DFT Conformational Study of Calix[6]arene: Hydrogen Bond

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We have performed *DFT* calculations to investigate the conformational characteristics and hydrogen bonds of the calix[6]arene (**1**) and *p-tert*-butylcalix[6]arene (**2**). The structures of various conformers of **1** were optimized by using the B3LYP/6-31G(d,p) and /6-31+G(d,p) methods followed by single point calculation of MPW1PW91/ 6-31G(d,p). The relative stability of the conformers of **1** is in the following order: cone (*pinched*: most stable) > partial-cone > cone (*winged*) ~ 1,2-alternate ~ 1,2,3-alternate > 1,4-alternate > 1,3-alternate > 1,3,5-alternate. The structures of different conformers of **2** were optimized by using the B3LYP/6-31G(d,p) method followed by single point calculation of MPW1PW91/6-31G(d,p). The relative stability of the conformers of **2** is in the following order: cone (*pinched*) > 1,2-alternate > cone (*winged*) > 1,4-alternate ~ partial-cone > 1,2,3-alternate > 1,3,5alternate > 1,3-alternate. One of the important factors affecting the relative stabilities of the various conformers of the **1** and **2** is the number and strength of the intramolecular hydrogen bonds.

Key Words: *DFT*. MPW1PW91. Calix[6]arene. Conformer. Hydrogen bond

Introduction

Calixarenes having four, six, or eight repeating units are well studied among the varying structures of calix[n]arenes.[1] Calix[4]arenes have proven to be useful building blocks in supramolecular chemistry. because of the possibility of selective functionalization and control over the conformation. The selective functionalization of calix[6]arenes has been explored.[2] but in contrast to calix[4]arenes. it is difficult to immobilize the conformations of calix[6]arenes.

Intramolecular hydrogen bond formation determines the stability of conformations of unsubstituted calix[n]arenes.[3] The conformational characteristics of calix[6]arene were studied by using the molecular mechanical method.[4] The most stable conformation of calix[6]arenes (**1**[5] and **2**[6,7]) (Chart 1) in the solid state is called a *pinched* cone because two methylene bridges are pointing into the cavity (Figures 1(a) and 2(a)). The skeleton of calix[6]arene is pinched to allow for a circular array of six hydrogen bonds. Early measurements by Gutsche *et al.* with ^{1}H NMR spectroscopy have shown that in solution *p-tert*-butylcalix[6]arene **2** is conformationally flexible.[3a] From the coalescence of the methylene hydrogens. they postulated the interconversion of two equivalent cone conformations. Molins *et al.*[8] published a sophisticated 2D NMR study of upper rim substituted trichlorocalix[6]arene. Their conformation is described as a *winged* cone. with four aryl groups in up alignment and two aryl groups located at opposite sites bent outside (Figures 1(c) and 2(c)). All six methylene bridges are pointing outward. The findings of Molins *et al.* have been disputed by Reinhoudt group.[9] This group claimed that the *pinched* cone found in the solid state is also the conformation in solution.

Recently we have reported the *DFT* calculation results for the conformers and hydrogen bondings of *t*-butylcalix[5]arene (**3**). *t*-butylcalix[4]arene (**4**) and monomethoxycalix[5]arene.[10,11] The first objective of this research is to determine the relative stability of different conformational isomers for calix-
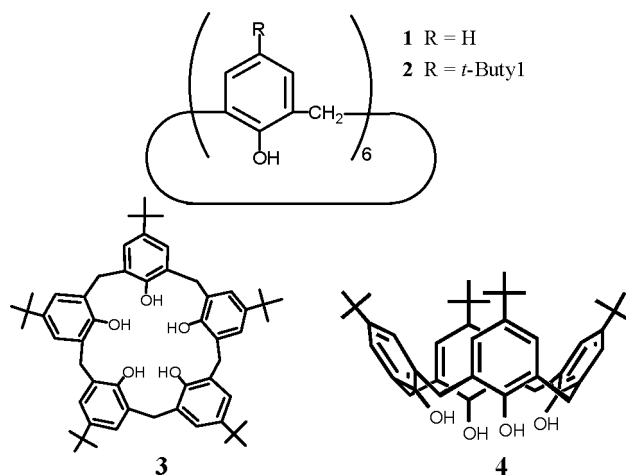

Chart 1. Chemdraw structures of calix[6]arene (**1**), *p-tert*-butylcalix [6] arene (**2**), *p-tert*-butylcalix[5]arene (**3**) and the cone conformer of *p-tert*-butylcalix[4]arene (**4**).
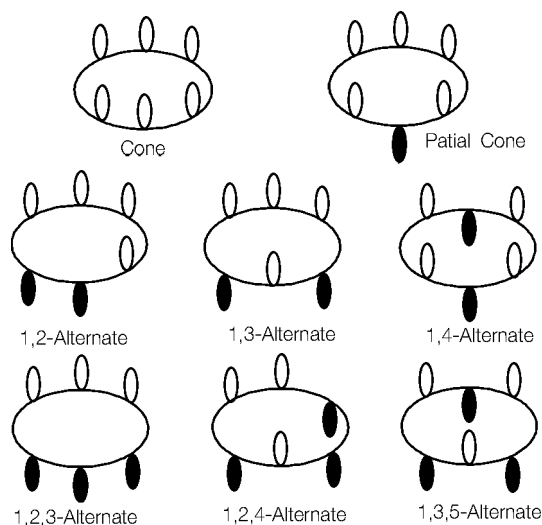

Chart 2. The sketches of the eight conformations of calix[6]arene.

[6]arene (1) and *p-tert*-butylcalix[6]arene (2) by using the *DFT* calculation. The second objective is to investigate the intramolecular hydrogen bonds by the hydroxyl groups of the 1 and 2.

