X-ray Diffraction Study of the Molecular Structure of a Spherohydridosilasesquioxane, $H_{10}Si_{10}O_{15}$, a Flexible Assembly of Rigid Tetrahedra

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The X-ray structure of $H_{10}Si_{10}O_{15}$ has been determined at 180 K and at 295 K. It crystallizes in the monoclinic space group $I2/a$, with $a = 14.141(8)$ Å, $b = 8.953(3)$ Å, $c = 15.022(8)$, $\beta = 94.91(3)°$, and $V = 1894.9$ Å^3 at 180 K, $a = 14.254(5)$ Å, $b = 9.053(2)$ Å, $c = 15.062(5)$ Å, $\beta = 94.87(1)°$, and $V = 1936.6$ Å^3 at 295 K, $Z = 8$, $D_x = 1.86$ g cm^{-3} (180 K), 1.82 g cm^{-3} (295 K), and fw = 530.92. Single-crystal diffraction data were collected with λ(Mo Kα) = 0.710 73 Å and μ(Mo Kα) = 7.45 cm^{-1} (180 K) and with λ(Ag Kα) = 0.560 83 Å, μ(Ag Kα) = 3.78 cm^{-1} (295 K). Refinement of 2089 observed reflections gave $R = 0.0294$ ($R_w = 0.0287$) for the 180 K data, and refinement of 1575 observed reflections gave $R = 0.0486$ ($R_w = 0.0661$) for the 295 K data. Using principal-component as well as rigid-body analysis, the molecular deformations from D_{5h} symmetry and the anisotropic displacement parameters are interpreted in terms of a molecular model built from rigid tetrahedra and connected through flexible oxygen atom joints. Results of the deformation analysis are compared to those in the structure of $(CH_3)_{10}Si_{10}O_{15}$.

Introduction

Homosubstituted spherosilasesquioxanes, $(RSiO_{1.5})_n$, are a family of oligomers composed of the building block $RSiO_{1.5}$ and commonly abbreviated as $(RT)_n$. The most frequently occurring substituents R are H, OH, halide, alkyl, allyl, and phenyl. The number of building blocks n is always even, 6 or larger for these spherical molecules. There are structural reports on only one hydrogen-substituted compound, namely $(HT)_8$.[1,2] Until recently, this could be attributed to the difficulties associated with their synthesis and purification. Nowadays the synthetic routes to spherohydridosilasesquioxanes of different sizes[3] and the techniques for their separation[4] are much more efficient.[5,6] Hydridosilasesquioxanes now constitute a family of molecules whose size and substitution may be varied in a controlled way.

$(RT)_n$ molecules, or parts of them, may be considered as molecular models of the building units found in infintely extended zeolite and silicate frameworks. With the help of these models, structure and flexibility of these building blocks may be explored without interference from Si/Al disorder, coordination to metal ions, and constraining effects of an infinite-framework structure usually present in zeolites and silicates. Such studies can provivde basic structural information necessary for the molecular modeling of zeolites.[7] Because of the small size and high symmetry of some $(RT)_n$ molecules, it is also feasible to investigate their flexibility by vibrational spectroscopy and normal-coordinate

analysis.[9,10] Such studies may be complemented by information on atomic mean-square displacements from high-resolution X-ray diffraction experiments.[11,12]

In this report we describe the crystal and molecular structure of the molecule $(HT)_{10}$ at 180 and 295 K; see Figure 1. The compound was first synthesized by Frye and Collins[13] and its atomic connectivity inferred from NMR data. The ten silicon atoms are arranged at the vertices of a pentagonal prism, and the fifteen oxygen atoms straddle its edges. The Si–O–Si angles and the nonbonded O···O 1,5-distances are discussed in relation to the associated Si–O distances and are compared to those of the room-temperature structure of $(CH_3)_{10}Si_{10}O_{15}$.[14a] The differences of the angles at oxygen in the molecules are discussed in terms of molecular flexibility and amplitudes of vibration of oxygen atoms which are distinctly larger than those of the silicon atoms.

