

## DFT Conformational Study of the Monomethoxycalix[5]arene

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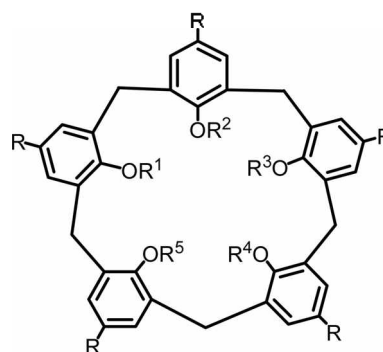
In this study, we have performed *DFT* calculations to investigate the conformational characteristics and the hydrogen bonds of the monomethyl ether of *p-tert*-butylcalix[5]arene (**1**: 5,11,17,23,29-Penta-*tert*-butyl-31-methoxy-32,33,34,35-tetrahydroxycalix[5]arene). The structures of different conformers of **1** were optimized by using B3LYP/6-31+G(d,p) method. The relative stability of the various conformers of **1** is in the following order: 2,3-alternate (most stable) > 1-partial-cone ~ 1,2-alternate > cone > 2-partial-cone > 3-partial-cone ~ 2,4-alternate ~ 1,3-alternate. The primary factor affecting the relative stabilities of the various conformers of the monomethoxy-*t*-butylcalix[5]arene (**1**) are the number of the intramolecular hydrogen bonds.

**Key Words** : *DFT*, B3LYP/6-31+G(d,p), Methoxycalix[5]arene, Conformer, Hydrogen bond

### Introduction

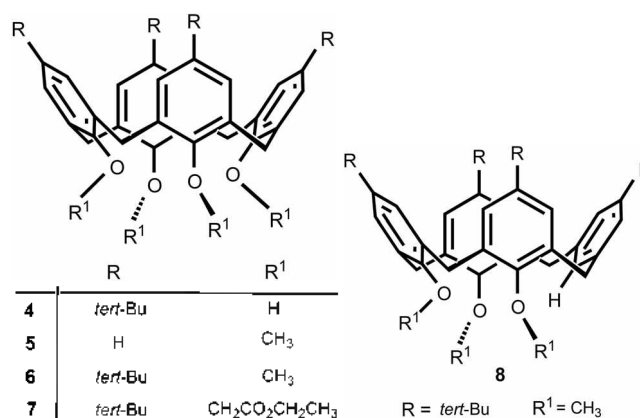
The calixarenes are particularly attractive as a basic skeleton for new supramolecular systems due to their well-defined molecular framework.<sup>1</sup> Among the varying structures of calix[*n*]arenes, pentameric analogue calix[5]arenes<sup>2</sup> (**1-3**) has received relatively less attention due to their difficulties both in the synthesis and in the selective derivatization compared to the other widely employed members of calixarenes having four (**4-8**), six, or eight repeating units. The relative stabilities of the various conformations of calix[4]aryl derivatives are determined by experimental and theoretical methods.<sup>3-10</sup>

Four different conformations of the tetramethoxy-*p-tert*-butylcalix[4]arene (**6**) have been calculated, and the trend (in the order of partial cone (most stable) > cone > 1,2-alternate ~ 1,3-alternate) is consistent with the relative free energies obtained from the NMR spectroscopic data.<sup>5</sup> Reinhoudt *et al.* have also reported both the calculated and the experimental results of conformational distributions of **6** and partially methylated calix[4]arenes.<sup>6</sup> We have studied the conformational characteristics of **6** by using the HF/6-31G(d,p) method, which reveals that the partial-cone conformer is 0.31 kcal/mol more stable than the cone.<sup>8</sup> However, our conformational studies of the tetraethyl ester (**7**) of the *p-tert*-butylcalix[4]arene by using B3LYP/6-311+G(d,p)//HF/6-31G calculations suggest that the cone conformational isomer is slightly more stable than the partial-cone analogue.<sup>9</sup> The relative stability of different conformers for the trimethyl ethers of the monodeoxycalix[4]arene (**8**) was investigated by performing a <sup>1</sup>H NMR experiment<sup>10a</sup> as well as by *ab initio* and *DFT* calculations.<sup>10b</sup> Recently we have reported the *DFT* calculation results for the conformers and hydrogen bondings of *t*-butylcalix[5]arene (**2**) and *t*-butylcalix[4]arene (**4**).<sup>11</sup> The first objective of this research is to determine the relative stability of different conformational isomers<sup>12</sup> for **1** by using the *DFT* calculation. The second objective is to investigate the intramolecular hydrogen bonds<sup>13</sup> by the four hydroxyl groups of the monomethoxy-*t*-butylcalix[5]arene (**1**).



