

Structure, Vibrational Spectra, and DFT and Ab Initio Calculations of Silacyclobutanes

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ABSTRACT

Ab initio calculations at a high level of theory have been carried out for silacyclobutane (SCB) and its 1,1-difluoro and 1,1-dichloro derivatives in order to compute the structures and dihedral angles of puckering for these molecules. For SCB the calculated dihedral angle of 35° agrees nicely with the 36° value obtained from far-infrared work. The calculated angles of 29° and 31° degrees for the fluoro and chloro derivatives, respectively, can be compared to electron diffraction results of 25° and 26°. The zero-point corrected barriers calculated using the MP2/cc-pVTZ level of theory were 523 (as compared to 440 cm⁻¹ experimental), 186, and 433 cm⁻¹ for SCB and its fluoro and chloro derivatives, respectively. Calculated structural changes in the dihalo derivatives can be ascribed to the high electronegativity of the halogen atoms. High level DFT computations were also carried out in order to calculate the infrared and Raman spectra of these three molecules as well as the SCB 1,1-d₂ isotopomer. The agreement between experimental and calculated spectra is remarkably good for all four molecules. The predicted frequencies and intensities were utilized to reassign several of the weaker spectral bands and also to characterize the 1130 cm⁻¹ signature band present in the infrared spectra of all silacyclobutanes. This arises from the α-CH₂ in-phase wagging vibration, which is very much affected by the neighboring silicon atom. The DFT calculations also demonstrated that two of the wagging and twisting motions of the CH₂ group next to the silicon atom have frequencies much lower than in typical organic molecules. This work also provides frequency ranges that can be expected for the six vibrations of SiX₂ groups (X = H, D, F, Cl) in organosilanes.

Keywords: silacyclobutane, infrared spectra, Raman spectra, *ab initio*, DFT, molecular structure.