Theoretical Confirmation of the Stereoselectivity in the Reverse Brook Rearrangement

Yigui Wang* and Michael Dolg

Max-Planck-Institut für Physik komplexer Systeme, Nöthnitzer Str. 38, D-01187 Dresden, Germany

Quantum chemical ab initio calculations (MP2/6-311++(3df,2dp)//MP2/6-31+G*, G2, CBS-Q, solvent effects at MP2/6-311+(2d,p) and B3LYP/6-311+G(2d,p) level within Onsager and IPCM models) on the systems $RCHM(SiH_3)$ (M=-,Li,Na; R=H,CH_3, CH_2=CH) and their silyl group migrations confirm the following facts: The methyl group favors the rention while the vinyl group with its delocalizing ability favors the inversion of the configuration of the central carbon. The migration of the silyl group is very facile and retains the configuration at the silicon center.