

Internal Rotation of Disilane and Related Molecules: a Density Functional Study

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Abstract

DFT calculations performed on Si₂H₆, Si₂F₆, Si₂Cl₆ and Si₂Br₆ are reported. The evolution of the energy, the chemical potential and the molecular hardness, as a function of torsion angle, is studied. Results at the DFT-B3LYP/6-311++G** level show that the molecules always favor the stable staggered conformations, with low but significant energy barriers that hinder internal rotation. Internal rotation is always accompanied by weakening and lengthening of the central Si–Si bond. In most cases this lengthening seems to be due to an interplay of electrostatic and hyperconjugative interactions. The chemical potential and hardness of Si₂H₆ remains quite constant as the silyl groups rotate around the Si–Si axis, whereas the other systems exhibit different degrees of rearrangement of the electronic density as a function of the torsion angle. A qualitative analysis of the frontier orbitals shows that the effect of torsional motion on electrophilic attack is negligible, whereas this internal rotation may generate different specific mechanisms for nucleophilic attack.