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Theoretical and Conformational Study of Pinched-cone Interconversion in monosubstituted tri-methylsilyle ethynyl Derivative of Calix[4]arene

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ABSTRACT

The conformational behavior of monosubstituted tri-methylsilyle ethynyl Derivative of Calix[4]arene as a new generation of Caliarene was compared with tetra alkylated calyx[4]arene. The most important conformational phenomena in these compounds which are pinched cone interconversion process were done by semi-empirical method and ab initio calculations with Gaussian 98w programming.

Keywords: Pinched-cone interconversion; Calix[4]arene; Conformational study

INTRODUCTION

The chemistry of calixarenes has been recently developed, and many papers have been published to investigate the attractive characteristics of them.[1, 2] The calixarene structure itself can behave as a soft donor group through its phenyl group π electrons, and this has been demonstrated by the inclusion of silver and thallium (I) ions.[3] They are basket-shaped compounds of potential interest for host-guest complexation studies[4]. One of the most significant changes in calixarene chemistry since the appearance of the previous volume in 1989 is the degree to which computational studies have been used to interpret and predict experimental results. One group of papers features molecular mechanics and dynamics calculations as their central focus,[5-9] while another group employs these techniques as an adjunct to experimental data,[10, 11] including complexation phenomena.[12] One of the earliest studies in the first category was carried out by the Reinhoudt group[13] and deals with calculations of structural and energetically characters of calix[4]arenes. The results are in generally good agreement with experiment with respect to the relative conformational stabilities. For example, the stability sequence for the parent calix[4]arene was correctly predicted by calculation to be cone > partial cone > 1,2-alternate > 1,3-alternate. Computational techniques are improving rapidly, however, and the now frequently used MM3 program [5] and improved CHARM program[14] appear to yield results that are usually in quite good agreement with experiment.

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DISCUSSION

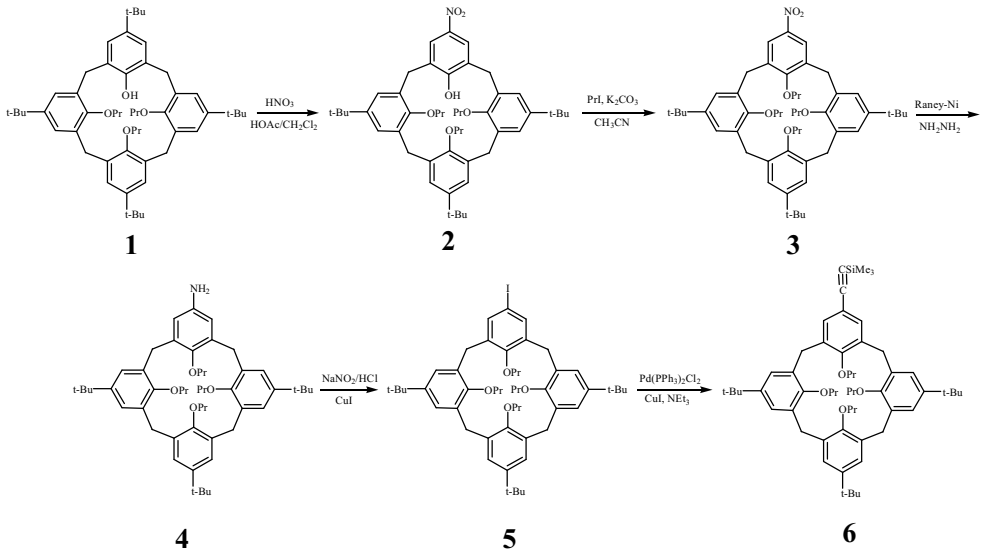
The subtle question has been addressed in some detail as to whether the cone conformers of calix[4]arenes exist as time-invariant structures with C_4 symmetry or as rapidly interconverting structures with C_2 symmetry. In this report the conformational study of pinched cone interconversion process was done for ethynyl derivative of calix[4]arene by semi-emperical method and low level ab initio calculations with Gaussian 98w programming in Hartree-Fock in STO-3G basis set. Scheme 1 is shown the synthetic rout of this derivative (**6**) from calix parent.