Computational Methods

The initial *pinched* cone-type structures of the calix[6]-arene (1) and *p-tert*-butylcalix[6]arene (2) were obtained from Cambridge Structure Database (CSD[12a] entry NOB-LEV[12b] (1) and KENBUA[12c] (2)), and other conformations are constructed by using the molecular mechanics (MM), molecular dynamics (MD), and AM1 calculations of HyperChem.[13] In order to find the optimized conformers, we executed a conformational search by using a simulated annealing method, which has been described in a previous publication.[14] The conformational isomers of 1 and 2 obtained from the MM/MD and AM1 semi-empirical calculations were fully re-optimized by using the *DFT* methods to determine the relative energies and the structures of eight distinct conformations in Chart 2. The level of theory used was Becke's three-parameter exchange functional in combination with the nonlocal correlation functional of Lee, Yang, and Parr (B3LYP)[15,16] and the 6-31G(d,p) basis set. Consecutive B3LYP/6-31G(d,p) and B3LYP/6-31+G(d,p) optimizations followed by single point calculation of MPW1PW91/6-31G(d,p) using Gaussian 03[17] were performed.

Results and Discussion

It is well known that the *p-tert*-butylcalix[5]arene (3) and *p-tert*-butylcalix[4]arene (4) form strong intramolecular hydrogen bonds among OH groups and represent the cone conformer as the most stable structure among four conformations (cone, partial cone, 1,2-alternate, and 1,3-alternate).[4]

The possible conformations of calix[6]arene (1) and *p-tert*-butylcalix[6]arene (2) are cone (*pinched* or *winged*), partial cone, 1,2-alternate, 1,3-alternate, 1,4-alternate, 1,2,3-alternate, 1,2,4-alternate, and 1,3,5-alternate. The *DFT* optimizations without any constraint were carried out for the distinct conformers of the 1 and 2, respectively.

Table 1 shows the total and relative energies of the conformers of calix[6]arene (1) calculated by the *DFT* B3LYP/6-31G(d,p), B3LYP/6-31+G(d,p) and MPW1PW91/6-31G(d,p) calculations, consecutively. During the *DFT* optimization of 1,2,4-alternate conformation, this structure spontaneously changed to the most stable *pinched* cone. Therefore, the energy of the 1,2,4-alternate conformer is omitted in Tables 1 and 2. The relative stabilities of B3LYP/6-31+G(d,p) calculation results of 1 are in the following order: cone (*pinched*: most stable) > partial-cone > cone (*winged*) ~ 1,2-alternate ~ 1,2,3-alternate > 1,4-alternate > 1,3-alternate > 1,3,5-alternate.

We also report the calculated results of the *DFT* B3LYP/6-31G(d,p) and MPW1PW91/6-31G(d,p) calculations for the conformers of *p-tert*-butylcalix[6]arene (2). The B3LYP/6-31+G

Table 1. *DFT* Calculated Energies[a] of the Various Conformers of 1

Conformer[b]	cone (*pinched*)	cone (*winged*)	pc	12a	13a	14a	123a	135a
B3LYP /6-31G(d,p)[c]	-2073.6287	-2073.6046	-2073.6098	-2073.6036	-2073.5935	-2073.5973	-2073.6030	-2073.5849
ΔE[d]	0.00	15.14	11.85	15.75	22.11	19.72	16.12	27.48
B3LYP /6-31+G(d,p)[e]	-2073.6982	-2073.6762	-2073.6817	-2073.6761	-2073.6687	-2073.6698	-2073.6766	-2073.6609
ΔE[d]	0.00	13.80	10.37	13.87	18.55	17.81	13.59	23.44
MPW1PW91 /6-31G(d,p)[e]	-2073.1652	-2073.1419	-2073.1480	-2073.1416	-2073.1324	-2073.1347	-2073.1407	-2073.1254
ΔE[d]	0.00	14.65	10.79	14.83	20.58	19.15	15.40	25.02

[a]The unit of DFT energy is in a.u. [b]Conformer: "pc" denotes partial cone. "12a" means 1,2-alternate, *etc*. (See Figure 1.) [c]Optimized Energy. [d]ΔE (kcal/mol) is the relative energy with respect to the most stable conformation (pinched cone). Error limits in these calculations are about 0.01 kcal/mol. [e]Single point energy: MPW1PW91/6-31G(d,p)// B3LYP/6-31+G(d,p)

Table 2. *DFT* Calculated Energies[a] of the Various Conformers of 2

Conformer[b]	cone (*pinched*)	cone (*winged*)	pc	12a	13a	14a	123a	135a
B3LYP /6-31G(d,p)[c]	-3017.2218	-3017.1987	-3017.1931	-3017.2047	-3017.1842	-3017.1999	-3017.1884	-3017.1786
ΔE[d]	0.00	14.48	18.03	10.72	23.58	13.77	20.99	27.12
MPW1PW91 /6-31G(d,p)[e]	-3016.5551	-3016.5340	-3016.5287	-3016.5402	-3016.5148	-3016.5290	-3016.5232	-3016.5173
ΔE[d]	0.00	13.27	16.58	9.37	25.32	16.41	20.01	23.73

[a,b,c,d]See the footnotes in Table 1. [e]Single point energy: MPW1PW91/6-31G(d,p)// B3LYP/6-31G(d,p)

(d,p) calculation of **2** was impossible to be completed with our computing resources. Table 2 shows the total and relative energies of the conformers of **2**. The relative stabilities of the MPW1PW91/6-31G(d,p) calculation results of **2** are in the following order: cone (*pinched*) > 1,2-alternate > cone (*winged*) > 1,4-alternate ~ partial-cone > 1,2,3-alternate > 1,3,5-alternate > 1,3-alternate.

One of the important factors affecting the relative stabilities of the various conformers of the calix[6]arenes is the number and strength of the intramolecular hydrogen bonds. The good stability of 1,2,3-alternate conformer of **1** among the less stable conformers can be explained by the four hydrogen bonds, whereas **1**(1,3-alternate) has three H-bonds and **1**(1,3,5-alternate) has none. We will explain the characteristics of the hydrogen bonds in various conformers later in

this section.

The MPW1PW91/6-31G(d,p) calculated relative stabilities of the conformations of **1** in Table 1 suggest that the cone (*pinched*) conformer is 10.79 kcal/mol more stable than partial-cone. about 15.0 kcal/mol more stable than cone (*winged*). 1,2-alternate and 1,2,3-alternate analogues. about 19.9 kcal/mol more stable than 1,3-alternate and 1,4-alternate. and 25.02 kcal/mol more stable than 1,3,5-alternate, respectively.