Experimental Section

The synthesis of the title compound was performed according to the procedure published by Frye and Collins,[13] and the crude product was isolated by size-exclusion chromatography.[4] Colorless transparent crystals

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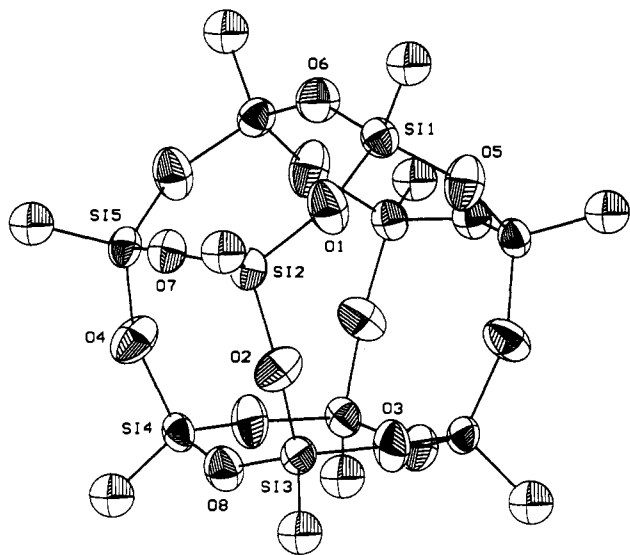
Figure 1. General view of (HT)$_{10}$, with vibrational ellipsoids at the 50% probability level and atomic numbering.

Table I. Crystallographic Data for the Two Measurements of (HT)$_{10}$

	data set	
	180 K	295 K
formula	(HSiO$_{1.5}$)$_{10}$	
fw	530.92	
space group	I2/a (No. 15)	
a, Å	14.141(8)	14.254(5)
b, Å	8.953(3)	9.053(2)
c, Å	15.022(8)	15.062(5)
β, deg	94.91(3)	94.87(1)
V, Å^3	1894.9	1936.6
Z	8	
D$_x$(calcd), g cm^{-3}	1.86	1.82
λ, Å	0.710 69 (Mo Kα)	0.560 83 (Ag Kα)
linear abs coeff μ, cm^{-1}	7.45	3.78
final R^a for obsd reflns	0.0294	0.0486
final R$_w$^{b} for obsd reflns	0.0287	0.0661
final R$_w$ for all reflns	0.0379	0.0767

^{a} $R = (\sum \|F_o\| - |F_c\|)/\sum|F_o|$. ^{b} $R_w = ((\sum(w\Delta F^2))/\sum(wF_o^2))^{-1/2}$.

were obtained by slow evaporation of a saturated solution of the compound in a 1:1 mixture of *n*-hexane/CH$_2$Cl$_2$.

Conditions for the X-ray diffraction experiments and the structure refinements are summarized in Table I. Diffraction data were collected on Enraf-Nonius CAD-4 instruments, using an Enraf-Nonius N$_2$ low-temperature device. In order to have as orthogonal a coordinate system as possible, a nonstandard setting of space group No. 15, *I2/a*, was chosen rather than the standard *C2/c*. The structure was solved by direct methods using SHELXS-86.[15] Full-matrix least-squares refinement with anisotropic displacement parameters for all non-H atoms was carried out with SHELX-76.[16] Five reflections showing unbalanced background measurements were omitted from the refinement of the 295 K data set. The positions of the H atoms were refined with restraints on the Si–H bond lengths, (1.480 ∓ 0.005 Å) and on two of the three H–Si–O angles (109.5 ∓ 0.1°). The largest magnitudes of residual densities in any of the difference-Fourier maps are 0.40 and –0.41 e Å^{-3}; they occur mainly around oxygen atoms and not in the vicinity of silicon atoms. The distances from refined oxygen positions to residual peaks are in the range 0.5–0.75 Å. The positions and magnitudes of these residual peaks are virtually the same at both temperatures; their significance is not clear. Final fractional atomic coordinates with their associated U$_{eq}$ values are given in Table II for both temperatures. Geometrical calculations were performed using PLATON.[17] Molecular images were produced with PEANUT[18] and SCHAKAL-88.[19]

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**Table II.** Fractional Non-Hydrogen Atomic Coordinates and U$_{eq}$ (Å^2) Values for (HT)$_{10}$

