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Theoretical Isomerization Study of $[(R)Calix^{TMS}{}_2]Ge$ Macrocycles

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Design, synthesis and study about the behaviours of liquid crystals and gauge theory for these compounds are two main concepts of this family of compounds. The calix[n]arenas are a class of chalice-like macrocyclic molecules that have recently attracted widespread attention as complex molecules with liquid crystal behaviours. The calix[n]arenas have been frequently used as ancilliary ligands for studying the chemistry of transition and main group metals. The 1,3-*bis*(trimethyl silyl)ether of *p-tert*-butyl calix[4]arene, $[(t\text{-Bu})calix^{TMS}{}_2]H_2$, has been synthesized and used as a dianionic ligand for Ge. The complex of $[(t\text{-Bu})calix^{TMS}{}_2]Ge$ exhibits *exo*/*endo* isomerism. The structural properties of $[(R_p)calix^{TMS}{}_2]Ge$, (R_{para} =H, CH_3, *t*-Bu) and the inter conversion of *exo* ↔ *endo* isomers were investigated by the use of PM3 data.

Key Words: Calix[4]arenes, Ge-complex, PM3, Molecular modeling, Liquid crystals.

INTRODUCTION

Calix[n]arenas are a class of macrocycles that have attracted much interest because of their potentiality for forming host-guest complexes and have been extensively investigated in various fields[1-5]. Calix[n]arenas with various functions have been developed with remarkable progress by modifying either the upper or lower rim[6]. Especially, for developing calix[n]arenas as analytical reagents, upper or lower rim-modified calix[n]arenas 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[11-14].

However, calix[n]arenas, 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,

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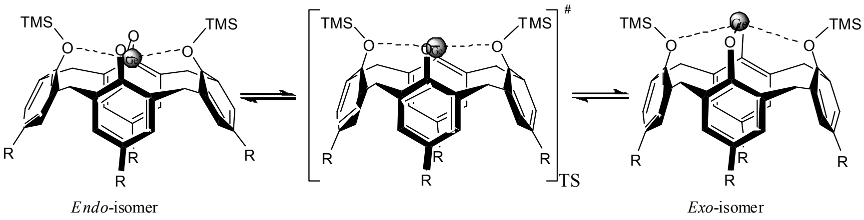
such as [(*t*-Bu)calix$^{TMS}{}_2$]Ge. Divalent Ge-complex *i.e.,* [(*t*-Bu)calix$^{TMS}{}_2$]Ge, are readily obtained by the reaction of [(*t*-Bu)calix$^{TMS}{}_2$]H_2 with Ge[N$(SiMe_3)_2$]$_2$. For the Ge-system, the reaction yields sequentially two isomers, namely *exo*- and *endo*-[(*t*-Bu)calix$^{TMS}{}_2$]Ge, which differ in location of the Ge-atom with respect to the calixarene cavity. The product of this reaction has been structurally characterized by X-ray diffraction[6,10].



R = H	**1**	**2**	**3**
R = CH_3	**4**	**5**	**6**
R = *t*-Bu	**7**	**8**	**9**

The *exo*- and *endo*- of [(R_p)calix$^{TMS}{}_2$]Ge, (R_{para} = H, CH_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. There is good agreement between the PM3 calculations and empirical results such as X-ray and ^{1}H NMR spectroscopy. The O-silylated calixarene complexes that combined from C, Si and Ge have been applied in various fields.

EXPERIMENTAL

Because of the large number of atoms in **1-9** the SCF-MO PM3 calculations were carried out on the geometries. In this study, the PM3 results show the best results in agree with the experimental data (X-ray and ^{1}H NMR) in comparison with the other SCF-MO methods. The energy minimum geometries were located by minimizing geometries of [(R_p)calix$^{TMS}{}_2$]Ge, (R_{para} =H, CH_3, *t*-Bu). The calculations were carried out by using MOPAC and PC-Model packages[15-18].

RESULTS AND DISCUSSION

***Exo*- and *Endo*-isomers of [(H)calix$^{TMS}{}_2$]Ge:** The data of semi-empirical PM3 calculations for the *exo*- and *endo*- of [(H)calix$^{TMS}{}_2$]Ge, **1-3** are summarized in Table-1 and Fig. 1. The heats of formations in kcal mol^{-1}, selected structural parameters and the transition state structure for inter-conversion of the *exo*- and *endo*-isomers were shown in Table-1 and Fig. 1. The energy surface for inter-conversion pathway of these isomers of [(H)calix$^{TMS}{}_2$]Ge was investigated in detail by changing the positin of Ge-atom in the cavity of the complex and the results are summarized in Fig. 1. The *endo*-form 15.75 kcal mol^{-1} is more stable than *exo*-isomer. The barrier energy for conversion of *endo*- to *exo*-isomer is 18.02 kcal mol^{-1}.

