

Calix[n]arenes and their derivatives are often used in supramolecular chemistry for their pronounced ability to form complexes. Thiocalix[4]arene is derived from the classical calix[4]arene by replacement of the methylene bridges between the phenol rings by sulfur atoms, which results in a slightly larger cavity and altered conformational behavior. Thiocalix[4]arene exists in a cone conformation, which is stabilized by an array of four hydrogen bonds between hydroxyl groups on the lower rim of the molecule. Its dynamic behavior in a non-polar solvent was studied by NMR spectroscopy methods based on the temperature dependence of ^{13}C spin relaxation. The rate constants of flip-flop motion of the hydrogen bond array were determined by measurements of dependence of spectral intensities on echo-time in the CPMG NMR pulse sequence. The activation enthalpy and entropy of this reaction were determined. Next, the correlation times of molecular tumbling were determined and found to follow the Arrhenius temperature dependence. The measurements were compared to those of the “classical” calix[4]arene.