Molecule	R	R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>	R <sup>5</sup>
<b>1</b> Methoxy- <i>t</i> -butylcalix[5]arene	<i>t</i> -Butyl	CH <sub>3</sub>	H	H	H	H
<b>2</b> <i>t</i> -Butylcalix[5]arene	<i>t</i> -Butyl	H	H	H	H	H
<b>3</b> Calix[5]arene	H	H	H	H	H	H

**Chart 1.** ChemDraw Structures of Calix[5]arene and Monomethoxy-*t*-butylcalix[5]arene.



**Chart 2.** ChemDraw Structures of calix[4]aryl derivatives. **4** = *p-tert*-Butylcalix[4]arene. **5** = Tetramethyl ether of calix[4]arene. **6** = Tetramethyl ether of *p-tert*-butylcalix[4]arene. **7** = Tetraethyl ester of *p-tert*-butylcalix[4]arene. **8** = Trimethyl ether of *p-tert*-butylmonodeoxycalix[4]arene.

**Table 1.** DFT B3LYP Optimized Energies<sup>a</sup> of the Various Conformers of **1**

Conformer <sup>b</sup>	cone	1pc	2pc	3pc	12a	13a	23a	24a
Method								
/6-31G(d,p)	-2553.6222	-2553.6245	-2553.6244	-2553.6038	-2553.6164	-2553.6043	-2553.6316	-2553.6041
$\Delta E$ (kcal/mol) <sup>c</sup>	5.91	4.46	9.54	17.13	4.50	17.40	0.00	17.22
/6-31+G(d,p)	-2553.6932	-2553.6949	-2553.6866	-2553.6770	-2553.6948	-2553.6831	-2553.7002	-2553.6753
$\Delta E$ (kcal/mol) <sup>c</sup>	4.50	3.41	8.62	14.66	3.45	10.79	0.00	15.71

<sup>a</sup>The unit of B3LYP energy is in a.u. <sup>b</sup>Conformer: 1pc (1-partial cone) denotes that the anisole group having methoxy moiety is inverted. 2pc (2-partial cone) means that one phenyl group which is next to the anisole group is inverted, etc. (See Figure 1.). <sup>c</sup> $\Delta E$  (kcal/mol) is the relative energy with respect to the most stable conformation (2,3-alternate). Error limits in these calculations are about 0.01 kcal/mol.

### Computational Methods

The initial structures of monomethoxy-*t*-butylcalix[5]arene (**1**) were constructed by using HyperChem.<sup>14</sup> In order to find optimized conformations, we executed a conformational search by using a simulated annealing method, which has been described in a previous publication.<sup>15</sup> The conformational isomers of **1** obtained from MM/MD calculations were fully re-optimized by using the quantum mechanical methods to estimate the absolute and relative energies of the different conformations of **1**. AM1 semi-empirical optimizations followed by DFT calculations of **1** by using Gaussian 98<sup>16</sup> were performed with an error limit of less than 0.01 kcal/mol for each conformer. The consecutive B3LYP/6-31G(d,p) and B3LYP/6-31+G(d,p) optimizations of the final structures are done to include the diffuse function, the effect of electron correlation and the basis set with polarization function.

### Results and Discussion

#### Conformational Characteristics of Monomethyl Ether of *p*-*tert*-Butylcalix[5]arene (**1**): (5,11,17,23,29-Penta-*tert*-butyl-31-methoxy-32,33,34,35-tetrahydroxycalix[5]arene).

