Theoretical Study of Exo-Endo Interconversion of [(R)CalixTMS2]Sn

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ABSTRACT

The 1, 3-bis(trimethyl silyl)ether of p-tert-butyl calix[4]arene, [(t-Bu)CalixTMS2]H2, has been synthesized and used as a dianionic ligand for “Sn”. The complex of [(t-Bu)CalixTMS2]Sn exhibits exo and endo isomerism. The structural properties of [(R)CalixTMS2]Sn, (Rpara= H, CH3, t-Bu) and the inter conversion of exo→endo isomers were investigated by using of SCF-MO PM3 method.

Keywords: Calix[n]arenes; Sn-complex; PM3; Molecular modeling; Liquid crystals; Isomerization.

INTRODUCTION

Calix[n]arenes are a class of macrocycles that have attracted much interest because of their potential for forming host-guest complexes and have been extensively investigated in various fields [1-14]. Calix[n]arenes with various functions have been developed with remarkable progress by modifying either the upper or lower rim [1-9, 15]. Especially, for developing calix[n]arenes as analytical reagents, upper or lower rim-modified calix[n]arenes have been applied for ion and molecular separations [7-10], as well as sensors such as ion-and molecular selective electrodes and also liquid crystals [8-23]. Calix[n]arenes have been combined with metal ions and functional units to give nice complexes with interesting properties.

With increasing size and structural complexity of the guest species this approach becomes increasingly demanding in terms of design and the number of steps in the synthesis of a host-guest compound. However, calix[n]arenes, which can be practically applied as effective analytical reagents with enzyme-like activity, have not yet been developed. Some of the complexes of these compounds were used as liquid crystals, such as [(t-Bu)CalixTMS2]Sn. Divalent Sn-complex i.e. [(t-Bu)CalixTMS2]Sn, are readily obtained by the reaction of [(t-Bu)CalixTMS2]H2 with Sn[N(SiMe3)2]2. For the Sn-system, the reaction yields sequentially two isomers, namely exo- and endo- [(t-Bu)CalixTMS2]Sn, which differ in location of the Sn-atom with respect to the calixarene cavity. The product of this reaction has been structurally characterized by X-ray diffraction [16,19].
The exo- and endo- of [(R_p)Calix\textsuperscript{TMS}\textsubscript{2}]Sn, (R\textsubscript{p}para=H, CH\textsubscript{3}, t-Bu) described here, therefore, constitute the first pair of the exo- and endo-isomers to be structurally characterized. The alkyl groups (R= Me, t-Bu) play the role of the "helm" for getting the two isomers. Also, the conformations, structural properties and inter conversion of the exo-endo-isomers were investigated by SCF-MO PM3 calculations.

RESULTS AND DISCUSSION

**Exo- and Endo-isomers of [(H)Calix\textsuperscript{TMS}\textsubscript{2}]Sn**: The results of semi-empirical PM3 calculations for the exo- and endo- of [(H)Calix\textsuperscript{TMS}\textsubscript{2}]Sn, 1-3 are summarized in Table-1 and Fig.-1. Selected structural parameters and the transition state structure for inter-conversion of the exo- and endo-isomers are shown in Table-1 and Fig.-1. The energy surface for inter-conversion pathway of these isomers of [(H)Calix\textsuperscript{TMS}\textsubscript{2}]Sn was investigated in detail by changing the position of Sn atom in the cavity of the complex and the results are summarized in Fig.-1. The endo-form 16.75 kcal mol\textsuperscript{-1} is more stable than exo-isomer. The barrier energy for conversion of endo- to exo-isomer is 21.1 kcal mol\textsuperscript{-1}.

For the endo- and exo-isomers the distances between Si-atoms are 5.42 and 6.75Å, respectively. As shown in Table-1, the distances between H-atoms at the para-position (r\textsubscript{13} and r\textsubscript{24}) on aromatic rings are 9.46 and 9.47Å for endo-, 8.28 and 9.41Å for exo- and 9.55 and 10.1Å for transition state form. The distances of Sn atom from oxygen atoms of O-TMS groups are 1.73, 1.66 and 1.73Å for endo-, exo-isomers and the [TS], respectively. The Sn-O bond lengths to the phenoxide moieties are 1.82, 2.27 and 1.87Å for endo-, exo-isomers and the [TS], respectively.

In this complex, the torsional angle between Si-0 bonds for endo-, exo-isomers is zero (0°) and for [TS] is equal to 18°. The summation distance of Sn-atom that it passes from endo- to exo-positions was calculated 0.76Å; (it was determined by geometrical calculations). The length of gradient positions of Sn atom from endo-isomer to [TS] is 0.27Å. This change position for exo-isomer to transition state is 0.50Å.

METHOD

Because of the large number of atoms in 1-9 the SCF-MO PM3 calculations were carried out on these molecules. The Energy minimum geometries were located by minimizing geometries of [(R_p)Calix\textsuperscript{TMS}\textsubscript{2}]Sn, (R\textsubscript{p}para=H, CH\textsubscript{3}, t-Bu). The calculations were carried out by using MOPAC and PC-Model packages.[24-26]
Table 1. Selected structural parameters for 1-9 ([R(CalixTMS)Sn]). The heats of formations in \((\Delta H^\circ)\) kcal mol\(^{-1}\), bond length \((r_{xy})\) in Å, bond angle \((\Theta_{xy})\) and torsional angle \((\Phi_{wxyz})\) in °

<table>
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<th>Endo-isomer</th>
<th>[TS]</th>
<th>Exo-isomer</th>
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Table-I continue:

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<td>(r_{fg})</td>
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Figure 1. Inter-conversion process of the exo- and endo- of [(H)Calix<sub>TMS</sub><sup>2</sup>]Sn, 1↔2↔3.
Exo-and Endo-isomers of [(CH₃)Calix⁴TMS]₂ Sn

The selected structural parameters, the heats of formation in kcal mol⁻¹ and the results of SCF-MO PM3 calculations for the exo- and endo isomers and the transition state of interconversion of [(CH₃)Calix⁴TMS]₂Sn are summarized in Table-1 and Fig.2.