atom	x	y	z	U$_{eq}$^{a}
	(a) 180 K			
Si(1)	0.35933(5)	0.26971(8)	–0.00589(5)	0.0360(2)
Si(2)	0.38411(5)	0.06665(8)	0.16411(4)	0.0339(2)
Si(3)	0.37296(5)	–0.26396(8)	0.10097(4)	0.0340(2)
Si(4)	0.15452(5)	–0.25957(8)	0.10867(4)	0.0329(2)
Si(5)	0.16521(5)	0.07064(8)	0.17627(4)	0.0337(2)
O(1)	0.3942(1)	0.1653(3)	0.0769(1)	0.0560(7)
O(2)	0.4048(1)	–0.1053(2)	0.1428(1)	0.0513(7)
O(3)	0.3791(1)	–0.2596(2)	–0.0047(1)	0.0487(6)
O(4)	0.1367(1)	–0.0981(2)	0.1492(1)	0.0523(7)
O(5)	0.3712(1)	0.1822(3)	–0.0969(1)	0.0529(7)
O(6)	0.25	0.3164(3)	0.0	0.0463(8)
O(7)	0.2787(1)	0.0840(2)	0.1958(1)	0.0390(5)
O(8)	0.2658(1)	–0.3019(2)	0.1232(1)	0.0448(6)
	(b) 295 K			
Si(1)	0.35805(8)	0.26962(13)	–0.00557(8)	0.0584(4)
Si(2)	0.38241(7)	0.06721(13)	0.16235(7)	0.0552(3)
Si(3)	0.37203(8)	–0.25954(12)	0.09965(6)	0.0532(3)
Si(4)	0.15584(8)	–0.25660(11)	0.10849(6)	0.0518(3)
Si(5)	0.16596(8)	0.06980(12)	0.17416(7)	0.0545(3)
O(1)	0.3932(2)	0.1704(4)	0.0780(2)	0.0827(14)
O(2)	0.4029(2)	–0.1010(3)	0.1383(2)	0.0801(12)
O(3)	0.3792(2)	–0.2629(4)	–0.0052(2)	0.0712(11)
O(4)	0.1377(2)	–0.0954(3)	0.1466(2)	0.0772(11)
O(5)	0.3701(2)	0.1816(4)	–0.0953(2)	0.0788(11)
O(6)	0.25	0.3157(5)	0.0	0.0740(16)
O(7)	0.2782(2)	0.0832(3)	0.1942(2)	0.0637(9)
O(8)	0.2665(2)	–0.2965(3)	0.1227(2)	0.0668(10)

^{a} $U_{eq} = \frac{1}{3}\sum_i\sum_j(U_{ij}a_i^*a_j^*\mathbf{a}_i\cdot\mathbf{a}_j)$.

The initial intention was to establish the structure of (HT)$_{10}$ at room temperature and at 100 K. Routine monitoring of the crystal during cooling revealed reflection broadening at temperatures below 165 K. For the reflections 400 and 004 a splitting into two well separated peaks was observed. No further splitting occurred below 155 K. This transition could be reversed and repeated, implying a reversible phase change; however, the nature of this change has not been investigated further.

Discussion

The ten HT units of (HT)$_{10}$ are arranged into two ten-membered rings, with alternating Si and O atoms (five-rings in silicate language), linked together via five oxygen atoms to a molecule of approximate D$_{5h}$ symmetry. In addition to the two ten-membered rings, there are five eight-membered rings (four-rings in silicate language). The feature of double five-membered rings is not known among zeolites (see **1**). However, other types

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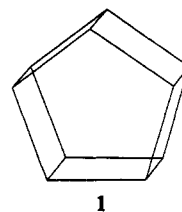
of double rings are well-known,[8] e.g. for zeolites: "A", double four-membered; "faujasite", double six-membered; "rho", double eight-membered rings. These structures also have in common a high symmetry, 4/*mmm*, $\bar{3}m$, and $\bar{4}2m$, respectively, likely as an effect of being part of a rigid framework. The unusual double five-membered rings in the molecular (HT)$_{10}$ structure, which is not confined to a rigid framework, have a crystallographic symmetry of only 2.

The 2-fold axis passes through one of the bridging oxygens and is parallel to the two five-ring planes. To our knowledge only two other crystal structures of (RT)$_{10}$ molecules have been reported so far, namely those of (CH$_3$T)$_{10}$[14a] and ([(CH$_3$)$_3$SiO]T)$_{10}$.[14b]

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Table III. Bond Distances (Å) and Angles (deg) for (HT)$_{10}$(180 K), (HT)$_{10}$(295 K), and (CH$_3$T)$_{10}$, Divided into Two Columns Representing the Two Crystallographically Independent Halves of (CH$_3$T)$_{10}$ Related by Rotation of 180°[a]

