

The authors would like to express their thanks to Professors K. H. Kuo and H. Endoh for their encouragement and comments. The present work is partly supported by National Natural Science Foundation of China. One of the authors (YDY) would like to express sincere thanks to Inoue Foundation for Science, for the support to work by staying in Japan.

#### References

- ABBOTT, W. H. (1974). *IEEE Trans. Parts Hybrids Packag.* **10**, 24–27.  
 FRANEY, J. P., KAMMLOTT, G. W. & GRAEDEL, T. E. (1985). *Corros. Sci.* **25**, 133–143.

- GUAN, R., HASHIMOTO, H. & KUO, K. H. (1984). *Acta Cryst.* **B40**, 560–566.  
 GUAN, R., HASHIMOTO, H. & KUO, K. H. (1985). *Acta Cryst.* **B41**, 219–225.  
 GUAN, R., HASHIMOTO, H. & KUO, K. H. (1986). *Ultramicroscopy*, **20**, 195–202.  
 GUAN, R., HASHIMOTO, H. & KUO, K. H. (1989). *Solid State Phenom.* **5**, 73–84.  
 GUAN, R., HASHIMOTO, H. & YOSHIDA, T. (1984). *Acta Cryst.* **B40**, 109–114.  
 GUAN, R., LU, J., KUO, K. H. & HASHIMOTO, H. (1986). Proc. XIth Int. Congr. on Electron Microscopy, Kyoto, Japan, pp. 831–832.  
 ISHII, M. & HASHIMOTO, H. (1967). *Jpn. J. Appl. Phys.* **6**, 173–180.  
 ISHIZUKA, K. (1982). *Acta Cryst.* **A38**, 773–779.  
 RICKERT, H. (1959). *Z. Phys. Chem.* **21**, 432–435.  
 SHOJIRI, M., MAEDA, S. & MURATA, Y. (1969). *Jpn. J. Appl. Phys.* **8**, 24–31.  
 VOLPE, L. & PETERSON, P. J. (1989). *Corros. Sci.* **29**, 1179–1196.

*Acta Cryst.* (1995). **B51**, 155–161

## The Crystal and Molecular Structure of Dodecahydridosilasesquioxane, H<sub>12</sub>Si<sub>12</sub>O<sub>18</sub>

BY KARL WILHELM TÖRNROOS

*Structural Chemistry, Stockholm University, 106 91 Stockholm, Sweden*

HANS-BEAT BÜRGI

*Institut für Chemische und Mineralogische Kristallographie, Universität Bern, 3012 Bern, Switzerland*

AND GION CALZAFERRI AND HERIBERT BÜRGI

*Institut für Anorganische, Analytische und Physikalische Chemie, Universität Bern, 3000 Bern 9, Switzerland*

(Received 23 February 1994; accepted 22 November 1994)

#### Abstract

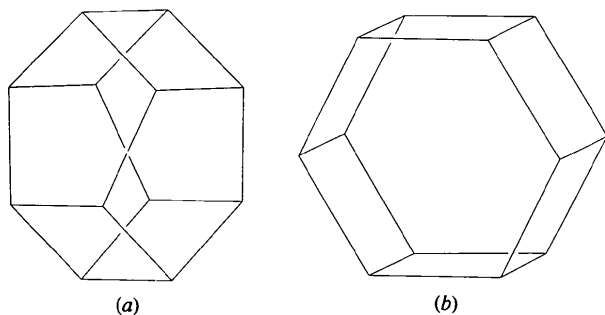
The title compound belongs to a family of cage-shaped spherosiloxane molecules which show, as a common and systematic feature, smaller or larger distortions from their respective ideal point-group symmetry. By means of statistical methods in combination with rigid-body analysis, the molecular distortions involved in the lowering of the molecular symmetry of H<sub>12</sub>Si<sub>12</sub>O<sub>18</sub> and (C<sub>6</sub>H<sub>5</sub>)<sub>12</sub>Si<sub>12</sub>O<sub>18</sub> have been analysed. The magnitudes and types of the deformations may be described in terms of a small number of symmetry displacement coordinates involving displacement of flexibly joined, but otherwise rigid, corner-sharing tetrahedra.

#### Introduction

In a series of studies the geometries of spherosilasesquioxane molecules are being analysed. Previous papers have reported results for H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> (Auf der Heyde,

Bürgi, Bürgi & Törnroos, 1991; Törnroos, 1994; Törnroos, Schwarzenbach, Larsen & Delley, 1995), Cl<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> (Törnroos, Calzaferri & Imhof, 1995), H<sub>10</sub>Si<sub>10</sub>O<sub>15</sub> (Bürgi, Törnroos, Calzaferri & Bürgi, 1993), Co(CO)<sub>4</sub>H<sub>7</sub>Si<sub>8</sub>O<sub>12</sub> (Calzaferri, Imhof & Törnroos, 1993) and (C<sub>6</sub>H<sub>13</sub>)H<sub>7</sub>Si<sub>8</sub>O<sub>12</sub> (Calzaferri, Imhof & Törnroos, 1994). The structures of two isomers, *D*<sub>3h</sub> (*6m2*) and *C*<sub>2v</sub> (*mm*), of H<sub>14</sub>Si<sub>14</sub>O<sub>21</sub> have been previously reported by Agaskar, Day & Klempner (1987). This report describes H<sub>12</sub>Si<sub>12</sub>O<sub>18</sub>, pictured in Fig. 1. The molecular connectivity shows four ten-membered rings and four eight-membered rings of alternating Si and O atoms. In zeolite language, where only the Si atoms are counted, it would be four five- and four four-membered rings, see scheme (a) below. The highest attainable point-group symmetry of this molecule is *D*<sub>2d</sub> (*42m*). In the crystalline state the molecule is strongly distorted, its symmetry being only *C*<sub>1</sub> (1). A second type of arrangement of this structure is also possible, namely that of two six-rings bridged by six O atoms, with molecular symmetry *D*<sub>6h</sub> (*6/mmm*), see

scheme (b). This latter form has not yet been observed as a molecular species. It is found as a building unit in double ring silicates, however.



