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Stereochemistry of Seven-membered Heterocycles. XXXVI. Unprecedented Solvent Effect on Thermodynamical Parameters of Conformational Equilibrium of Model 1,2,3-Trithia-5-6-benzocycloheptene: Donor-Acceptor Interactions of Conformers with the Medium

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Abstract

Medium effect on the conformational equilibrium of a model seven-membered trisulfide represented in solutions by chair and boat conformations is studied by dynamic 1H NMR spectroscopy. Thermodynamic equilibrium parameters (Δ GO, Δ HO, and Δ SO) in nine solvents substantially differing in polar, acceptor, and donor properties, as well as in 5 M solution of lithium perchlorate in acetone are obtained. A pronounced compensation effect is revealed. The difference in the Δ HO values in the studied media are as high as 6.6 kcal/mol, magnitudes of Δ SO differ by up to 22 e.u. Analysis of the solvation energy components led us to conclusion that the observed effect depends on the donor-acceptor interaction of two conformers with the medium. Increasing acceptor properties of solvent result in the enthalpy stabilization of the boat form.