However. The MPW1PW91/6-31G(d,p) calculated relative stabilities of the conformations of **2** in Table 2 suggest that the cone conformer is 9.37 kcal/mol more stable than 1,2-alternate. 13.27 kcal/mol more stable than cone (*winged*). about 16.5 kcal/mol more stable than 1,4-alternate and partial-cone, 20.01 kcal/mol more stable than 1,2,3-alternate conformers. 23.73 kcal/mol more stable than 1,3,5-alternate, and 25.32
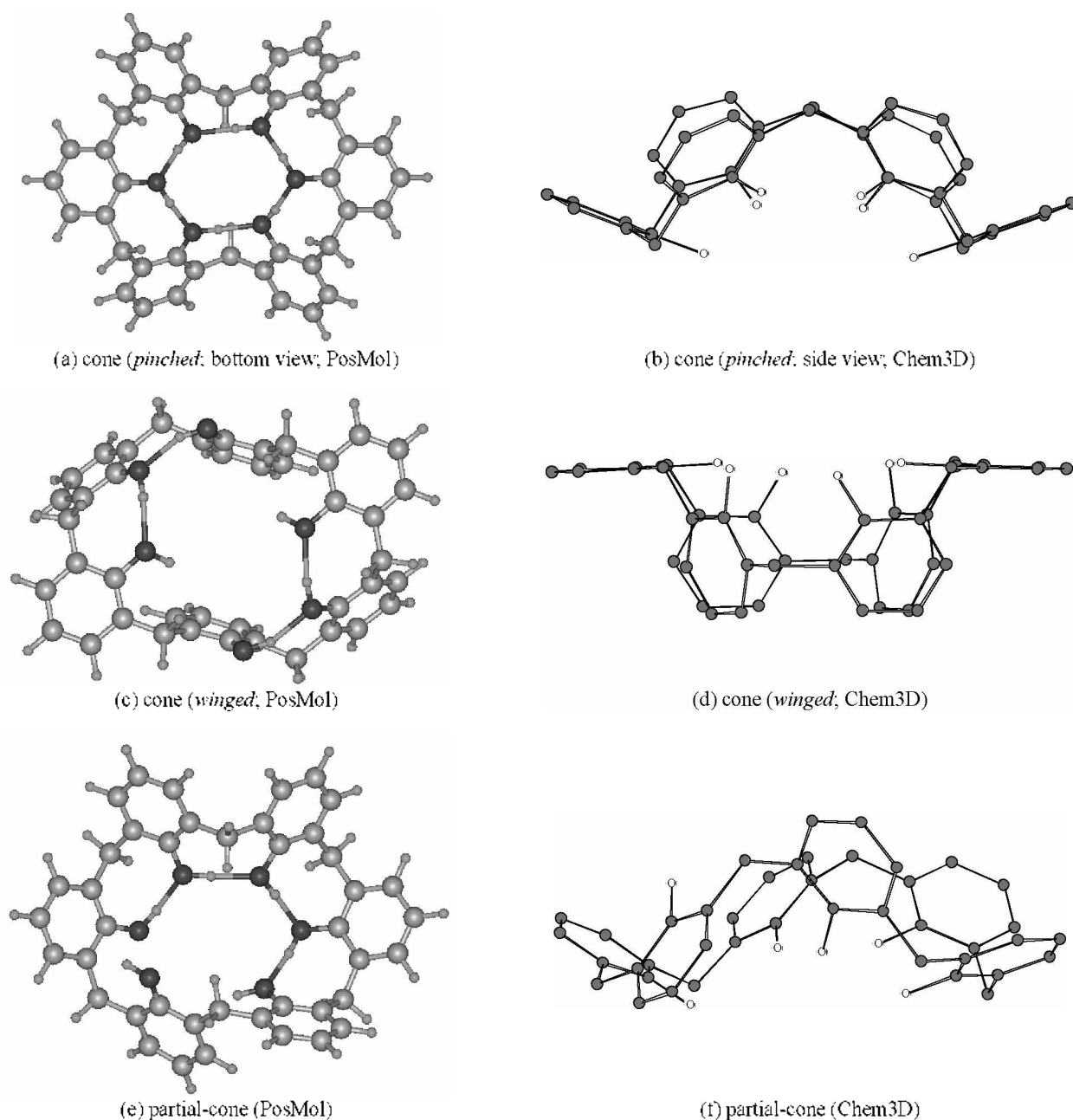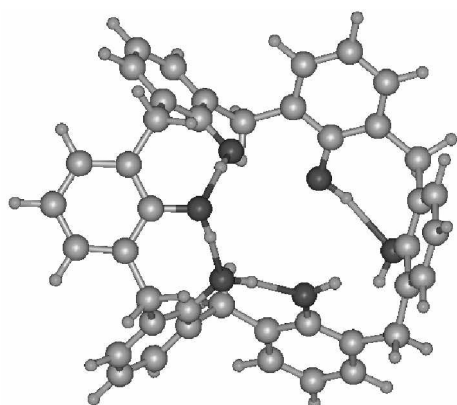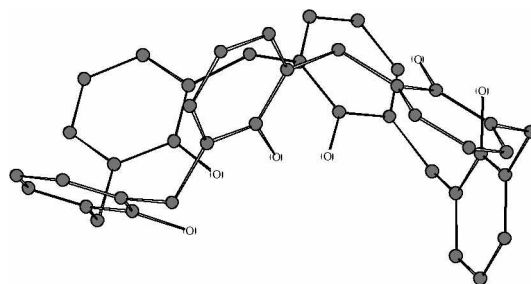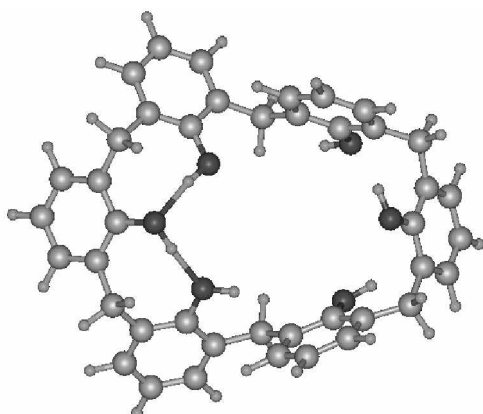
(a) cone (*pinched*, bottom view; PosMol)

