

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 [(Rp)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[4]arenes; Sn-complex; PM3; Molecular modeling; Liquid crystals; Izomerization.

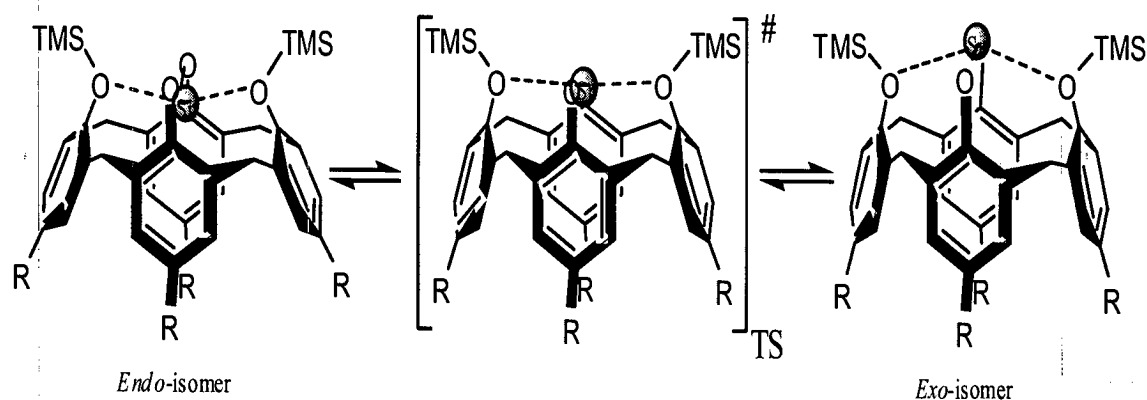
INTRODUCTION

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 calyx[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[4]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].

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R=H	1	2	3
R=CH ₃	4	5	6
R= <i>t</i> -Bu	7	8	9

The *exo*- and *endo*- of [(R_p)Calix^{TMS}₂]Sn, (R_{para}=H, CH₃, *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. There is good agreement between the PM3 calculations and X-ray and ¹H-NMR data. The *O*-silylated calixarene complexes that combined from C, Si and Sn have been applied in various fields. This is achieved at the expense of a high molecular weight which might be even larger when the electronic activities are purposed.

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^{TMS}₂]Sn, (R_p=H, CH₃, *t*-Bu). The calculations were carried out by using MOPAC and PC-Model packages.[24-26]

RESULTS AND DISCUSSION

Exo- and *Endo*- isomers of [(H)Calix^{TMS}₂]Sn:

The results of semi-empirical PM3 calculations for the *exo*- and *endo*- of [(H)Calix^{TMS}₂]Sn, 1-3 are summarized in Table-1 and Fig.-1. Selected structural parameters and the transition state

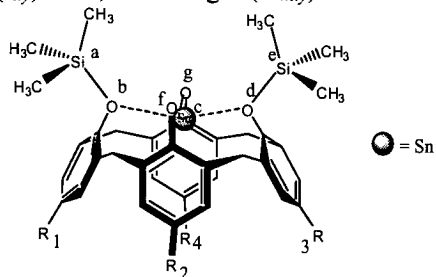
structure for inter-conversion of the *exo*- and *endo*- isomers are shown in Table-1 and Fig.-1.

The energy surface for inter-conversion pathway of these isomers of [(H)Calix^{TMS}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⁻¹ is more stable than *exo*-isomer. The barrier energy for conversion of *endo*- to *exo*-isomer is 21.1 kcal mol⁻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*₁₃ and *r*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 *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-O 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.

Table 1. Selected structural parameters for 1-9 ($[(R)\text{Calix}^{\text{TMS}}_2]\text{Sn}$). The heats of formations in (ΔH_f°) kcal mol⁻¹, bond length (r_{xy}) in Å, bond angle (Θ_{wxy}) and torsional angle (Φ_{wxyz}) in °