It is well known that the calix[5]arenes (**2** and **3**) and calix[4]arene (**4**) form strong intramolecular hydrogen bonds among OH groups and represent the cone conformer as the most stable structure.<sup>3,11</sup> Substitution of all the phenolic protons of a calix[4]arene by bulky alkyl groups generally leads to conformationally rigid structures like **7**.<sup>9</sup> However, when the substituent is small enough such as a methyl group, the resulting methyl ether **6** is no longer rigid, and any anisole ring can rotate via oxygen-through-the-annulus to give a mixture of the four possible conformers.<sup>5-8</sup>

The barrier for conformational interconversion diminish progressively as the OH groups of **2** are changed to OMe groups, ascribed to continuously diminishing intramolecular hydrogen bonding that is not offset by the corresponding increase in steric hindrance.<sup>12</sup> It is interesting to investigate what kind of influence on the relative stabilities for the different conformers of monomethoxy-*p*-*tert*-butylcalix[5]arene (**1**) will be made by the substitution of one of the five *p*-*tert*-butylphenol rings in **2** with a methoxy-*p*-*tert*-butylbenzene. Although the rings of **1** are able to move through the annulus of the lower rim, the hydrogen bonds restrict the

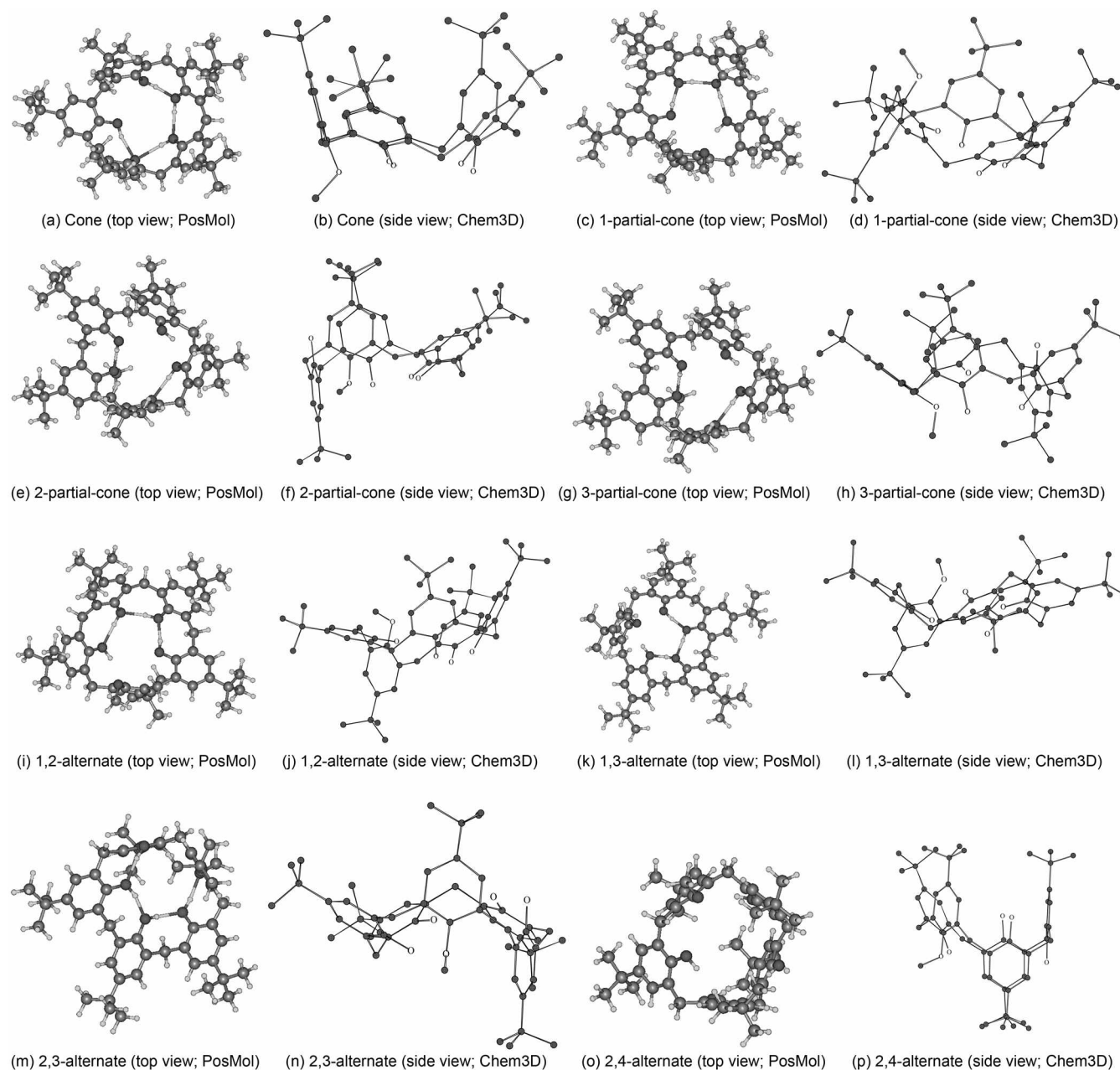
free rotation. Various conformations of **1** can be generated by the up/down orientation of the benzene rings.