(b) cone (*pinched*, side view; Chem3D)

(c) cone (*winged*, PosMol)

(d) cone (*winged*, Chem3D)

(e) partial-cone (PosMol)

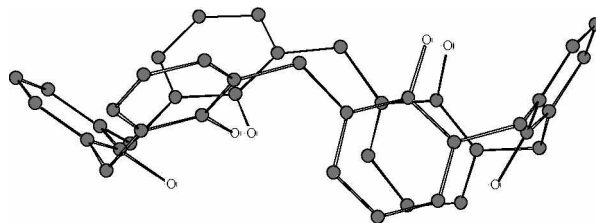(f) partial-cone (Chem3D)

Figure 1. (continued)
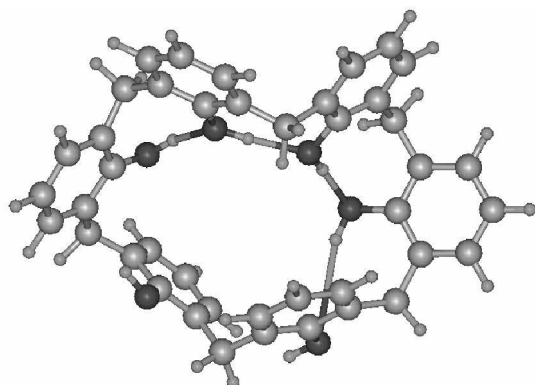
(g) 1,2-alternate (PosMol)
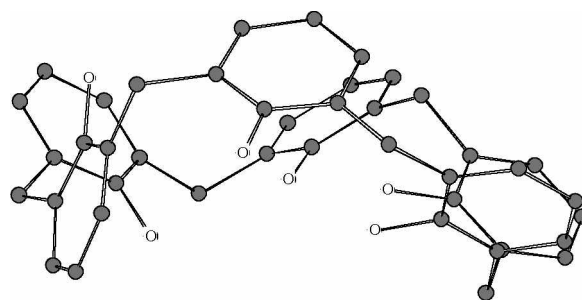

(h) 1,2-alternate (Chem3D)
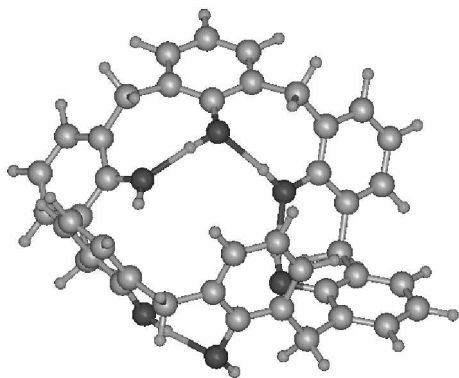

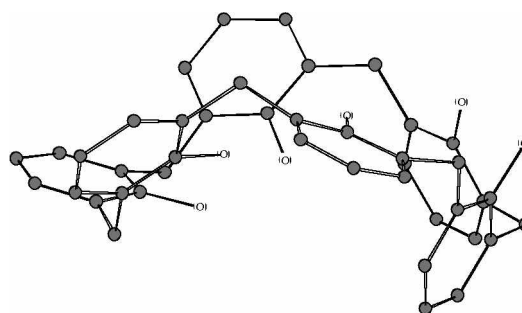(i) 1,3-alternate (PosMol)

(j) 1,3-alternate (Chem3D)

(k) 1,4-alternate (PosMol)

(l) 1,4-alternate (Chem3D)

(m) 1,2,3-alternate (PosMol)

(n) 1,2,3-alternate (Chem3D)
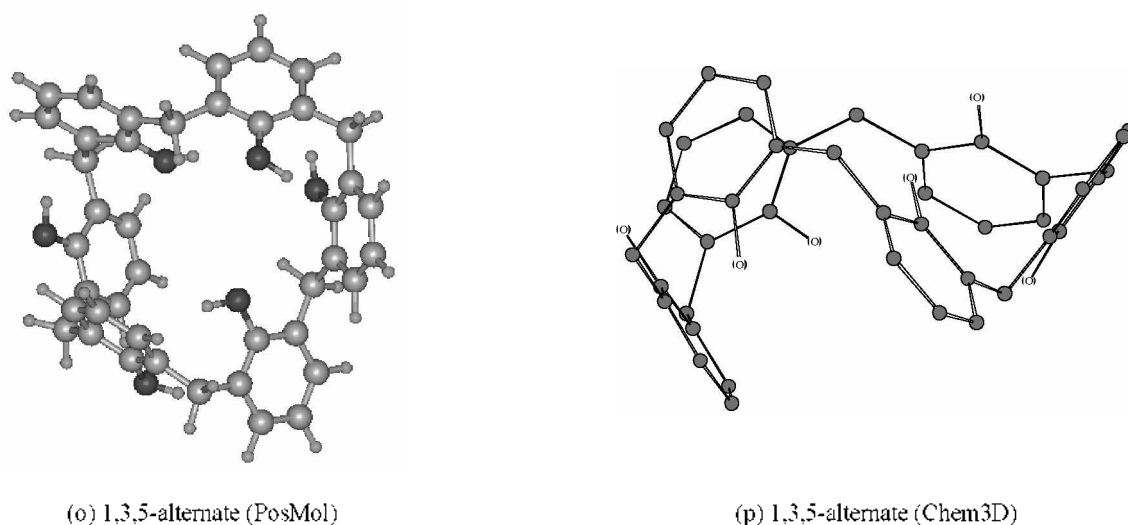
Figure 1. (continued)

(o) 1,3,5-alternate (PosMol)

(p) 1,3,5-alternate (Chem3D)

