



DOI #: 10.6564/JKMRS.2010.14.2.144

## Conformational Characteristics of *p*-*tert*-Butylcalix[6]arene Mono-Alkyl Ester Derivatives

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(Received Nov 10, 2010; accepted Dec 9, 2010)*

**Abstract** : Conformational properties of several mono-alkyl ester derivatives of *p*-*tert*-butylcalix[6]arene depending on temperatures have been investigated by solution NMR spectroscopy. It is found out that all derivatives can adopt a cone-like conformation around room temperature, while the conformational characteristics at high temperatures seem to be quite different each other.

Keywords : calix[6]arene, mono-alkyl ester, conformation, NMR

### INTRODUCTION

It is well known that the calixarenes can be good hosts toward various guests as well as building blocks for large supramolecular assemblies due to their recognition ability.<sup>1,2</sup> A great number of researchers have made efforts to manifest the conformation of calixarenes, because it is one of major factors determining their properties and activities as hosts or building blocks.<sup>1-4</sup>

Among calixarene families, calix[4]arenes are the most widely studied compounds and much have been elucidated about their conformational behaviors by means of diverse analytical tools such as X-ray crystallography, computer calculations, and NMR spectroscopy.<sup>5-7</sup> The higher homologue,

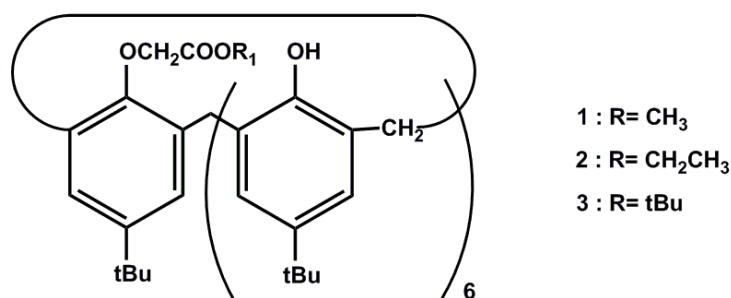
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calix[6]arenes have been expected to have more versatile platforms for the formation of inclusion complexes with various types of guest substances since they have the larger cavity and flexibility compared to calix[4]arenes.<sup>1</sup> This higher degree of conformational complexity can give more possibility for practical applications of calix[6]arenes. On the other hand, it has also been a constraint to the wide research about them. Proper functionalization in the upper and/or lower rim can envisaged as a mean of controlling the conformation, thus modulating the properties of calix[6]arenes. For example, introducing some bulky group substituents could produce good ionophoric ligands arranged to form rigid of specific conformations with remarkable complexing abilities toward certain metal or organic ions.<sup>8,9</sup>

In this work, we have investigated the conformational properties of mono-substituted calix[6]arene derivatives by solution NMR spectroscopy. The calix[6]arenes used were substituted by *tert*-butyl group at upper rim to give them more rigidity and substituted by alkyl (methyl, ethyl, *tert*-butyl) ester groups at the lower rim of only 'one' phenyl unit to investigate the substituent effects on conformation. With our previous studies on the 'hexakis' and 'mono-penta' type ester derivatives,<sup>3,10</sup> this research about the 'mono' alky ester derivatives will be helpful to increase the information on controlling the structure of calix[6]arenes.

## EXPERIMENTAL

All kinds of mono-functionalized *p*-*tert*-butylcalix[6]arenes, 1 ~ 3 used for this study were synthesized following the reported standard procedures.<sup>11</sup> The NMR solvents ( $\text{CDCl}_3$  and  $\text{C}_2\text{D}_2\text{Cl}_4$ ) used were purchased from Sigma-Aldrich Chemical Co. Inc. and used without further purification. Each sample was placed in a standard 5 mm o.d. solution NMR tube. The chemical shift values for  $^1\text{H}$  NMR spectra were referenced to the residual protons in the solvents and the  $^{13}\text{C}$  chemical shifts were referenced to observed solvent peaks. Most of the NMR experiments were performed on a Varian VNS600 spectrometer operating at 600 MHz for protons, and the NMR experiments at high temperatures were recorded on a Varian VXR-200S spectrometer operating at 200 MHz for protons.