We compare our structural results with those for the structure of  $(C_6H_5)_{12}Si_{12}O_{18}$  (Clegg, Sheldrick & Vater, 1980), which has molecular symmetry  $S_4$  ( $\bar{4}$ ), and a framework structure close to  $D_{2d}$  symmetry. Our objectives are to determine the nature of the deformations from the ideal  $D_{2d}$  symmetry for the two structures, as well as the degree of the deformations and to test a simple model describing the flexibility of  $R_{2n}Si_{2n}O_{3n}$  molecules, as well as  $T_{2n}O_{3n}$  fragments in zeolites.

### Experimental

$H_{12}Si_{12}O_{18}$  was synthesized according to the procedure published by Frye & Collins (1970), and separated by size-exclusion chromatography (Bürgy & Calzaferrri, 1990). Colourless transparent crystals were obtained

Table 1. *Crystal data, data collection and refinement parameters*

Crystal data	
Chemical formula	$H_{12}Si_{12}O_{18}$
Molecular weight	637.11
Crystal system	Orthorhombic
Space group	$Pbca$
$a$ (Å)	14.605 (2)
$b$ (Å)	20.738 (3)
$c$ (Å)	15.420 (2)
$V$ (Å <sup>3</sup> )	4670.4 (1)
$Z$	8
$D_c$ (g cm <sup>-3</sup> )	1.812
Radiation type	Mo $K\alpha$
Wavelength (Å)	0.71073
No. of reflections for cell parameters	18
Transmission factor range	0.9832–0.9993
$\mu$ (cm <sup>-1</sup> )	7.39
Temperature (K)	130
Crystal colour	Colourless
Crystal form	Transparent prism
Crystal size (mm)	0.2 × 0.2 × 0.2
Data collection	
Data collection method	$\omega/2\theta$ scans
No. of measured reflections	5124
No. of independent reflections	5073
No. of observed reflections	2849
Observation criterion	$[F_o^2 > 3.0\sigma(F_o^2)]$
$R_{int}$	0.0170
$2\theta_{max}$ (°)	53.92
Range of $h, k, l$	0 → $h$ → 18 0 → $k$ → 26 0 → $l$ → 19
Maximum $\sin \theta/\lambda$ (Å <sup>-1</sup> )	0.6379
Refinement	
Final $R^*$	0.0355
Final $wR^\dagger$	0.0844
$S^\ddagger$	1.102
No. of refined parameters	284
$(\Delta/\sigma)_{mean,max}$	< 0.001
$\Delta\rho_{max}$ (e Å <sup>-3</sup> )	0.50
$\Delta\rho_{min}$ (e Å <sup>-3</sup> )	-0.32

\*  $R = \sum ||F_o| - |F_c|| / \sum |F_o|$ ; conventional  $R$ -value based on  $F_o > 4\sigma(F_o)$  observation criterion.

†  $wR = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$ ;  $w = 1/[\sigma^2(F_o^2) + (0.0329P)^2 + 8.10P]$ ,  $P = [\max.(F_o^2, 0) + 2F_c^2]/3$ .

‡  $S = \{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{1/2}$ .

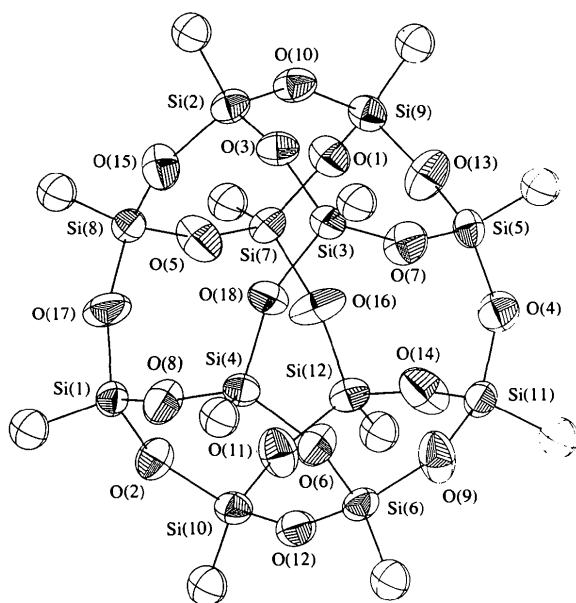


Fig. 1. Structure of the title compound with atomic numbering and displaying displacement ellipsoids at 50% probability.

through slow evaporation of a saturated solution of the compound in a 1:1 mixture of  $CH_2Cl_2/n$ -hexane.

Details on the X-ray experiment and structure refinement are given in Table 1. Intensities were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromated Mo  $K\alpha$  radiation. Four reflections were monitored at intervals of 100 reflections. The intensity decay amounting to 12.9% was corrected for by linear interpolation. Semi-empirical psi-scan absorption correction was applied. The structure was solved by direct methods using *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Structural least-squares refinement with respect to  $F^2$  was carried out using *SHELXL92* (Sheldrick, 1992), refining anisotropic displacement parameters for all non-H atoms. H atoms were given geometrically idealized positions and the Si—H distances restrained to 1.460 Å, as found from a

Table 2. Atomic coordinates and isotropic displacement parameters (Å) for H<sub>12</sub>Si<sub>12</sub>O<sub>18</sub>

