

NOVEL MACROCYCLIC COMPOUNDS AS BUILDING BLOCKS IN
SUPRAMOLECULAR CHEMISTRY

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ABSTRACT

Resorcinarenes and pyrogallolarenes have been widely used as building blocks for novel synthetic receptors and supramolecular self-assemblies. To explore new chemistry of these compounds, new substituted macrocyclic arenes were synthesized. Introduction of functionalities such as nitro, cyano, and amido groups into the resorcin[4]arene molecule can significantly change the chemical properties of these macrocycles. The spectroscopic data and X-ray crystal structures of the new tetracyano resorcin[4]arenes show that these compounds adopt a crown conformation and that all alkyl substituents are in the axial position. No hydrogen-bonded self-assembly is observed suggesting that the presence of a cyano group inhibits the formation of the hydrogen bonds between the macrocycles. The complex of silver(I) ion and tetracyano resorcin[4]arene is a three-dimensional polymer in which the silver center is coordinated by three cyano groups of the macrocycle and possesses an unusual trigonal planar geometry. No new tetranitro and tetraamido resorcin[4]arenes were synthesized under the studied conditions.

Additionally, molecular hosts with a spacious inner cavity have also received a lot of interest because of their ability to encapsulate and stabilize several guest molecules. To obtain such valuable receptors, palladium-catalyzed Suzuki-Miyaura cross coupling and aldehyde-amine condensation are used as the synthetic pathways to functionalize calix[4]arenes and cavitands with a trimethoxyphenyl moiety. The Suzuki coupling attempts afford only mixtures of products and no pure desired macrocycles can be isolated. In a similar fashion, condensation reactions of tetraformyl- and tetraamino calix[4]arenes produce mixtures of imino calix[4]arene derivatives. The poor solubility of these calix[4]arenes could result in incompleteness of the reactions.

Finally, a new calix[4]arene derivative possessing the versatile 2,4-diamino-1,3,5-triazine moieties has been prepared. Its ability to participate in a large hydrogen-bonded system and to serve as a potential ligand for transition metal complexes was examined by X-ray crystal structure analysis and ¹H-NMR titration. The results from this study reveal that the new diamino-triazine calix[4]arene derivative has a poor solubility in most organic solvents except dimethylsulfoxide. No hydrogen-bonded network is detected for the hydrochloride salt of this new macrocycle. Very polar solvents such as dimethylsulfoxide probably disturb the formation of a hydrogen-bonded assembly, even in the presence of compatible barbituric acid. The complexation study of the new triazine calix[4]arene with zinc(II) trifluoromethanesulfonate also suggests that no complex is formed between the new calix[4]arene compound and a zinc ion.