Figure 1. *DFT* B3LYP/6-31+G(d,p) optimized molecular structures of the conformers of **1** (calix[6]arene). (a) Bottom view of the pinched cone conformer by PosMol[19] with hydrogen bonds shown, (b) side view of the *pinched* cone conformer by Chem3D[20] without hydrogen atoms, (c) bottom view of the *winged* cone, (d) side view of the *winged* cone, (e) bottom view of the partial-cone, (f) side view of the partial-cone conformer, (g) bottom view of the 1,2-alternate, (h) side view of the 1,2-alternate, (i) bottom view of the 1,3-alternate, and (j) side view of the 1,3-alternate, (k) bottom view of the 1,4-alternate, and (l) side view of the 1,4-alternate, (m) bottom view of the 1,2,3-alternate, and (n) side view of the 1,2,3-alternate, (o) bottom view of the 1,3,5-alternate, and (p) side view of the 1,3,5-alternate. Atoms that are within a certain distance (the bond proximate distance) from one another were automatically marked as bonded.[19] Therefore, the hydrogen bonds in the figures of 1 and 2 drawn by PosMol[19] are not real covalent bonds.
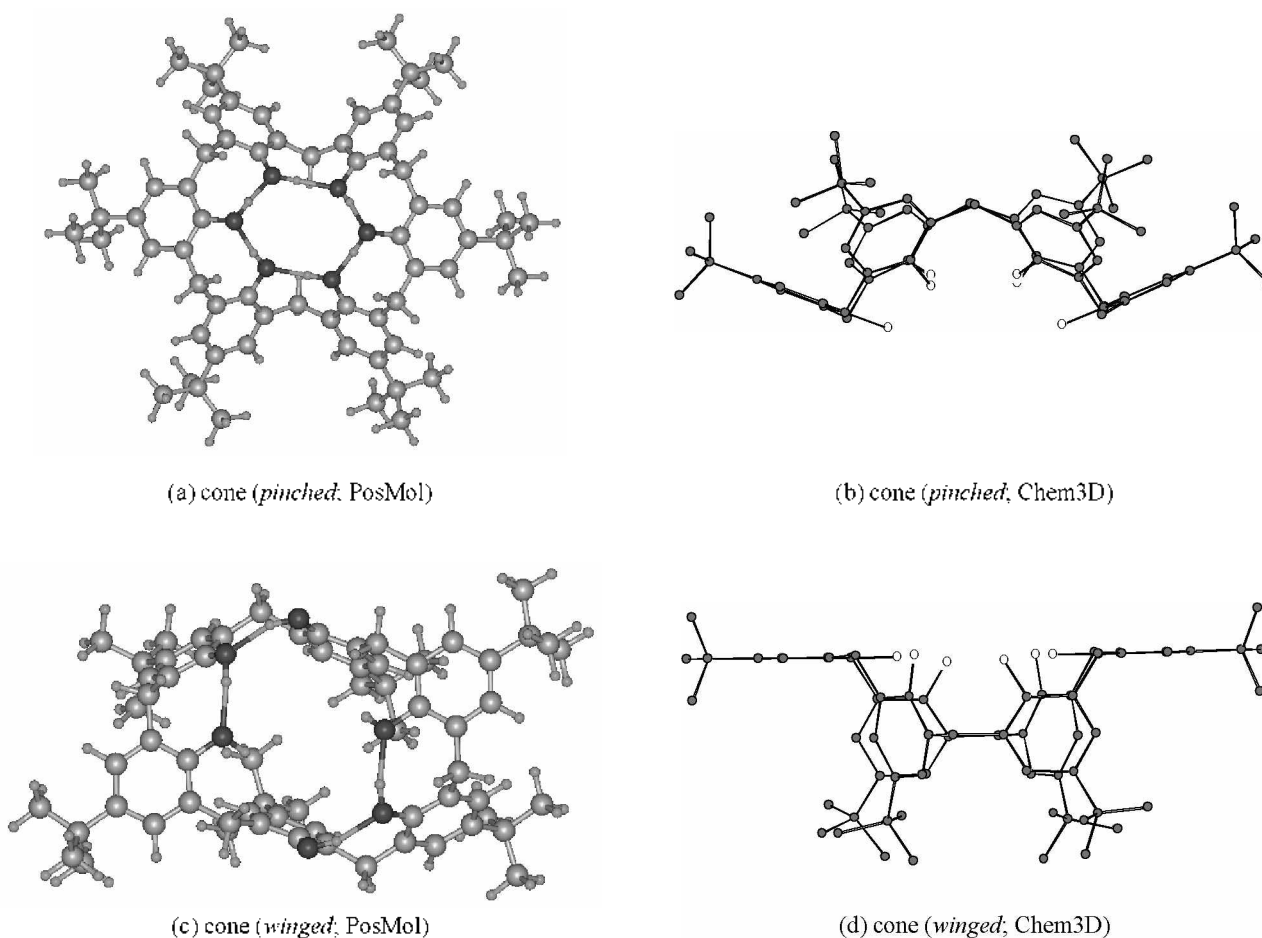

(a) cone (*pinched*, PosMol)

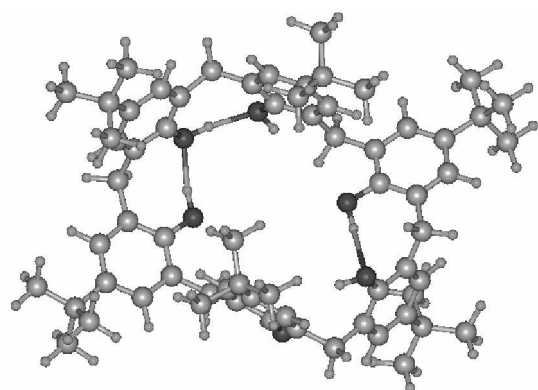(b) cone (*pinched*, Chem3D)

