

Chirality Studies of Electrostatically Stabilized Silanates with NMR, X-Ray and Quantum Chemistry

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Electrostatically stabilized (ES) silanates were first synthesized at the Latvian Institute of Organic Synthesis [1]. These compounds can be used as an effective and ecologically safe growth factor for plants [2], as chiral co-catalysts and chiral ionic liquids³.

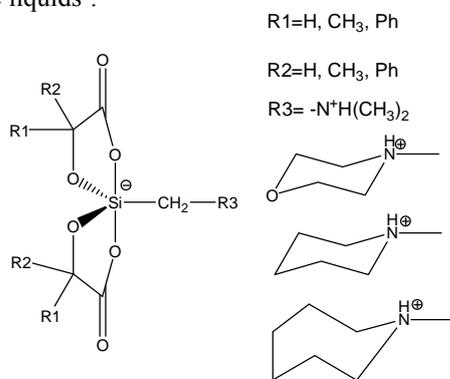


Figure 1. Overall structure of ES-silanates

According to ²⁹Si, ¹³C and ¹H NMR spectra and X-ray data, these compounds exist as trigonal bipyramid (TBP) with chiral pentacoordinated silicon in both solutions and solid state. These compounds exist as Δ or Λ enantiomers.

In compounds, where R1=R2=CH₃, the methyl groups are prochiral in NMR spectra. This non-equivalence can be removed at higher temperatures due to the fast Δ – Λ exchange of the chirality on silicon. The free activation energy for this process is ΔG[‡]₃₅₈=18.5 kcal/mol. According to literature, the loss of silicon chirality could be caused by Berry pseudorotation, “turnstile” rotation, or dissociation mechanism.

DFT quantum chemistry calculations were performed to establish the possible mechanisms of the process. The “turnstile” rotation for our bicyclic compounds is sterically impossible. For Berry pseudorotation, the energy differences for 6 possible transition states were calculated. These energy differences for stereomutation of spirocycles on TBP were adjusted to partial Levi-Desargues graph [3]. The lowest energy difference found was 30.0 kcal/mol. Thus, the Berry pseudorotation energy is too high to explain the experimentally observed energies. The dissociation mechanism of apical Si-O bonds in TBP seems to be the best explanation and was confirmed by quantum chemistry

calculations. Accordingly, the experimentally determined ΔS[‡] value for the process was negative [4] as well as the experimentally observed exchange of heterocycles on TBP in CDCl₃ solutions.

The chirality of silicon determines the non-equivalence of SiCH₂N protons. The protons and carbons in R3 substituents become prochiral only when nitrogen inversion is slowed down by the protonation. The free energy barrier for “ammonium–amine” equilibrium was determined to be ΔG[‡]₃₁₀=16.4±0.4 kcal/mol when R3=N⁺H(CH₃)₂.

In the ES-silanates, where R1≠R2, several isomers were observed in NMR spectra. The derivative, where R1=H, R2=Ph and R3=perhydroazepine, formed from optically active mandelic acid, according to X-ray data, was crystallized in specific Δ,S,S conformation. After dissolution of the crystal in DMSO solution, the formation of three new isomers in ¹H NMR spectra by the cleavage of Si–O bond in solution was observed. In 2D EXSY spectra, the chemical exchange peaks between CH groups in different isomers were found related to the allowed transitions between the isomers. The scheme leading to the formation of all possible enantiomeric/diastereomeric pairs for different R1≠R2 derivatives was proposed. The scheme was analysed together with available literature and X-ray data. The quantum chemical calculations of the energy differences for these compounds suggest the populations of the structures.

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