

Abstract

Azacalixarenes were synthesized as being new type of macrocyclic molecules. Bis(hydroxymethyl)-*p*-*tert*-butylphenol tetramer **18**, dimer **20** and monomer **21** were treated with benzylamine in refluxing xylene with continuous removal of water as an azeotropic mixture to afford dihomoozacalix[4]arenes **6** (22%), tetrahomodiazacalix[4]arenes **7** (20%), and hexahomotriazacalix[3]arenes **8** (29%), respectively. Predominant formation of the cyclic products suggests that the reaction proceeds under the influence of the template effect of the hydrogen bonds among phenolic hydroxyl groups and nitrogen lone pairs in nonpolar solvents like xylene. The variable temperature ^1H NMR studies of **6** and **7** reveal that their preferred conformations are cone. These compounds are much more conformationally stable than their oxa analogues **2** and **3**, while **8** is conformationally flexible ligand whose geometry meets the requirement to act as uranophile. The energy barrier of 17.8 kcal/mole ($T_c=110^\circ\text{C}$, xylene- d_{10}) for aryl ring inversion in **6** is 4.8 or 2.1 kcal/mole higher than that of the oxa analogue **2** or calix[4]arene **1** itself, respectively. This shows that **6** is conformationally more stable than calix[4]arene irrespective of the increased ring size. ^1H NMR and IR data of the phenolic hydroxyl groups in this series of macrocyclic molecules suggest the existence of strengthened intramolecular hydrogen bonds formed by the participation of the nitrogen lone pairs in the cyclic array of the phenolic hydroxyl groups. We conclude, therefore, that the conformation of calixarenes can be substantially stabilized by introducing the nitrogen functions in the neighborhood of phenolic moieties. The results presented in this report thus, differ from the general view that the conformational flexibility of the calixarenes is expected to increase with the increase in the ring size of the macrocyclic compound.