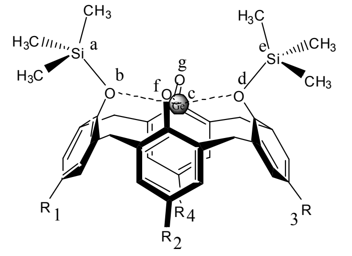
For the *endo*- and *exo*-isomers the distances between Si-atoms are 5.42 and 6.75 Å, respectively. As shown in Table-1, the distances between H-atoms at the *para*-position (r_{13} and r_{24}) on aromatic rings are 9.50 and 9.54 Å for *endo*-, 8.28 and 9.42 Å for *exo*- and 9.55 and 10.1 Å for transition state form. The distances of Ge-atom from oxygen atoms of O-TMS groups are 2.31, 1.88 and 1.91 Å *endo*-, *exo*-isomers and the [TS], respectively. The Ge-O bond lengths to the phenoxide moieties are 1.75, 1.67 and 1.74 Å 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 17°. The summation distance of Ge-atom that it passes from *endo*- to *exo*- positions was calculated 0.7 Å (it was determined by geometrical calculations). The length of gradient positions of Ge-atom from endo-isomer to [TS] is 0.24 Å. This change position for *exo*-isomer to transition state is 0.46 Å.

***Exo*- and *Endo*-isomers of [(CH_3)calix$^{TMS}{}_2$]Ge:** 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$^{TMS}{}_2$]Ge were summarized in Table-1 and Fig. 2. The energy surface and the barrier energy for the pathway of the isomers inter-conversion of [(CH_3)calix$^{TMS}{}_2$]Ge were investigated in detail by changing the position of Ge-atom in the cavity of the complex. The *exo*- form (18.75 kcal mol^{-1}) is less stable than *endo*- isomer. The barrier energy for the isomerization of *endo*- and *exo*-isomers was obtained 26.44 kcal mol^{-1}. The distances between Si-atoms for *endo*- and *exo*-isomers are 5.32 and 5.96 Å, respectively. This length for [TS] of **4** and **6** were obtained 6.0 Å. The distances between C-atoms of *para*-CH_3 groups (r_{13} and r_{24}) on aromatic rings are 10.05 and 9.92Å for *endo*-, 9.00 and 11.00 Å for *exo*- and 9.60 and 10.50 Å for transition state form. The distances of Ge-atom from oxygen atoms of O-TMS groups are 2.38, 1.96 and 1.92Å *endo*-, *exo*-isomers and the [TS], respectively. The Ge-O bond lengths to the phenoxide moieties are 1.81, 1.82 and 1.80 Å for *endo*-, *exo*-isomers and the [TS], respectively.

The O-Ge-O bond angle for the *exo*-isomer (153°) is notably larger than is observed for simple $(RO)_2Ge$ complexes (*ca.* 86-92°). This bond angle for endo-isomer was obtained 134° and it is more near to the O-Ge-O bond angle of $(RO)_2Ge$ complex.

TABLE-1
SELECTED STRUCTURAL PARAMETERS FOR **1-9** ([(R)calix$^{TMS}{}_2$]Ge), THE HEATS OF FORMATIONS IN ($\Delta H°_f$) 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				
	$\Delta H°_f$	-231.3	-213.28	-215.55
	$\Delta\Delta H°_f$	0.00	18.02	15.75
	r_{ab}	1.74	1.74	1.67
	r_{bc}	1.89	1.91	2.31
	r_{cd}	1.89	1.91	2.31
	r_{de}	1.74	1.74	1.67
	r_{fc}	1.81	1.80	1.75
	r_{cg}	1.81	1.80	1.75
	r_{ae}	5.42	5.72	6.75
	r_{fg}	3.62	3.59	3.16
	r_{13}	9.50	9.55	8.28
	r_{24}	9.54	10.10	9.42
	Θ_{bcd}	168	170	159
	Θ_{fcg}	172	180	130
	Φ_{abde}	0	17	0
R=CH$_3$				
	$\Delta H°_f$	-268.46	-242.02	-249.71
	$\Delta\Delta H°_f$	0.00	26.44	18.75
	r_{ab}	1.74	1.75	1.74
	r_{bc}	1.96	1.91	2.38
	r_{cd}	1.96	1.91	2.38
	r_{de}	1.74	1.75	1.74
	r_{fc}	1.81	1.80	1.82
	r_{cg}	1.81	1.80	1.82
	r_{ae}	5.32	6.00	5.96
	r_{fg}	3.62	3.61	3.27
	r_{13}	10.05	9.60	9.00
	r_{24}	9.92	10.50	11.00
	Θ_{bcd}	134	170	153
	Θ_{fcg}	171	180	128
	Φ_{abde}	0	23	8