$$U_{eq} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	x	y	z	$U_{eq}$
Si(1)	0.10035 (9)	0.48044 (6)	0.16465 (8)	0.0340 (3)
Si(2)	0.14232 (9)	0.23069 (6)	0.21647 (9)	0.0361 (3)
Si(3)	0.09907 (8)	0.25670 (6)	0.02258 (9)	0.0326 (3)
Si(4)	0.04708 (9)	0.40183 (6)	-0.00178 (8)	0.0331 (3)
Si(5)	0.30643 (8)	0.24225 (6)	-0.02176 (9)	0.0346 (3)
Si(6)	0.21256 (9)	0.46114 (7)	-0.10112 (8)	0.0361 (3)
Si(7)	0.39012 (9)	0.35287 (6)	0.24674 (9)	0.0340 (3)
Si(8)	0.17784 (8)	0.36946 (6)	0.28271 (8)	0.0328 (3)
Si(9)	0.35025 (9)	0.21876 (6)	0.17572 (9)	0.0366 (3)
Si(10)	0.26931 (9)	0.53571 (6)	0.06764 (9)	0.0361 (3)
Si(11)	0.38524 (9)	0.37351 (7)	-0.08404 (8)	0.0363 (3)
Si(12)	0.43720 (9)	0.44367 (6)	0.09057 (9)	0.0360 (3)
O(1)	0.4012 (2)	0.2781 (2)	0.2226 (2)	0.0448 (9)
O(2)	0.1891 (2)	0.5212 (2)	0.1356 (2)	0.0429 (8)
O(3)	0.1019 (2)	0.2287 (2)	0.1195 (2)	0.0400 (8)
O(4)	0.3601 (2)	0.2988 (2)	-0.0699 (3)	0.0497 (9)
O(5)	0.2837 (2)	0.3701 (2)	0.2562 (2)	0.0555 (10)
O(6)	0.1235 (2)	0.4211 (2)	-0.0715 (2)	0.0459 (9)
O(7)	0.1996 (2)	0.2582 (2)	-0.0190 (2)	0.0523 (10)
O(8)	0.0536 (3)	0.4480 (2)	0.0812 (2)	0.0505 (9)
O(9)	0.2965 (3)	0.4126 (2)	-0.1147 (2)	0.0563 (10)
O(10)	0.2485 (2)	0.2100 (2)	0.2152 (2)	0.0418 (8)
O(11)	0.3606 (3)	0.4979 (2)	0.0969 (2)	0.0518 (9)
O(12)	0.2383 (3)	0.5136 (2)	-0.0282 (2)	0.0433 (8)
O(13)	0.3445 (2)	0.2327 (2)	0.0740 (2)	0.0580 (11)
O(14)	0.4238 (3)	0.4029 (2)	0.0034 (3)	0.0622 (11)
O(15)	0.1321 (2)	0.3030 (2)	0.2546 (3)	0.0486 (9)
O(16)	0.4341 (3)	0.3965 (2)	0.1719 (3)	0.0612 (11)
O(17)	0.1281 (3)	0.4276 (2)	0.2342 (3)	0.0590 (11)
O(18)	0.0585 (3)	0.3281 (2)	0.0250 (3)	0.0569 (10)

single-crystal neutron diffraction study on H<sub>8</sub>Si<sub>8</sub>O<sub>12</sub> (Törnroos, 1994). A single isotropic displacement parameter common to all H atoms was refined.\* Molecular drawings were made with *PEANUT* (Hummel, Hauser & Bürgi, 1990) and *SCHAKAL92* (Keller, 1992). Rigid-body calculations were made using *THMA11* (Trueblood, 1985), and additional geometrical calculations with *PLATON90* (Spek, 1990).

### Discussion

Table 2 gives the fractional coordinates of the title compound and Table 3 lists distances and angles for the H<sub>12</sub>Si<sub>12</sub>O<sub>18</sub> cage structure. The Si—O distances  $d$  are inversely correlated to the Si—O—Si angle  $\alpha$ , and follow the equation  $d = 1.59 + [(180 - \alpha)^4 \times 2.1 \times 10^{-8}]$  deduced earlier for the R<sub>10</sub>Si<sub>10</sub>O<sub>15</sub> compounds (Bürgi, Törnroos, Calzaferri & Bürgy, 1993). Si—O distances and O—Si—O angles vary relatively little, 1.582–1.617 Å and 108.3–111.5°, respectively; Si—O—Si angles vary substantially more, 142.9–164.2°. Population means and standard deviations are 1.601 (8) Å [1.611 (4)] for Si—O distances,

\*Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, and extracts from the Principal Components Analysis have been deposited with the IUCr (Reference: CR0477). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. Bond distances (Å) and angles (°) in H<sub>12</sub>Si<sub>12</sub>O<sub>18</sub>

Si(1)—O(2)	1.611 (3)	Si(7)—O(1)	1.602 (3)
Si(1)—O(8)	1.605 (4)	Si(7)—O(5)	1.602 (3)
Si(1)—O(17)	1.587 (3)	Si(7)—O(16)	1.601 (3)
Si(2)—O(3)	1.608 (3)	Si(8)—O(5)	1.599 (3)
Si(2)—O(10)	1.609 (3)	Si(8)—O(15)	1.592 (3)
Si(2)—O(15)	1.617 (4)	Si(8)—O(17)	1.593 (3)
Si(3)—O(3)	1.603 (3)	Si(9)—O(1)	1.609 (3)
Si(3)—O(7)	1.603 (3)	Si(9)—O(10)	1.616 (3)
Si(3)—O(18)	1.596 (3)	Si(9)—O(13)	1.597 (4)
Si(4)—O(6)	1.601 (3)	Si(10)—O(2)	1.601 (3)
Si(4)—O(8)	1.600 (3)	Si(10)—O(11)	1.611 (4)
Si(4)—O(18)	1.592 (3)	Si(10)—O(12)	1.613 (4)
Si(5)—O(4)	1.593 (3)	Si(11)—O(4)	1.608 (4)
Si(5)—O(7)	1.594 (3)	Si(11)—O(9)	1.601 (4)
Si(5)—O(13)	1.591 (3)	Si(11)—O(14)	1.582 (4)
Si(6)—O(6)	1.609 (3)	Si(12)—O(11)	1.590 (4)
Si(6)—O(9)	1.600 (3)	Si(12)—O(14)	1.601 (4)
Si(6)—O(12)	1.608 (3)	Si(12)—O(16)	1.591 (4)
Si(7)—O(1)—Si(9)	142.9 (2)	O(6)—Si(4)—O(8)	110.3 (2)
Si(1)—O(2)—Si(10)	150.4 (2)	O(6)—Si(4)—O(18)	109.9 (2)
Si(2)—O(3)—Si(3)	150.1 (2)	O(8)—Si(4)—O(18)	111.1 (2)
Si(5)—O(4)—Si(11)	152.2 (3)	O(4)—Si(5)—O(7)	109.9 (2)
Si(7)—O(5)—Si(8)	163.7 (3)	O(4)—Si(5)—O(13)	110.7 (2)
Si(4)—O(6)—Si(6)	152.0 (2)	O(7)—Si(5)—O(13)	110.0 (2)
Si(3)—O(7)—Si(5)	154.6 (3)	O(6)—Si(6)—O(9)	109.4 (2)
Si(1)—O(8)—Si(4)	156.5 (3)	O(6)—Si(6)—O(12)	109.9 (2)
Si(6)—O(9)—Si(11)	154.2 (3)	O(9)—Si(6)—O(12)	109.7 (2)
Si(2)—O(10)—Si(9)	149.4 (2)	O(1)—Si(7)—O(5)	109.6 (2)
Si(10)—O(11)—Si(12)	155.4 (3)	O(1)—Si(7)—O(16)	109.8 (2)
Si(6)—O(12)—Si(10)	154.0 (2)	O(5)—Si(7)—O(16)	109.2 (2)
Si(5)—O(13)—Si(9)	162.4 (2)	O(5)—Si(8)—O(15)	110.1 (2)
Si(11)—O(14)—Si(12)	164.2 (3)	O(5)—Si(8)—O(17)	108.3 (2)
Si(2)—O(15)—Si(8)	149.6 (2)	O(15)—Si(8)—O(17)	109.7 (2)
Si(7)—O(16)—Si(12)	158.0 (3)	O(1)—Si(9)—O(10)	110.0 (2)
Si(1)—O(17)—Si(8)	163.0 (3)	O(1)—Si(9)—O(13)	109.1 (2)
Si(3)—O(18)—Si(4)	157.5 (3)	O(10)—Si(9)—O(13)	110.0 (2)
O(2)—Si(1)—O(8)	109.9 (2)	O(2)—Si(10)—O(11)	109.3 (2)
O(2)—Si(1)—O(17)	110.1 (2)	O(2)—Si(10)—O(12)	110.0 (2)
O(8)—Si(1)—O(17)	111.2 (2)	O(11)—Si(10)—O(12)	110.5 (2)
O(3)—Si(2)—O(10)	109.6 (2)	O(4)—Si(11)—O(9)	110.1 (2)
O(3)—Si(2)—O(15)	109.1 (2)	O(4)—Si(11)—O(14)	109.7 (2)
O(10)—Si(2)—O(15)	109.9 (2)	O(9)—Si(11)—O(14)	110.2 (2)
O(3)—Si(3)—O(7)	110.8 (2)	O(11)—Si(12)—O(14)	109.8 (2)
O(3)—Si(3)—O(18)	108.9 (2)	O(11)—Si(12)—O(16)	111.5 (2)
O(7)—Si(3)—O(18)	109.4 (2)	O(14)—Si(12)—O(16)	109.5 (2)