The DFT optimizations without any constraint were carried out for the various conformers of the monomethyl ether of *p*-*tert*-butylcalix[5]arene (**1**). Table 1 shows the total and relative energies of the eight distinct conformers of **1** obtained by the B3LYP/6-31G(d,p) and B3LYP/6-31+G(d,p) calculations. The calculation results suggest that 2,3-alternate conformer is the most stable one among the conformers of **1** in the following order: 2,3-alternate (most stable) > 1-partial-cone ~ 1,2-alternate ~ cone > 2-partial-cone > 1,3-alternate > 3-partial-cone ~ 2,4-alternate.

We can sort the relative stabilities of eight conformers in Table 1 into four groups: the 2,3-alternate conformer is 3.4-4.5 kcal/mol more stable than cone, 1-partial-cone and 1,2-alternate analogues, 8.8-10.8 kcal/mol more stable than 2-partial-cone and 1,3-alternate conformers, and 14.7-15.7 kcal/mol more stable than 3-partial-cone and 2,4-alternate analogues. The primary factor affecting the relative stabilities of the various conformers of the monomethoxy-*t*-butylcalix[5]arene (**1**) are the number and strength of the intramolecular hydrogen bonds. Although there are many factors such as steric hindrances and electrostatic interactions determining the stability, each additional hydrogen bond contributes 4-5 kcal/mol for the stability of the conformers of **1**.

Figure 1 shows the calculated stable structures showing the hydrogen bonds of the various conformers of the monomethyl ether of *p*-*tert*-butylcalix[5]arene. The 2,3-alternate conformer (Fig. 1(m)) of the **1** having four hydrogen bonds is the most stable. This result may be a kind of unusual outcome, since the adjacent *t*-butylbenzene rings of the 2,3-alternate conformers produce more steric hindrance than other cases such as 1,3-alternate and 2,4-alternate. However, the hydrogen bondings of the 2,3-alternate conformer overcome the steric interferences.

**Intramolecular Hydrogen Bonds of the Monomethyl Ether of *p*-*tert*-Butylcalix[5]arene (**1**):** The DFT calculated distances and angles of intramolecular hydrogen bonds (O-H...O) of **1** are listed in Table 2. In general, if O...O distance is less than 3.0 Å, one interprets that the (O-H...O) hydrogen bond is relatively strong for this intramolecular case.<sup>13</sup> The O...O calculated distances of 2.66-2.96 Å in Table 2 suggest that our optimized values in **1** are in accord with the experimental distances (2.7-2.9 Å in Table 3) of the intra-