	Selected structural parameters	*Endo*-isomer	[TS]	*Exo*-isomer
R=CMe$_3$				
	$\Delta H°_f$	-343.43	-304.68	-315.33
	$\Delta\Delta H°_f$	0.00	38.75	28.10
	r_{ab}	1.74	1.75	1.75
	r_{bc}	1.90	1.91	2.80
	r_{cd}	1.90	1.91	2.80
	r_{de}	1.74	1.75	1.75
	r_{fc}	1.82(1.84)	1.81	1.82(1.82)
	r_{cg}	1.82(1.84)	1.81	1.82(1.82)
	r_{ae}	5.28	6.10	5.86
	r_{fg}	3.60	3.65	3.40
	r_{13}	10.50	9.70	9.22
	r_{24}	12.00	11.00	11.20
	Θ_{bcd}	130	170	151
	Θ_{fcg}	168	180	128
	Φ_{abde}	0	28	15

The torsional angle between Si-O bonds for *endo*-, *exo*-isomers are 1° and 9° and for [TS] is equal to 23°. The summation distance of Ge-atom that it passes from *endo*- to *exo*-positions was calculated 0.71 Å (it was determined by geometrical calculations). The length of gradient positions of Ge-atom from endo-isomer to [TS] is 0.25 Å. This change position for exo-isomer to transition state is 0.47 Å.

***Exo*- and *Endo*-isomers of [(*t*-Bu)calix$^{TMS}{}_2$]Ge:** The data of semi-empirical PM3 calculations for the *exo*- and *endo*- of [(*t*-Bu)calix$^{TMS}{}_2$]Ge, **7-9** are summarized in Table-1 and Fig. 3. The heats of formation in kcal mol^{-1}, selected structural parameters and the transition state structure for inter-conversion of the *exo*- and *endo*-isomers were shown in Table-1 and Fig. 3. The energy surface and the barrier energy for the pathway of the isomers inter-conversion of [(*t*-Bu)calix$^{TMS}{}_2$]Ge, **7** and **9** were investigated in detail by changing the position of Ge-atom in the cavity of the complex. The *endo*- form 28.10 kcal mol^{-1} is more stable than *exo*-isomer. The barrier energy for the isomerization of *endo*- and *exo*-isomers was obtained 38.75 kcal mol^{-1}.

The conversion of [(*t*-Bu)calix$^{TMS}{}_2$]Ge to its *endo*-isomer has been observed to occur over a 1 h at 80 °C, as monitored by ^{1}H NMR spectroscopy.

The distances between Si-atoms for *endo*- and *exo*-isomers are 5.28 and 5.86 Å, respectively. This length for [TS] of **7** and **9** were obtained 6.1 Å. The distances between C-atoms of *para*-CH$_3$ groups (r_{13} and r_{24}) on aromatic rings are 10.5 and 12.00 Å for *endo*-, 9.22 and 11.20 Å for *exo*- and 9.70 and 11.00 Å for transition state form. The distances of Ge-atom