Selected Structural Parameters		Endo-isomer	[TS]	Exo-isomer
R=H				
$\Delta\Delta H_f^\circ$		0.00	21.10	16.75
r_{ab}		1.73	1.73	1.66
r_{bc}		1.82	1.87	2.27
r_{cd}		1.82	1.87	2.27
r_{de}		1.73	1.73	1.66
r_{fe}		1.77	1.79	1.76
r_{cg}		1.77	1.79	1.76
r_{ae}		5.44	5.74	6.80
r_{fg}		3.64	3.61	3.21
r_{13}		9.46	9.51	8.28
r_{24}		9.47	10.03	9.41
Θ_{bcd}		166	170	160
Θ_{feg}		170	180	131
Φ_{abde}		0	18	0
R=CH₃				
$\Delta\Delta H_f^\circ$		0.00	35.55	26.53
r_{ab}		1.73	1.73	1.66
r_{bc}		1.95	1.87	2.27
r_{cd}		1.95	1.87	2.27
r_{de}		1.73	1.73	1.66
r_{fe}		1.80	1.80	1.76
r_{cg}		1.80	1.80	1.76
Table-1 continue:				
r_{ae}		5.46	5.79	6.80
r_{fg}		3.65	3.61	3.21
r_{13}		10.00	9.51	8.28
r_{24}		9.96	10.03	9.41
Θ_{bcd}		138	170	160
Θ_{feg}		171	180	130
Φ_{abde}		1	22	9
R=CMe₃				
$\Delta\Delta H_f^\circ$		0.00	54.88	38.73
r_{ab}		1.73	1.73	1.66
r_{bc}		1.90	1.87	2.87
r_{cd}		1.90	1.87	2.87
r_{de}		1.73	1.73	1.66
r_{fe}		1.84(1.82)	1.80	1.82(1.82)
r_{cg}		1.84(1.82)	1.80	1.82(1.82)
r_{ae}		5.27	6.14	5.84
r_{fg}		3.61	3.70	3.42
r_{13}		10.22	9.78	9.55
r_{24}		11.80	11.10	10.90
Θ_{bcd}		133	170	150
Θ_{feg}		169	180	130
Φ_{abde}		4	30	17

