The monofunctionalized cyclohexasilanes XSi₆Me₁₁ [X = -OH (2); -NH₂ (3)] are easily accessible from XSi₆Me₁₁ and H₂O/Et₃N or NH₃, respectively. The crystal structure of 2 as determined by single crystal X-ray crystallography exhibits the cyclohexasilane ring in chair conformation with the OH group in an unusual equatorial position due to intermolecular hydrogen bonding. Full geometry optimization (B3LYP/6-31+G*) of the gas-phase structures of 2 and 3 affords six minima on the potential energy surface for chair, twist and boat conformers with the heterosubstituents either in axial or equatorial positions all being very close in energy. According to time-dependent DFT B3LYP/TZVP calculations contributions of several conformers to the observed solution UV absorption spectra of dodecamethylcyclohexasilane (1), 2 and 3 need to be considered in order to achieve satisfactory agreement of calculated and experimental data.

Key words: Cyclopolysilanes, Aminosilanes, Silanols, UV Absorption Spectra, Molecular Structure