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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 (ΔG0, ΔH0, and ΔS0) 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 ΔH0 values in the studied media are as high as 6.6 kcal/mol, magnitudes of ΔS0 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.