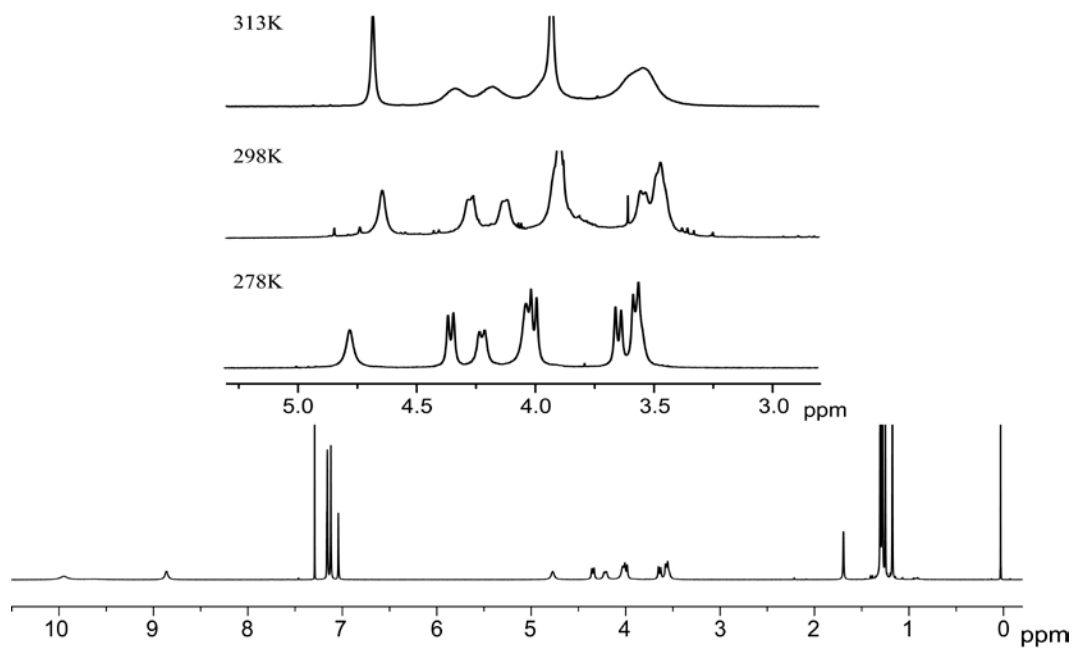


## RESULTS AND DISCUSSION

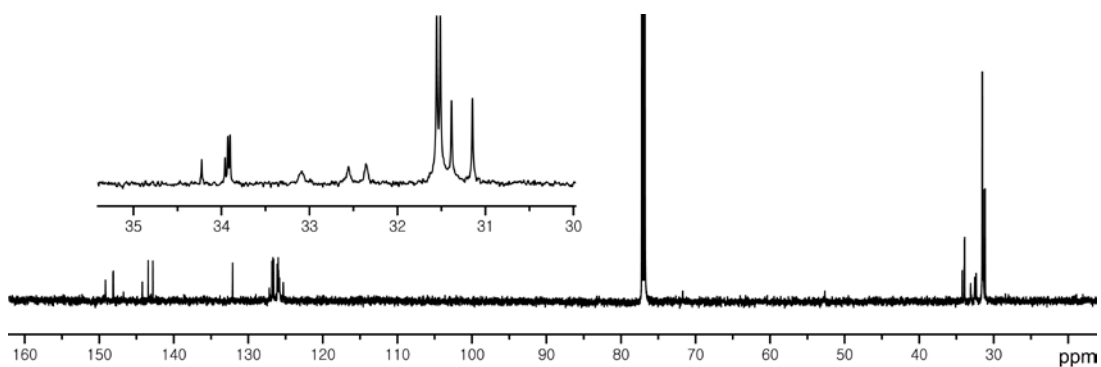
The bridging ( $\text{ArCH}_2\text{Ar}$ ) methylene proton resonance lines of mono methyl ester 1 split clearly into three pairs of doublets (exhibiting like 3 AX spin systems) at 278 K as shown in Figure 1, indicating that the compound has a cone-like conformation. Although the lines were broadened as

temperature was raised, the conformation seemed to be maintained until at room temperature.  $^{13}\text{C}$  NMR spectrum of mono methyl ester 1 also supports that it adopts a cone conformation at 298 K. The  $\text{ArCH}_2\text{Ar}$  methylene carbon peak was divided into three parts at the range of 32 ~ 33 ppm (see Figure 2), which represented that all the connected phenyl rings took *syn* orientations rather than *anti* orientations.<sup>12,13</sup> However, the chemical shifts values strongly suggest some of phenyl rings were somewhat flattened. It could be predicted by the chemical shifts differences between two protons in bridging methylenes (0.77, 0.55, and 0.46 ppm). Additionally, the signals from both methyl and quaternary carbons of *t*-butyl groups on the upper rims split into four peaks with a ratio of 1:1:2:2. It is the typical splitting pattern for mono-substituted calix[6]arenes when they adopt the cone-like conformation having a symmetry plane.