(a) Distances

	(HT)$_{10}$(180 K)	(HT)$_{10}$(295 K)	(CH$_3$T)$_{10}$	(CH$_3$)T$_{10}$
Si(1)–O(1)	1.599(3)	1.592(3)	1.606(4)	1.600(5)
Si(1)–O(5)	1.597(2)	1.591(3)	1.608(4)	1.597(4)
Si(1)–O(6)	1.611(1)	1.605(2)	1.617(3)	1.605(3)
Si(2)–O(1)	1.597(2)	1.595(3)	1.602(5)	1.582(4)
Si(2)–O(2)	1.604(2)	1.598(3)	1.582(5)	1.600(6)
Si(2)–O(7)	1.611(2)	1.607(3)	1.609(3)	1.619(3)
Si(3)–O(2)	1.602(2)	1.597(3)	1.617(6)	1.592(5)
Si(3)–O(3)	1.598(2)	1.591(3)	1.613(2)	1.606(5)
Si(3)–O(8)	1.616(2)	1.607(3)	1.613(3)	1.611(3)
Si(4)–O(3a)	1.593(2)	1.594(3)	1.596(2)	1.603(5)
Si(4)–O(4)	1.597(2)	1.597(3)	1.591(5)	1.611(5)
Si(4)–O(8)	1.615(2)	1.615(3)	1.621(2)	1.626(2)
Si(5)–O(4)	1.607(2)	1.595(3)	1.599(5)	1.589(5)
Si(5)–O(5a)	1.606(2)	1.611(3)	1.593(5)	1.596(5)
Si(5)–O(7)	1.611(2)	1.607(3)	1.610(3)	1.623(3)

(b) Angles

	(HT)$_{10}$(180 K)	(HT)$_{10}$(295 K)	(CH$_3$T)$_{10}$	(CH$_3$T)$_{10}$
Si(1)–O(1)–Si(2)	156.67(14)	156.2(2)	150.0(2)	158.0(2)
Si(2)–O(2)–Si(3)	151.51(14)	152.8(2)	157.9(2)	158.4(2)
Si(3)–O(3)–Si(4a)	159.53(15)	157.9(2)	148.1(3)	152.6(2)
Si(4)–O(4)–Si(5)	154.61(14)	154.9(2)	158.1(2)	160.5(2)
Si(1)–O(5)–Si(5a)	152.90(14)	152.9(2)	155.6(2)	151.0(2)
Si(1)–O(6)–Si(1a)	149.93(19)	149.9(3)	152.7(4)	
Si(2)–O(7)–Si(5)	150.64(12)	150.2(2)	149.5(3)	148.0(3)
Si(3)–O(8)–Si(4)	147.43(13)	147.8(2)	147.4(3)	148.6(3)

[a] Note that the alignment of the (CH$_3$T)$_{10}$ molecule with the (HT)$_{10}$ molecule is arbitrary.

However, crystallographic data are only available to us for the (CH$_3$T)$_{10}$ compound. The fact that the (CH$_3$T)$_{10}$ molecule has a different kind of substituent makes it possible to evaluate the influence of substitution on the T$_{10}$ core. Individual bonding distances and angles, excluding those of substituents, for (HT)$_{10}$ at two temperatures and for (CH$_3$T)$_{10}$ are compared in Table III. Average Si–O distances for the three structures (given in the order as in Table III) are 1.612(2), 1.608(4), and 1.616(3) Å in eight-membered rings and 1.601(5), 1.596(6), and 1.599(5) Å in ten-membered rings. The average Si–O–Si angles between the two ten-membered rings are 149.5(1.7), 149.3(1.3), and 149.2-(2.1)°; within the ten-membered rings they are 154.7(3.1), 154.9-(2.2), and 155.0(4.3)°. Finally, the average O–Si–O angles are 110.0(2), 110.1(2), and 109.3(6)° in the eight-membered rings and 109.5(2), 109.9(2), and 108.6(7)° in the ten-membered rings. (Numbers in parentheses indicate standard deviations of populations.)

The mean distances and angles reveal a rather consistent average geometry, but the distributions of individual values show nevertheless that the T$_{10}$ molecule deviates significantly from an ideal D_{5h} symmetry. These deviations are generally small for Si–O distances and O–Si–O angles but considerable for Si–O–Si angles and especially for the O···O 1,5-nonbonded distances in the eight- and ten-membered rings, as can be seen from Table IV.

Although Si–O distances, d, vary only slightly, they are correlated inversely to the Si–O–Si angles, α, as illustrated by the scatter plot in Figure 2. The correspondence between angle and distance follows the equation $d = 1.59 + ((180 - \alpha)^4 \times 2.1 \times 10^{-8})$. The reason for the bond length shortening with increasing angle has been the subject of some debate throughout the years. The best interpretation of this correlation seems to have been given by Gibbs, Meagher, Newton, and Swanson,[20,21] by means of *ab initio* calculations on, among others, the disiloxane molecule.
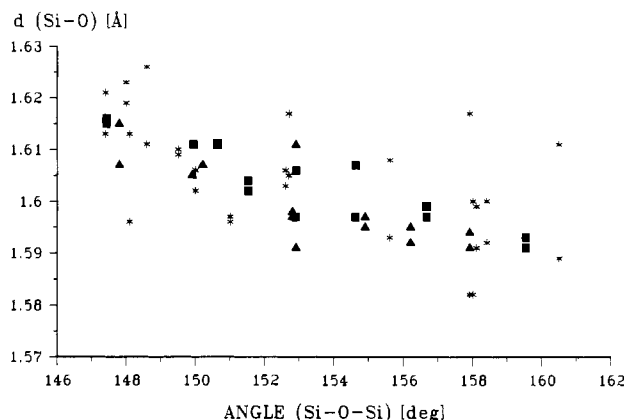
d (Si–O) [Å]