109.9 (6)° [109.0 (1)] for O—Si—O angles, and 155.0 (6)° [150.5 (4)] for Si—O—Si angles [values within square brackets refer to (C<sub>6</sub>H<sub>5</sub>)<sub>12</sub>Si<sub>12</sub>O<sub>18</sub>].

The large range of Si—O angles shows that spherosilasesquioxane molecules of the type R<sub>2n</sub>Si<sub>2n</sub>O<sub>3n</sub> are quite flexible. Not only the Si—O—Si bond angles, but also the Si—O torsion angles may be deformed with very little cost in energy (Gibbs, Meagher, Newton & Swanson, 1981) compared with deformations of Si—O distances and O—Si—O angles. This makes it expedient to describe the geometry of the R<sub>2n</sub>Si<sub>2n</sub>O<sub>3n</sub> framework in terms of corner-sharing rigid tetrahedra, whose connections at oxygen behave like flexible ball joints (Bürgi, Törnroos, Calzaferri & Bürgy, 1993; Bieniok & Bürgi, 1994a,b). The number of geometric degrees of freedom to describe the geometry of the Si<sub>2n</sub>O<sub>3n</sub> skeleton is thereby reduced from 3(2n + 3n) - 6 = 15n - 6 to 15n - 6 - 6(2n) = 3n - 6, *i.e.* from 54 to 6 for Si<sub>8</sub>O<sub>12</sub>, from 69 to 9 for Si<sub>10</sub>O<sub>15</sub> and from 84 to 12 for Si<sub>12</sub>O<sub>18</sub>.

Since known  $R_{2n}Si_{2n}O_{3n}$  molecules show topological but only approximate geometric symmetry, it is convenient to describe their structures in relation to their highest attainable point-group symmetries, [ $O_h$  ( $m3m$ ),  $D_{5h}$  ( $10m2$ ) and  $D_{2d}$  for  $R_8Si_8O_{12}$ ,  $R_{10}Si_{10}O_{15}$  and  $R_{12}Si_{12}O_{18}$ , respectively], using symmetry deformation coordinates which transform as irreducible representations of these point groups; for  $R_{12}Si_{12}O_{18}$ :  $7A_1$ ,  $5A_2$ ,  $5B_1$ ,  $7B_2$  and  $12E$ . Assuming distances and angles at Si to be approximately constant leaves  $2A_1$ ,  $1A_2$ ,  $1B_1$ ,  $2B_2$  and  $3E$  coordinates, *i.e.* 12 degrees of freedom. Deformation along each of these coordinates separately leaves some or all of the original symmetry intact (kernel symmetries; Murray-Rust, Bürgi & Dunitz, 1979):  $D_{2d}$  for  $A_1$ ,  $S_4$  for  $A_2$ ,  $D_2$  (222) for  $B_1$ ,  $C_{2v}$  for  $B_2$  and  $C_s$  ( $m$ ) for  $E$  (deformation along one of the two degenerate components). The degree of distortion along each of these is thus a measure of the degree of loss in symmetry or, expressed positively, distortion coordinates give a quantitative expression to the notion of approximate symmetry (Murray-Rust, Bürgi & Dunitz, 1978; Bürgi & Dunitz, 1993).

