6-}$ is formed in a variety of reaction media, for example aqueous or aqueous methanolic solutions derived from reactions involving silica gel or $Si(OEt)_4$ and tetraalkylammonium hydroxides. (See, for example, references [2 – 4], and references therein.) Under appropriate reaction conditions [2 – 4] the $[Si_6O_{15}]^{6-}$ anion can be formed in strong preference to the $[Si_8O_{20}]^{8-}$ anion, and this allows derivatisation of the anion *via* silylation reactions [3, 5]. Thus, reaction of $[Si_6O_{15}]^{6-}$ with excess Me_3SiCl affords $Si_6O_9(OSiMe_3)_6$ as an air-stable white solid [5].

This current study of $Si_6O_9(OSiMe_3)_6$ provides the first experimental determination of the structure of a hexasilsesquioxane in the gas phase, giving structural parameters for the polyhedral compound that are not perturbed by solid-state packing effects, and which may therefore be compared to calculated structures. This is also the first gas-phase structure of a molecule with only oxygen atoms bonded to silicon, with the consequence that it relates to the silicate anion, $[Si_6O_{15}]^{6-}$, and potentially to a zeolite structure containing six- and eight-membered rings. As with the determination of experimental equilibrium structures for other silsesquioxane structures [6 – 8], molecular-dynamics simulations have been used to predict vibrational quantities required for use in the gas electron diffraction (GED) refinement. Several different semi-empirical molecular-dynamics (SE-MD) methods have been tested to gauge the importance, or otherwise, of d-type orbitals for calculating amplitudes of vibration and vibrational distance corrections for silsesquioxanes.

Experimental Section

Computational studies

Previous geometry optimisations for silsesquioxanes [6, 8] have shown that the inclusion of basis sets with extra

0932–0776 / 09 / 1100–1269 $ 06.00

polarisation functions is necessary to calculate accurate Si–O bond lengths. They have also shown that MP2 and B3LYP calculations give broadly similar results for these sorts of systems. Geometry optimisations for $Si_6O_9(OSiMe_3)_6$ were therefore performed (using the GAUSSIAN03 suite of programs [9], with the resources of the EPSRC National Service for Computational Chemistry Software [10]) with the 6-311G(d) [11] and 6-311++G(3df,3pd) basis sets, using the B3LYP [12] method. Calculated coordinates from the highest level calculation are given in Table S1 (see note at the end of the paper for Supporting Information available online).

As electron-diffraction experiments yield time-averaged structures, in which the effects of vibrations may affect measured interatomic distances, it is common to compute corrections to apply to the distances. This allows more accurate comparison of theoretical and experimental structures to be made. Here, the molecular dynamics (MD) method of obtaining distance corrections, starting values of amplitudes of vibrations, and anharmonic constants has been used. This method is discussed in greater detail elsewhere [6, 7], and only details of the calculations pertinent to this work are given.

Previous GED studies using the MD method have employed plane-wave DFT-MD simulations to estimate the vibrational quantities. $Si_6O_9(OSiMe_3)_6$ is a much bigger molecule than those previously studied, and test simulations suggested that a DFT-MD simulation would be prohibitively expensive to perform. Some semi-empirical molecular dynamics (SE-MD) simulations have been performed previously for the $Si_8O_{12}Me_8$ and $Si_{10}O_{15}H_{10}$ silsesquioxanes, although these results were never published. They suggested that SE-MD should be suitable for this class of compounds, although no in-depth investigation of the most appropriate methods was undertaken. All SE-MD calculations for $Si_6O_9(OSiMe_3)_6$ were performed using the resources of the EaStCHEM research computing facility [13] running the CP2K code [14]. A geometry optimisation was initially carried out using the PM6 method [15], before the optimised geometry was used as the starting geometry for an SE-MD simulation in the NVT ensemble. The canonical sampling *via* velocity rescaling (CSVR) thermostat was used to control the temperature [16]. A time step of 0.5 fs was used, and the simulation was run for 30 ps. The process of performing geometry optimisations followed by SE-MD simulations was repeated using the PM3 [17], AM1 [18], MNDO [19] and MNDO/D [20] methods, allowing the effects of different levels of theory on vibrational quantities to be determined.

Following the completion of the molecular-dynamics simulations, amplitudes of vibration, distance corrections, and anharmonic constants were determined using MDSIM v0.4.0 [21], which computes this information from the calculated equilibrium geometry and the many interatomic distances assumed by each atom pair during the MD simulation.

Preparation of $Si_6O_9(OSiMe_3)_6$

The silsesquioxane $Si_6O_9(OSiMe_3)_6$ was prepared in 51 % yield by trimethylsilylation of $[Et_4N]_6[Si_6O_{15}]^{6-}$ using the procedures previously described [3, 5]. NMR spectroscopic data for solutions in $CDCl_3$ are: ^1H: $\delta = 0.19$ ppm; ^{13}C: $\delta = 1.20$ ppm; ^{29}Si: $\delta = 14.5$ ppm ($SiMe_3$), -99.1 ppm (SiO_4).

Gas electron diffraction

Data were collected for $Si_6O_9(OSiMe_3)_6$ using the Edinburgh gas-phase electron diffraction (GED) apparatus [22] with an accelerating voltage of 40 kV (equivalent to an electron wavelength of approximately 6.0 pm). The experiments were performed at two different nozzle-to-film distances to maximise the range of scattering data available. The scattering intensities were recorded on Kodak Electron Image films; nozzle-to-film distances and nozzle and sample temperatures are given in Table 2. The camera distances were calculated using diffraction patterns of benzene recorded immediately after each of the sample runs. The scattering intensities were measured using an Epson Expression 1680 Pro flat-bed scanner and converted to mean optical densities using a method described elsewhere [23]. The data were then reduced and analysed using the ed@ed least-squares refinement program v3.0 [24], employing the scattering factors of Ross *et al.* [25]. The weighting points for the off-diagonal weight matrix, correlation parameters and scale factors are shown in Table S2.

The GED refinement procedure used here for $Si_6O_9(OSiMe_3)_6$ gives interatomic distances that we have termed $r_{e,MD}$, indicating that corrections of the form $r_a - r_e$ have been determined from the PM6 SE-MD simulations described above. The calculated amplitudes of vibration used as starting values in the refinement were also taken from MD simulations, and are termed u_{MD}.

Results and Discussion

Computational studies

Geometry optimisations

All calculations indicate that D_{3h}-symmetric structures are real. The $OSiMe_3$ groups are bent at the oxygen atom, although the value is very dependent on method and basis set. The direction of the bend is away from the C_3 rotation axis as shown in Fig. 1.

Molecular-dynamics simulations

The calculated amplitudes of vibration and distance corrections for selected bonded and non-bonded distances using AM1, PM3, PM6, MNDO and MNDO/D, are given in Table 1. The results from the PM6 level

Table 1. Amplitudes of vibration and vibrational corrections from a variety of semi-empirical calculations.[a]

	AM1		PM3		PM6		MNDO		MNDO/D	
Atom pair	u	$r_a - r_e$	u	$r_a - r_e$	u	$r_a - r_e$	u	$r_a - r_e$	u	$r_a - r_e$
Si(1)–O(4)	3.5	0.7	3.5	0.6	4.6	0.4	3.3	0.4	3.9	0.5
Si(1)–O(7)	3.5	0.2	3.4	−0.7	4.4	1.0	3.4	0.4	3.7	0.5
O(16)–Si(35)	3.6	1.6	3.7	0.8	4.4	1.2	3.3	0.9	3.8	1.0
C(22)–Si(33)	4.8	1.1	6.0	0.9	4.4	0.9	4.2	0.9	4.1	1.1
C(23)–Si(33)	4.9	1.0	5.8	1.4	4.3	0.7	4.2	0.8	4.3	0.8
Si(1) ··· Si(2)	7.4	−1.0	7.3	−1.1	6.9	1.3	5.7	0.3	5.9	1.2
Si(1) ··· O(10)	7.6	1.1	8.2	7.4	6.8	−2.1	6.3	−1.0	6.0	−1.8
Si(1) ··· Si(11)	14.3	−0.7	12.6	4.0	9.8	−0.9	10.3	−0.9	10.0	−0.9
Si(1) ··· Si(35)	8.4	−7.2	9.1	−2.8	6.3	−2.4	5.7	−2.5	5.6	−2.1

[a] See Fig. 1 for atom numbering. Distances and amplitudes of vibration are in pm.

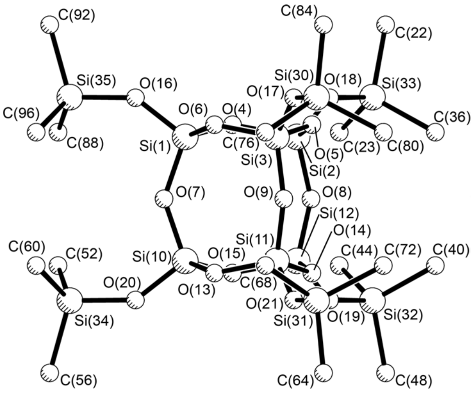

Fig. 1. Molecular structure of $Si_6O_9(OSiMe_3)_6$ including atom numbering. Hydrogen atoms have been omitted for clarity.

of theory were judged to be best based on the values for the Si–O amplitudes of vibration. In the previous study of $Si_8O_{12}H_8$ [6], the refined Si–O amplitude of vibration was observed to be 4.5(1) pm. While the PM6 method gives Si–O amplitudes close to this value, the other methods give significantly lower values. The amplitudes of vibration and distance corrections from the PM6 method were subsequently used for the GED refinement. Values for all atoms pairs are given in Table S3. Generally the amplitudes of vibration for the bonded distances are smaller for methods other than PM6 and larger for the non-bonded distances. AM1, PM3 and MNDO all produce large distance corrections, especially for the non-bonded distances across the cage. There is also disagreement between the vibrational corrections calculated from the simulations using these three methods and those using PM6 and MNDO/D. The major difference between the two groups of methods is the inclusion of d-orbitals for the PM6 and MNDO/D levels of theory. This is important when carrying out calculations for molecules that include second-row main-group elements. The MD simulations identified very large-amplitude motions of the $OSiMe_3$ groups. The inclusion of d-type orbitals is therefore important to obtain realistic barriers for these motions and has proven to be essential in these semi-empirical simulations.

As was the case for light-atom bonded pairs in previous GED studies of silsesquioxanes [6 – 8], the MD method underestimates the C–H amplitudes of vibration because the simulations are performed using classical dynamics. (See ref. [7] for a more detailed discussion of this problem.) This results in the neglect of zero-point energy contributions to the thermal motion and prohibits the possibility of quantum-mechanical tunnelling. For $Si_8O_{12}Me_8$ and $Si_{10}O_{15}H_{10}$ this was not a substantial problem, but resulted in the calculation of C–H and Si–H amplitudes of vibration, respectively, that were about 50 % too small. Similar sorts of vibrations and low-frequency oscillations of the $OSiMe_3$ groups are seen here, and as a result the C–H amplitudes of vibration have also been underestimated. The starting values used for the GED refinement were therefore taken to be refined values from the $Si_8O_{12}Me_8$ structure [6].

GED refinement

A model was written for $Si_6O_9(OSiMe_3)_6$ to allow the refinable geometrical parameters to be converted to Cartesian coordinates. The high symmetry of the molecule (D_{3h}) indicated by the *ab initio* calculations allowed the geometry to be described using 15 parameters (see Table 2).