Figure 2. Scatter plot of Si–O–Si angles (α) vs corresponding Si–O distances (d). The points are distributed about the line $d = 1.59 + ((180 - \alpha)^4 \times 2.1 \times 10^{-8})$: ■, (HT)$_{10}$(180 K); ▲, (HT)$_{10}$(295 K); ✳ (CH$_3$T)$_{10}$.

Table IV. O···O 1,5-Nonbonded Distances (Å) for (HT)$_{10}$(180 K), (HT)$_{10}$(295 K), and (CH$_3$T)$_{10}$

	(HT)$_{10}$(180 K)	(HT)$_{10}$(295 K)	(CH$_3$T)$_{10}$	(CH$_3$T)$_{10}$
(a) Eight-Membered Rings				
O(1)···O(5a)	3.793(3)	3.785(4)	3.830(4)	3.751(4)
O(6)···O(7)	3.598(3)	3.599(4)	3.573(6)	3.605(6)
O(2)···O(4)	3.801(3)	3.793(4)	3.629(4)	3.659(4)
O(7)···O(8)	3.623(3)	3.602(4)	3.655(7)	3.662(7)
O(3)···O(3a)	3.667(3)	3.698(4)	3.793(3)	
O(8)···O(8a)	3.691(3)	3.685(4)	3.622(5)	
(b) Ten-Membered Rings				
O(1)···O(3)	3.997(4)	4.118(5)	4.629(9)	4.195(7)
O(1)···O(4a)	4.127(4)	4.144(5)	4.199(7)	3.866(6)
O(2)···O(4a)	4.376(4)	4.281(4)	3.705(6)	4.021(5)
O(2)···O(5)	4.419(4)	4.343(5)	3.880(6)	4.378(6)
O(3)···O(5)	4.189(4)	4.245(5)	4.453(9)	4.502(7)

The fact that angular variations of Si–O–Si are by far larger than those of O–Si–O is not surprising, considering the difference in bending force constants between Si–O–Si and O–Si–O; their approximate ratio is 10^{21}. We are thus dealing with a structure composed of ten approximately regular and rigid RSiO$_3$ tetrahedra, connected via flexible Si–O–Si angles.

In order to interpret the averages given above and the distribution of individual values, we have analyzed the implications of such a model. First, we discuss the flexibility of the model under the constraint of D_{5h} symmetry, which implies that the relative positions of all atoms are fixed by specifying only five parameters, e.g. atomic Cartesian coordinates (n = 0–4):

	x	y	z
Si	$x(Si) \times$ $\cos(n \times 72°)$	$x(Si) \times$ $\sin(n \times 72°)$	$\pm z(Si)$
O$_A$(in ten-ring)	$x(O_A) \times$ $\cos(n \times$ $72° + 36°)$	$x(O_A) \times$ $\sin(n \times$ $72° + 36°)$	$\pm z(O_A)$
O$_B$(bridging)	$x(O_B) \times$ $\cos(n \times 72°)$	$x(O_B) \times$ $\sin(n \times 72°)$	0

As mentioned earlier, the Si–O distances and O–Si–O angles vary only little. If we assume that the two independent Si–O distances in the model are equal at 1.61 Å, and if we further assume that the two O–Si–O angles are also the same and equal 110.0°, we obtain four relationships among the five independent coordinates. This leaves only 1 degree of freedom; i.e., we are free to assign a magnitude to the Si–O–Si angle in either the eight- or the ten-membered ring; whichever we choose, this will fix the value of the other angle. The analytical relationship between the two seems complicated, but in the range of interest,