Figure 2. Inter-conversion process of the exo- and endo- of [(CH₃)Calix⁴TMS]₂Sn, 4→[5]→6.
The exo-form 26.53 kcal mol\(^{-1}\) is less stable than endo-isomer. The barrier energy for the isomerization of endo- and exo-isomers was obtained 35.55 kcal mol\(^{-1}\). The distances between Si-atoms for endo- and exo-isomers are 5.38 and 6.12Å respectively. This length for [TS] of 4 and 6 were obtained 6.03Å. The distances between C-atoms of para-CH\(_3\) groups (r\(_{13}\) and r\(_{24}\)) on aromatic rings are 10.00 and 9.96Å for endo-, 8.28 and 9.41Å for exo- and 9.51 and 10.03Å for transition state form. The distances of Sn atom from oxygen atoms of O-Sn groups are 2.27, 1.95 and 1.87Å endo-, exo-isomers and the [TS], respectively. The TMS-O bond lengths to the phenoxide moieties are 1.73, 1.66 and 1.73Å for endo-, exo-isomers and the [TS], respectively.

The torsional angle between Si-O bonds for endo-, exo-isomers are 1° and 9° and for [TS] is equal to 22°. The summation distance of Sn atom that it passes from endo- to exo- positions was calculated 0.75Å (it was determined by geometrical calculations). The length of gradient positions of Sn atom from endo-isomer to [TS] is 0.26Å. This change position for exo-isomer to transition state is 0.49Å.

**Exo- and Endo-isomers of [(t-Bu)Calix\(^{TMS}\)\(_2\)]Sn**

The data of the PM3 calculations for the exo- and endo- of [(t-Bu)Calix\(^{TMS}\)\(_2\)]Sn, 7-9 are summarized in Table-1 and Fig.-3. The endo-form 38.73 kcal mol\(^{-1}\) is more stable than exo-isomer.

![Figure 3. Inter-conversion process of the exo- and endo- of [(t-Bu)Calix\(^{TMS}\)\(_2\)]Sn, 7\(-\rightarrow\)8\(-\rightarrow\)9.](image)
The barrier energy for the isomerization of endo- and exo-isomers was obtained 54.88 kcal mol\(^{-1}\). The conversion of [(t-Bu)Calix\(^{TMS}\)\(_2\)]Sn to its endo-isomer has been monitored by \(^1\)H-NMR spectroscopy [19].

The distances between Si atoms for endo- and exo-isomers are 5.38 and 5.93Å, respectively. This length for [TS] of 7 and 9 were obtained 5.87Å. The distances between C-atoms of para-CH\(_3\) groups \((r_{13}\) and \(r_{24}\)) on aromatic rings are 10.22 and 11.80Å for endo-, 9.55 and 10.90Å for exo- and 9.78 and 11.10Å for transition state form. The distances of Sn atom from oxygen atoms of O-Sn groups are 2.87, 1.90 and 1.87Å endo-, exo-isomers and the [TS], respectively. The TMS-O bond lengths to the phenoxide moieties are 1.73, 1.66 and 1.73Å for endo-, exo-isomers and the [TS], respectively.

It has worth to mention that, despite the observation that the dative interaction between Sn atom and the trimethylsilyl ether groups is shorter for the exo-isomer, the endo-isomer is evidently the more thermodynamically stable as judged by the observed endo- and exo-isomerization. Thus, the Sn-O dative interactions in the exo-isomer are presumably weak and insufficient to compensate for other structural changes which accompany for the isomerization.

One factor which favors the endo-isomer being the more stable is concerned with the possibility that the calixarene conformation is such that it furnishes a more appropriate bite angle for Sn atom in the endo-position than for Sn atom in the exo-position.

Thereby, suggesting that there is less strain for the endo-isomer, so that it may be more thermodynamically favored than exo-isomer. The torsional angle between Si-O bonds for endo-, exo-isomers are 4° and 17° and for [TS] is equal to 30°. The summation distance of Sn-atom that it passes from endo- to exo- positions was calculated 0.75Å (it was determined by geometrical calculations). The length of gradient positions of Sn-atom from endo-isomer to [TS] is 0.25Å. This change position for exo-isomer to transition state is 0.50Å.

CONCLUSION

In conclusion, the PM3 calculations provide a picture of isomerizations of the exo- and endo- of [(R)Calix\(^{TMS}\)\(_2\)]Sn, compounds as examples of O-silylated calixarenes both from the structural and energetic points of view. The results show that the alkyl groups \((R=Me, t-Bu)\) play the role of the “helm” for getting the endo-, exo-geometries. It seems that, the sizes of \(R_{para}\) groups of aromatic rings are affected on the barrier energy of conversion endo\(\leftrightarrow\)exo isomers and the structural parameters.

REFERENCES