The pinched cone interconversion of **6** (Scheme 2) has been detected by semi-emperical calculations by AM1 method and low level ab initio calculations.

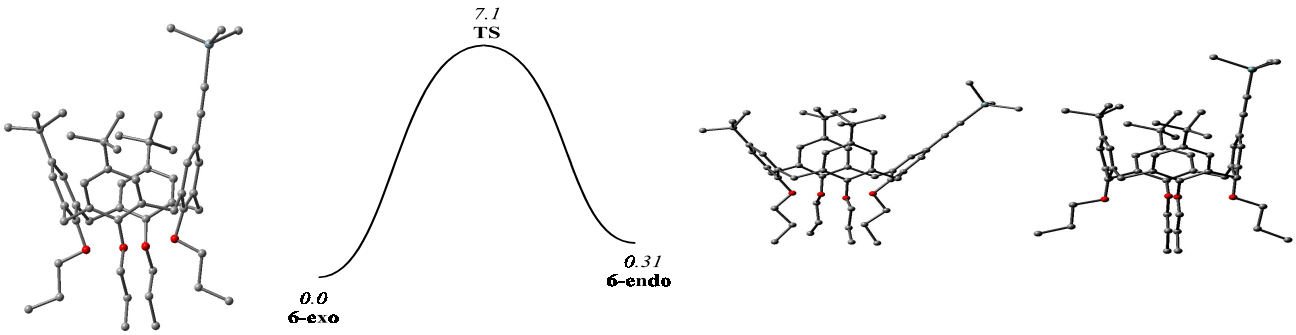
For investigation of barrier in this interconversion, the symmetrically tetra-propoxy calix[4]arene has been chosen as a model (Scheme 3).

Scheme 2, 3 show the structures of ground and transition states of related conformers, and table 1 shows the total and relatives energies of conformers in ground states and transition state both for model and compound **6,** and also the structural parameters for conformers.

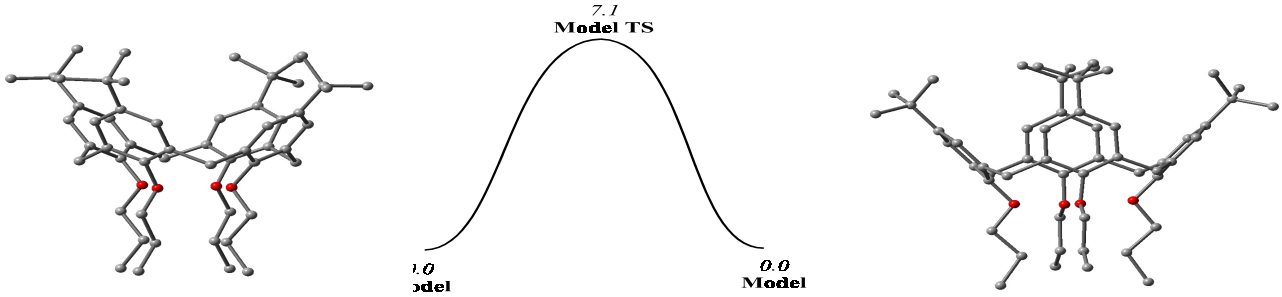
According to data showed in table 1, the barrier for pinched cone interconversion in monosubstiuted silyle compound **6** is 5.3 kcal mol^{-1}. It is 1.8 kcal mol^{-1} less than such interconversion phenomena in model system. It seems that the tri-methylsilyle moiety has a positive π-π^* interaction with phenolic rings in calix[4]arene system.



Scheme 1. The synthetic rout of ethynyl derivative of calixarene (**6**).