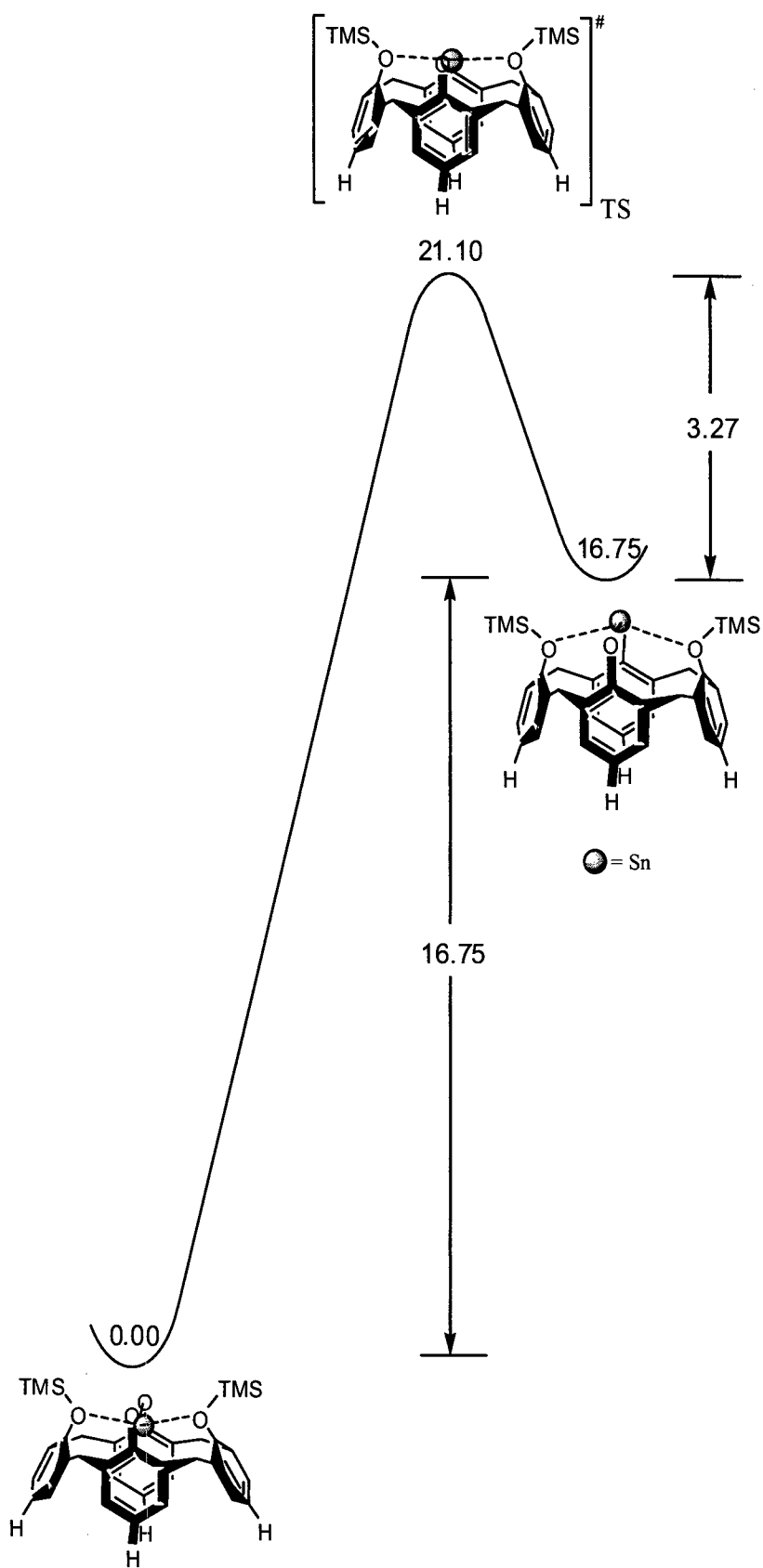


Figure 1. Inter-conversion process of the *exo*- and *endo*- of $[(H)Calix^{TMS}_2]Sn$, $1 \leftrightarrow [2] \leftrightarrow 3$.

Exo-and Endo-isomers of $[(CH_3)Calix^{TMS}_2]Sn$

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 inter-conversion of $[(CH_3)Calix^{TMS}_2]Sn$ are summarized in Table-1 and Fig.2.