**Figure 1.** DFT B3LYP/6-31+G(d,p) optimized molecular structures of the conformers of **1** (*p*-*tert*-butyl monomethoxycalix[5]arene). (a) Top view of the cone conformer by PosMol<sup>22</sup> with hydrogen bonds shown. (b) side view of the cone conformer by Chem3D<sup>25</sup> without hydrogen atoms. (c) top view of the 1-partial-cone conformer. (d) side view of the 1-partial-cone conformer. (e) top view of the 2-partial-cone conformer. (f) side view of the 2-partial-cone conformer. (g) top view of the 3-partial-cone conformer. (h) side view of the 3-partial-cone conformer. (i) top view of the 1,2-alternate conformer. (j) side view of the 1,2-alternate conformer. (k) top view of the 1,3-alternate conformer. (l) side view of the 1,3-alternate conformer. (m) top view of the 2,3-alternate conformer. (n) side view of the 2,3-alternate conformer. (o) top view of the 2,4-alternate conformer, and (p) side view of the 2,4-alternate conformer.

molecular hydrogen bonds (O $\cdots$ O) of the calixarenes (**2**, **3**, **4**, and **5**) obtained from Cambridge Structure Database.<sup>17-21</sup>

Table 2 also lists the DFT calculated H $\cdots$ O distances of **1**. If H $\cdots$ O distance is less than 2.0 Å, one judges that the (O-H $\cdots$ O) hydrogen bond is relatively strong for intramolecular case.<sup>13</sup> The H $\cdots$ O distances of 1.71-2.00 Å in Table 2 suggest that the hydrogen bondings in the molecule (**1**) are fairly strong. Also, one recognizes that the (O-H $\cdots$ O) hydrogen bond is stronger if the (O-H $\cdots$ O) angle is closer to 180°.

Our calculated (O-H $\cdots$ O) angles of 153°-178° in Table 2 tell that the hydrogen bondings in the molecule (**1**) are pretty strong.

In order to compare our calculated distances with the values of the stronger intramolecular hydrogen bonds of *t*-butylcalix[5]arene (**2**) and *t*-butylcalix[4]arene (**4**), we have tabulated the calculated hydrogen-bond data of **1**, **2**<sup>11</sup> and **4**<sup>11</sup> in Table 4. The average calculated O $\cdots$ O distances (2.65-2.80 Å in Table 4) of the intramolecular hydrogen bonds of *t*-

**Table 2.** DFT Calculated Distances (Å) and Angles (O-H...O) of Intramolecular Hydrogen Bonds of **1**

Conformer	H-bond	1	2	3	4	# <sup>a</sup>	Average
1(cone)	O...O	3.208	2.904	2.830	2.905	4	2.962
	H...O	2.239	1.929	1.886	1.958		2.003
	O-H	0.971	0.976	0.975	0.971		0.973
	Angle(°)	174.3	177.0	162.1	164.3		169.4
1(1-partial-cone)	O...O	2.853	2.757	2.748		3	2.786
	H...O	1.873	1.781	1.785			1.813
	O-H	0.982	0.984	0.978			0.981
	Angle(°)	176.5	170.7	167.1			171.4
1(2-partial-cone)	O...O	2.906	2.861			2	2.884
	H...O	1.933	1.916				1.924
	O-H	0.976	0.975				0.975
	Angle(°)	174.2	162.4				168.3
1(3-partial-cone)	O...O	2.754	2.990			2	2.872
	H...O	1.805	2.018				1.912
	O-H	0.974	0.973				0.974
	Angle(°)	164.0	175.0				169.5
1(1,2-alternate)	O...O	2.857	2.762	2.755		3	2.791
	H...O	1.876	1.785	1.793			1.818
	O-H	0.981	0.984	0.978			0.981
	Angle(°)	177.5	171.4	166.8			171.9
1(1,3-alternate)	O...O	2.606	2.600	2.787		3	2.664
	H...O	1.624	1.634	1.888			1.715
	O-H	0.986	0.986	0.976			0.983
	Angle(°)	173.0	164.8	151.8			163.2
1(2,3-alternate)	O...O	2.757	2.791	2.867	2.789	4	2.801
	H...O	1.846	1.851	1.907	1.822		1.857
	O-H	0.978	0.979	0.978	0.979		0.979
	Angle(°)	153.7	159.6	166.6	168.7		162.2
1(2,4-alternate)	None					0	

<sup>a</sup>The number of intramolecular hydrogen bonds in the particular conformer.