Four different Si–O bond lengths were described using the average value and three difference parameters:

$$\begin{aligned} p_1 = [&r\mathrm{Si(1)O(16)} + r\mathrm{Si(35)O(16)} \\ &+ r\mathrm{Si(1)O(7)} + 2 \times r\mathrm{Si(1)O(4)}]/5 \end{aligned}$$

Table 2. Refined $r_{\mathrm{e,MD}}$ parameters from the GED refinement for $Si_6O_9(OSiMe_3)_6$.[a]

Parameter		$r_{\mathrm{e,MD}}$	r_{e}[b]	Restraint
Independent				
p_1	rSi−O average	161.89(9)	163.12	–
p_2	rSi−O difference 1	−1.3(4)	−1.6	−1.6(5)
p_3	rSi−O difference 2	6.4(5)	5.5	5.5(5)
p_4	rSi−O difference 3	0.3(5)	0.7	0.7(5)
p_5	rSi−C mean	186.3(3)	187.3	–
p_6	rC−H mean	109.3(4)	109.6	109.6(5)
p_7	∠Si(1)−O(4)−Si(2)	129.2(7)	130.8	–
p_8	∠Si(1)−O(7)−Si(10)	141.8(14)	136.4	–
p_9	∠Si(1)−O(16)−Si(35)	142.7(10)	156.9	–
p_{10}	∠X−A−O[c]	154.4(16)	163.6	–
p_{11}	∠O−Si−C average	106.9(4)	107.7	–
p_{12}	∠O−Si−C difference	1.3(5)	1.2	1.2(5)
p_{13}	∠C−Si−C	111.5(10)	111.2	111.2(1)
p_{14}	∠Si−C–H mean	110.8(7)	111.4	111.4(8)
p_{15}	∠X−Si−O[c]	142.1(7)	138.1	–
Dependent				
p_{16}	rSi(1)−O(4)	162.5(3)	164.0	–
p_{17}	rSi(1)−O(7)	162.2(4)	163.3	–
p_{18}	rSi(1)−O(16)	157.9(4)	159.4	–
p_{19}	rSi(16)−O(35)	164.3(4)	164.9	–
p_{20}	∠O(16)−Si(35)−C(88)	107.5(5)	108.3	–
p_{21}	∠O(16)−Si(35)−C(92)	106.2(5)	107.1	–

[a] Distances are in pm, angles are in degrees. See Fig. 1 for atom numbering. The numbers in parentheses are estimated standard deviations of the last digits; [b] theoretical results from B3LYP/6-311++G(3df,3pd) calculations; [c] X is the point at the centre of the triangle formed by three Si atoms and A is the Si ··· Si midpoint for two Si atoms on that face.

$$p_2 = [r\mathrm{Si(1)O(16)} + r\mathrm{Si(35)O(16)}]/2 - [r\mathrm{Si(1)O(7)} + 2 \times r\mathrm{Si(1)O(4)}]/3$$

$$p_3 = r\mathrm{Si(35)O(16)} - r\mathrm{Si(1)O(16)}$$

$$p_4 = r\mathrm{Si(1)O(4)} - r\mathrm{Si(1)O(7)}$$

Two further distance parameters were used, namely the mean Si–C bond length (the calculations showed that the variation in Si–C distances was small) and a mean value for the C–H bond length (p_{5-6}).

Three Si−O−Si angles (p_{7-9}) were used, two to determine the geometry of the cage and one for positioning the ligand. ∠X−A−O (p_{10}) was the final parameter required to generate the cage geometry. X is the point at the centre of the triangle formed by three silicon atoms that form part of one of the six-sided faces of the cage, and A lies half way between two of those silicon atoms. The final five angles complete the definition of the ligand groups. The $OSiMe_3$ groups are modelled with local C_s symmetry. As such they require two O−Si−C angles, which are described as the average of the two different ones and the difference between them (p_{11-12}), and one of the two different C–Si–C angles must also be defined (p_{13}). The methyl groups are modelled with local C_{3v} symmetry and are assumed to be perfectly staggered with no tilt about their axes of rotation (calculations suggest that these are both reasonable approximations), and so a single Si–C–H angle is defined (p_{14}). Finally, the X–Si–O angle (p_{15}) is used to position the $OSiMe_3$ groups relative to the cage. (See Fig. 1 for a picture of the molecular structure complete with atom numbering.)

For the refinement of the structure of $Si_6O_9(OSiMe_3)_6$ flexible SARACEN restraints [26] were applied to parameters that could otherwise not be refined. As can be seen from Table 2, these are primarily difference parameters and those related to the hydrogen-atom positions. These parameters were restrained to values obtained from B3LYP/6-311++G(3df,3pd) calculations, and the uncertainties were estimated from observations of the spread of values when different basis sets and levels of theory were used for the geometry optimisations. Amplitudes of vibration for distances under the same peak in the radial-distribution curve (RDC) were constrained by ratios fixed at the calculated values, and only one amplitude for each group was refined. The amplitudes of vibration for the C–H bonded pairs were underestimated as a result of the classical nature of the MD simulations. We have previously shown that the use of path-integral MD methods can overcome this problem [7]. However, the unstable implementation of the path-integral code in CP2K renders the collection of MD-simulated data impossible and so we have not been able to do this for $Si_6O_9(OSiMe_3)_6$. Instead the C–H amplitudes of vibration (the only parameter that is significantly affected by the classical MD approach) were started from the refined value (8.3 pm) obtained for $Si_8O_{12}Me_8$ [6]. A list of amplitudes of vibration, their constraints and the corresponding distances for the most significant atom pairs is given in Table S3. Some amplitudes were also restrained using the SARACEN method. Also given are the anharmonicity (Morse) constants derived using the MDSIM code as described elsewhere [7]. These values seem to be reliable, with bonded atom pairs having values that are positive and generally in the region of 10 − 20 nm^{-1}. For the non-bonded pairs the values are generally smaller, and some are small and negative.

The final R_G factor for the fit between the theoretical scattering (generated from the model) and the ex-

Table 3. Structural data for $Si_6O_9R_6$ compounds and $[Si_6O_{15}]^{6-}$ salts. Adapted from reference [1].

R or $[Si_6O_{15}]^{6-}$ salt	Si–O (pm) Si_3O_3 and Si_4O_4 rings Range	Mean	Si–O–Si (deg) Si_4O_4 rings only Range	Mean	Si–O–Si (deg) Si_3O_3 and Si_4O_4 rings Range	Mean	Method	Reference
H	163.4 – 164.3	163.8	139		131		calc.	[32]
Cl	–		136.6		126.9		calc.	[33]
OH[a]	162.7		135.7		135.7		calc.	[34]
OH[b]	162.8		134.9		134.9		calc.	[34]
OH[c]	165 – 169		not reported		not reported		calc.	[35]
OH[d]	165 – 177		not reported		not reported		calc.	[35]
Me	163.3 – 164.2	163.7	141.3		131.3		calc.	[36]
$OSiMe_3$	163.3 – 164.0	163.8	136.4		130.8		calc.	this work
i-Pr	161.7(4)–164.1(5)	163.1	138.9(2)–139.4(3)	139.1	130.1(2)–130.6(3)	130.4	X-ray	[37]
t-Bu	162.3(2)–164.2(2)	163.3	137.10(12)–141.08(13)	138.59	129.69(13)–131.12(13)	130.32	X-ray	[38]
CMe_2CHMe_2	160.1(9)–165.6(9)	162.6	137.9(5)–139.7(5)	139.0	130.6(5)–132.5(5)	131.6	X-ray	[39]
c-C_6H_{11}	162.5(6)–164.9(6)	164.0	139.3(4)–144.7(5)	141.1	128.8(4)–130.8(5)	129.5	X-ray	[40]
$(CH_2)_3C_6H_4$p-OMe	162.2 – 164.2	163.1	137.69 – 142.37	139.3	130.04 – 132.15	130.82	X-ray	[41]
2,4,6-*i*$Pr_3C_6H_2$[e]	162.2(2)–164.6(4)	163.4	138.3(3)–141.7(3)	139.8	131.8(2)–134.0(2)	132.0	X-ray	[42]
$OSiMe_3$	156(1)–163(1)	161	136.8(8)–138.6(6)	137.9	128.9(8)–131.7(9)	130.3	X-ray	[5, 43]
$OSiMe_3$	162.2(4)–162.5(3)	162.4	141.8(14)	141.8	129.2(7)	129.2	GED	this work
$Na_3Y[Si_6O_{15}]^{6-}$	164 – 169		not reported		not reported		calc.	[44]
$Na_3Y[Si_6O_{15}]^{6-}$	162.3(2) – 165.1(1)	164.1	132.8(2) – 135.8(2)	134.8	130.3(2) – 134.1(1)	132.8	X-ray	[45]
$(NEt_4)_6[Si_6O_{15}]^{6-}$[f]	163.0(4) – 164.7(4)	163.8	137.8(3) – 146.0(3)	141.3	129.6(2) – 132.5(3)	131.0	X-ray	[46]

[a] For the D_{3h} isomer; [b] for the C_{3v} isomer; [c] for a single molecule; [d] for a molecule hydrated by 16 water molecules; [e] for the right-handed enantiomer; [f] structure contains 40.8 H_2O molecules per unit cell.

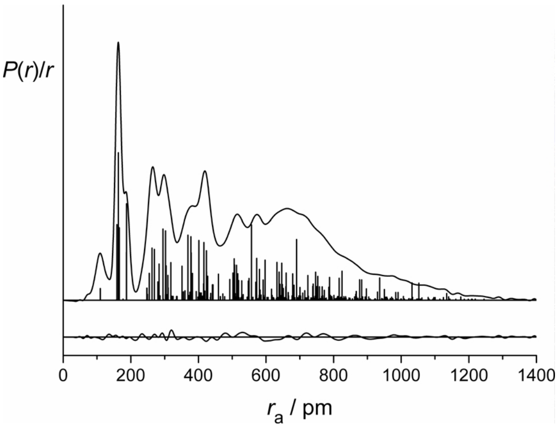

Fig. 2. Experimental and difference (experimental minus theoretical) radial-distribution curves, $P(r)/r$, for $Si_6O_9(OSiMe_3)_6$. Before Fourier inversion the data were multiplied by $s \cdot \exp(-0.00002s^2)/(Z_{Si} - f_{Si})(Z_O - f_O)$.

perimental data for $Si_6O_9(OSiMe_3)_6$ was 0.091 (R_D = 0.070). The final radial-distribution curve is shown in Fig. 2, and the corresponding molecular-intensity scattering curves are shown in Fig. S1. Coordinates for the final structure are given in Table S1, and the least-squares correlation matrix is in Table S4.

Solid-state structural studies of $Si_6O_9(OSiMe_3)_6$ and a range of alkyl and aryl derivatives of the hexasilsesquioxane cage, as well as for salts of $[Si_6O_{15}]^{6-}$, have been undertaken in the literature, as have some computational studies of $Si_6O_9H_6$ and other $Si_6O_9R_6$ derivatives with small substituents; data from these studies and this work are given in Table 3. The Si–O bond lengths shown in Table 3 are generally close to those found in a wide variety of other compounds containing Si–O bonds (*ca.* 162.9 pm) [27], with the Si–O distances within the Si_3O_3 rings being slightly longer than those found solely within the Si_4O_4 rings, as has been noted previously [27]. The Si–O–Si angles fall in a fairly narrow range of 129 – 133° for the angles within the Si_3O_3 rings and 138 – 141° for the angles within only the Si_4O_4 rings. A similar difference has been described for simple cyclosiloxanes $(R_2SiO)_n$, where the averages are 132.8 and 148.9°, respectively, for n = 3 and 4 [6]. It should be noted that several single-crystal X-ray structural studies have been carried out for related $Ge_6O_9R_6$ compounds (for example, R = ^{i}Pr [28, 29], ^{t}Bu [30] and *cyclo*-C_6H_{11} [28, 29]), and the structure of the related $Sn_6O_9H_6$ cage compound has been calculated [31].