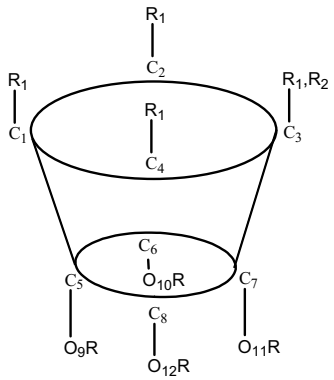
Scheme 2. The pinched cone interconversion of **6**.



Scheme 3. The pinched cone interconversion of tetra-propoxy derivativr of calixarene.

Table 1. Total energies (hartree) and relative energies (kcal mol^{-1}) for pinched-cone interconversion of calix[4]arene **6** and model and structural parameters(distance(A°), angle(degree))

Structure	**6-***exo*	**6-***TS*	**6-***endo*	**Model**	**Model-***TS*
RAM1	-0.216852	-0.208406	-0.216560	-0.266114	-0.254799
	(0.0)	(5.3)	(0.3)	(0.0)	(7.1)
ZPVE(NIMAG)	790.06871(0)	790.98434(1)	790.20656(0)	792.19684(0)	792.82196(1)
STO-3G	-3082.79225	-3082.78380	-3082.78978	-2436.78594	-2436.77342
	(0.0)	(10.6)	(1.5)	(0.0)	(7.8)
$H°_{298}$-$H°_{0}$*(kcal/mol)*	157.3	164.3	157.6	116.8	124.9
	(0.0)	(6.9)	(1.4)	(0.0)	(8.1)
$G°_{298}$-$G°_{0}$*(kcal/mol)*	-287.4	-301.9	-289.7	-232.4	-239.0
	(0.0)	(-14.4)	(-2.3)	(0.0)	(-6.6)
$S°_{298}$*(cal/mol.°)*	411.31	427.66	423.77	364.12	367.95
	(0.0)	(16.3)	(12.4)	(0.0)	(3.8)
Distance(A°)					
C_1-C_3	8.83	6.69	6.41	8.77	8.17
C_2-C_4	6.20	7.07	8.75	6.21	8.17
C_5-C_7	5.51	4.93	5.53	5.51	5.16
C_6-C_8	5.51	5.48	5.49	5.52	5.16
O_9-O_{11}	3.91	4.06	5.19	3.34	3.25
O_{10}-0_{12}	5.23	4.65	3.92	5.13	3.25
Angle(degree)					
$C_1C_5C_7$	123.79	106.17	99.45		
$C_3C_7C_5$	129.11	107.96	101.73	124.50	121.42
$C_2C_6C_8$	97.22	112.27	125.26	96.55	121.42



(R = Pr, R_1 = t-Bu, R_2 = C≡CSiMe_3)

As a mater of fact, the hindrance effect of TMS-ethynyl group in transition state is less than propyl group and there is of course depends to distance between acetylene group and phenolic moieties. For model molecule two interconverted conformers have equal energies. This fact is related to high symmetrically structure of models molecule. The model has C_{2V} symmetry in ground state and C_{4V} symmetry in transition state. For compound **6** all conformers have only plane of symmetry.

In **6-exo** (more stable conformer) the acetylenic group is in exo form and in **6-endo** this group is in endo form (0.31 kcal mol^{-1}more stable than **6-exo**).

CALCULATIONS

Initial estimates of the geometries of structures were obtained by Cs *Chem office 7.0* [15] followed by full minimization using the semi-emperical AM1 method in the chem 3D ultra program. Optimum geometries were located by minimizing energy with respect to all geometrical coordinates, and without imposing any symmetry constrain. The structures of the transition state geometries were obtained by using the optimized geometries of the equilibrium structures according to the procedure of the Dewar *etal*. Final estimates of the geometries of ground states and transition states were carried out by *GAUSSIAN 98W* [16] programs followed by full minimization using the semi-emperical AM1 method and ab initio calculations at Hartree-Fock level in STO-3G basis set. The optimization of transition state carried out with QST2 keyword.

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