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IR and NMR spectra, intramolecular hydrogen bonding and conformations of para-tert-butyl-aminothiacalix[4]arene in solid state and chloroform solution

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ABSTRACT

It is demonstrated that dissolution of aminothiacalix[4]arene in chloroform results in transformation of 1,3-alternate conformation, adopted in single-crystal and bulk polycrystalline solids, to the pinched-cone form. This conformer is stabilised by the intramolecular hydrogen bonds of two distal amino-groups acting as H-donors with another two amino moieties that appear as H-acceptors. The H-bonds cause quite small (ca. 10–20 cm^{-1}) red shift of the IR bands of the NH_2 stretching vibrations, which suggests rather weak NH···N hydrogen bonding. This latter is sufficient to stabilize the pinched-cone conformation in the chloroform solution, but the energy gap between the pinched-cone and other conformations is small, and solid-state intermolecular forces easily overcome it, leading to realisation of the 1,3-alternate conformer. The comparison of the DFT computed and experimental vibrational and NMR spectra demonstrates good quality of present quantum-chemical computations, allows complete interpretation of the spectra and reveals simple IR and NMR spectroscopic markers of the conformers of aminothiacalix[4]arenes.

1. Introduction

Calixarenes are macrocyclic compounds consisting of phenol rings that are connected via the ortho positions by methylene groups. In thiacalixarenes the methylene bridges are replaced by the S atoms. Both types of calixarenes, especially calix[4]arene (**1**, Fig. 1) and thiacalix[4]arene (**2**), comprising four phenolic units, and their para-tert-butyl derivatives (**3** and **4** respectively) are among the most used macrocyclic frameworks [1–4]. Recently the synthesis of para-tert-butyl-aminothiacalix[4]arene (**5**), in which four OH groups were replaced by four NH_2 groups was reported [5]. The amino substituent is not only a potential metal-ligating moiety but also the most reliable functional group in synthetic aromatic chemistry for transformation to various entities. So, the compound **5** should provide a new molecular platform for functional materials and supramolecular assembly.

The conformation of a macrocyclic receptor is a key feature, which determines the use of such molecules in many applications. Therefore, the study of the conformational behaviour of calixarenes has been in the focus since the beginning of their chemistry. The calix[4]arenes (**1**, **3**) and the thiacalix[4]arenes (**2**, **4**) are known to have the cone conformation both in the solid state and CCl_4 solutions [1–4]. In full accord with the experiment, both ab initio and DFT computations (e.g. [6] and references cited therein) predict the cone conformations of individual molecules **1**–**4** to be much more energetically stable than other possible conformers—partial cone (paco), 1,3-alternate (1,3-alt) and 1,2-alternate (1,2-alt). In case of aminothiacalix[4]arenes quantum-chemical computations [7,8] seem to contradict the X-ray data [5]: the former predict the cone and paco conformations of the molecule **6** to be more stable than the other conformers, while according to the latter, closely related p-tert-butyl derivative **5** adopts the 1,3-alt conformation in the crystalline phase.

Similar situation was encountered in case of tetramercaptothiacalix[4]arenes **7** and **8**: according to DFT predictions [7,8], the cone should be preferable conformation of the molecule **8**, but 1,3-alt was found by X-ray [9] in crystal of p-tert-butyl derivative **7**. Subsequently we were able to demonstrate [10] that the introduction of p-tert-butyl groups to the molecule **8** dramatically influenced the conformational behaviour of the mercaptothiacalix[4]arene molecules. Quantum-chemical computations in combination with IR and NMR spectroscopy indicated that, in contrast to **8**, the 1,3-alt became a dominant conformer of p-tert-butyl-derivative **7** not only in crystal state, but also in solutions and in vacuum.

In the present work we use the same hyphenated spectroscopic-quantum-chemical technique to study conformational behaviour of the compound **5** both in the solid state and in solutions. As any experiment is impossible for the molecule **6**, which has not yet

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