Given the flexibility of Si–O–Si moieties, the remarkable feature of the data in Table 3 is the invariance of the structures. The ring Si–O distances are at the short end of their recorded range in $Si_6O_9(OSiMe_3)_6$, although that can simply be attributed to the effect of the electronegative substituents. However, the Si–O–Si angles in the six-membered rings are also at the narrow end of their reported range, while those that are in both six-membered and eight-membered rings are at the wide end of their range. The values of these angles are of course correlated, so it may be that the less extreme values found in other molecules may be attributed to vibrational effects, rather than to inherent chemical differences.

Another interesting feature of the structure of $Si_6O_9(OSiMe_3)_6$ is the pendent ligands attached to the cage silicon atoms. These effectively form the linker atoms that would be required to extend this structure in additional dimensions – in short, this isolated molecule is the closest yet to a fragment of a zeolite structure (although admittedly zeolites with only six- and eight-membered rings have not yet been observed). An obvious next step in the study of gas-phase silsesquioxanes would be to study cage structures known in the zeolite literature with $OSiMe_3$ ligands attached [for example $Si_8O_{12}(OSiMe_3)_8$].

Supporting Information

Tables of calculated coordinates at the B3LYP/6-311++(3df,3pd) level and final GED-determined coordinates (Table S1), experimental parameters for the GED analysis of $Si_6O_9(OSiMe_3)_6$ (Table S2), refined and calculated RMS amplitudes of vibration (u), associated r_a distances, corresponding correction values and anharmonic constants (Table S3), and least-squares correlation matrix (Table S4) for the refinement of $Si_6O_9(OSiMe_3)_6$. Molecular-intensity scattering and difference curves for $Si_6O_9(OSiMe_3)_6$ (Fig. S1). This material is available online: http://www.znaturforsch.com/ab/v64b/c64b.htm.

Acknowledgements

The EPSRC is acknowledged for funding the electron-diffraction research in Edinburgh (EP/C513649) and the related visit of F. R. to Edinburgh. A. M. R. thanks the School of Chemistry, University of Edinburgh for funding a PhD studentship, and F. R. thanks the UK Energy Research Centre for funding. Mr. Cameron Jackson is acknowledged for performing some of the initial MD simulations and preliminary DFT-MD studies. The EaStCHEM RCF, NSCCS and EPCC provided valuable computational hardware and software.

---

[1] P. D. Lickiss, F. Rataboul, *Adv. Organomet. Chem.* **2008**, *57*, 1.

[2] D. Hoebbel, A. Vargha, B. Falke, G. Engelhardt, *Z. Anorg. Allg. Chem.* **1985**, *521*, 61.

[3] P. G. Harrison, R. Kannengiesser, C. J. Hall, *Main Group Met. Chem.* **1997**, *20*, 137.

[4] S. Caratzoulas, D. G. Vlachos, *J. Phys. Chem. B* **2008**, *112*, 7.

[5] D. Hoebbel, G. Engelhardt, A. Samoson, K. Újszászy, Y. I. Smolin, *Z. Anorg. Allg. Chem.* **1987**, *552*, 236.

[6] D. A. Wann, R. J. Less, F. Rataboul, P. D. McCaffrey, A. M. Reilly, H. E. Robertson, P. D. Lickiss, D. W. H. Rankin, *Organometallics* **2008**, *27*, 4183.

[7] D. A. Wann, A. V. Zakharov, A. M. Reilly, P. D. McCaffrey, D. W. H. Rankin, *J. Phys. Chem. A* **2009**, *113*, 9511.

[8] D. A. Wann, F. Rataboul, A. M. Reilly, H. E. Robertson, P. D. Lickiss, D. W. H. Rankin, *Dalton Trans.* **2009**, 6843.

[9] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, GAUSSIAN03, (revision C.01); Gaussian, Inc.; Wallingford, CT (USA) 2004.

[10] National Service for Computational Chemistry Software (NSCCS). URL http://www.nsccs.ac.uk.

[11] a) R. Krishnan, J. S. Binkley, R. Seeger, J. A. Pople, *J. Chem. Phys.* **1980**, *72*, 650; b) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639.

[12] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1992**,

37, 785; c) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200.

[13] EaStCHEM Research Computing Facility (http://www.eastchem.ac.uk/rcf). This facility is partially supported by the eDIKT initiative (http://www.edikt.org).

[14] J. VandeVondele, M. Krack, F. Mohamed, M. Parrinello, T. Chassaing, J. Hutter, *Comp. Phys. Comm.* **2005**, *167*, 103.

[15] J. J. P. Stewart, *J. Mol. Model.* **2007**, *13*, 1173.

[16] G. Bussi, D. Donadio, M. Parrinello, *J. Chem. Phys.* **2007**, *126*, 014101.

[17] J. J. P. Stewart, *J. Comp. Chem.* **1989**, *10*, 209.

[18] M. J. S. Dewar, E. G. Zoebisch, E. F. Healy, J. J. P. Stewart, *J. Am. Chem. Soc.* **1985**, *107*, 3902.

[19] M. J. S. Dewar, *J. Am. Chem. Soc.* **1977**, *99*, 4899.

[20] W. Thiel, A. A. Voityuk, *Theor. Chim. Acta* **1992**, *81*, 391.

[21] A. V. Zakharov, personal communication.

[22] C. M. Huntley, G. S. Laurenson, D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.* **1980**, 954.

[23] H. Fleischer, D. A. Wann, S. L. Hinchley, K. B. Borisenko, J. R. Lewis, R. J. Mawhorter, H. E. Robertson, D. W. H. Rankin, *Dalton Trans.* **2005**, 3221.

[24] S. L. Hinchley, H. E. Robertson, K. B. Borisenko, A. R. Turner, B. F. Johnston, D. W. H. Rankin, M. Ahmadian, J. N. Jones, A. H. Cowley, *Dalton Trans.* **2004**, 2469.

[25] A. W. Ross, M. Fink, R. Hilderbrandt in *International Tables for Crystallography*, Vol. C, (Ed.: A. J. C. Wilson), Kluwer Academic Publishers, Dordrecht, Netherlands, **1992**, p. 245.

[26] a) A. J. Blake, P. T. Brain, H. McNab, J. Miller, C. A. Morrison, S. Parsons, D. W. H. Rankin, H. E. Robertson, B. A. Smart, *J. Phys. Chem.* **1996**, *100*, 12280; b) P. T. Brain, C. A. Morrison, S. Parsons, D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.* **1996**, 4589; c) N. W. Mitzel, D. W. H. Rankin, *Dalton Trans.* **2003**, 3650.

[27] M. Kaftory, M. Kapon, M. Botoshansky in *The Chemistry of Organic Silicon Compounds*, Vol. 2, (Eds.: Z. Rappoport, Y. Apeloig), Wiley, Chichester, **1998**, p. 181.

[28] H. Puff, K. Braun, S. Franken, T. R. Kok, W. Schuh, *J. Organomet. Chem.* **1988**, *349*, 293.

[29] M. Nanjo, T. Sasage, K. Mochida, *J. Organomet. Chem.* **2003**, *667*, 135.

[30] H. Puff, S. Franken, W. Schuh, *J. Organomet. Chem.* **1983**, *256*, 23.

[31] T. Kudo, M. Akasaka, M. S. Gordon, *J. Phys. Chem. A* **2008**, *112*, 4836.

[32] C. W. Earley, *J. Phys. Chem.* **1994**, *98*, 8693.

[33] K. Jug, D. Wichmann, *Theochem* **1997**, *398 – 399*, 365.

[34] V. Moravetski, J.-R. Hill, U. Eichler, A. K. Cheetham, J. Sauer, *J. Am. Chem. Soc.* **1996**, *118*, 13015.

[35] C. L. Schaffer, K. T. Thomson, *J. Phys. Chem. C* **2008**, *112*, 12653.

[36] J. Shen, W.-D. Cheng, D.-S. Wu, X.-D. Li, Y.-Z. Lan, Y.-J. Gong, F.-F. Li, S.-P. Huang, *J. Chem. Phys.* **2005**, *122*, 204709.

[37] M. Unno, A. Suto, K. Takada, H. Matsumoto, *Bull. Chem. Soc. Jpn.* **2000**, *73*, 215.

[38] S. Spirk, M. Nieger, F. Belaj, R. Pietschnig, *Dalton Trans.* **2009**, 163.

[39] M. Unno, S. B. Alias, H. Saito, H. Matsumoto, *Organometallics* **1996**, *15*, 2413.

[40] H. Behbehani, B. J. Brisdon, M. F. Mahon, K. C. Molloy, *J. Organomet. Chem.* **1994**, *469*, 19.

[41] A. R. Bassindale, I. A. MacKinnon, M. G. Maesano, P. G. Taylor, *Chem. Commun.* **2003**, 1382.

[42] M. Unno, Y. Imai, H. Matsumoto, *Silicon Chem.* **2003**, *2*, 175.

[43] Y. I. Smolin, Y. F. Shepelev, D. Hoebbel, *Kristallografiya* **1994**, *39*, 558.

[44] J.-L. You, H. Chen, G.-C. Jiang, H.-Y. Hou, H. Chen, Y.-Q. Wu, K. D. Xu, *Chinese Phys. Lett.* **2004**, *21*, 640.

[45] S. M. Haile, J. Maier, B. J. Wuensch, R. A. Laudise, *Acta Crystallogr.* **1995**, *B51*, 673.

[46] M. Wiebcke, J. Felsche, *Microporous Mesoporous Mater.* **2001**, *43*, 289.

The Gas-phase Structure of the Hexasilsesquioxane $Si_6O_9(OSiMe_3)_6$

Derek A. Wann, Anthony M. Reilly, Franck Rataboul, Paul D. Lickiss and David W. H. Rankin

Supplementary Information

Table S1. Coordinates/Å for $Si_6O_9(OSiMe_3)_6$.

	Calculated [a]			Experimental GED		
	x	*y*	*z*	*x*	*y*	*z*
Si(1)	0.0000	1.7214	1.5162	-0.8479	1.4686	-1.5322
Si(2)	1.4908	-0.8607	1.5162	-0.8479	-1.4686	-1.5322
Si(3)	-1.4908	-0.8607	1.5162	1.6958	0.0000	-1.5322
O(4)	1.3128	0.7579	1.7093	-1.4733	0.0000	-1.8358
O(5)	0.0000	-1.5159	1.7093	0.7367	-1.2760	-1.8358
O(6)	-1.3128	0.7579	1.7093	0.7367	1.2760	-1.8358
O(7)	0.0000	2.3286	0.0000	-1.1140	1.9296	0.0000
O(8)	2.0166	-1.1643	0.0000	-1.1140	-1.9296	0.0000
O(9)	-2.0166	-1.1643	0.0000	2.2281	0.0000	0.0000
Si(10)	0.0000	1.7214	-1.5162	-0.8479	1.4686	1.5322
Si(11)	-1.4908	-0.8607	-1.5162	1.6958	0.0000	1.5322
Si(12)	1.4908	-0.8607	-1.5162	-0.8479	-1.4686	1.5322
O(13)	-1.3128	0.7579	-1.7093	0.7367	1.2760	1.8358
O(14)	0.0000	-1.5159	-1.7093	0.7367	-1.2760	1.8358
O(15)	1.3128	0.7579	-1.7093	-1.4733	0.0000	1.8358
O(16)	0.0000	2.9079	2.5813	-1.4706	2.5471	-2.5037
O(17)	-2.5183	-1.4539	2.5813	2.9412	0.0000	-2.5037
O(18)	2.5183	-1.4539	2.5813	-1.4706	-2.5471	-2.5037
O(19)	2.5183	-1.4539	-2.5813	-1.4706	-2.5471	2.5037
O(20)	0.0000	2.9079	-2.5813	-1.4706	2.5471	2.5037
O(21)	-2.5183	-1.4539	-2.5813	2.9412	0.0000	2.5037
C(22)	3.8200	-2.2055	4.9830	-2.5456	-4.4091	-4.3018
C(23)	3.8318	-3.9910	2.4615	-3.9145	-3.6765	-1.6417
H(24)	2.9170	-2.7240	5.3518	-1.5859	-4.5171	-4.8143
H(25)	4.6911	-2.7084	5.4073	-3.0901	-5.3523	-4.3975
H(26)	3.8176	-1.1642	5.3518	-3.1190	-3.6320	-4.8143
H(27)	4.7007	-4.5571	2.8028	-4.5108	-4.5924	-1.6125
H(28)	2.9374	-4.5171	2.7995	-3.7501	-3.3451	-0.6129
H(29)	3.8335	-4.0047	1.3706	-4.4968	-2.9081	-2.1573
Si(30)	-3.8693	-2.2339	3.1142	4.5847	0.0000	-2.5091
Si(31)	-3.8693	-2.2339	-3.1142	4.5847	0.0000	2.5091
Si(32)	3.8693	-2.2339	-3.1142	-2.2924	-3.9705	2.5091
Si(33)	3.8693	-2.2339	3.1142	-2.2924	-3.9705	-2.5091