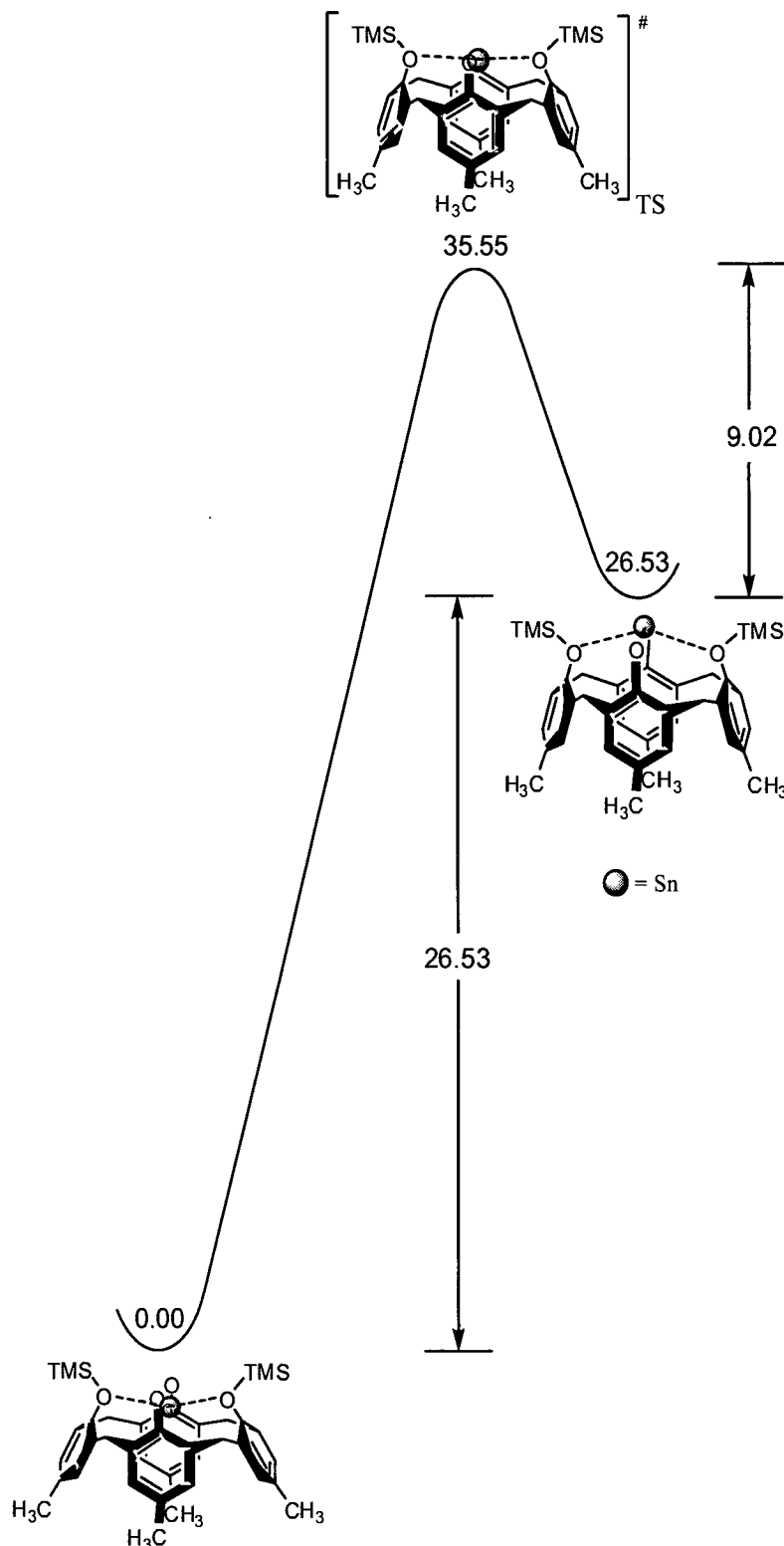


Figure 2. Inter-conversion process of the *exo*- and *endo*- of $[(CH_3)Calix^{TMS}_2]Sn$, $4 \leftrightarrow [5] \leftrightarrow 6$.

The *exo*- form $26.53 \text{ kcal mol}^{-1}$ is less stable than *endo*- isomer. The barrier energy for the isomerization of *endo*- and *exo*-isomers was obtained $35.55 \text{ kcal mol}^{-1}$. The distances between Si-atoms for *endo*- and *exo*-isomers are 5.38 and 6.12 \AA respectively. This length for [TS] of **4** and **6** were obtained 6.03 \AA . The distances between C-atoms of *para*-CH₃ groups (r_{13} and r_{24}) on aromatic rings are 10.00 and 9.96 \AA for *endo*-, 8.28 and 9.41 \AA for *exo*- and 9.51 and 10.03 \AA for transition state form. The distances of Sn atom from oxygen atoms of O-Sn groups are 2.27 , 1.95 and 1.87 \AA *endo*-, *exo*-isomers and the [TS], respectively. The TMS-O bond lengths to the phenoxide moieties are 1.73 , 1.66 and 1.73 \AA 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 0.75 \AA (it was determined by geometrical calculations). The length of gradient positions of Sn atom from *endo*-isomer to [TS] is 0.26 \AA . This change position for *exo*-isomer to transition state is 0.49 \AA .

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

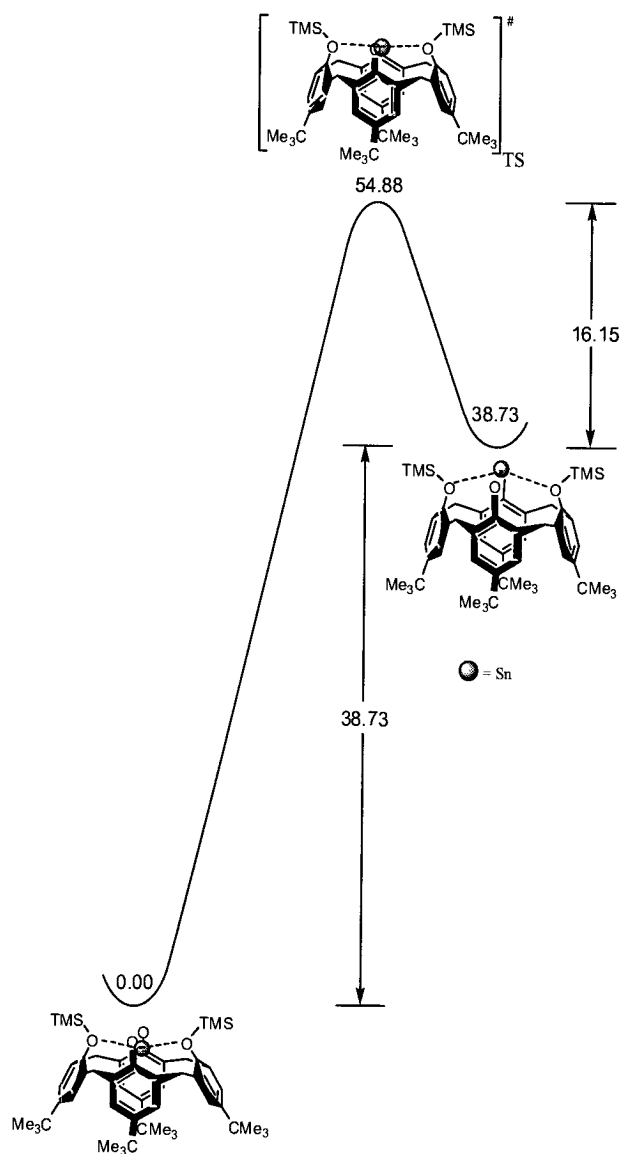


Figure 3. Inter-conversion process of the *exo*- and *endo*- of $[(t\text{-Bu})\text{Calix}^{\text{TMS}}_2]\text{Sn}$, **7**↔**[8]**↔**9**.

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 ¹H-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*-CH₃ 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*↔*exo* isomers and the structural parameters.

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