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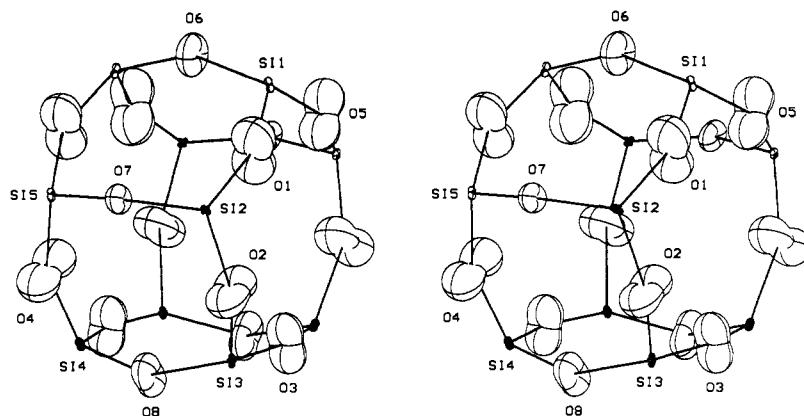
Figure 3. Stereoimage displaying difference root-mean-square displacement surfaces[18] scaled up 3.08 times for $(HT)_{10}(180 K)$: solid outlines, positive differences; dotted, imaginary. Hydrogen atoms omitted.
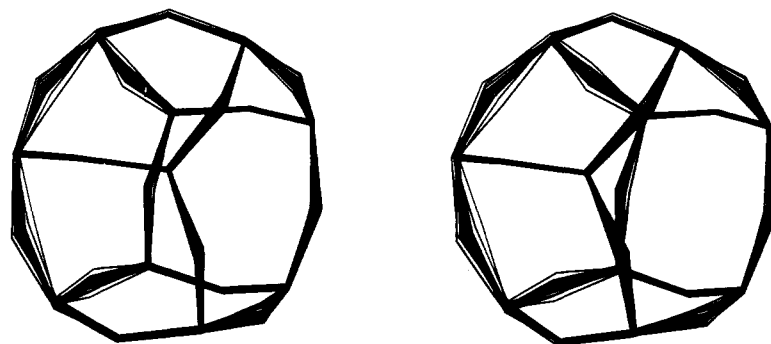

Figure 4. Optimized superposition of the Si atoms of 10, 10, and 20 isometric images of $(HT)_{10}(180 K)$, $(HT)_{10}(295 K)$, and $(CH_3T)_{10}$, respectively (see text).

Table V. Lengths of Deformation Vectors (Å) in the Planes of the Degenerate Principal Components 1,2, 3,4, 6,7, and 8,9 and along the Nondegenerate Principal Component 5

	1,2	3,4	5	6,7	8,9
$(HT)_{10}(180 K)$	0.36	0.35	0.07	0.10	0.02
$(HT)_{10}(295 K)$	0.14	0.24	0.08	0.08	0.06
$(CH_3T)_{10}$	0.88	0.33	−0.08	0.08	0.04

$140° < Si-O_A-Si < 160°$, it follows the numerical relationship $\angle(Si-O_A-Si) = (-0.57\angle(Si-O_B-Si)) + 240.5°$. The mean values given above follow this relationship well for all three data sets.

The mean values of the two types of Si–O–Si angles differ by 5.2–5.8° in the three structures, even though their interdependence would allow them to be equal at 153.2°. Why is this? The nonbonded distances $O_A \cdots O_A$ and $O_B \cdots O_B$ in the eight-membered rings may provide an answer. For equal angles at oxygens, 153.2°, these distances are 3.85 and 3.57 Å. Conversely for equal nonbonded distances, 3.71 Å, the bond angles are 157.6 and 145.4°. The observed structures with averages angles of 155.0 and 149.2° and average nonbonded distances of 3.73–3.76 and 3.62–3.64 Å would seem to be a compromise between equal angles and equal $O \cdots O$ 1,5-nonbonded distances.

Next we consider the deformations of the assembly of ten rigid tetrahedra, linked flexibly across their corners, from D_{5h} symmetry. Fixing the relative arrangement of all Si, O, and H(Si) or C(Si) atoms requires fixing 99 internal coordinates $((3 \times 35) - 6)$. For the ten rigid tetrahedral $RSiO_{1.5}$ building blocks, 90 internal coordinates, namely the four distances and the five independent angles about Si, may be assumed fixed. This leaves 9 degrees of freedom unaccounted for. These are algebraically complicated combinations of the 15 Si–O–Si angles and of the torsion angles about the 30 Si–O bonds. Alternatively, the 9 degrees of freedom could be expressed in terms of similarly complicated relationships involving the $O \cdots O$ 1,5-nonbonded distances within the eight- and ten-membered rings. We do not attempt to calculate these relationships algebraically but make use of principal-component analysis (PCA) instead[22] to obtain numerical relationships. In