Si(34)	0.0000	4.4679	-3.1142	-2.2924	3.9705	2.5091
Si(35)	0.0000	4.4679	3.1142	-2.2924	3.9705	-2.5091
C(36)	5.3722	-1.3229	2.4615	-1.2266	-5.2283	-1.6417
H(37)	5.3849	-1.3176	1.3706	-0.2701	-5.3484	-2.1573
H(38)	5.3806	-0.2854	2.7995	-1.0219	-4.9202	-0.6129
H(39)	6.2969	-1.7924	2.8028	-1.7218	-6.2026	-1.6125
C(40)	5.3722	-1.3229	-2.4615	-1.2266	-5.2283	1.6417
H(41)	5.3849	-1.3176	-1.3706	-0.2701	-5.3484	2.1573
H(42)	6.2969	-1.7924	-2.8028	-1.7218	-6.2026	1.6125
H(43)	5.3806	-0.2854	-2.7995	-1.0219	-4.9202	0.6129
C(44)	3.8318	-3.9910	-2.4615	-3.9145	-3.6765	1.6417
H(45)	4.7007	-4.5571	-2.8028	-4.5108	-4.5924	1.6125
H(46)	3.8335	-4.0047	-1.3706	-4.4968	-2.9081	2.1573
H(47)	2.9374	-4.5171	-2.7995	-3.7501	-3.3451	0.6129
C(48)	3.8200	-2.2055	-4.9830	-2.5456	-4.4091	4.3018
H(49)	2.9170	-2.7240	-5.3518	-1.5859	-4.5171	4.8143
H(50)	3.8176	-1.1642	-5.3518	-3.1190	-3.6320	4.8143
H(51)	4.6911	-2.7084	-5.4073	-3.0901	-5.3523	4.3975
C(52)	-1.5404	5.3139	-2.4615	-3.9145	3.6765	1.6417
H(53)	-1.5962	6.3495	-2.8028	-4.5108	4.5924	1.6125
H(54)	-2.4432	4.8024	-2.7995	-3.7501	3.3451	0.6129
H(55)	-1.5514	5.3222	-1.3706	-4.4968	2.9081	2.1573
C(56)	0.0000	4.4109	-4.9830	-2.5456	4.4091	4.3018
H(57)	0.9006	3.8882	-5.3518	-3.1190	3.6320	4.8143
H(58)	-0.9006	3.8882	-5.3518	-1.5859	4.5171	4.8143
H(59)	0.0000	5.4169	-5.4073	-3.0901	5.3523	4.3975
C(60)	1.5404	5.3139	-2.4615	-1.2266	5.2283	1.6417
H(61)	1.5514	5.3222	-1.3706	-0.2701	5.3484	2.1573
H(62)	2.4432	4.8024	-2.7995	-1.0219	4.9202	0.6129
H(63)	1.5962	6.3495	-2.8028	-1.7218	6.2026	1.6125
C(64)	-3.8200	-2.2055	-4.9830	5.0912	0.0000	4.3018
H(65)	-4.6911	-2.7084	-5.4073	6.1803	0.0000	4.3975
H(66)	-3.8176	-1.1642	-5.3518	4.7049	0.8851	4.8143
H(67)	-2.9170	-2.7240	-5.3518	4.7049	-0.8851	4.8143
C(68)	-3.8318	-3.9910	-2.4615	5.1412	1.5519	1.6417
H(69)	-4.7007	-4.5571	-2.8028	6.2325	1.6102	1.6125
H(70)	-2.9374	-4.5171	-2.7995	4.7720	1.5751	0.6129
H(71)	-3.8335	-4.0047	-1.3706	4.7669	2.4403	2.1573
C(72)	-5.3722	-1.3229	-2.4615	5.1412	-1.5519	1.6417
H(73)	-5.3849	-1.3176	-1.3706	4.7669	-2.4403	2.1573
H(74)	-5.3806	-0.2854	-2.7995	4.7720	-1.5751	0.6129
H(75)	-6.2969	-1.7924	-2.8028	6.2325	-1.6102	1.6125
C(76)	-3.8318	-3.9910	2.4615	5.1412	1.5519	-1.6417
H(77)	-3.8335	-4.0047	1.3706	4.7669	2.4403	-2.1573
H(78)	-2.9374	-4.5171	2.7995	4.7720	1.5751	-0.6129
H(79)	-4.7007	-4.5571	2.8028	6.2325	1.6102	-1.6125

C(80)	-5.3722	-1.3229	2.4615	5.1412	-1.5519	-1.6417
H(81)	-6.2969	-1.7924	2.8028	6.2325	-1.6102	-1.6125
H(82)	-5.3806	-0.2854	2.7995	4.7720	-1.5751	-0.6129
H(83)	-5.3849	-1.3176	1.3706	4.7669	-2.4403	-2.1573
C(84)	-3.8200	-2.2055	4.9830	5.0912	0.0000	-4.3018
H(85)	-2.9170	-2.7240	5.3518	4.7049	-0.8851	-4.8143
H(86)	-3.8176	-1.1642	5.3518	4.7049	0.8851	-4.8143
H(87)	-4.6911	-2.7084	5.4073	6.1803	0.0000	-4.3975
C(88)	-1.5404	5.3139	2.4615	-3.9145	3.6765	-1.6417
H(89)	-1.5514	5.3222	1.3706	-4.4968	2.9081	-2.1573
H(90)	-2.4432	4.8024	2.7995	-3.7501	3.3451	-0.6129
H(91)	-1.5962	6.3495	2.8028	-4.5108	4.5924	-1.6125
C(92)	0.0000	4.4109	4.9830	-2.5456	4.4091	-4.3018
H(93)	0.0000	5.4169	5.4073	-3.0901	5.3523	-4.3975
H(94)	-0.9006	3.8882	5.3518	-1.5859	4.5171	-4.8143
H(95)	0.9006	3.8882	5.3518	-3.1190	3.6320	-4.8143
C(96)	1.5404	5.3139	2.4615	-1.2266	5.2283	-1.6417
H(97)	1.5962	6.3495	2.8028	-1.7218	6.2026	-1.6125
H(98)	2.4432	4.8024	2.7995	-1.0219	4.9202	-0.6129
H(99)	1.5514	5.3222	1.3706	-0.2701	5.3484	-2.1573

Calculated energy (not zero-point corrected) = –5323.72365 Hartrees.

[a] B3LYP/6-311++G(3df,3pd).

Table S2. Experimental parameters for the GED analysis of $Si_6O_9(OSiMe_3)_6$.[a]

Nozzle-to-film distance/mm	253.07	92.41
T_{nozzle}, K	441	461
T_{sample}, K	450	473
Δs, nm^{-1}	0.2	0.4
s_{min}, nm^{-1}	20	100
sw_1, nm^{-1}	40	120
sw_2, nm^{-1}	128	344
s_{max}, nm^{-1}	150	400
Correlation parameter	0.291	0.207
Scale factor (k)	0.791(10)	0.665(27)
Electron wavelength, pm	6.18	6.18

[a] Values in parentheses are estimated standard deviations of the last digits.

Table S3. Refined and calculated RMS amplitudes of vibration (u), associated r_a distances, corresponding distance correction values (r_a–r_e) and anharmonic Morse constants (a) for $\mathrm{Si_6O_9(OSiMe_3)_6}$.[a]

	Atom pair	r_a	$u_\mathrm{(GED)}$	r_a–r_e	a	$u_\mathrm{MD(calc.)}$
u_{4}	C(22)–H(25)	109.6(4)	8.7(tied to u_1)	0.2	11	8.3
u_{5}	C(23)–H(27)	109.7(4)	8.7(tied to u_1)	0.3	12	8.3
u_{2}	C(23)–H(28)	109.7(4)	8.7(tied to u_1)	0.3	12	8.3
u_{3}	C(23)–H(29)	109.7(4)	8.7(tied to u_1)	0.4	14	8.3
u_{1}	C(22)–H(24)	109.8(4)	8.7(6)	0.5	14	8.3
u_{6}	Si(1)–O(16)	158.6(4)	4.2(tied to u_8)	0.6	4	4.2
u_{8}	Si(1)–O(4)	162.9(2)	4.6(2)	0.4	10	4.6
u_{7}	Si(1)–O(7)	163.2(4)	4.4(tied to u_8)	1.0	14	4.4
u_{9}	O(16)–Si(35)	165.5(4)	4.4(tied to u_8)	1.2	16	4.4
u_{14}	H(24)...H(25)	176.8(11)	7.9(fixed)	-0.3	0	7.9
u_{12}	H(27)...H(29)	176.8(11)	7.8(fixed)	-0.3	0	7.8
u_{11}	H(24)...H(26)	176.8(11)	7.9(fixed)	-0.2	0	7.9
u_{13}	H(27)...H(28)	176.8(11)	7.7(fixed)	-0.2	0	7.7
u_{10}	H(28)...H(29)	176.9(11)	7.7(fixed)	-0.1	0	7.7
u_{16}	C(23)–Si(33)	187.0(3)	5.4(3)	0.7	17	4.3
u_{15}	C(22)–Si(33)	187.2(3)	5.5(tied to u_{16})	0.9	20	4.4
u_{17}	H(24)...Si(33)	247.0(9)	10.2(fixed)	-0.2	0	10.2
u_{21}	H(27)...Si(33)	247.2(9)	10.3(fixed)	0.0	0	10.3
u_{20}	H(29)...Si(33)	247.3(9)	10.2(fixed)	0.1	0	10.2
u_{19}	H(28)...Si(33)	247.6(9)	10.1(fixed)	0.4	0	10.1
u_{18}	H(25)...Si(33)	248.8(9)	10.4(fixed)	1.6	0	10.4
u_{22}	O(4)...O(5)	254.4(20)	5.5(tied to u_{25})	-0.8	1	9.3
u_{25}	O(4)...O(16)	262.6(6)	6.4(14)	-0.8	0	10.9
u_{23}	O(7)...O(16)	262.6(12)	6.1(tied to u_{25})	2.3	6	10.4
u_{24}	O(4)...O(7)	269.5(12)	6.1(tied to u_{25})	0.8	4	10.3
u_{26}	O(16)...C(92)	279.7(10)	6.5(tied to u_{25})	-0.6	1	10.9
u_{27}	O(16)...C(88)	283.4(8)	6.5(tied to u_{25})	0.7	4	11.0
u_{112}	C(23)...H(47)	286.3(90)	204.1(tied to u_{28})	57.8	1	154.3
u_{28}	Si(1)...Si(2)	295.0(9)	9.1(5)	1.3	4	6.9
u_{91}	H(24)...H(37)	297.0(47)	15.6(fixed)	-11.0	0	15.6
u_{33}	O(16)...H(94)	302.3(16)	37.6(tied to u_{28})	-1.6	0	28.4
u_{40}	Si(1)...Si(35)	302.6(9)	8.3(tied to u_{28})	-2.4	0	6.3
u_{30}	Si(1)...Si(10)	304.4(14)	8.9(tied to u_{28})	-2.1	0	6.8
u_{92}	H(28)...H(38)	304.5(85)	15.5(fixed)	-10.6	0	15.5
u_{84}	O(7)...H(54)	304.8(44)	88.1(tied to u_{28})	-0.7	-1	66.6
u_{34}	O(16)...H(90)	307.4(15)	37.0(tied to u_{28})	0.7	0	28.0
u_{35}	O(16)...H(89)	308.1(15)	37.0(tied to u_{28})	1.4	1	28.0
u_{32}	C(22)...C(23)	309.5(18)	14.1(tied to u_{28})	1.5	4	10.7
u_{31}	C(23)...C(36)	310.4(42)	14.3(tied to u_{28})	0.0	2	10.8
u_{204}	H(28)...H(43)	311.5(102)	159.2(fixed)	-26.6	0	159.2
u_{41}	Si(1)...O(5)	318.3(8)	13.4(tied to u_{28})	-0.1	0	10.1
u_{61}	C(23)...H(26)	321.2(29)	16.5(tied to u28)	-5.9	0	12.5

