VIBRATIONAL SPECTRA, AB INITIO CALCULATIONS AND CONFORMER STABILITY OF 1,3-DIMETHYL-1,1,3,3-TETRAKIS(TRIMETHYLSILYL)TRISILANE (SiMe₃)₂MeSiH₂SiMe(SiMe₃)₂

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Abstract: Quantum chemical ab initio calculations at the RHF level of theory predict five minima with very unusual SiSiSiSi dihedral angles on the internal rotation potential energy surface for (SiMe₃)₂MeSiH₂SiMe(SiMe₃)₂. Temperature dependent Raman spectroscopy has been used to correlate these results with vibrational spectra.

1,3-Disubstituted propanes, for instance XCH₂CH₂CH₂X with X = halogen, possess four minima on the potential energy surface (PES) for internal rotation, commonly named anti/anti, anti/gauche, gauche(+)/gauche(+) and gauche(+)/gauche(-) as illustrated in Figure 1 below. Ab initio calculations predict that 1,3-disubstituted trisilanes XSiH₂SiH₂SiH₂X with monoatomic substituents X behave identical in this respect [1].

![Figure 1: Perspective drawings of the conformers of 1,3-dihalopropanes and 1,3-dihalotrisilanes](image)

However, when the substituents at the SiSi-bond get bigger this simple picture changes drastically due to 1,3- and 1,4-substituent interactions [2]. For instance, a new minimum at around 90° exists for SiMe₃SiMe₂SiMe₂SiMe₃, termed ortho by the authors. With substituents such as C₄H₉ or larger, up to five minima with dihedral angles ω~40° (termed cisoid), ω~55° (gauche), ω~90° (ortho), ω~150° (deviant) and ω~165° (transoid) appear, as in SiMe₃SiEt₂SiEt₂SiMe₃ [3]. To the best knowledge of the authors, no one has yet investigated the conformational compositions of trisilanes with large polyatomic substituents such as SiMe₃.

We have prepared the title compound with the intention to do that. With the help of ab initio calculations, five minima were located so far at the HF/STO-3G level of theory. In a second step the equilibrium geometries were optimized at the HF/6-311G* level of theory. Figure 2 presents molecular models of these conformers, with the relative energies (kJ/mol) increasing from left to right.

![Figure 2: Ball/stick models for the five conformers of the title compound](image)
Figure 3 presents perspective views from two different angles of the two-dimensional PES for internal rotation ($\omega_1$, $\omega_2=\omega(H_3)CSiSi$) calculated at the HF/STO-3G level.

Figure 3: Two views of the PES for internal rotation of the title compound ($180^\circ > \omega_1 > 0^\circ$, $360^\circ > \omega_2 > 0^\circ$).

The Raman spectrum in the range of the SiSi stretching vibrations (300-500 cm$^{-1}$) which are expected to be sensitive towards conformations is given in Figure 4. At 20°C in the crystalline solid state, it is straightforwardly interpreted as originating from a single conformer. At higher temperature, a second conformer appears which is higher in energy by about 6 kJ/mol, a value obtained from a Van’t Hoff plot for the band pair 329/340 cm$^{-1}$.

Figure 4: Raman spectrum of the title compound at 20°C and 100°C (left) and Van’t Hoff plot for the band pair 329/340 cm$^{-1}$ (right).

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References:
1. K. Hassler, unpublished results.