

# diffusion-fundamentals

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## Molecular motions of calix[4]arene and thiacalix[4]arene in solution studied by NMR relaxation

Jan Lang,<sup>1,2</sup> Kateřina Šetková,<sup>2</sup> Veronika Deckerová,<sup>2</sup> Pavel Lhoták,<sup>3</sup> Jiří Czernek<sup>4</sup>

<sup>1</sup>Laboratory of NMR Spectroscopy, Institute of Chemical Technology in Prague, Czech Republic

<sup>2</sup>Department of Low Temperature Physics, Faculty of Mathematics and Physics, Charles University in Prague, Czech Republic

<sup>3</sup>Department of Organic Chemistry, Institute of Chemical Technology in Prague, Czech Republic

<sup>4</sup>Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Czech Republic

Corresponding author:

Jan Lang

Laboratory of NMR Spectroscopy

Institute of Chemical Technology

Technická 5

166 28 Prague 6

Czech Republic

E-Mail: Jan.Lang@vscht.cz

### Abstract

Calixarenes have been well established as one of the major structural motifs in supramolecular chemistry. Preorganization of their cavity and availability of many kinds of chemical modifications of the basic scaffold make them particularly useful as molecular receptors, sensors, containers, catalyzers etc. [1].

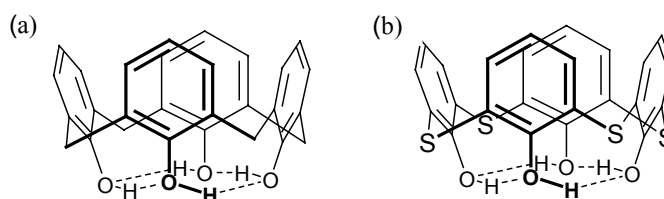


Fig. 1: Calix[4]arene (a) and thiacalix[4]arene (b) with the circular hydrogen bond array on the lower rim

The properties of non-covalent binding towards various molecular guests can be gently tuned by specific chemical substitutions. Thiacalix[4]arene is derived from the “classical” calix[4]arene (Fig. 1) by replacement of the methylene bridges between the phenolic rings by sulfur atoms, which results in a slightly larger cavity and altered conformational behavior.

In principle, calix[4]arene or thiacalix[4]arene can adopt four basic conformations defined by orientation of its phenyl rings (*cone*, *partial cone*, *1,3-alternate*, *1,2-*

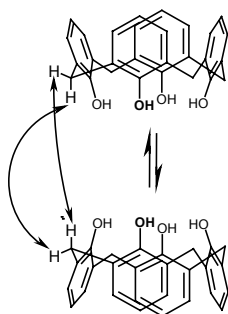


Fig. 2: *Cone* - "*inverted cone*" transition

*alternate*). The transitions between the conformers are possible if the lower rim substituent is small enough to pass through the cavity when the phenyl ring rotates. When the lower rim carries just hydroxyl groups, the *cone* conformation becomes stabilized by a circular array of hydrogen bonds, and, consequently, other conformations are not populated. However, the rotation of the phenyl rings can lead to the inversion of the whole structure "inside out" (Fig. 2). The starting and the resulting structures are identical, but the process can be monitored using  $^1\text{H}$  resonances of  $\text{CH}_2$  bridging groups of calix[4]arene, whose chemically non-equivalent hydrogens exchange their positions.

Next type of molecular motion in calixarenes is flip-flop of the circular hydrogen bond array. The arrays can be oriented in clockwise or anti-clockwise direction. Rate of this motion can be assessed by means of measurements of transverse  $^{13}\text{C}$  spin relaxation. However, besides the slower molecular motions (termed as "chemical exchange"), the spin relaxation is governed by fluctuations of local magnetic fields caused by molecular rotational diffusion and by molecular internal motions in picosecond – nanosecond timescale. Therefore, in order to separate the chemical exchange contributions, the nature of molecular tumbling must be determined. This can be accomplished by analysis of the longitudinal  $^{13}\text{C}$  spin relaxation (and  $^{13}\text{C}$ - $^1\text{H}$  cross-relaxation), which is not affected by the chemical exchange.

Thus, employing the nuclear magnetic resonance (NMR) techniques relying mainly on measurements of nuclear spin relaxation, several kinds of molecular motions in calix[4]arene [2] and thiacalix[4]arene were characterized (in the temperature range 223 – 313 K):

- i. Molecular tumbling with the correlation time the range of 70 ps – 3 ns.
- ii. Flip-flop motion of circular hydrogen bond array occurring every 1  $\mu\text{s}$  – 3.5 ms.
- iii. *Cone* - "*inverted cone*" conformational transition occurring ca. one time each second.

### Acknowledgement

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### References

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- [2] J. Lang, V. Deckerová, J. Czernek, P. Lhoták, J. Chem. Phys., 122 (2005) 044506.