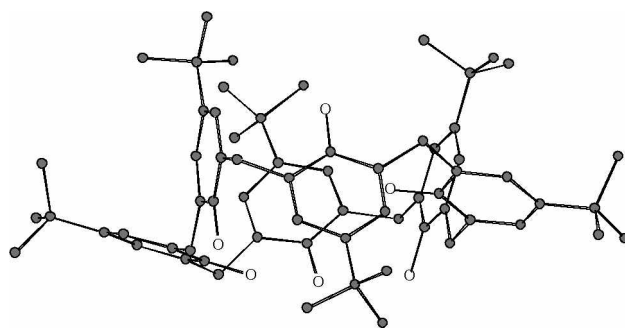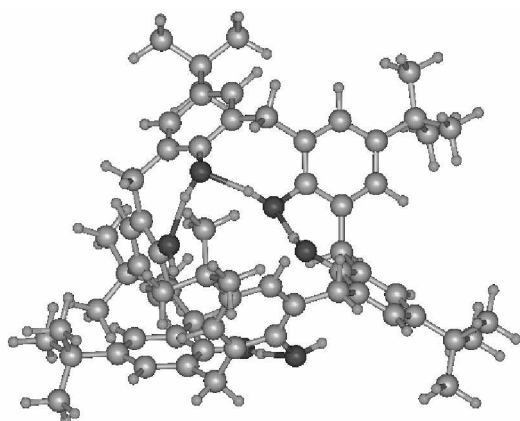(c) cone (*winged*, PosMol)

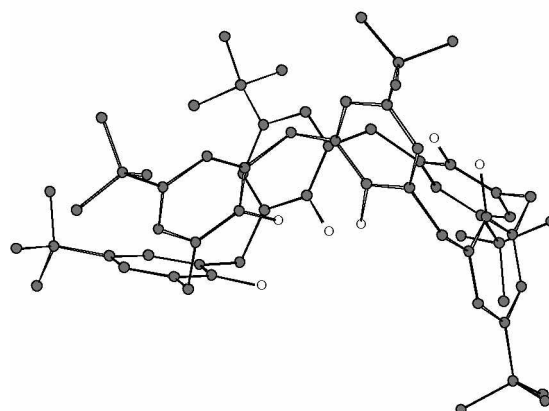(d) cone (*winged*, Chem3D)

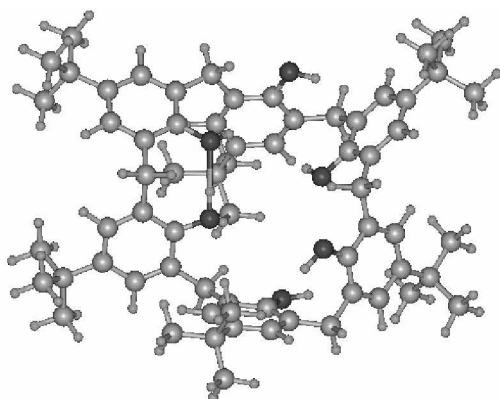**Figure 2.** (continued)

(e) partial-cone (PosMol)
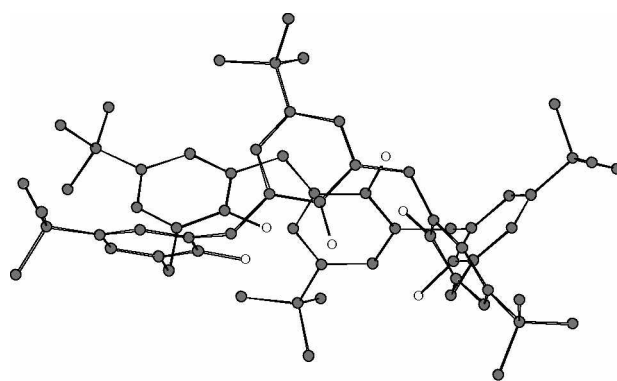

(f) partial-cone (Chem3D)
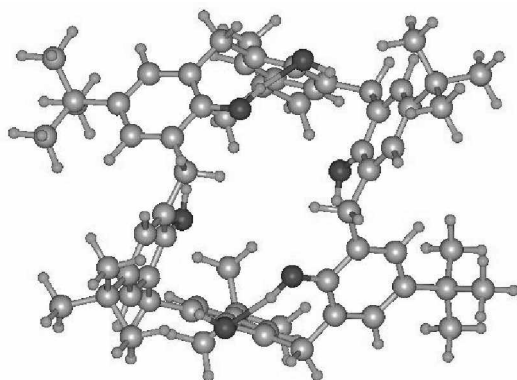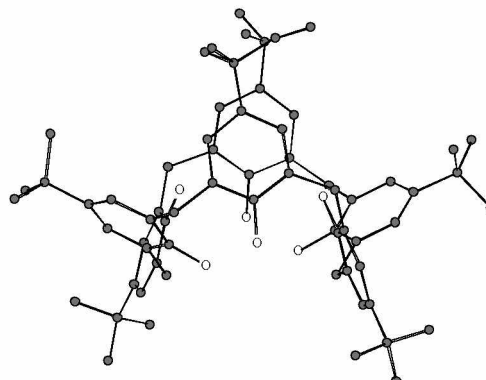

(g) 1,2-alternate (PosMol)

(h) 1,2-alternate (Chem3D)

(i) 1,3-alternate (PosMol)

(j) 1,3-alternate (Chem3D)

(k) 1,4-alternate (PosMol)

(l) 1,4-alternate (Chem3D)

Figure 2. (continued)

(m) 1,2,3-alternate (PosMol)

(n) 1,2,3-alternate (Chem3D)

