

Stereochemistry of seven-membered heterocycles: XLII. A theoretical study of stereochemistry of H complexes formed by conformationally nonuniform 2-R-1- 3-dioxacyclohept-5-enes with some proton donors

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Abstract

According to semiempirical AM1 calculations, the stability of the boat and twist forms of 2-R-1-3-dioxacyclohept-5-enes depends on the size of substituents at the acetal carbon atom. The twist form gives diastereomeric H complexes with chloroform and methanol of the cis and trans structure, containing monocentered hydrogen bonds, whereas the chair conformation preferably forms complexes with a two-centered hydrogen bond. Based on theoretical data (Γ_{OH} , ΔH , geometry of complexes), the specific features of H complexes of the conformers in electrophilic addition and cycloaddition were revealed. Considerable preferableness of the exo attack of the diastereotopic double bond in the H complex having the chair form is due to the steric accessibility of the exo side, whereas in the complexes of the twist form the facial selectivity is appreciably lower.

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