PCA a parameter space is defined, one dimension for each kind of parameter. PCA itself analyzes the distribution of data points by identifying directions in parameter space with a wide spread of points (principal components) and others with a small or even vanishing spread of points. For our analysis of $(RT)_{10}$ structures we have chosen the 20 different $O \cdots O$ 1,5-nonbonded distances in each of the three molecules as parameters. We expect to find at most 9 significant principal components, corresponding to degrees of freedom not specified by the distances and angles about Si. Since we are interested in deformations from D_{5h} symmetry, we have to take into account that for a given molecular deformation the labels of the atoms can be permuted in 20 different ways, each permutation being associated with a symmetry operation of D_{5h}. Alternatively, for a fixed atomic labeling, the molecule can undergo a given deformation in 20 different but symmetry equivalent ways;[23] for example, each of the ten substituents can be displaced to either side of the mirror plane it occupies in a D_{5h}-symmetrical configuration. Whichever point of view we adopt, we get 20 isometric copies of the C_1-symmetric $(CH_3)_{10}$-$Si_{10}O_{15}$ and 10 isometric copies of the C_2-symmetric $H_{10}Si_{10}O_{15}$ at each of the two temperatures. The 20-dimensional parameter space of $O \cdots O$ 1,5-nonbonded distances is thus populated with 40 data points.

The first four principal components come in two degenerate pairs (1,2 and 3,4). They account for 97% of all distortions from D_{5h} symmetry. The form of the first and second principal components implies extension/compression of both five-rings along one of two orthogonal directions perpendicular to the 5-fold axis. The third and fourth principal components correspond to compression of one five-ring and extension of the other along one (or the other) of the two directions perpendicular to the 5-fold axis. The degrees of deformation in angstrom units are listed in Table V for the three structures. The deformation is largest along the first four principal components, irrespective of sub-

(22) *SAS User's Guide*; SAS Institute Inc.: Cary, NC, 1982.
(23) *Structure Correlation*; Bürgi, H.-B., Dunitz, J. D., Eds.; Verlag Chemie: Weinheim, Germany, 1993; Chapter 2.
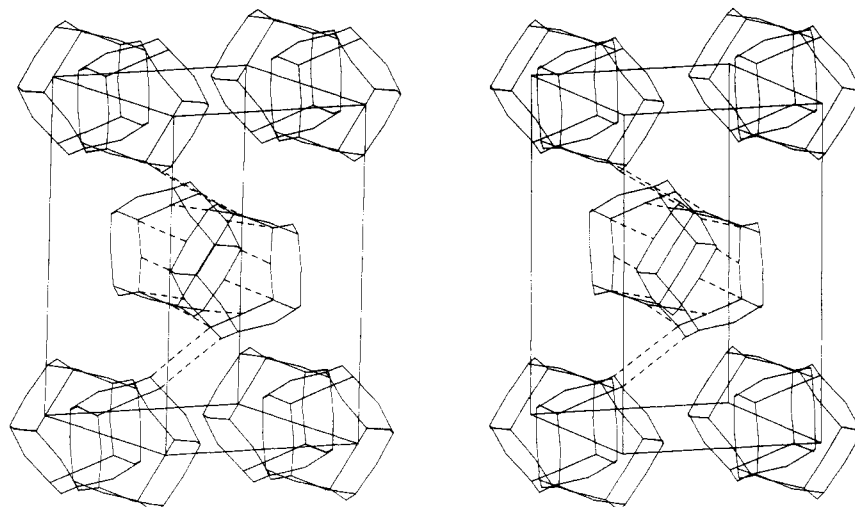
Figure 5. Stereoimage of the packing arrangement of $(HT)_{10}$. Intermolecular contacts are indicated with dashed lines. Hydrogen atoms are omitted.

stitution and temperature. Note, however, that the deformations of $(HT)_{10}$ increase significantly as temperature is lowered. This observation might be connected with the occurrence of a phase transition at ~ 160 K (see Experimental Section).

Deformations along principal component 5 and along the degenerate pairs 6,7 and 8,9 are smaller but still significant. The nondegenerate principal component 5 and the degenerate pair 6,7 are about the same in magnitude. Together they account for another 2.5% of the distortions. The deformation corresponding to principal component 5 implies an extension/compression of the molecule along the 5-fold axis. It is the deformation discussed in detail above, in connection with the D_{5h} average structure. Deformations along the principal components 10 etc. are ≤ 0.01 Å for $(HT)_{10}$ and ≤ 0.03 Å for the less accurately determined $(CH_3T)_{10}$. These values are in the range of the experimental estimated standard deviations and need not be discussed. Overall, the results of the PCA support our assumption that the $(RT)_{10}$ molecules may be considered as built from essentially rigid tetrahedra joined flexibly at the oxygen atoms. There are at most nine significant distortion modes of the D_{5h}-symmetric reference structure; of these only the first four are substantial. Eigenvalues and eigenvectors of the PCA are given as supplementary material.