(o) 1,3,5-alternate (PosMol)
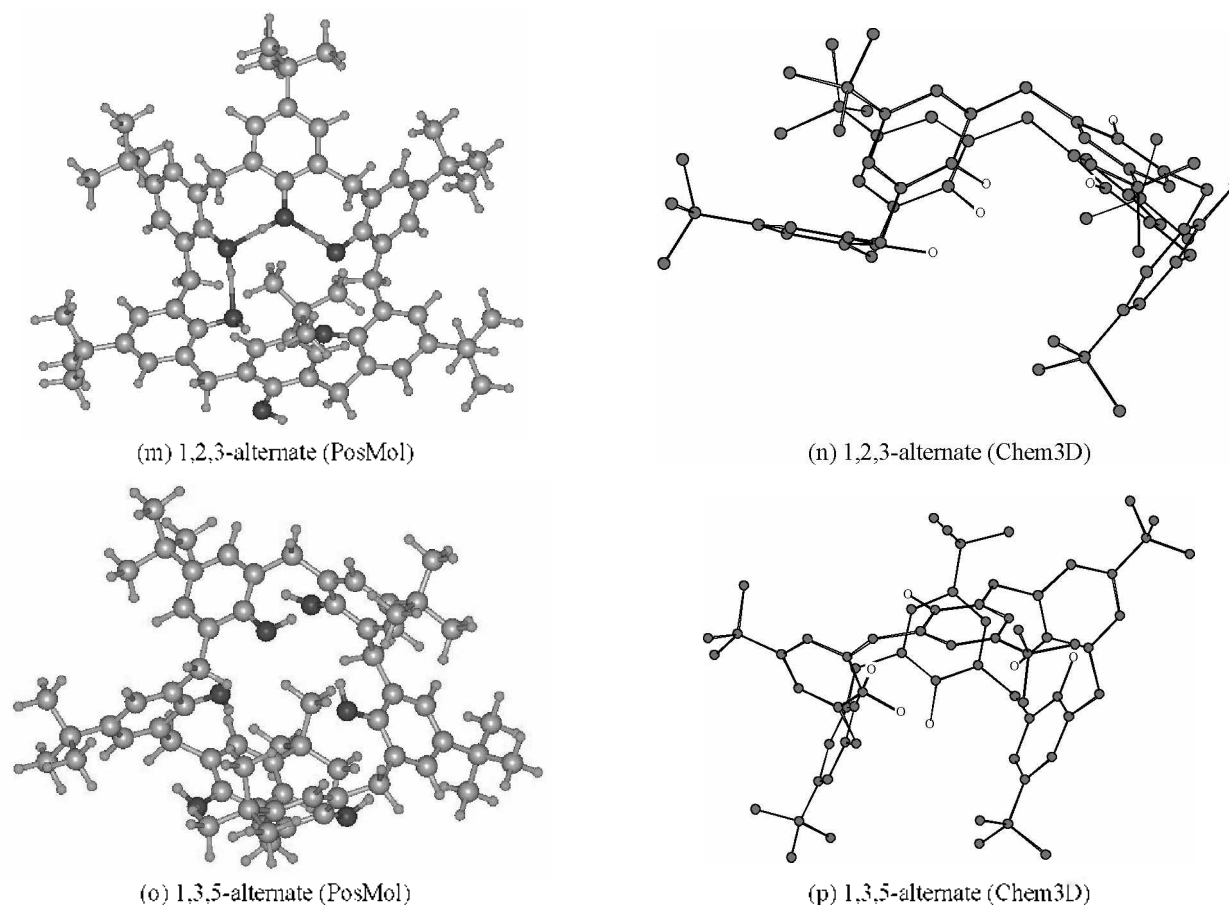

(p) 1,3,5-alternate (Chem3D)

Figure 2. *DFT* B3LYP/6-31G(d,p) optimized molecular structures of the conformers of **2** (*p-tert*-butylcalix[6]arene). (a) Top view of the *pinched* cone conformer with hydrogen bonds shown, (b) side view of the *pinched* cone conformer without hydrogen atoms, (c) bottom view of the *winged* cone, (d) side view of the *winged* cone, (e) top view of the partial-cone, (f) side view of the partial-cone, (g) top view of the 1,2-alternate, (h) side view of the 1,2-alternate, (i) top view of the 1,3-alternate, and (j) side view of the 1,3-alternate, (k) bottom view of the 1,4-alternate, and (l) side view of the 1,4-alternate, (m) bottom view of the 1,2,3-alternate, (n) side view of the 1,2,3-alternate, (o) bottom view of the 1,3,5-alternate, (p) side view of the 1,3,5-alternate.

kcal/mol more stable than 1.3-alternate, respectively. Due to the steric hindrances of *p-tert*-butyl groups of **2**, the energy differences between conformers of **2** are bigger than the values of **1**.

Figure 1 shows the *DFT* B3LYP/6-31+G(d,p) optimized stable structures showing hydrogen bondings of the various conformers of the calix[6]arene (**1**). The **1**(*pinched* cone) (Figure 1(a)) having six hydrogen bonds is the most stable, and the conformers (partial cone, *winged* cone, 1.2-alternate and 1.2.3-alternate) having four hydrogen bonds are next in the order. The 1.3.5-alternate (Figure 1(o)) which has no H-bond is the least stable conformation.

Figure 2 shows the *DFT* B3LYP/6-31G(d,p) optimized stable structures showing hydrogen bondings of the various conformers of the *tert*-butylcalix[6]arene (**2**). The *pinched* cone conformer (Figure 2(a)) of **2** having six hydrogen bonds is the most stable, and **2**(1.2-alternate: Figure 2(g)) having four hydrogen bonds is next in the order. The steric hindrances between adjacent *p-tert*-butylbenzyl groups are not much critical in the relative stability of the various conformations of the *p-tert*-butylcalix[6]arene, since the cavity size made of six benzene rings are big enough. (See Chart 2 and Figure 2.) We have changed the up-down direction in the

Figures 1(d) and 2(d) to show the structure better for the *winged* cone conformers of **1** and **2**.

Table 3 lists the *DFT* calculated distances and angles of intramolecular hydrogen bonds of **1**. 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.[18] The O···O distances of 2.64 ~ 2.80 Å in Table 3 suggest that these calculated values in the calix[6]arene (**1**) display strong hydrogen bonds.

In order to compare our calculated H-bond distances of **1** with the values of the intramolecular hydrogen bonds of *t*-butylcalix[6]arene (**2**), we have tabulated the *DFT* calculated H-bond distances of **2** (Table 5). The average calculated O···O distances (2.638 Å in Table 3 and 2.640 Å in Table 5) of the intramolecular hydrogen bonds of the cone conformers of calix[6]arene (**1**) and *t*-butylcalix[6]arene (**2**) are similar to the experimental crystal structure values (2.585 and 2.597 Å, respectively) in Table 4. The calculated O···O distances (2.71 ~ 2.79 Å) of the less stable conformations are 0.07 ~ 0.15 Å longer than the most stable cone conformer.