**Table 3.** Experimental Distances (O...O) of Intramolecular Hydrogen Bonds of Calixarenes

Molecule #	Molecule (CSD <sup>17</sup> entry)	Average (Å)
2	<i>t</i> -Butylcalix[5]arene (VETXUO <sup>18</sup> )	2.894
3	Calix[5]arene (VETYAV <sup>18</sup> )	2.780
3	Calix[5]arene (UKAGIW <sup>19</sup> )	2.764
4	<i>t</i> -Butylcalix[4]arene (XAHMOI <sup>20</sup> )	2.779
5	<i>t</i> -Butylcalix[4]crown-5-ether (VERLUA <sup>21</sup> )	2.727

butylcalix[4]arene (**4**) are shorter than the values (2.76-2.86 Å) of *t*-butylcalix[5]arene (**2**) and the values (2.79-2.96 Å) of monomethoxy-*t*-butylcalix[5]arene (**1**).

The conformational study of **6** (tetramethyl ether of the *p*-*tert*-butylcalix[4]arene) by using the HF/6-31G(d,p) method suggested that the cone and partial-cone conformers are 3-6 kcal/mol more stable than the 1,2-alternate or 1,3-alternate.<sup>8</sup> And, conformational studies of **7** (tetraethyl ester of the *p*-*tert*-butylcalix[4]arene) by using B3LYP/6-311+G(d,p)/HF/6-31G calculations report that the cone and partial-cone

**Table 4.** DFT B3LYP/6-31+G(d,p) Calculated Average Distances (Å) and Angles of Intramolecular Hydrogen Bonds of **1**, **2**, and **4**

Conformer	H-bond	1 <sup>a</sup>	2 <sup>b</sup>	4 <sup>b</sup>
cone	O...O	2.962	2.765	2.650
	H...O	2.003	1.783	1.683
	O-H	0.973	0.986	0.991
	Angle(°)	169.4	173.1	164.0
1-partial-cone	O...O	2.786	2.810	2.718
	H...O	1.813	1.841	1.767
	O-H	0.981	0.979	0.982
	Angle(°)	171.4	170.1	163.5
1,2-alternate	O...O	2.791	2.768	2.796
	H...O	1.818	1.823	1.842
	O-H	0.981	0.982	0.978
	Angle(°)	171.9	162.3	164.2
1,3-alternate	O...O	2.664	2.861	
	H...O	1.715	1.890	
	O-H	0.983	0.976	
	Angle(°)	163.2	172.6	

<sup>a</sup>The average data from Table 2. <sup>b</sup>Values from reference 11.

conformers are also 5-11 kcal/mol more stable than the 1,2-alternate or 1,3-alternate.<sup>9</sup> However, the B3LYP/6-31+G(d,p) calculated relative stabilities of **1** report that the energy difference between the most stable group (2,3-alternate cone, 1-partial-cone, 1,2-alternate and cone conformers) and the least stable group (3-partial-cone and 2,4-alternate analogues) is about 11-15 kcal/mol.

## Conclusion

The relative stabilities of the various conformers of the monomethoxy-*p*-*tert*-butylcalix[5]arene (**1**) are more dependent upon the number of the intramolecular hydrogen bonds than steric hindrance of adjacent rings.

DFT B3LYP/6-31+G(d,p) calculations of **1** suggest that the 2,3-alternate conformer is most stable. The most stable group (2,3-alternate, 1-partial-cone, 2-partial-cone and cone) is about 11-15 kcal/mol more comfortable than the least stable group (3-partial-cone and 2,4-alternate). Each hydrogen bond contributes 4-5 kcal/mol for the stability of the conformers of the calixarenes **1-4**.

The O...O hydrogen bond distances of 2.66-2.96 suggest that the calculated values in the molecule **1** are in accord with the experimental distances (2.7-2.9 Å) of the intramolecular hydrogen bonds (O...O) of the calixarenes (**2**, **3**, **4**, and **5**).

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