u_{62}	C(22)...H(29)	321.3(30)	16.3(tied to u_{28})	-5.2	0	12.3
u_{136}	H(27)...H(47)	322.0(83)	166.2(fixed)	55.8	1	166.2
u_{60}	C(23)...H(38)	325.0(59)	15.7(tied to u_{52})	-6.2	0	12.4
u_{38}	H(27)...H(39)	331.0(55)	43.4(fixed)	8.9	2	43.4
u_{39}	H(25)...H(27)	334.0(31)	44.1(fixed)	12.3	2	44.1
u_{45}	C(23)...H(39)	335.3(44)	36.6(tied to u_{52})	0.7	0	28.8
u_{47}	C(22)...H(27)	335.4(21)	37.0(tied to u_{52})	1.8	1	29.1
u_{46}	C(23)...H(25)	336.8(21)	37.3(tied to u_{52})	3.9	1	29.3
u_{57}	O(7)...Si(34)	351.2(20)	24.3(tied to u_{52})	7.0	2	19.2
u_{76}	H(24)...H(39)	355.4(29)	28.5(fixed)	-6.7	0	28.5
u_{65}	Si(1)...H(90)	355.6(31)	53.9(tied to u_{52})	-2.1	0	42.4
u_{77}	H(25)...H(29)	356.2(30)	28.2(fixed)	-4.0	0	28.2
u_{75}	H(27)...H(38)	357.5(59)	28.3(fixed)	-6.9	0	28.3
u_{48}	O(4)...O(15)	360.2(31)	27.1(tied to u_{52})	-7.0	0	21.3
u_{52}	Si(1)...O(13)	368.8(16)	17.6(8)	-3.9	0	13.8
u_{53}	O(16)...H(93)	369.2(11)	15.7(tied to u_{52})	-6.0	0	12.4
u_{55}	O(16)...H(91)	371.6(10)	15.4(tied to u_{52})	-5.5	0	12.2
u_{155}	H(28)...Si(32)	374.5(72)	158.2(tied to u_{52})	24.4	1	124.5
u_{56}	Si(1)...O(8)	377.5(19)	17.1(tied to u_{52})	3.8	4	13.4
u_{63}	Si(1)...C(88)	378.5(21)	26.5(tied to u_{52})	0.5	0	20.8
u_{85}	H(28)...H(46)	380.0(92)	160.2(fixed)	89.8	2	160.2
u_{74}	O(7)...C(52)	382.2(35)	55.4(tied to u_{52})	13.5	0	43.6
u_{58}	O(7)...O(8)	393.5(39)	17.4(tied to u_{67})	7.6	3	20.3
u_{166}	C(23)...H(43)	398.1(92)	128.7(tied to u_{67})	10.9	0	150.1
u_{67}	O(4)...Si(33)	401.4(7)	17.9(10)	-9.6	0	20.8
u_{42}	C(23)...H(37)	404.1(32)	24.4(tied to u_{67})	-0.2	0	28.5
u_{59}	Si(1)...H(89)	404.2(22)	36.4(tied to u_{67})	7.0	1	42.5
u_{43}	C(23)...H(24)	404.5(16)	24.7(tied to u_{67})	2.1	1	28.7
u_{114}	O(4)...H(28)	404.7(34)	34.2(tied to u_{67})	-18.0	-4	39.8
u_{44}	C(22)...H(28)	405.1(16)	23.8(tied to u_{67})	2.7	1	27.8
u_{126}	Si(1)...H(54)	408.2(49)	67.9(tied to u_{67})	1.4	-1	79.2
u_{110}	O(4)...H(29)	411.8(22)	34.6(tied to u_{67})	-9.0	-3	40.4
u_{66}	O(4)...O(9)	415.3(14)	13.1(tied to u_{67})	2.1	2	15.3
u_{68}	Si(1)...O(17)	416.0(8)	9.6(tied to u_{67})	-1.8	0	11.2
u_{102}	C(23)...C(44)	419.3(96)	112.7(tied to u_{67})	90.9	3	131.5
u_{73}	H(24)...H(38)	419.6(31)	28.0(fixed)	-6.3	0	28.0
u_{72}	H(24)...H(29)	419.8(31)	28.5(fixed)	-5.9	0	28.5
u_{128}	H(27)...H(45)	421.3(126)	161.0(fixed)	98.8	2	161.0
u_{71}	H(28)...H(37)	422.3(54)	28.1(fixed)	-7.9	0	28.1
u_{70}	Si(1)...Si(11)	423.6(8)	8.4(tied to u_{67})	-0.9	0	9.8
u_{69}	Si(1)...O(20)	424.0(13)	9.5(tied to u_{67})	1.6	2	11.1
u_{80}	Si(1)...C(92)	424.0(11)	17.6(tied to u_{67})	-14.2	0	20.5
u_{49}	H(27)...H(37)	426.7(37)	49.9(fixed)	-7.5	0	49.9
u_{109}	O(4)...C(23)	427.4(21)	17.9(tied to u_{67})	-14.4	0	20.9
u_{50}	H(24)...H(27)	428.0(21)	50.8(fixed)	-5.8	0	50.8
u_{191}	H(27)...H(43)	428.7(90)	162.4(fixed)	13.5	0	162.4

u_{51}	H(25)...H(28)	429.7(21)	50.4(fixed)	-3.8	-1	50.4
u_{117}	C(23)...H(45)	435.4(105)	124.0(tied to u_{67})	92.2	2	144.6
u_{82}	Si(1)...H(94)	436.4(18)	36.7(tied to u_{67})	-17.6	-3	42.8
u_{78}	O(4)...O(13)	441.1(22)	14.1(tied to u_{67})	-6.0	0	16.4
u_{54}	O(7)...H(55)	442.4(36)	53.7(tied to u_{67})	29.5	2	62.6
u_{83}	O(4)...O(17)	442.9(14)	11.8(tied to u_{67})	-3.6	0	13.7
u_{86}	Si(1)...O(14)	459.2(12)	11.3(tied to u_{67})	-3.2	0	13.2
u_{185}	O(4)...H(47)	464.5(44)	59.1(tied to u_{67})	-8.5	-2	68.9
u_{105}	O(7)...H(53)	465.3(38)	38.7(tied to u_{67})	4.5	-2	45.1
u_{99}	Si(1)...H(91)	472.0(21)	17.9(tied to u_{67})	-9.4	0	20.8
u_{90}	O(4)...H(26)	477.6(23)	55.7(tied to u_{67})	-20.1	-1	64.9
u_{95}	O(4)...C(22)	492.8(15)	42.4(tied to u_{108})	-23.7	-5	44.7
u_{36}	H(29)...H(37)	495.0(22)	42.9(fixed)	6.9	2	42.9
u_{37}	H(24)...H(28)	498.2(17)	42.3(fixed)	11.3	3	42.3
u_{93}	O(4)...O(19)	502.1(14)	15.1(tied to u_{108})	-1.1	0	15.9
u_{98}	O(16)...O(17)	502.2(18)	18.8(tied to u_{108})	-7.2	0	19.8
u_{107}	O(7)...C(56)	504.4(19)	18.5(tied to u_{108})	-12.4	0	19.5
u_{130}	C(23)...C(40)	505.6(88)	127.0(tied to u_{108})	53.8	1	133.8
u_{108}	Si(1)...Si(34)	505.6(21)	21.3(8)	8.8	2	22.4
u_{104}	O(4)...H(24)	506.0(21)	64.1(tied to u_{108})	-35.2	-3	67.6
u_{133}	C(23)...Si(32)	507.0(73)	93.4(tied to u_{108})	60.3	2	98.4
u_{100}	O(16)...O(20)	508.6(27)	19.1(tied to u_{108})	7.8	2	20.1
u_{81}	O(4)...H(38)	509.7(29)	62.6(tied to u_{108})	0.7	0	66.0
u_{106}	Si(1)...H(93)	510.7(12)	19.8(tied to u_{108})	-21.5	0	20.9
u_{129}	H(28)...H(41)	511.5(92)	164.9(fixed)	23.7	0	164.9
u_{118}	Si(1)...C(52)	512.7(40)	51.2(tied to u_{108})	19.2	0	54.0
u_{103}	O(7)...O(17)	516.3(15)	13.5(tied to u_{108})	2.2	1	14.2
u_{64}	C(23)...H(46)	517.4(101)	132.4(tied to u_{108})	125.5	4	139.5
u_{89}	O(4)...C(36)	518.7(17)	44.8(tied to u_{108})	-5.1	-2	47.2
u_{256}	C(22)...H(43)	520.8(75)	118.7(tied to u_{108})	3.7	0	125.1
u_{165}	H(27)...H(42)	523.1(103)	162.8(fixed)	67.3	1	162.8
u_{152}	C(23)...H(42)	525.3(93)	139.2(tied to u_{108})	58.6	1	146.7
u_{148}	O(4)...H(27)	527.1(22)	22.9(tied to u_{108})	-23.9	0	24.1
u_{124}	O(16)...C(52)	528.0(53)	71.3(tied to u_{108})	33.7	1	75.1
u_{373}	H(29)...H(89)	528.3(45)	67.6(fixed)	-53.3	-4	67.6
u_{115}	O(7)...H(57)	529.4(22)	37.5(tied to u_{108})	-19.2	-4	39.5
u_{293}	H(24)...H(43)	529.7(74)	119.2(fixed)	-17.4	-1	119.2
u_{158}	H(27)...Si(32)	532.5(85)	104.2(tied to u_{108})	60.3	1	109.8
u_{87}	H(27)...H(46)	539.0(109)	151.2(fixed)	126.1	3	151.2
u_{88}	O(4)...H(37)	544.1(20)	66.4(tied to u_{108})	-5.0	-1	70.0
u_{146}	Si(30)...Si(31)	547.5(62)	54.6(tied to u_{108})	45.7	7	57.5
u_{178}	Si(1)...H(28)	548.3(37)	46.5(tied to u_{108})	-21.3	-4	49.0
u_{127}	O(16)...Si(34)	549.6(38)	34.9(tied to u_{108})	22.1	3	36.8
u_{282}	H(25)...H(43)	555.9(76)	135.0(fixed)	12.1	0	135.0
u_{120}	Si(1)...Si(30)	556.9(8)	25.5(14)	-14.2	0	21.4
u_{138}	O(4)...H(43)	561.2(47)	76.2(tied to u_{108})	9.7	0	80.2