One usually recognizes that the (O-H···O) hydrogen bond is stronger if the (O-H···O) angle is closer to 180°.[18] Our calculated average (O-H···O) angles of 163° ~ 171° in Table

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Table 3. *DFT* Calculated Distances (Å) and Angles (O-H···O) of Intramolecular Hydrogen Bonds of 1

Conformer	H-bond	1	2	3	4	5	6	#	Average
1(cone)	O···O	2.637	2.650	2.632	2.637	2.650	2.632	6	2.640
(pinched)	H···O	1.664	1.670	1.643	1.664	1.670	1.643		1.659
	O-H	0.990	0.991	0.991	0.990	0.991	0.991		0.991
	Angle(°)	166.6	168.9	175.8	166.6	168.9	175.8		170.4
1(cone)	O···O	2.778	2.745	2.778	2.745			4	2.762
(winged)	H···O	1.844	1.822	1.844	1.822				1.833
	O-H	0.978	0.978	0.978	0.978				0.978
	Angle(°)	158.6	156.0	158.6	156.0				157.3
1(pc)	O···O	2.796	2.698	2.673	2.681			4	2.712
	H···O	1.707	1.695	1.714	1.856				1.743
	O-H	0.984	0.987	0.985	0.979				0.984
	Angle(°)	169.8	170.5	176.5	160.1				169.2
1(12a)	O···O	2.729	2.659	2.711	2.941			4	2.760
	H···O	1.739	1.695	1.773	2.001				1.802
	O-H	0.980	0.984	0.979	0.971				0.979
	Angle(°)	171.1	165.4	164.8	162.6				166.0
1(13a)	O···O	2.712	2.752	2.883				3	2.782
	H···O	1.751	1.787	1.961					1.833
	O-H	0.981	0.980	0.976					0.979
	Angle(°)	165.3	167.9	156.6					163.3
1(14a)	O···O	2.732	2.764					2	2.748
	H···O	1.762	1.788						1.775
	O-H	0.981	0.980						0.981
	Angle(°)	169.1	173.7						171.4
1(123a)	O···O	2.729	2.840	2.845	2.764			4	2.795
	H···O	1.749	1.865	1.898	1.800				1.828
	O-H	0.981	0.981	0.977	0.977				0.979
	Angle(°)	174.8	172.6	162.5	168.3				169.6
1(135a)	O···O							0	

Table 5. *DFT* Calculated Distances (Å) and Angles(O-H···O) of Intramolecular Hydrogen Bonds of 2

Conformer	H-bond	1	2	3	4	5	6	#	Average
2(cone)	O···O	2.650	2.632	2.629	2.637	2.650	2.632	6	2.638
(pinched)	H···O	1.673	1.644	1.660	1.664	1.670	1.643		1.659
	O-H	0.991	0.991	0.990	0.990	0.991	0.991		0.991
	Angle(°)	167.8	175.1	164.7	166.6	168.9	175.8		169.8
2(cone)	O···O	2.757	2.729	2.751	2.730			4	2.742
(winged)	H···O	1.825	1.794	1.817	1.796				1.808
	O-H	0.980	0.980	0.980	0.980				0.980
	Angle(°)	157.9	158.6	158.2	158.3				158.3
2(pc)	O···O	2.795	2.767					2	2.781
	H···O	1.793	1.827						1.810
	O-H	0.980	0.978						0.979
	Angle(°)	171.9	169.7						170.8
2(12a)	O···O	2.677	2.659	2.694	2.941			4	2.743
	H···O	1.711	1.689	1.720	2.001				1.780
	O-H	0.984	0.987	0.982	0.971				0.981
	Angle(°)	166.1	166.5	170.7	162.6				166.5
2(13a)	O···O	2.778						1	2.778
	H···O	1.816							1.816
	O-H	0.976							0.976
	Angle(°)	168.1							168.1
2(14a)	O···O	2.776	2.769					2	2.773
	H···O	1.812	1.804						1.808
	O-H	0.978	0.978						0.978
	Angle(°)	167.9	168.3						168.1
2(123a)	O···O	2.708	2.679	2.764				3	2.717
	H···O	1.741	1.694	1.796					1.744
	O-H	0.984	0.986	0.979					0.983
	Angle(°)	166.5	175.1	169.8					170.5
2(135a)	O···O							0	

Table 4. Experimental O···O Distances (Å) of Intramolecular Hydrogen Bonds of 1 and 2

Molecule	H-bond	1	2	3	4	5	6	#	Average
1(cone)[12b]	O···O	2.570	2.631	2.554	2.570	2.631	2.554	6	2.585
2(cone)[12c]	O···O	2.648	2.609	2.621	2.610	2.522	2.573	6	2.597

3 and 166° ~ 171° in Table 5 tell that the hydrogen bondings in the calix[6]arenes (**1** and **2**) are almost linear and very strong.

Conclusion

The relative stabilities of the conformers of the calix[6]-arene (**1**) and *t*-butylcalix[6]arene (**2**) are mainly dependent upon the number and strength of the intramolecular hydrogen bonds than steric hindrance of adjacent rings. The relative stability of the various conformers of **1** is in the following order: cone (*pinched*: most stable) > partial-cone > cone (*winged*) ~ 1,2-alternate ~ 1,2,3-alternate > 1,4-alternate > 1,3-alternate > 1,3,5-alternate. The *pinched*-cone conformers of **1** and **2** are 14.65 and 13.27 kcal/mol more stable than the *winged*-cones. respectively. The relative stability of the different conformers of **2** is in the following order: cone (*pinched*) > 1,2-alternate > cone (*winged*) > 1,4-alternate ~ partial-cone > 1,2,3-alternate > 1,3,5-alternate > 1,3-alternate. The *DFT* optimized average O···O distances (2.638 and 2.640 Å) for

the *pinched* cone conformations of **1** and **2** are similar to the experimental distances (2.585 Å and 2.597 Å. respectively). Our calculated average (O-H···O) angles of 163° ~ 171° tell that the hydrogen bondings in the calix[6]arenes (**1** and **2**) are very strong.

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