

The conformation and dynamic behaviour of tetrathiacalix[4]arenes functionalized by hydrazide and hydrazone groups

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Abstract

The ^1H , ^{13}C and ^{15}N NMR data, conformation and dynamic behaviour of the new tetrathiacalix[4]arenes functionalized by hydrazide and hydrazone groups are reported and compared with the result of earlier investigations of 4-*tert*-butylphenoxyacetylhydrazones. The unusual fact of formation of *N,N'*-diacetylhydrazine bridge and factors leading to its formation in the *cone* conformer of calixarene has been discussed. The barriers of rotation of hydrazone fragments of tetrathiacalix[4]arenes were determined by NMR-measurements at various temperatures. The structure of 1,3-*alternate* conformer of 5,11,17,23-tetra-*tert*-butyl-25,26,27,28-tetrakis[hydrazinocarbonylmethyl]-2,8,14,20-tetrathiacalix[4]arene in solution is compared with crystal structure obtained by the X-ray analysis.

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1. Introduction

In the last decades it has been shown that preorganization plays a fundamental role in molecular recognition [1,2]. Preorganization and rigidity of host molecules are usually obtained by covalent linking of binding groups by means of rigid spacers to suitable templates [3,4]. Calix[4]arenes are very interesting host molecules and their complexation ability can be varied either by changing the nature and the number of the binding sites located on both rims or by controlling the conformation of the calix[4]arene molecule [1,5,6].

To investigate this problem the series of new calix[4]phenols, calix[4]resorcinols and calix[4]pyrogallols with acetylhydrazide substituents has been designed and synthesized [7]. The presence of carbonyl oxygen and amine nitrogen atoms in acylhydrazides promotes the formation of chelate

binding center and provides their unique complexation properties [8]. The comparison of extraction properties of synthesized calix[4]phenol derivatives and their acyclic monomeric analogue has clearly showed, that the preorganization of acetylhydrazide groups on the calix[4]arene platform is the cause of dramatic improvement of their binding ability [9]. The presence of additional “soft” nitrogen atom in ion-binding sites of acetylhydrazide derivatives of calix[4]arenes leads to the shift of classical selectivity from alkali and alkaline earth cations which is observed for amide derivatives to transitional metal ions.

It is known that hydrazides of carboxylic acids are key reagents for the synthesis of other nitrogen containing derivatives, particularly, acylhydrazones [10,11]. The condensation of hydrazides with aldehydes leads as a rule to the conversion of acetylhydrazide groups to acetylhydrazone ones. Thus, the acetylhydrazones (**4**, **5**) (see Fig. 1) have been obtained on the base of 4-*tert*-butylphenoxyacetylhydrazide (**1**), which is the monomer structure block of tetrahydrazide derivatives of calix[4]phenols (**2**, **3**) [12,13].