It is known that some of 'hexakis' and 'mono-penta' type *p*-*tert*-butylcalix[6]arene ester derivatives have specific conformations such as an 1,2,3-alternate or an 1,2-alternate.<sup>3,10</sup> But the mono substituted derivatives generally adopt a cone-like conformation since they have five phenolic OH groups which enable to form intramolecular hydrogen bonds. As seen in Figure 1, the phenolic protons signals were found to appear at far down field (around 9~10 ppm) due to the effects of hydrogen bonding.

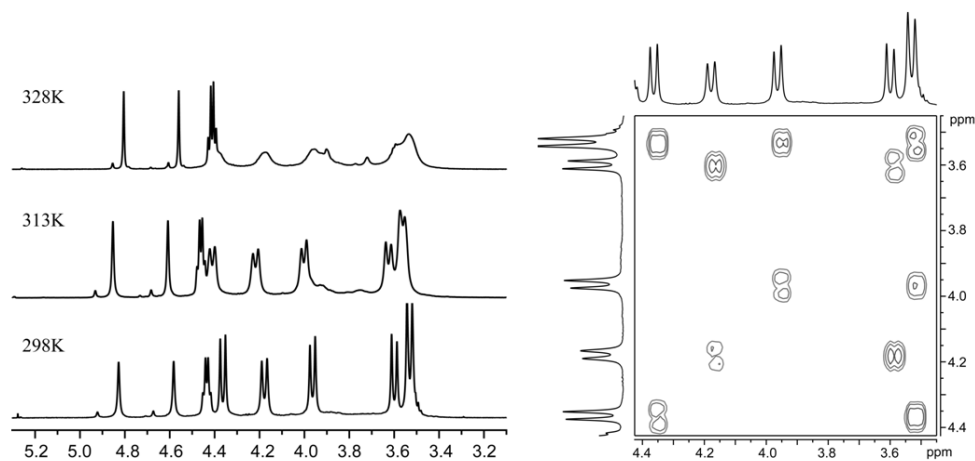


**Figure 1.** Variable temperature partial <sup>1</sup>H NMR spectra and the full spectrum (at 278 K) of calix[6]arene mono-methyl ester 1 in CDCl<sub>3</sub> (600 MHz).

