

SELF-ASSEMBLY OF MONO-O-ALKYLATED CALIX[4]ARENES IN SOLID STATE: EFFECT OF THE CHAIN LENGTH

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Amphiphilic calix[n]arenes and amphiphilic resorcinarenes have attracted a large interest¹ during last decade due to their possible application in design of ion- and molecule-selective electrodes, chromogenic and fluorescent sensors, and Solid Lipid Nanoparticles. O-Alkylated calixarenes are also known because of their complexation ability to proteins and DNA. The geometry of molecules apt to aggregate in micellar structures requires conical molecular shapes, with control over the ration of polar head group size to the length of the hydrophobic chain. In order to produce such a geometry based on a calix[4]arene skeleton, mono-O-alkylated derivatives would appear to be good targets (Fig. 1a). In this study, we present self-assembly of pseudo-amphiphilic

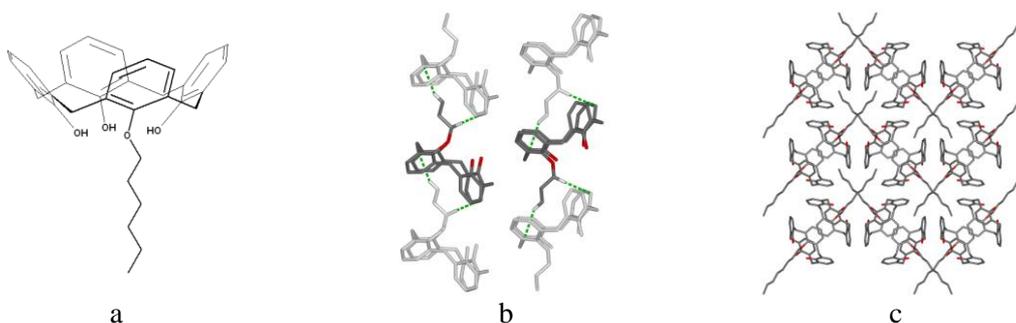


Figure 1. (a) Schematic view of mono-O-alkylated calix[4]arene; (b) two parallel head-to-tail chains in crystal structure of monoproxy-calix[4]arene; (c) packing of dimers in crystal structure of mono-octoxy-calix[4]arene.

calix[4]arenes monosubstituted at the phenolic face by alkyl chains of varying length (2, 3, 5, 6, 8, and 9 carbon atoms) in single crystals. All mono-O-alkylated calix[4]arene molecules in crystal structures adopt the cone conformation, which is stabilized by O–H···O hydrogen bonding at the lower rim. The calix[4]arenes with shorter alkyl chains (1²–5 carbon atoms) assemble into the head-to-tail mode. Alkyl group of one calixarene molecule is located within another calixarene bowl and weak C–H··· π interactions are presented between the two molecules. Repetition of this construction mode creates infinite parallel the head-to-tail chains (Fig. 1b). In the crystal structures of higher homologs (6–9 carbon atoms) the head-to-head dimer formation, due to both C–H··· π

and π - π interactions, is observed (Fig. 1c). Details of head-to-tail and head-to-head assembly, spatial orientation and packing, as well as role of solvent will be discussed.

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2. Maharaj F., Craig D., Scudder M., Bishop R., Kumar N. *J. Incl. Phenom. Macrocycl. Chem.* **55**, 315 (2006).