The observed anisotropic displacement parameters for the two $(HT)_{10}$ measurements have been studied by rigid-body analysis[24] in two ways. Including all Si and O atoms in the calculations leads to systematically negative differences U(obs) – U(model) for Si, positive differences for O, and a poor goodness of fit, GOF $= \Sigma_{Si,O} w [U(\text{obs}) - U(\text{model}))^2 / \text{obs} - \text{par})$. When the rigid-body calculations are performed on the Si atoms alone, the GOF is significantly better; this indicates that the motion of the Si's alone can be modeled quite well by a rigid-body model. On the basis of the translation, libration, and screw coupling tensors T, L, and S derived from U(Si), the U(O)'s were calculated. As expected, the residual motion U(O;obs) – U(O;model) is still positive and even larger than in the case where both Si and O atoms are included in the analysis. The residual atomic motion not accounted for by this model is exemplified for the 180 K data in Figure 3. Very small vibrational components remain for the Si atoms, but considerable components remain for the O atoms and must be due to intramolecular vibrations. Residual components of the oxygen atoms are generally large perpendicular to the Si–O–Si plane, intermediate along the bisector of the Si–O–Si angle, but small along the Si–O bond direction. The residual displacements are generally larger for the oxygens in the ten-membered rings than for the oxygens connecting these rings.

Disregarding the temperature-dependent difference in absolute magnitudes, the results are consistent at both temperatures.

We interpret the residual displacements at oxygens as being due to the flexibility of the Si–O–Si angles, as discussed above. A conclusive confirmation of this hypothesis would require a normal-coordinate analysis based on the 9 degrees of freedom describing the relative orientation of the ten rigid tetrahedra. At present, we cannot offer such an analysis for $(HT)_{10}$; for $(HT)_8$ such an analysis has been performed and has confirmed the above hypothesis.[11] Here we give a qualitative argument relating the residual, intramolecular motions to the static deviations of the three structures from D_{5h} symmetry. For this purpose the Si atoms of the 10, 10, and 20 isometric structures used in the PCA were superimposed by least-squares fitting of corresponding Si atoms in the 40 isometric structures.[25] As shown in Figure 4, the Si atoms superimpose much better than the O atoms. The O's in the ten-membered rings are spread out primarily in the direction perpendicular to the Si–O–Si planes; the O's connecting the ten-membered rings show a smaller spread. Both observations are in qualitative agreement with the intramolecular motions derived from the displacement parameters (Figure 3). We therefore conclude that the model of rigid $RSiO_3$ tetrahedra flexibly interconnected via the oxygen atoms accounts for the static displacements from D_{5h} symmetry as well as for the large-amplitude intramolecular motions.

A corresponding analysis[26] has been performed for the cube-shaped T_8O_{12} fragments found in molecular compounds $R_8T_8O_{12}$ as well as in zeolites (e.g. zeolite A). Analogous observations have been made with respect to both the O···O 1,5-nonbonded distances and the oxygen displacement parameters; significantly, the latter are invariably larger than those of silicon, not only in the molecular but also in the framework compounds.

Molecular Packing

As illustrated in Figure 5, the $(HT)_{10}$ molecules in the crystal are stacked into hexagonally arranged columns. Adjacent molecules within the stacks are related by an inversion center. Because of the small size of the hydrogen substituent, this arrangement allows short Si···O contacts between adjacent molecules. Further Si···O contacts appear between molecules in different stacks. The contact distances are in the ranges 3.609-(3)–3.767(3) Å for $(HT)_{10}(180$ K) and 3.676(3)–3.814(3) Å for $(HT)_{10}(295$ K) and are indicated by dashed lines in Figure 5. The associated O–Si···O angles are in the ranges 163.1(1)–179.2(1)° for $(HT)_{10}(180$ K) and 163.2(1)–178.7(1)° for $(HT)_{10}(295$ K). Such nonbonded O···Si contacts in $(HT)_n$ crystal structures are

(24) Trueblood, K. N. *THMA11: Thermal Motion Analysis*; University of California: Los Angeles, CA, 1985.

(25) *QUANTA*; Molecular Simulations Inc.: Burlington, MA, 1990.
(26) Bieniok, A. M.; Bürgi, H. B. In preparation.

reminiscent of incipient stages of nucleophilic substitution reactions with Walden inversion[2] and might reflect the instability of these compounds in the presence of base. Steric factors prevent contacts of this kind in $(CH_3T)_{10}$, the shortest intermolecular Si···O distance being 4.728(6) Å.

Supplementary Material Available: Tables of detailed experimental conditions, anisotropic displacement parameters, positions and isotropic displacement factors for hydrogen atoms, and numerical results of principal-component and rigid-body analyses (16 pages). Ordering information is given on any current masthead page.