We find it useful to utilize the non-bonded O...O 1,5-distances within the two different ring types, as a measure of the molecular deformation, and have consequently analysed the distortions of  $(C_6H_5)_{12}Si_{12}O_{18}$  and  $H_{12}Si_{12}O_{18}$  in terms of these non-bonded distances using principal component analysis, PCA (The SAS System, 1992). There are 28 such 1,5-distances within each cage molecule, and their values are listed in Table 4. Since the crystallographic symmetry of  $(C_6H_5)_{12}Si_{12}O_{18}$  is  $S_4$ , and that of  $H_{12}Si_{12}O_{18}$  is  $C_1$ , it follows from the above symmetry analysis that the only deformation types possible for the phenyl-substituted compound are  $A_1$  and  $A_2$ ; all 12 types are possible for  $H_{12}Si_{12}O_{18}$ , but only eight are found to be of significant magnitudes. The PCA thus indicates that only eight of the 12 degrees of freedom are necessary to account for 100% of the deformation. The six largest still account for 95.4% of the total deformation. The six significant magnitudes, presented in Table 5, are in descending order of importance,  $B_2$ ,  $A_2$ ,  $A_1$ ,  $E$ ,  $B_1$  and  $E$ . By way of example, the first three are illustrated in Figs. 2(a)–(c), displaying the deformation vectors between the non-bonded O...O 1,5-atoms. The coordinate  $A_1$ , Fig. 2(a), is an expansion/contraction type of deformation along the  $S_4$ -axis of the undistorted molecule;  $H_{12}Si_{12}O_{18}$  is elongated relative to  $(C_6H_5)_{12}Si_{12}O_{18}$ , as may also be seen from the O(10)...O(12) distances from the top to the bottom of the molecule, which are 7.33 (1) and 7.06 (1) Å, respectively. The  $B_2$  coordinate, Fig. 2(b), is related to the  $A_1$  coordinate in that the top half of the molecule is compressed, whereas the bottom half is elongated (or *vice versa*), thus deforming the molecule towards a pear shape. This coordinate contributes most to the total deformation of  $H_{12}Si_{12}O_{18}$ . In the  $A_2$  deformation, Fig. 2(c), the two groups of four equivalent O atoms

Table 4. Non-bonded O...O 1,5-distances (Å) in  $H_{12}Si_{12}O_{18}$  and  $(C_6H_5)_{12}Si_{12}O_{18}$  (atomic labelling of the former has been applied to the latter)

	$H_{12}Si_{12}O_{18}$	$(C_6H_5)_{12}Si_{12}O_{18}$
Eight-membered rings		
O(1)...O(15)	3.994 (4)	3.947 (7)
O(2)...O(6)	3.929 (5)	3.947 (7)
O(3)...O(13)	3.611 (5)	3.947 (7)
O(5)...O(10)	3.418 (5)	3.447 (7)
O(7)...O(10)	3.814 (5)	3.447 (7)
O(8)...O(12)	3.461 (5)	3.447 (7)
O(9)...O(11)	3.829 (5)	3.947 (7)
O(12)...O(14)	3.584 (5)	3.447 (7)
Ten-membered rings		
O(1)...O(4)	4.570 (5)	4.486 (7)
O(1)...O(14)	4.269 (5)	3.720 (7)
O(2)...O(5)	3.896 (5)	3.720 (7)
O(2)...O(16)	4.450 (5)	4.486 (7)
O(3)...O(8)	4.639 (5)	3.720 (7)
O(3)...O(17)	4.504 (5)	4.486 (7)
O(4)...O(6)	4.286 (5)	4.348 (7)
O(4)...O(16)	4.380 (5)	4.769 (8)
O(4)...O(18)	4.682 (5)	4.769 (8)
O(5)...O(11)	3.785 (5)	3.626 (7)
O(6)...O(7)	3.648 (5)	3.626 (7)
O(7)...O(9)	3.799 (6)	3.720 (7)
O(8)...O(15)	4.184 (5)	3.626 (7)
O(9)...O(18)	4.449 (5)	4.486 (7)
O(11)...O(17)	4.259 (5)	4.348 (7)
O(13)...O(14)	3.871 (6)	3.626 (7)
O(13)...O(16)	3.942 (6)	4.348 (7)
O(15)...O(18)	3.737 (6)	4.348 (7)
O(16)...O(17)	4.616 (5)	4.769 (8)
O(17)...O(18)	3.962 (6)	4.769 (8)

Table 5. Degree of deformation (Å) for various deformation types in  $H_{12}Si_{12}O_{18}$  and  $(C_6H_5)_{12}Si_{12}O_{18}$

Deformation type	$H_{12}Si_{12}O_{18}$	$(C_6H_5)_{12}Si_{12}O_{18}$
$A_1$	0.65	-0.65
$A_2$	0.73	0.24
$B_1$	0.42	0
$B_2$	0.85	0
$E$	0.55	0
$E$	0.32	0
Total	1.50	0.69

at the top and bottom of the molecule move most. In both groups the oxygen displacements are up-down-up-down and preserve overall  $S_4$  symmetry. The ten-membered rings are thereby elongated. The  $B_1$  coordinate is similar to the  $A_2$  coordinate in the up-down-up-down displacements within each of the two groups of four O atoms, but here the correlation between the top and bottom group is such as to maintain  $D_2$  symmetry. The  $A_2$ ,  $B_1$  and  $B_2$  coordinates contribute to distort  $H_{12}Si_{12}O_{18}$  substantially, 1.2 Å. In comparison, the deviation of  $(C_6H_5)_{12}Si_{12}O_{18}$  from  $D_{2d}$  to  $S_4$  symmetry is quite small, 0.24 Å. The  $E$  coordinates are more complicated in nature and are not discussed further here; their shape may be derived from the information given in the supplementary material.

We have applied a rigid-body analysis (Trueblood, 1985) using the observed harmonic displacement

parameters for the cage-framework atoms of  $\text{H}_{12}\text{Si}_{12}\text{O}_{18}$ . The analysis was based upon the Si atoms only, since a Hirshfeld rigid-body test and a comparison of figures of merit showed that the Si atoms follow the rigid-body hypothesis much better than the O atoms. Based on the translation, libration and screw-coupling tensors derived from  $\text{U}(\text{Si})$ , the  $\text{U}(\text{O})$ 's were subsequently calculated. The graphical representation (Hummel, Hauser & Bürgi, 1990) of