u_{172}	O(4)...C(44)	569.5(36)	58.6(tied to u_{120})	7.7	-2	49.0
u_{121}	Si(1)...O(19)	572.4(7)	14.3(tied to u_{120})	-0.3	0	12.0
u_{140}	O(7)...H(59)	575.9(22)	26.9(tied to u_{120})	-15.4	0	22.5
u_{380}	H(28)...H(89)	577.3(60)	78.6(fixed)	-71.1	-4	78.6
u_{161}	O(16)...H(53)	579.4(60)	98.6(tied to u_{120})	28.3	0	82.5
u_{233}	O(7)...H(28)	579.9(44)	58.6(tied to u_{120})	-13.0	-3	49.0
u_{94}	Si(1)...H(55)	580.0(42)	88.5(tied to u_{120})	41.5	2	74.1
u_{174}	Si(1)...C(23)	580.6(23)	29.9(tied to u_{120})	-18.4	0	25.0
u_{131}	O(4)...H(25)	580.7(13)	55.8(tied to u_{120})	-34.3	-6	46.7
u_{173}	Si(1)...H(29)	582.4(23)	69.4(tied to u_{120})	9.1	1	58.0
u_{157}	Si(1)...H(53)	585.3(45)	69.4(tied to u_{120})	10.3	-1	58.0
u_{363}	H(28)...H(90)	590.0(89)	101.0(fixed)	-79.0	-4	101.0
u_{134}	O(4)...Si(30)	591.3(14)	26.4(tied to u_{120})	-18.2	0	22.1
u_{29}	H(29)...H(46)	591.9(119)	145.7(fixed)	160.4	5	145.7
u_{248}	Si(1)...H(47)	592.3(44)	69.3(tied to u_{120})	-9.3	-2	58.0
u_{265}	H(24)...H(47)	595.0(73)	133.9(fixed)	-0.9	0	133.9
u_{239}	O(16)...H(29)	595.6(28)	53.7(tied to u_{120})	-29.2	-5	45.0
u_{372}	C(23)...H(89)	596.5(47)	71.6(tied to u_{120})	-66.6	-1	59.9
u_{143}	O(4)...Si(32)	597.3(18)	29.0(tied to u_{120})	3.0	0	24.3
u_{119}	O(4)...H(39)	603.0(17)	57.7(tied to u_{120})	-18.1	-4	48.3
u_{145}	O(4)...H(46)	606.3(40)	87.0(tied to u_{120})	27.1	0	72.7
u_{137}	O(4)...O(21)	616.1(11)	12.3(tied to u_{189})	-2.9	0	13.9
u_{97}	H(29)...Si(32)	617.5(72)	136.1(tied to u_{120})	90.6	3	113.8
u_{96}	O(16)...H(55)	617.6(56)	110.8(tied to u_{120})	60.7	2	92.7
u_{132}	Si(1)...H(26)	617.9(26)	64.1(tied to u_{189})	-29.7	-2	72.6
u_{234}	O(16)...H(28)	621.6(40)	66.9(tied to u_{120})	-37.8	-4	56.0
u_{101}	C(23)...H(41)	623.4(88)	178.8(tied to u_{120})	71.0	1	149.6
u_{367}	C(23)...H(90)	630.7(70)	94.3(tied to u_{120})	-79.1	-6	78.9
u_{149}	O(16)...Si(30)	632.2(18)	31.3(tied to u_{189})	-24.7	0	35.5
u_{206}	O(7)...H(29)	634.7(28)	46.9(tied to u_{189})	6.2	-1	53.1
u_{171}	O(4)...H(78)	637.1(38)	58.5(tied to u_{189})	-18.5	-2	66.3
u_{147}	Si(1)...C(22)	638.8(17)	44.8(tied to u_{189})	-32.8	-5	50.7
u_{229}	O(16)...C(23)	639.3(26)	31.0(tied to u_{189})	-34.9	-10	35.1
u_{125}	Si(1)...H(38)	639.7(32)	65.4(tied to u_{189})	-6.0	-1	74.1
u_{300}	H(24)...H(83)	640.3(52)	105.1(fixed)	-79.0	-2	105.1
u_{221}	O(7)...C(23)	641.5(31)	25.0(tied to u_{189})	-6.3	0	28.3
u_{150}	Si(1)...H(24)	643.5(24)	67.5(tied to u_{189})	-43.1	-3	76.5
u_{135}	O(16)...H(26)	646.4(39)	77.9(tied to u_{189})	-33.6	-1	88.2
u_{164}	O(7)...Si(30)	646.5(19)	18.6(tied to u_{189})	-5.4	0	21.0
u_{144}	O(4)...C(40)	648.2(35)	47.9(tied to u_{189})	19.8	0	54.2
u_{224}	O(4)...H(45)	648.6(42)	46.8(tied to u_{189})	-1.1	-3	53.0
u_{111}	H(27)...H(41)	649.7(92)	160.8(fixed)	77.3	1	160.8
u_{421}	H(28)...H(54)	650.8(88)	79.6(fixed)	-29.4	-2	79.6
u_{225}	C(22)...C(40)	651.0(80)	87.4(tied to u_{189})	36.7	1	99.0
u_{151}	O(4)...H(85)	653.8(31)	66.2(tied to u_{189})	-37.7	-2	74.9
u_{182}	O(4)...H(77)	656.1(27)	51.3(tied to u_{189})	-14.7	-3	58.1

u_{180}	Si(1)...C(56)	658.6(18)	19.9(tied to u_{189})	-16.5	0	22.5
u_{364}	C(23)...C(88)	659.2(52)	50.8(tied to u_{189})	-76.1	0	57.5
u_{181}	O(4)...C(76)	659.5(26)	36.2(tied to u_{189})	-20.2	-7	41.0
u_{142}	Si(1)...C(36)	659.6(19)	45.9(tied to u_{189})	-11.3	-3	51.9
u_{261}	C(22)...H(42)	660.4(100)	99.1(tied to u_{189})	36.9	1	112.2
u_{160}	O(4)...C(84)	665.7(24)	44.7(tied to u_{189})	-35.6	-6	50.6
u_{263}	C(23)...H(50)	666.0(79)	85.0(tied to u_{189})	15.5	0	96.3
u_{409}	H(27)...H(89)	666.2(50)	67.1(fixed)	-85.8	-6	67.1
u_{317}	H(29)...Si(35)	666.5(28)	49.7(tied to u_{189})	-56.7	-5	56.3
u_{276}	H(25)...H(42)	674.7(110)	125.6(fixed)	52.4	1	125.6
u_{232}	Si(1)...H(27)	677.3(24)	24.9(tied to u_{189})	-31.0	-12	28.2
u_{299}	H(24)...H(42)	679.0(100)	108.8(fixed)	14.5	0	108.8
u_{236}	Si(1)...C(44)	679.1(33)	32.4(tied to u_{189})	1.2	-3	36.7
u_{139}	Si(1)...H(37)	679.2(20)	65.7(tied to u_{189})	-7.8	-2	74.4
u_{405}	H(28)...H(55)	679.7(63)	81.8(fixed)	-8.3	-1	81.8
u_{252}	C(23)...H(51)	680.3(87)	97.2(tied to u_{189})	48.1	0	110.1
u_{188}	Si(1)...H(43)	681.6(44)	64.2(tied to u_{189})	7.4	0	72.7
u_{190}	Si(1)...H(57)	682.3(22)	38.5(tied to u_{189})	-25.6	-5	43.6
u_{163}	O(16)...C(22)	683.0(31)	61.9(tied to u_{189})	-43.5	-4	70.0
u_{168}	O(16)...H(24)	685.1(36)	86.3(tied to u_{189})	-58.3	-2	97.7
u_{249}	O(4)...H(70)	685.2(47)	57.4(tied to u_{189})	-3.9	-1	65.0
u_{189}	Si(1)...Si(31)	690.5(13)	16.2(8)	-2.4	0	18.4
u_{324}	O(16)...H(47)	691.0(44)	52.6(tied to u_{189})	-13.4	-3	59.6
u_{156}	O(7)...H(38)	693.9(45)	64.4(tied to u_{189})	6.1	0	72.9
u_{113}	H(24)...H(85)	695.1(79)	137.6(fixed)	-31.3	0	137.6
u_{205}	Si(1)...H(46)	697.4(34)	55.2(tied to u_{189})	18.6	0	62.4
u_{331}	C(22)...H(83)	697.9(41)	78.8(tied to u_{189})	-89.2	-4	89.2
u_{251}	C(22)...Si(32)	700.4(67)	49.1(tied to u_{189})	17.4	1	55.6
u_{310}	H(28)...Si(35)	702.6(46)	61.8(tied to u_{189})	-67.0	-5	70.0
u_{406}	H(27)...H(90)	704.6(75)	86.4(fixed)	-99.1	-6	86.4
u_{213}	O(16)...C(56)	708.8(37)	30.2(tied to u_{189})	-5.0	0	34.2
u_{418}	C(23)...H(54)	714.3(71)	57.7(tied to u_{189})	-23.3	-2	65.4
u_{186}	O(16)...O(19)	714.6(9)	13.7(tied to u_{189})	0.3	0	15.5
u_{192}	O(4)...H(42)	717.8(40)	52.5(tied to u_{189})	7.7	-1	59.4
u_{247}	C(23)...H(49)	718.4(76)	94.3(tied to u_{189})	27.0	0	106.7
u_{116}	O(4)...H(41)	720.8(37)	65.7(tied to u_{189})	42.5	2	74.3
u_{304}	C(23)...Si(35)	723.8(29)	47.5(tied to u_{189})	-62.7	-9	53.8
u_{228}	Si(1)...H(59)	724.9(24)	23.7(tied to u_{189})	-18.5	0	26.8
u_{278}	C(23)...H(95)	725.0(46)	94.9(tied to u_{189})	-75.7	-2	107.5
u_{201}	Si(1)...H(25)	725.4(16)	48.6(tied to u_{189})	-47.7	-7	55.0
u_{79}	H(29)...H(41)	730.1(88)	164.7(fixed)	78.6	2	164.7
u_{283}	H(24)...H(45)	730.8(95)	118.7(fixed)	24.6	0	118.7
u_{392}	H(29)...H(55)	731.3(68)	88.4(fixed)	7.1	-1	88.4
u_{285}	O(16)...H(27)	733.0(27)	37.4(tied to u_{189})	-48.1	-10	42.4
u_{197}	O(7)...H(26)	733.6(21)	62.4(tied to u_{189})	-28.9	-3	70.7
u_{404}	C(23)...H(91)	734.2(56)	59.4(tied to u_{189})	-94.8	0	67.3