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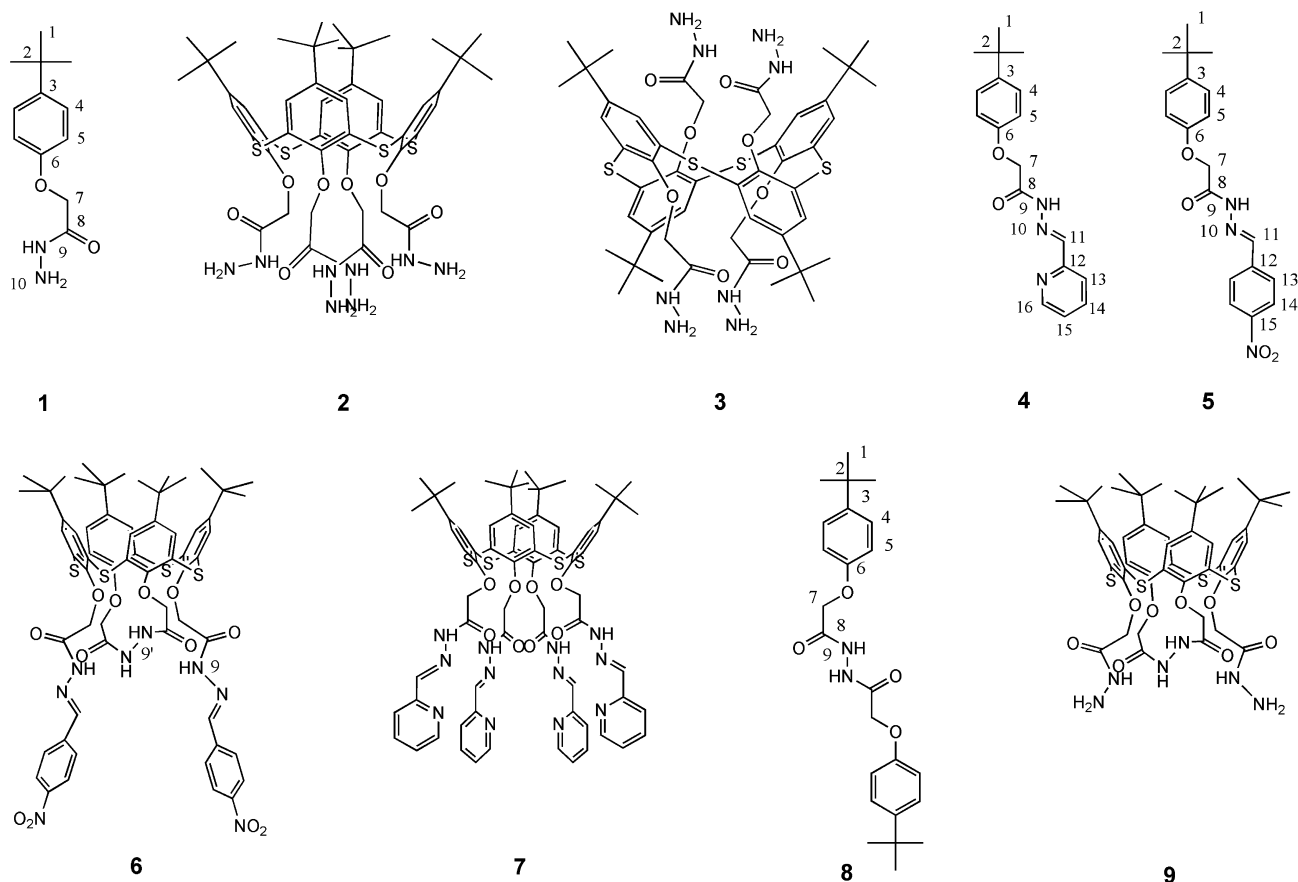


Fig. 1. Compounds investigated. Numbering system used in Tables.

However, the reaction of tetrathiacalix[4]arene **2** with an excess of 4-*tert*-butylphenoxyacetylhydrazide leads to the preferable formation of unconventional tetrathiacalix[4]arene (**6**) with additional *N,N'*-diacetylhydrazine bridge [14]. The calix[4]arene **6** is formed as a result of intramolecular reaction. When using of pyridine-2-carboxaldehyde as a reagent, only formation of tetrathiacalix[4]arene functionalized by four acetylhydrazone fragments has been observed (**7**) [14].

The properties and reaction ability of compounds are determined in many cases by their conformation and/or configuration [15]. It is generally known that the energies of conformational transitions in organic molecules are too small in comparison with activation energy of chemical reactions. Therefore, the conformational effects usually influence weakly on the reaction rate and its direction. However, in the large molecules, especially in supramolecules, the influence of weak effects can be considerably increased by cooperative interactions in these molecules. The hydrogen bonds determine intramolecular interactions, the self-assembly of supramolecular structures and also effect on the conformational properties of molecules. Therefore, the conformational and hydrogen bonding control is a rational way to predict the physical and chemical behaviour of the molecules.

Following to our previous studies on reactivity and binding properties of tetrathiacalix[4]arenes functionalized by hydrazide and hydrazone groups synthesized earlier

[7,9,14] we present therein the results of the complete assignment of ^1H , ^{13}C and ^{15}N NMR spectra and the investigation of conformational and dynamic behaviour of these compounds. The conformation of **3** in solution is compared with the structure obtained by the X-ray analysis.

2. Experimental

2.1. Materials and methods

All reagents were used as commercially received without further purification. CDCl_3 (99.8% isotopic purity) and $\text{DMSO}-d_6$ (99.5% isotopic purity) from Aldrich were used for NMR spectroscopy. Microanalyses of C, H, N were carried out with a CHN-S analyzer (Carlo Erba). The IR spectra were recorded on a Vector-22 Bruker FT-IR spectrophotometer using KBr pellets with a resolution of 4 cm^{-1} . Mass spectra were detected on a Finnigan MALDI-TOF Dynamo mass spectrometer.

The hydrazides **1–3** and hydrazones **4–7**, the derivatives of 4-*tert*-butylphenoxyacetylhydrazide **1** and tetrathiacalix[4]arene **2**, were obtained as described earlier [7,9,12,14].

2.1.1. *N,N'*-di(4-*tert*-butylphenoxyacetyl)hydrazine **8**

To the 4-*tert*-butylphenoxyacetyl hydrazide **1** (0.22 g; 1 mmol) in water (5 ml) under stirring HCl solution (37%, 0.09 ml; 1 mmol) was added. The reaction mixture

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