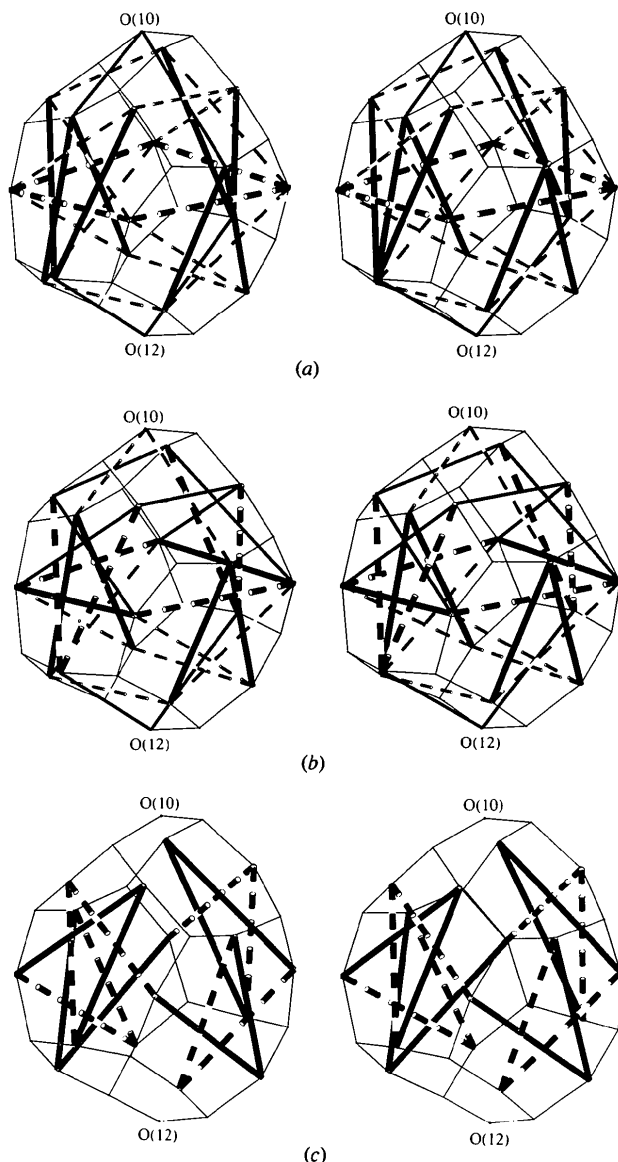


Fig. 2. Stereoscopic illustrations of molecular deformations in the  $\text{Si}_{12}\text{O}_{18}$  skeleton. Full lines indicate a lengthening, broken lines a shortening of the corresponding  $\text{O}\cdots\text{O}$  distance (or *vice versa*) and thick lines a large magnitude of deformation. The  $S_4$ -axis runs along the vector  $\text{O}_{10}\cdots\text{O}_{12}$ . (a) Deformation of type  $A_1$ , (b) deformation of type  $B_2$  and (c) deformation of type  $A_2$ .

$[\text{U}(\text{O,obs}) - \text{U}(\text{O,calc})]^{1/2}$  is presented in Fig. 3. The difference in magnitude of the residual r.m.s. displacements between Si and O atoms is obvious. The residual components for the O atoms are most pronounced in the out-of-plane direction, along the bisector of the  $\text{Si}-\text{O}-\text{Si}$  plane, and negligible along the  $\text{Si}-\text{O}$  bond direction. In general, the O atoms at the top and bottom of the molecule appear less effected, which agrees well with the observations from the deformation analysis discussed above, see also Fig. 2. The results of the rigid-body analysis of the  $(\text{C}_6\text{H}_5)_{12}\text{Si}_{12}\text{O}_{18}$  molecule are qualitatively the same. The conclusion is that the residual components represent intramolecular vibrations consistent with the concept of the soft  $\text{Si}-\text{O}-\text{Si}$  angles in contrast to the stiffer  $\text{O}-\text{Si}-\text{O}$  angles.

In our earlier analysis of  $R_{10}\text{Si}_{10}\text{O}_{15}$  molecules, it was shown how the residual atomic displacements from the rigid-body analysis can be related to the static distortions without performing an extensive normal coordinate analysis. The procedure of accomplishing this involves generating all isometric structures of the cage framework of each of the molecules studied, by permuting the non-bonded distances according to the point-group symmetry in question. In the present case we obtain eight isometric copies for each of the two molecules. We then superimpose the Si atoms of these isometric copies

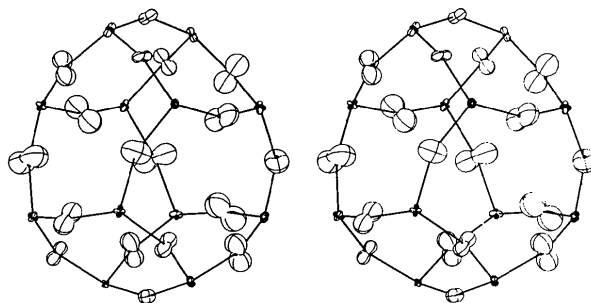


Fig. 3. Difference r.m.s. displacement surfaces,  $[\text{U}(\text{obs}) - \text{U}(\text{TLS})]^{1/2}$ , for the title compound at 130 K. Solid outlines represent positive differences. Scale: 3.08.

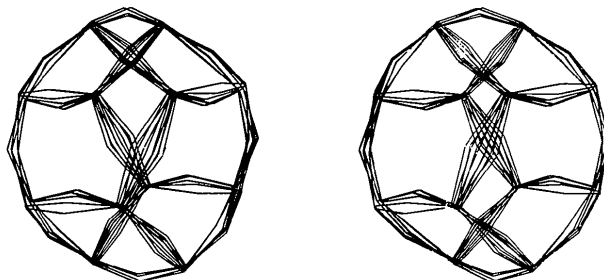


Fig. 4. Composite drawing of all isometric structures of  $\text{H}_{12}\text{Si}_{12}\text{O}_{18}$  and  $(\text{C}_6\text{H}_5)_{12}\text{Si}_{12}\text{O}_{18}$ , obtained by superimposing the Si atoms with a least-squares algorithm.