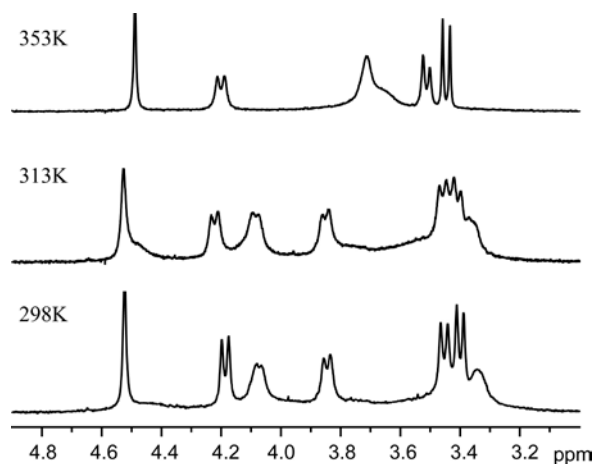


**Figure 2.** <sup>13</sup>C NMR spectrum of calix[6]arene mono-methyl ester 1 in CDCl<sub>3</sub> at 298 K (600 MHz).

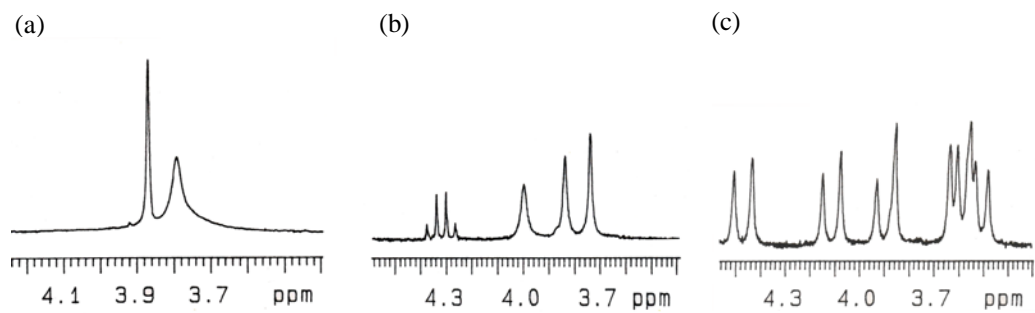
The higher homologues, mono ethyl and mono *tert*-butyl esters 2 and 3, also adopt a cone-like conformation, but the conformational fluctuations seem to be different each other (see Figures 3 and 4). For example, differing from the mono methyl ester 1, the proton NMR signal of the bridging ArCH<sub>2</sub>Ar methylene of 2 splits clearly into three sets of doublet pairs even at room temperature. However, in contrast to simple expectation, those peaks for *tert*-butyl ester 3 seemed to be broader than those of 2. Considering only the effects of bulkiness of substituent, the conformation of 3 must be more stable. This implies that the conformational behaviors of calix[6]arenes depend predominantly both on the size and property of substituents.



**Figure 3.** Temperature varied partial <sup>1</sup>H NMR spectra (left) and COSY spectrum (right, at 298 K) of calix[6]arene mono ethyl ester 2 in CDCl<sub>3</sub> (600 MHz).



**Figure 4.** Temperature varied partial  $^1\text{H}$  NMR spectra of calix[6]arene mono *tert*-butyl ester ester 3 in  $\text{C}_2\text{D}_2\text{Cl}_4$  (600 MHz).



**Figure 5.** High temperature  $^1\text{H}$  NMR spectra of calix[6]arene (a) mono methyl ester 1 in  $\text{CDCl}_3$  at 328 K (b) mono ethyl ester 2 in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403K (c) mono *t*-butyl ester 3 in  $\text{C}_2\text{D}_2\text{Cl}_4$  at 403 K (200 MHz).

The conformational characteristics depending on the substituents are shown well on the spectra obtained at high temperatures. As seen in Figure 5 a, on raising the temperature the bridging methylene proton lines of mono methyl ester 1 were coalesced into one broad singlet line at 328 K, which were divided into three sets of double pairs at low temperature. (Note that the sharp singlet around 3.9 ppm corresponds to the signal from methoxyl protons on the methyl ester substituent.) In contrast to this, those of mono ethyl ester 2 were found to collapse into three singlets corresponding to three doublet pairs (Figure 5 b). These results imply that “turn-inside-out” inversion (simultaneous flips of all six benzene rings) of mono ethyl ester 2 might take place at high temperatures keeping a cone conformation, while the inversion of mono methyl ester 1 probably occurs without a specific preferential conformation. This observation as well as the previous studies<sup>3,10</sup> shows that the methyl ester moiety plays some exquisite role in determining the conformation of *p-tert*-butyl calix[6]arene derivatives.

Especially, in the case of mono *tert*-butyl ester 3 which has the bulkier substituent than the compound 1 and 2, the conformational preference has been changed as temperature raised to 353 K and 403 K. As illustrated in Figure 4 and discussed earlier, 3 adopts a cone-like conformation at room temperature. But the <sup>1</sup>H NMR spectrum at 353 K showed that one doublet pair of bridging methylene proton lines was coalesced, which could be interpreted as the result of a partial cone conformation. The conformation seemed to be changed into a cone-like again at 403 K as can be seen from the fact that the bridging methylene proton line split clearly again into three sets of doublet pairs (see Figure 5



c). Mono *tert*-butyl ester 3 would look like to have a less tendency to collapse and remain nearly intact at 403 K due to the bulky substituent.

In summary, we have investigated the conformational characteristics of mono alkyl ester substituted derivatives of *p-tert*-butyl calix[6]arene. All derivatives adopt a cone-like conformation around room temperature or at low temperature, however the behaviors with temperature raising seem to be quite different from each other. The methyl substituted compound 1 couldn't maintain its cone conformation at high temperature while ethyl ester 2 keeps a cone conformation during turn-inside-out inversion. On the other hand, *tert*-butyl ester 3 looks like to change the preferential conformation twice over the observed temperature range.

### ***Acknowledgment***

This work was supported by the Young Investigator Research Program of Chung-Ang University 2007 year (K.-C. Chung).

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