

„Self-assembly of selected amphiphilic calix[4]arenes and calix[6]arenes in solid state – single crystal X-ray diffraction studies”

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SUMMARY

Hydrophobic effect plays a key role in living organisms: protein folding, ligand-protein and protein-protein binding, micelle and membrane formation *etc.* It is widely applied in surfactant and block copolymer chemistry for rational design of supramolecular assemblies and molecular recognition in, *e.g.* drug delivery and sensing. However, in the field of crystal engineering, spatial unpredictability of the hydrophobic effect is still an open question.

The aim of this work is to show that even apparently non-polar O-alkylated calix[4]arenes and calix[6]arenes in molecular crystals mimic microstructures observed in surfactant assemblies and block copolymers. As good model compounds three classes of O-alkylated calix[n]arenes ($n = 4, 6$) have been chosen: non-substituted at the upper rim (possible C–H $\cdots\pi$ and π - π stacking interactions), substituted at *para*-positions with *tert*-butyl groups (possibility for π - π stacking interactions are blocked), and substituted at *para*-positions with nitro groups calix[n]arenes (more polar molecules with additional possibility for C–H \cdots O hydrogen bonding). Self-assembly of such calixarenes in twenty seven crystal structures were analysed in this thesis.

Structural analysis of investigated compounds and thirty five their analogues from Cambridge Structural Database show localisation of aliphatic and aromatic regions in crystals. Topological analysis of the surface between these regions reveals that topology of crystal structure depends on relationship between volumes of aromatic and aliphatic parts of molecules.

Crystal structures of fully O-alkylated calix[4]arenes in the cone conformation with short alkyl chains [HC[4]OC $_n$ ($n = 3,4$), tBuC[4]OC $_n$ ($n = 3,4$) and NO $_2$ C[4]OC $_n$ ($n = 2-8$)] reveals *bicontinuous* topology. For crystal structures of HC[4]OC $_n$ ($n = 7-14$) and NO $_2$ C[4]OC $_n$, ($n = 12-14$), the *layered* topology is proper. For tBuC[4]OC $_n$ with number of carbon atoms in the alkyl chains larger than 4, two homologous series are observed: the *inverted perforated layers* topology has been found for odd n (5,9 and 11) and the *inverted ribbons* topology for even n (6–14).

Changes in calix[4]arene conformation may be followed by changes in the topology. Thus, tBuC[4]OC $_n$ (partial cone) ($n = 1-8$) is the largest group of the calix[4]arenes which adopts other than the cone conformation. Crystal structures of all tBuC[4]OC $_n$ (partial cone) show the *inverted perforated layers* topology.

In the case of calix[6]arenes, only 7 structures are known so far. The resulting topology strongly depends on both presence of solvent molecules in the structure and calix[6]arene conformation. The only one common feature for all the known structures is self-inclusion of methyl or methylene group(s) into calix[6]arene cavity.

Apparently non-polar fully O-alkylated calix[4]arenes and calix[6]arenes reveal amphiphilic behaviour in the solid state. Hydrophobic-to-total volume analysis is a powerful tool for understanding the crystal chemistry of amphiphilic compounds and provides the possibility of rational design of crystals with 0-, 1-, 2- or 3-dimensional distribution of domains of desired nature, which is important in designing, *e.g.* organic semiconductors.