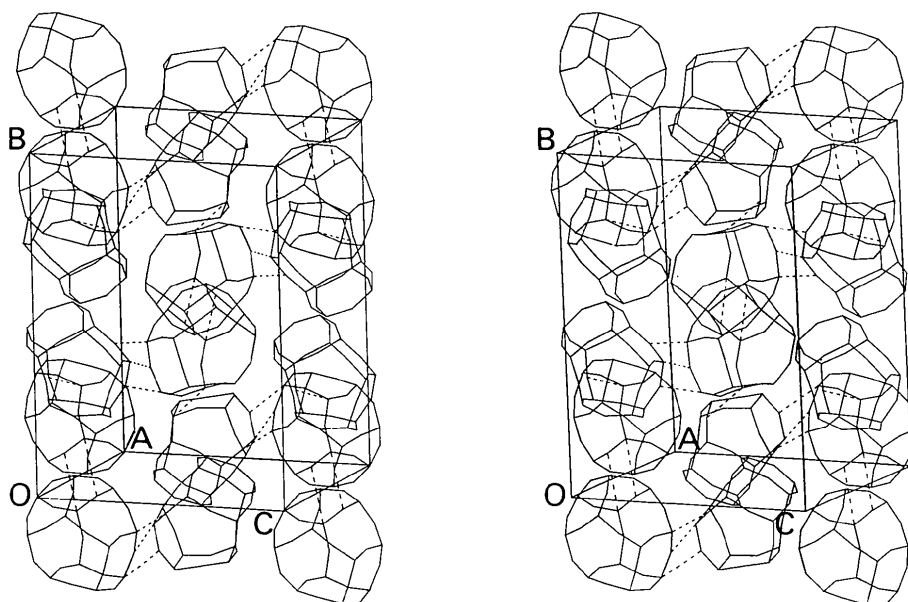


Fig. 5. Stereoscopic illustration of the packing arrangement of  $H_{12}Si_{12}O_{18}$ . H atoms have been omitted, dashed lines indicate the shortest intermolecular  $O \cdots Si$  contacts.

using a least-squares algorithm. The result is shown in Fig. 4 (*QUANTA*; Molecular Simulations Inc., 1990). The Si atoms superimpose quite well, whereas the O atoms do not. The pattern of oxygen displacements is reminiscent of the residual displacements found in the rigid-body analysis. A simple comparison of Fig. 3 and 4 thus shows congruent results of the two different types of analyses.

The packing of the  $H_{12}Si_{12}O_{18}$  molecules in the crystal is illustrated in Fig. 5. The molecules are arranged in columns running along the *b*-axis. The small hydrogen substituent renders possible an extensive network of intermolecular  $Si \cdots O$  contacts, indicated with dashed lines in Fig. 5. Such contacts are also observed in the packing of  $H_8Si_8O_{12}$ ,  $H_{10}Si_{10}O_{15}$ ,  $Co(CO)_4H_7Si_8O_{12}$  and  $(C_6H_{13})H_7Si_8O_{12}$ . They are interpreted as indications of incipient nucleophilic attack of O on Si, or of incipient five-coordination of the Si atoms. The distances in question are in the range 3.656–3.775 (4) Å, and the associated  $O \cdots Si-O$  angles are 159.6–174.1 (2)°. Due to steric congestion, short contacts of this kind are obviously not present in  $(C_6H_5)_{12}Si_{12}O_{18}$  and  $Cl_8Si_8O_{12}$ . Typically, the crystal density is also considerably larger in the case of  $H_{12}Si_{12}O_{18}$  (1.81 g cm<sup>-3</sup>) compared with  $(C_6H_5)_{12}Si_{12}O_{18}$  (1.19 g cm<sup>-3</sup>).

In conclusion, we argue that the relatively close  $Si \cdots O$  contacts between the  $H_{2n}Si_{2n}O_{3n}$  molecules exercise a major rôle on the magnitudes of the molecular deformations, as is particularly well reflected by the magnitudes and directions of the atomic displacement parameters for the O atoms. The ensuing complicated and extensive lowering of the molecular symmetry

occurs almost exclusively along only a few soft deformation coordinates.

Similar analyses have been performed for  $R_8Si_8O_{12}$  molecules,  $T_8O_{12}$  fragments in zeolites A [ $T = Si$  or Al, usually disordered; Bieniok & Bürgi (1994a)],  $R_{10}Si_{10}O_{15}$  molecules and  $T_{16}O_{24}$  fragments in zeolite rho, merlinoite and paulingite (Bieniok & Bürgi, 1994b). In all cases the general conclusions are substantially the same and show that the spherosiloxane molecules as well as corresponding zeolite fragments are flexible entities which may be modelled in terms of rigid corner-sharing tetrahedra, joined flexibly through the O atoms.

The Swedish Natural Science Research Council and the Swiss National Science Foundation are gratefully acknowledged for their financial support of this work.

#### References

- AGASKAR, P. A., DAY, V. W. & KLEMPERER, W. G. (1987). *J. Am. Chem. Soc.* **109**, 5554–5556.
- AUF DER HEYDE, T. P. E., BÜRGI, H.-B., BÜRGI, H. & TÖRNROOS, K. W. (1991). *Chimia*, **45**, 38–40.
- BIENIOK, A. & BÜRGI, H.-B. (1994a). *J. Phys. Chem.* **98**, 10735–10741.
- BIENIOK, A. & BÜRGI, H.-B. (1994b). *Studies in Surface Science and Catalysis*, Vol. 84, Part A, *Zeolites and Related Microporous Materials: State of the Art 1994*, edited by J. WEITKAMP, H. G. KARGE, H. PFEIFER & W. HÖLDERICH, pp. 567–574. Amsterdam: Elsevier.
- BÜRGI, H.-B. & DUNITZ, J. D. (1993). *Structure Correlation*, edited by H.-B. BÜRGI & J. D. DUNITZ, pp. 23–70. Weinheim: Verlag Chemie.
- BÜRGI, H.-B., TÖRNROOS, K. W., CALZAFERRI, G. & BÜRGI, H. (1993). *Inorg. Chem.* **32**, 4914–4919.

