Stereochemistry of Seven-Membered Heterocycles: XLII.[1] A Theoretical Study of Stereochemistry of H Complexes Formed by Conformationally Nonuniform 2-R-1,3-Dioxacyclohept-5-enes with Some Proton Donors

V. Yu. Fedorenko, V. V. Zverev, Yu. G. Shtyrlin,
G. R. Shaikhutdinova, and E. N. Klimovitskii

Butlerov Research Chemical Institute, Kazan State University, Kazan, Tatarstan, Russia

Arbuzov Institute of Organic and Physical Chemistry, Kazan Scientific Center, Russian Academy of Sciences, Kazan, Tatarstan, Russia

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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 mono-centered hydrogen bonds, whereas the *chair* conformation preferably forms complexes with a two-centered hydrogen bond. Based on theoretical data (ϑ_{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.