u_{284}	O(7)...H(27)	734.4(34)	26.9(tied to u_{189})	-18.4	-8	30.4
u_{280}	H(25)...Si(32)	734.8(77)	58.6(tied to u_{189})	26.0	0	66.3
u_{334}	H(24)...H(89)	736.9(45)	115.6(fixed)	-103.7	-2	115.6
u_{287}	H(24)...H(82)	737.8(53)	118.3(fixed)	-79.1	-2	118.3
u_{175}	O(7)...C(36)	738.2(32)	45.2(tied to u_{189})	3.8	0	51.1
u_{214}	O(4)...C(48)	739.6(15)	29.4(tied to u_{189})	-23.7	-8	33.3
u_{211}	O(4)...Si(31)	739.6(15)	14.5(tied to u_{189})	-5.9	0	16.4
u_{273}	H(24)...Si(32)	740.1(63)	55.8(tied to u_{189})	2.3	-1	63.2
u_{238}	O(16)...H(57)	741.3(36)	42.2(tied to u_{189})	-16.7	-3	47.8
u_{194}	Si(1)...H(39)	745.2(19)	48.3(tied to u_{189})	-26.9	-5	54.7
u_{179}	H(24)...Si(30)	745.7(45)	93.3(tied to u_{189})	-53.0	-2	105.6
u_{212}	O(4)...H(50)	746.1(22)	52.2(tied to u_{189})	-29.3	-3	59.1
u_{210}	Si(30)...Si(33)	746.7(18)	48.6(tied to u_{189})	-47.4	-7	55.0
u_{154}	C(22)...H(85)	749.7(71)	114.8(tied to u_{189})	-58.1	-1	130.0
u_{208}	O(7)...C(22)	750.2(13)	40.9(tied to u_{189})	-29.1	-6	46.3
u_{159}	H(24)...H(86)	750.3(76)	150.9(fixed)	-79.0	-1	150.9
u_{370}	H(25)...H(83)	752.2(40)	100.6(fixed)	-115.1	-4	100.6
u_{241}	O(4)...H(79)	752.4(26)	38.2(tied to u_{189})	-35.1	-10	43.2
u_{200}	Si(1)...C(40)	753.1(32)	42.7(tied to u_{189})	11.0	0	48.4
u_{215}	O(4)...H(87)	754.3(23)	48.9(tied to u_{189})	-52.8	-6	55.4
u_{170}	O(16)...C(36)	758.0(21)	64.8(tied to u_{189})	-24.7	-3	73.3
u_{260}	O(16)...H(59)	760.2(45)	37.3(tied to u_{189})	-2.2	-2	42.2
u_{403}	C(23)...H(55)	760.7(59)	65.0(tied to u_{189})	-1.7	-1	73.6
u_{203}	H(24)...H(41)	761.3(79)	113.5(fixed)	47.0	1	113.5
u_{169}	C(22)...H(41)	761.4(79)	101.6(tied to u_{189})	70.1	2	115.0
u_{296}	Si(1)...H(45)	764.7(39)	34.7(tied to u_{189})	-10.2	-6	39.3
u_{222}	O(7)...H(24)	765.6(20)	61.0(tied to u_{189})	-40.4	-4	69.1
u_{216}	O(16)...H(25)	765.8(30)	68.9(tied to u_{189})	-62.5	-4	78.0
u_{250}	O(4)...C(68)	766.1(35)	35.6(tied to u_{189})	2.8	0	40.3
u_{141}	O(16)...H(38)	767.6(31)	87.0(tied to u_{189})	-4.1	-1	98.5
u_{235}	O(4)...H(49)	768.2(20)	43.1(tied to u_{189})	-35.8	-4	48.8
u_{313}	C(22)...C(80)	772.7(37)	82.2(tied to u_{189})	-89.5	-4	93.0
u_{177}	O(16)...H(37)	772.8(25)	84.2(tied to u_{189})	-26.6	-2	95.4
u_{318}	C(22)...H(82)	776.1(46)	93.9(tied to u_{189})	-91.0	-3	106.3
u_{162}	O(7)...H(37)	778.2(30)	67.0(tied to u_{189})	14.4	0	75.9
u_{312}	O(16)...C(44)	785.8(34)	36.6(tied to u_{189})	-0.9	-4	41.5
u_{389}	H(28)...Si(34)	786.5(52)	55.8(tied to u_{189})	-22.2	-3	63.2
u_{218}	C(22)...Si(30)	788.1(36)	80.5(tied to u_{189})	-69.2	-3	91.2
u_{440}	H(27)...H(54)	790.0(78)	68.2(fixed)	-37.9	-3	68.2
u_{414}	C(23)...C(52)	790.8(61)	46.0(tied to u_{189})	-14.5	-3	52.1
u_{231}	H(24)...Si(35)	794.8(42)	117.9(fixed)	-87.6	-2	117.9
u_{291}	O(16)...H(46)	795.5(36)	60.1(tied to u_{189})	16.7	-1	68.0
u_{187}	H(25)...H(41)	795.8(86)	124.9(fixed)	82.3	2	124.9
u_{196}	H(24)...H(94)	797.9(77)	160.5(fixed)	-105.6	-1	160.5
u_{199}	C(22)...C(84)	800.9(62)	121.0(fixed)	-81.0	-2	121.0
u_{217}	O(4)...H(71)	801.5(35)	57.1(tied to u_{189})	21.5	1	64.7

u_{202}	C(22)...H(86)	802.1(69)	143.2(fixed)	-97.2	-1	143.2
u_{429}	H(27)...H(91)	804.4(62)	79.0(fixed)	-114.1	0	79.0
u_{316}	C(23)...H(94)	805.6(40)	120.5(fixed)	-103.4	-2	120.5
u_{311}	H(24)...H(81)	807.0(47)	116.3(fixed)	-86.4	-2	116.3
u_{271}	O(4)...H(51)	809.3(20)	36.5(fixed)	-28.1	-10	36.5
u_{305}	H(28)...H(82)	809.4(64)	114.8(fixed)	-61.0	-1	114.8
u_{341}	H(27)...Si(35)	811.6(30)	64.1(fixed)	-77.5	-7	64.1
u_{257}	Si(1)...H(50)	813.1(21)	63.3(fixed)	-32.2	-3	63.3
u_{262}	Si(1)...C(48)	816.4(11)	36.7(fixed)	-28.9	-10	36.7
u_{309}	H(24)...H(90)	817.4(47)	132.4(fixed)	-100.0	-2	132.4
u_{195}	H(24)...H(87)	818.7(72)	141.9(fixed)	-80.7	-1	141.9
u_{240}	O(7)...H(39)	819.1(34)	54.9(fixed)	-12.2	-3	54.9
u_{326}	C(23)...H(83)	821.1(33)	102.9(fixed)	-57.3	-3	102.9
u_{430}	H(27)...H(55)	824.4(67)	77.6(fixed)	-15.0	-2	77.6
u_{270}	O(16)...Si(31)	824.9(14)	24.5(fixed)	-1.5	0	24.5
u_{255}	O(16)...H(43)	825.1(46)	80.8(fixed)	14.7	0	80.8
u_{335}	C(23)...H(82)	827.4(51)	93.4(fixed)	-72.2	-3	93.4
u_{297}	H(28)...H(83)	827.8(50)	115.0(fixed)	-42.6	-1	115.0
u_{264}	Si(1)...H(42)	830.3(36)	52.6(fixed)	-3.3	-2	52.6
u_{350}	C(23)...H(93)	831.2(37)	105.9(fixed)	-116.4	-4	105.9
u_{356}	H(25)...H(82)	831.6(48)	118.0(fixed)	-119.2	-3	118.0
u_{274}	O(7)...H(25)	831.9(14)	50.0(fixed)	-41.4	-9	50.0
u_{183}	H(24)...H(46)	834.7(74)	120.6(fixed)	62.2	1	120.6
u_{272}	Si(1)...H(49)	835.6(19)	57.7(fixed)	-39.9	-4	57.7
u_{226}	O(16)...H(39)	837.1(21)	79.4(fixed)	-42.7	-3	79.4
u_{412}	H(24)...H(74)	842.4(46)	104.0(fixed)	-43.8	-2	104.0
u_{338}	C(22)...C(48)	845.4(76)	52.8(fixed)	-15.0	-3	52.8
u_{303}	O(4)...H(69)	848.8(41)	42.6(fixed)	-10.6	-4	42.6
u_{343}	C(22)...H(81)	855.7(38)	103.7(fixed)	-104.1	-3	103.7
u_{277}	H(25)...Si(30)	862.2(35)	103.1(fixed)	-92.4	-3	103.1
u_{437}	C(23)...H(53)	863.1(69)	56.8(fixed)	-27.5	-5	56.8
u_{290}	C(23)...H(98)	863.3(50)	114.5(fixed)	-49.6	-1	114.5
u_{289}	O(4)...C(64)	865.6(15)	33.8(fixed)	-33.1	-11	33.8
u_{349}	O(16)...H(45)	866.7(42)	45.8(fixed)	-11.7	-6	45.8
u_{319}	C(23)...C(80)	867.0(35)	92.1(fixed)	-63.1	-4	92.1
u_{351}	H(29)...Si(34)	867.8(42)	75.0(fixed)	7.9	-1	75.0
u_{381}	H(28)...H(62)	868.2(71)	101.3(fixed)	-10.8	-1	101.3
u_{359}	C(22)...H(51)	870.1(92)	64.3(fixed)	-6.6	-2	64.3
u_{254}	C(22)...H(87)	870.6(63)	134.6(fixed)	-107.1	-1	134.6
u_{288}	O(4)...H(66)	872.2(24)	59.1(fixed)	-39.8	-4	59.1
u_{362}	H(27)...H(83)	874.6(32)	103.9(fixed)	-79.4	-3	103.9
u_{259}	H(24)...H(93)	875.0(70)	155.2(fixed)	-124.2	-1	155.2
u_{378}	C(23)...Si(34)	877.1(42)	49.0(fixed)	-8.0	-4	49.0
u_{340}	H(28)...H(99)	879.2(51)	108.0(fixed)	-69.8	-2	108.0
u_{420}	C(22)...H(54)	880.2(46)	83.4(fixed)	-45.7	-3	83.4
u_{328}	H(29)...H(83)	880.7(38)	116.1(fixed)	-46.9	-2	116.1

u_{230}	C(23)...Si(30)	883.0(21)	96.5(fixed)	-47.1	-2	96.5
u_{377}	H(27)...H(82)	884.4(52)	104.1(fixed)	-96.8	-3	104.1
u_{383}	H(25)...H(51)	885.0(111)	77.2(fixed)	5.5	-1	77.2
u_{353}	C(22)...H(49)	885.7(71)	62.5(fixed)	-31.1	-3	62.5
u_{184}	H(28)...Si(30)	886.1(34)	117.6(fixed)	-31.8	-1	117.6
u_{347}	H(24)...H(91)	889.2(41)	130.1(fixed)	-119.7	-2	130.1
u_{314}	Si(1)...H(51)	893.3(13)	39.3(fixed)	-37.9	-12	39.3
u_{268}	O(16)...C(40)	897.0(33)	57.3(fixed)	15.6	0	57.3
u_{193}	C(23)...H(85)	897.2(42)	139.7(fixed)	-62.8	-1	139.7
u_{227}	H(24)...H(77)	900.1(53)	152.1(fixed)	-78.8	-1	152.1
u_{243}	H(29)...Si(30)	903.8(25)	116.7(fixed)	-50.4	-2	116.7
u_{396}	C(23)...H(74)	908.0(61)	82.0(fixed)	-13.7	-2	82.0
u_{387}	H(25)...H(81)	909.7(38)	118.8(fixed)	-132.8	-3	118.8
u_{382}	H(24)...H(51)	912.4(88)	71.7(fixed)	-24.7	-2	71.7
u_{365}	H(24)...H(49)	919.0(68)	77.7(fixed)	-43.9	-3	77.7
u_{295}	H(24)...H(99)	919.1(51)	149.8(fixed)	-111.0	-2	149.8
u_{266}	C(23)...H(86)	921.9(39)	144.1(fixed)	-103.6	-2	144.1
u_{358}	C(23)...H(97)	924.1(34)	103.3(fixed)	-87.9	-4	103.3
u_{423}	H(24)...H(54)	925.3(45)	98.7(fixed)	-54.3	-2	98.7
u_{336}	H(28)...H(73)	925.5(68)	115.5(fixed)	25.3	0	115.5
u_{153}	H(24)...H(78)	928.2(41)	158.7(fixed)	-47.5	0	158.7
u_{376}	H(24)...H(50)	930.0(67)	66.1(fixed)	-49.0	-3	66.1
u_{244}	C(22)...C(76)	930.1(32)	126.6(fixed)	-78.3	-2	126.6
u_{446}	H(27)...H(53)	933.3(78)	62.4(fixed)	-40.2	-6	62.4
u_{298}	H(25)...H(87)	934.1(65)	151.2(fixed)	-136.4	-2	151.2
u_{337}	Si(30)...Si(32)	936.3(25)	34.8(fixed)	-3.0	-5	34.8
u_{269}	C(22)...H(77)	936.6(41)	138.7(fixed)	-88.0	-2	138.7
u_{223}	H(24)...H(98)	940.9(38)	162.7(fixed)	-93.7	-1	162.7
u_{323}	O(16)...H(50)	942.1(22)	71.6(fixed)	-29.8	-3	71.6
u_{333}	O(4)...H(65)	943.9(16)	35.5(fixed)	-43.2	-12	35.5
u_{442}	H(25)...H(54)	945.1(49)	87.0(fixed)	-60.8	-3	87.0
u_{352}	C(23)...H(62)	945.7(64)	97.4(fixed)	11.1	0	97.4
u_{332}	O(16)...C(48)	950.3(12)	44.4(fixed)	-28.8	-9	44.4
u_{198}	C(22)...H(78)	951.6(31)	147.1(fixed)	-63.2	-1	147.1
u_{286}	H(27)...Si(30)	954.4(21)	106.4(fixed)	-68.5	-3	106.4
u_{401}	C(23)...H(57)	954.9(41)	94.9(fixed)	-23.5	-2	94.9
u_{411}	H(27)...Si(34)	957.6(50)	55.0(fixed)	-18.3	-5	55.0
u_{321}	H(27)...H(98)	958.7(52)	125.2(fixed)	-59.5	-1	125.2
u_{348}	C(23)...H(81)	959.1(37)	103.6(fixed)	-76.4	-3	103.6
u_{237}	O(16)...H(41)	959.3(33)	80.4(fixed)	34.6	1	80.4
u_{242}	H(24)...H(79)	964.4(46)	149.7(fixed)	-79.3	-1	149.7
u_{369}	H(24)...H(73)	965.1(45)	113.4(fixed)	-0.7	-1	113.4
u_{320}	O(16)...H(42)	967.6(38)	64.0(fixed)	0.3	-2	64.0
u_{427}	H(27)...H(74)	969.3(63)	87.7(fixed)	-31.9	-2	87.7
u_{308}	H(28)...Si(31)	971.8(50)	89.6(fixed)	21.0	0	89.6
u_{339}	O(16)...H(49)	975.0(19)	62.5(fixed)	-42.2	-5	62.5