- BÜRGI, H. & CALZAFERRI, G. (1990). *Chromatography*, **507**, 481–486.
- CALZAFERRI, G., IMHOF, R. & TÖRNROOS, K. W. (1993). *J. Chem. Soc. Dalton Trans.* pp. 3741–3748.
- CALZAFERRI, G., IMHOF, R. & TÖRNROOS, K. W. (1994). *J. Chem. Soc. Dalton Trans.* pp. 3123–3128.
- CLEGG, W., SHELDRIK, G. M. & VATER, N. (1980). *Acta Cryst.* **B36**, 3162–3164.
- FRYE, C. L. & COLLINS, W. T. (1970). *J. Am. Chem. Soc.* **92**, 5586–5588.
- GABE, E. J., LE PAGE, Y., CHARLAND, J.-P., LEE, F. L. & WHITE, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.
- GIBBS, G. V., MEAGHER, E. P., NEWTON, M. D. & SWANSON, D. K. (1981). *Structure and Bonding in Crystals*, edited by M. O'KEEFFE & A. NAVROTSKY, Vol. 1, pp. 195–225. New York: Academic Press.
- HUMMEL, W., HAUSER, J. & BÜRGI, H.-B. (1990). *J. Mol. Graphics*, **8**, 214–220.
- KELLER, E. (1992). *SCHAKAL92. Program for the Graphic Representation of Molecular and Crystallographic Models*. Univ. of Freiburg, Germany.
- MURRAY-RUST, P., BÜRGI, H.-B. & DUNITZ, J. D. (1978). *Acta Cryst.* **B34**, 1787–1793.
- MURRAY-RUST, P., BÜRGI, H.-B. & DUNITZ, J. D. (1979). *Acta Cryst.* **A35**, 703–713.
- Molecular Simulations Inc. (1990). *QUANTA*. Burlington, Massachusetts, USA.
- SHELDRIK, G. M. (1992). *SHELXL92. Test version. Program for the Refinement of Crystal Structures*. Univ. of Göttingen, Germany.
- SPEK, A. L. (1990). *PLATON90. Vakgroep Algemene Chemie, Univ. of Utrecht, The Netherlands*.
- The SAS System (1992). SAS Institute Inc., Cary, North Carolina, USA.
- TÖRNROOS, K. W. (1994). *Acta Cryst.* **C50**, 1646–1648.
- TÖRNROOS, K. W., CALZAFERRI, G. & IMHOF, R. (1995). *Acta Cryst.* Submitted.
- TÖRNROOS, K. W., SCHWARZENBACH, D., LARSEN, F. K. & DELLEY, B. (1995). *Acta Cryst.* In preparation.
- TRUEBLOOD, K. N. (1985). *THMA11. Thermal Motion Analysis*. Univ. of California, Los Angeles, USA.

*Acta Cryst.* (1995). **B51**, 161–166

## Structure and Thermal Motion of Sulfonylbis(phosphorimidic trichloride), $\text{SO}_2(\text{NPCl}_3)_2$ , at 100 K

BY FERDINAND BELAJ

*Institut für Anorganische Chemie, Universität Graz, Schubertstrasse 1, A-8010 Graz, Austria*

(Received 8 August 1994; accepted 4 October 1994)

### Abstract

Sulfonylbis(phosphorimidic trichloride),  $\text{SO}_2(\text{NPCl}_3)_2$ ,  $M_r = 366.74$ , monoclinic,  $P2_1/c$ ,  $a = 11.843(1)$ ,  $b = 7.751(1)$ ,  $c = 12.374(2)$  Å,  $\beta = 95.11(1)^\circ$ ,  $V = 1131.4(2)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 2.153$  g cm<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 19.56$  cm<sup>-1</sup>,  $F(000) = 712$ ,  $T = 100$  K,  $R = 0.0284$ ,  $wR = 0.0296$ ,  $S = 1.33$  for 3806 unique observed reflections and 118 parameters. The P—N distances observed [1.5405(15) and 1.5342(14) Å] are the shortest of all compounds known to contain a non-cyclic S—N—P fragment. The S—N—P angles [129.56(10) and 132.27(9)°] are smaller than the bond angles observed in non-cyclic P—N—P compounds. The preference of the more folded conformation with approximate  $C_2$  symmetry over the stretched conformation with  $C_{2v}mm2$  symmetry is most probably due to some electron delocalization over the two almost planar O=S—N=P—Cl fragments. The N=P—Cl and O=S—N angles in these fragments [107.55(6), 108.12(6) and 105.54(7), 105.85(8)°, respectively] are markedly smaller than the remaining related angles [115.57(6)–117.56(6) and 110.57(8), 111.20(7)°, respectively]. Therefore, the angle between the O—S—O plane and the N—S—N plane [86.4(1)°] deviates significantly from 90°. The thermal motion of the molecule can best be described as almost independent

motions of rigid  $\text{SO}_2\text{N}_2$  and  $\text{NPCl}_3$  tetrahedra, coupled by a 'ball joint'.

### 1. Introduction

In the course of the structural investigations of the phosphorimidic trichlorides,  $\text{Cl}_3\text{PNP}(\text{O})\text{Cl}_2$  (Belaj, 1993),  $[\text{Cl}—\text{P}(\text{NPCl}_3)_3]^+\text{X}^-$  [ $\text{X} = \text{Cl}^-, \text{PCl}_6^-$  (Belaj, 1992)] and  $[\text{P}(\text{NPCl}_3)_4]^+\text{ICl}_2^-$  (Belaj, 1995), the structure determination of  $\text{SO}_2(\text{NPCl}_3)_2$  was desired in order to study the flexibility of the  $\text{NPCl}_3$  group at the N atoms. The title compound was synthesized for the first time by reaction of sulfamide with phosphopentachloride (Kirsanov, 1952); the hydrolysis (Haubold & Becke-Goehring, 1967), alcoholysis (Schöning, Klingebiel & Glemser, 1974) and several reactions with silylamines yielding open-chained and cyclic compounds (Becke-Goehring, Bayer & Mann, 1966; Klingebiel & Glemser, 1971, 1972) are described in the literature. No structural data are known for open-chained derivatives; the heterocyclic compound 1-methyl-bis(dichlorophosphazo)-sulphonamide,  $\text{SO}_2(\text{NPCl}_2)_2\text{NCH}_3$ , is the only derivative of  $\text{SO}_2(\text{NPCl}_3)_2$  of which the crystal structure is known (Nuber & Ziegler, 1977). The non-rigid body motion of the exceptionally flexible cation in  $[\text{P}(\text{NPCl}_3)_4]^+\text{ICl}_2^-$  could not be explained by intramolecular torsion. Despite