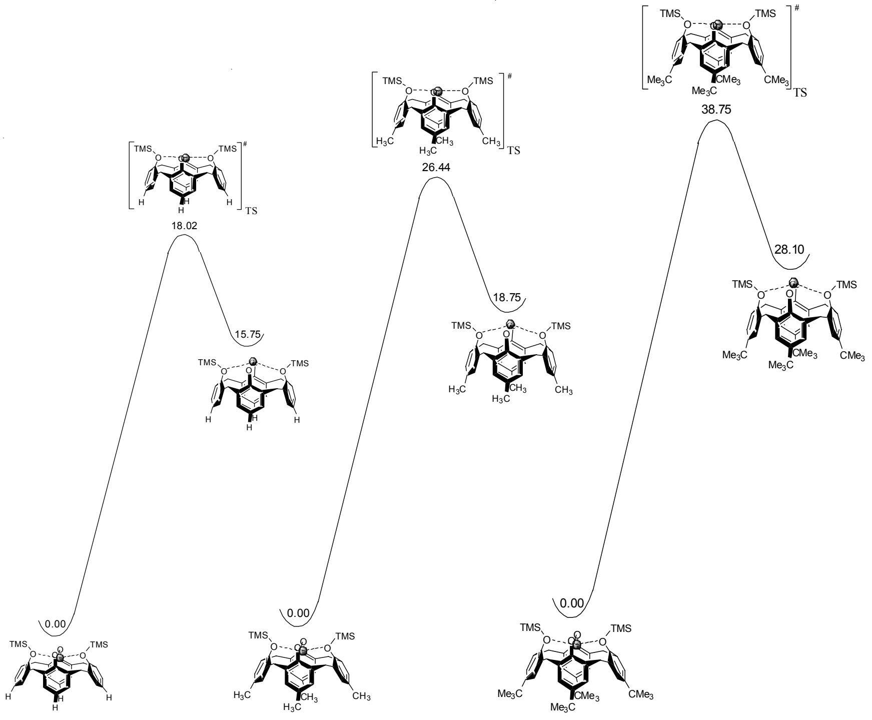


Fig. 1 Fig. 2 Fig.3

Fig. 1. Inter-conversion process of the *exo*- and *endo*- of [(H)calix$^{TMS}{}_2$]Ge, **1** ↔ [**2**] ↔ **3**
Fig. 2. Inter-conversion process of the exo- and *endo*- of [(CH$_3$)calix$^{TMS}{}_2$]Ge, **4** ↔ [**5**] ↔ 6
Fig. 3. Inter-conversion process of the *exo*- and *endo*- of [(*t*-Bu)calix$^{TMS}{}_2$]Ge, **7** ↔ [**8**] ↔ **9**

from oxygen atoms of O-TMS groups are 3.10 Å (X-ray: 3.50 Å), 1.95 Å (X-ray: 2.5 Å) and 1.91 Å *endo*-, *exo*-isomers and the [TS], respectively. The Ge-O bond lengths to the phenoxide moieties are 1.82 Å (X-ray: 1.84 Å), 1.82Å (X-ray: 1.77 Å) and 1.81 Å for *endo*-, *exo*-isomers and the [TS], respectively.

It is worth to mention that, despite the observation that the dative interaction between Ge-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 Ge-O dative interactions in the *exo*-isomer are presumably weak and insufficient to compensate for other structural changes which accompany for the isomerization.

The O-Ge-O bond angle of **3** for the *exo*-isomer is 138° (X-ray: 100°) and is notably larger than simple $(RO)_2Ge$ complexes (*ca.* 86-92°). One factor which favours 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 Ge-atom in the *endo*-position than for Ge-atom in the *exo*-position. Thereby, suggesting that there is less strain for the *endo*-isomer, so that it may be more thermodynamically favoured than *exo*-isomer.

The tensional angle between Si-O bonds for *endo*-, *exo*-isomers are 4° and 16° and for [TS] is equal to 28°. The summation distance of Ge-atom that it passes from *endo*- to *exo*-positions was calculated 0.73 Å (it was determined by geometrical calculations). The length of gradient positions of Ge-atom from *endo*-isomer to [TS] is 0.25 Å. This change position for *exo*-isomer to transition state is 0.48 Å.

Conclusion

In conclusion, the PM3 calculatins provide a picture of isomerizations of the *exo*- and *endo*- of [(R)calix$^{TMS}{}_2$]Ge, compounds as examples of O-silylated calixarenes both 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. The isomer inter-conversion of [(*t*-Bu)calix$^{TMS}{}_2$]Ge has been observed by X-ray and ^{1}H NMR spectroscopy. There are good agreement results between PM3 calculations and ^{1}H NMR spectroscopy. The structures of *exo*- and *endo*- of [(*t*-Bu)calix$^{TMS}{}_2$]Ge have been determined by X-ray diffraction. The results of X-ray and PM3 calculations show good agreement.

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