u_{379}	H(28)...H(61)	977.5(60)	98.6(fixed)	0.9	-1	98.6
u_{413}	C(22)...C(52)	983.8(39)	71.5(fixed)	-29.0	-4	71.5
u_{123}	H(28)...H(78)	986.5(72)	161.1(fixed)	2.4	1	161.1
u_{391}	C(22)...H(55)	986.8(43)	94.0(fixed)	-8.6	-1	94.0
u_{375}	C(23)...C(60)	990.8(54)	76.9(fixed)	4.4	-1	76.9
u_{306}	H(24)...H(97)	994.6(42)	155.2(fixed)	-124.2	-2	155.2
u_{292}	C(22)...H(79)	998.8(34)	138.3(fixed)	-99.0	-2	138.3
u_{167}	C(23)...H(78)	1000.8(54)	149.3(fixed)	-19.5	0	149.3
u_{209}	C(23)...C(76)	1006.7(37)	134.9(fixed)	-39.0	-1	134.9
u_{357}	H(27)...H(99)	1007.5(37)	121.9(fixed)	-74.6	-3	121.9
u_{294}	C(23)...H(87)	1009.5(30)	140.1(fixed)	-99.7	-2	140.1
u_{393}	H(27)...H(81)	1012.5(36)	116.9(fixed)	-102.5	-3	116.9
u_{176}	H(28)...H(77)	1015.7(53)	165.5(fixed)	-25.5	0	165.5
u_{315}	H(25)...H(77)	1020.5(40)	151.3(fixed)	-108.5	-2	151.3
u_{402}	H(27)...H(73)	1021.7(59)	105.4(fixed)	-2.6	-1	105.4
u_{426}	H(24)...H(75)	1021.9(49)	101.4(fixed)	-31.1	-2	101.4
u_{220}	C(23)...H(77)	1022.2(37)	153.5(fixed)	-41.0	-1	153.5
u_{368}	O(16)...H(51)	1023.2(15)	48.9(fixed)	-38.2	-8	48.9
u_{416}	C(23)...H(58)	1028.2(39)	86.9(fixed)	-40.6	-2	86.9
u_{330}	C(23)...Si(31)	1032.0(38)	67.8(fixed)	17.2	0	67.8
u_{346}	H(24)...H(70)	1032.1(49)	125.0(fixed)	-2.3	0	125.0
u_{219}	H(29)...H(77)	1032.4(43)	171.2(fixed)	-37.3	-1	171.2
u_{246}	H(25)...H(78)	1033.3(32)	159.6(fixed)	-80.8	-1	159.6
u_{371}	H(24)...Si(31)	1033.9(25)	80.7(fixed)	-24.9	-2	80.7
u_{422}	H(25)...H(55)	1039.5(45)	99.6(fixed)	-24.3	-2	99.6
u_{399}	H(24)...H(55)	1040.2(42)	106.7(fixed)	-19.1	-1	106.7
u_{390}	H(27)...H(62)	1043.3(66)	103.9(fixed)	5.9	-1	103.9
u_{436}	C(23)...H(59)	1046.2(42)	77.1(fixed)	-43.2	-4	77.1
u_{342}	H(29)...H(61)	1046.7(57)	114.4(fixed)	23.7	0	114.4
u_{415}	C(23)...H(63)	1049.4(56)	84.7(fixed)	-13.6	-2	84.7
u_{253}	H(28)...H(70)	1052.2(79)	127.9(fixed)	60.5	1	127.9
u_{388}	C(22)...Si(31)	1052.2(20)	54.2(fixed)	-27.9	-6	54.2
u_{434}	C(22)...H(53)	1056.2(49)	78.1(fixed)	-38.7	-4	78.1
u_{360}	C(22)...H(62)	1059.5(45)	104.5(fixed)	-6.0	-1	104.5
u_{386}	H(24)...H(62)	1061.0(46)	109.3(fixed)	-29.1	-1	109.3
u_{355}	C(23)...H(61)	1061.3(53)	97.3(fixed)	16.5	-1	97.3
u_{329}	H(25)...H(79)	1072.9(33)	154.8(fixed)	-123.6	-2	154.8
u_{207}	H(27)...H(78)	1079.8(55)	160.6(fixed)	-39.2	0	160.6
u_{400}	H(24)...Si(34)	1079.9(22)	69.2(fixed)	-43.4	-4	69.2
u_{408}	C(23)...H(75)	1082.4(58)	83.9(fixed)	-3.1	-2	83.9
u_{267}	C(23)...H(79)	1082.7(36)	146.9(fixed)	-61.5	-1	146.9
u_{279}	C(23)...H(70)	1093.9(66)	111.7(fixed)	54.1	1	111.7
u_{301}	H(29)...Si(31)	1096.4(36)	89.6(fixed)	34.8	0	89.6
u_{366}	H(27)...Si(31)	1100.5(42)	76.5(fixed)	1.4	-1	76.5
u_{438}	H(24)...H(53)	1100.6(47)	91.9(fixed)	-52.0	-3	91.9
u_{275}	H(27)...H(77)	1101.4(36)	164.4(fixed)	-64.0	-1	164.4

u_{354}	C(23)...H(67)	1114.4(36)	107.5(fixed)	1.9	-1	107.5
u_{445}	H(25)...H(53)	1117.8(51)	84.7(fixed)	-52.9	-5	84.7
u_{417}	H(25)...Si(31)	1125.2(24)	60.2(fixed)	-37.8	-6	60.2
u_{374}	C(22)...C(60)	1134.7(34)	84.9(fixed)	-5.2	-1	84.9
u_{433}	H(27)...H(63)	1139.6(60)	92.8(fixed)	-21.1	-2	92.8
u_{245}	H(28)...H(71)	1139.6(66)	125.7(fixed)	73.4	1	125.7
u_{302}	C(23)...C(68)	1140.2(55)	94.9(fixed)	44.2	0	94.9
u_{394}	C(23)...H(66)	1143.7(35)	93.3(fixed)	-25.9	-2	93.3
u_{419}	H(24)...H(67)	1148.8(38)	99.7(fixed)	-57.4	-2	99.7
u_{398}	H(25)...H(62)	1150.8(48)	110.9(fixed)	-10.7	-1	110.9
u_{395}	H(27)...H(61)	1154.2(56)	102.3(fixed)	9.5	-1	102.3
u_{307}	H(27)...H(79)	1154.2(36)	161.9(fixed)	-86.3	-1	161.9
u_{424}	C(22)...H(57)	1161.4(27)	82.3(fixed)	-55.6	-3	82.3
u_{397}	H(24)...H(69)	1173.1(40)	115.6(fixed)	-10.1	-1	115.6
u_{428}	C(22)...C(56)	1176.1(21)	59.7(fixed)	-55.9	-7	59.7
u_{322}	H(27)...H(70)	1177.6(68)	120.9(fixed)	41.1	0	120.9
u_{281}	C(23)...H(71)	1186.5(54)	113.1(fixed)	58.6	1	113.1
u_{431}	H(24)...H(57)	1197.5(35)	86.3(fixed)	-73.2	-3	86.3
u_{410}	C(22)...H(63)	1198.4(38)	93.4(fixed)	-19.3	-2	93.4
u_{327}	H(24)...H(71)	1200.4(39)	122.6(fixed)	28.3	0	122.6
u_{435}	C(22)...H(58)	1207.9(24)	69.4(fixed)	-71.5	-5	69.4
u_{425}	H(24)...H(63)	1209.6(39)	100.1(fixed)	-40.4	-2	100.1
u_{345}	C(22)...H(61)	1209.8(35)	103.8(fixed)	17.8	0	103.8
u_{361}	H(24)...H(61)	1212.2(38)	112.0(fixed)	-2.9	-1	112.0
u_{344}	C(23)...H(69)	1218.6(57)	105.0(fixed)	29.1	0	105.0
u_{407}	C(23)...H(65)	1219.2(36)	92.2(fixed)	-13.2	-2	92.2
u_{258}	H(29)...H(71)	1219.8(56)	130.8(fixed)	66.3	1	130.8
u_{441}	H(24)...H(65)	1226.3(32)	87.9(fixed)	-60.5	-3	87.9
u_{439}	H(24)...H(58)	1236.5(34)	79.7(fixed)	-83.9	-4	79.7
u_{443}	C(22)...H(59)	1244.9(24)	65.6(fixed)	-63.7	-6	65.6
u_{325}	H(27)...H(71)	1266.3(56)	122.1(fixed)	42.6	0	122.1
u_{444}	H(24)...H(59)	1277.8(27)	73.5(fixed)	-80.6	-5	73.5
u_{432}	H(25)...H(63)	1281.9(40)	101.8(fixed)	-27.7	-2	101.8
u_{384}	H(25)...H(61)	1294.6(36)	110.6(fixed)	8.4	-1	110.6
u_{385}	H(27)...H(69)	1295.7(59)	116.2(fixed)	14.0	0	116.2
u_{447}	H(25)...H(59)	1313.4(29)	72.4(fixed)	-72.0	-1	72.4

[a] Distances are in pm, anharmonicities are in nm^{-1}. Values in parentheses are the standard deviations on the last digits. See Fig. 1 for atom numbering.

Table S4. Least-squares correlation matrix (×100) for the GED refinement of $Si_6O_9(OSiMe_3)_6$.[a]

	p_8	u_{25}	u_{58}	u_{68}	k_2
p_7	–59	–66			
p_8			58	–54	
p_{10}		77			
u_8					75

[a] Only absolute values ≥ 50 are shown. k_2 is a scale factor.

Fig. S1. Molecular-intensity scattering and difference (experimental minus theoretical) curves for $Si_6O_9(OSiMe_3)_6$.