Poster Presentations

[MS25-P15] Fine tuning of the inclusion behaviour of calixarenes depending on the bridge substituents

Petra Bombicz,[a] Conrad Fischer,[b] Wilhelm Seichter[b], Edwin Weber[b]

[a]*Dept. Struct. Chem., Inst. of Org. Chem., Research Centre for Natural Sciences, Hungarian Academy of Sciences, Hungary,* [b]*Institut für Organische Chemie, Technische Universität Bergakademie Freiberg, Germany.*
E-mail: bombicz.petra@ttk.mta.hu

The conformational variability makes calixarenes ideal target compounds both in the field of crystal engineering and supramolecular complex formation. Until recently less was known about the effect of a bridge modification on the supramolecular properties. To study the effect of lateral substitution series of laterally non-, mono-or disubstituted tetra-*tert*-butyltetramethoxycalix[4]arene compounds were synthesised [1, 2, 3, Scheme 1]. Either one or two bridge substituents on opposite methylene units of the parent tetramethoxycalix[4]arene exercise a distinct influence on the molecular conformation of the host as well as on the supramolecular architecture of the crystal packing.

Scheme 1. Bridge non-(R^1=H, R^2=H), mono-(R^2=H) and disubstituted calix[4]arenes.

The calixarene molecules in the different laterally monosubstituted structures [1] all adopt the partial cone conformation with different affection of the included guest molecules. As a consequence of bridge monosubstitution, the serpentine like channels observed in the laterally unsubstituted calixarene structure are straightened to linear channels [1]. The introduction of a lateral substituent may expand the total room available for guest molecule inclusion by nearly 30%, being another promising fact for crystal inclusion chemistry. A conformational change upon attachment of a second lateral substituent to the opposite methylene bridge site in the diametrically bridge-disubstituted calix[4]arenes transform molecular geometry from partial cone to 1,2alternate [2, 3], resulting in dense packing with highly reduced solvent accessible voids. Concluding this, the inclusion behaviour seems to be tuneable depending on the bridge substituents, which is a promising tool for supramolecular host guest design. Moreover, the increase of the sterical demand of the bridge substituents results in a more efficient utilisation of the crystal volume and a gradual reduction of residual empty voids of the lattice. If a size limit is exceeded, the bridge substituents are forced to participate in the supramolecular bonding system [2, 3]. In all examined structures, the lateral substituents act as a spacer. The bridge substitution clearly influences the packing arrangement of the host molecules, which can be fine-tuned very sensitively by size and functionality of the substituents. In these series of calixarenes the spatial requirement of the bridge substituents has a determining role in the crystal packing. This directed manipulation of the molecular packing arrangement by the system of secondary interactions, could be understood as a kind of "synthon engineering".

P.B. acknowledges the support from the Hungarian Scientific Research Fund (OTKA K-100801).

[1] C. Fischer, G. Lin, P. Bombicz, W. Seichter, E. Weber, *Struct Chem 2011*, 22, 433–439.
[2] C. Fischer, P. Bombicz, W. Seichter, F. Katzsch, E. Weber, *Crystal Growth and Design 2012*, 12, 2445-2454.
[3] C. Fischer, P. Bombicz, W. Seichter, E. Weber, *Struct Chem 2013*, 24, 535-541.

Keywords: inclusion compounds; calixarenes; crystal engineering