

DFT Conformational Study of Calix[5]arene and Calix[4]arene: Hydrogen Bond

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We have performed *DFT* calculations to investigate the conformational characteristics and hydrogen bonds of the *p*-*tert*-butylcalix[5]arene (**1**) and *p*-*tert*-butylcalix[4]arene (**2**). 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: cone (most stable) > 1,2-alternate > partial-cone > 1,3-alternate. The relative stability of four conformers of **2** is in the following order: cone (most stable) > partial-cone > 1,2-alternate > 1,3-alternate. The primary factor affecting the relative stabilities of the various conformers of the **1** and **2** are the number and strength of the intramolecular hydrogen bonds. The hydrogen-bond distances are discussed based on different calculation methods.

Key Words : *DFT*, B3LYP/6-31+G, Calix[5]arene, Calix[4]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.¹ Among the varying structures of calixarenes, pentameric analogue calix[5]arenes^{2,3} 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, six, or eight repeating units. The relative stabilities of the various conformations of calix[4]aryl derivatives are determined by experimental and theoretical methods.⁴⁻⁹ Previously, the relative stability of calix systems was reported.¹⁰ For calix[4]quinone (CQ) and calix[4]hydroquinone (CHQ), the order in stability is as follows: CQ: partial cone > 1,3 alternative > cone > 1,2 alternative, CHQ: cone > partial cone > 1,2-alternative > 1,3-alternative.

We reported the calculation results for the molecular recognition behaviors of penta-O-alkylated derivative of cone-shaped *p*-*tert*-butylcalix[5]arene toward a series of alkyl ammonium guests.^{11,12}

The first objective of this research is to determine the relative stability of different conformational isomers for *p*-*tert*-butylcalix[5]arene^{2b} (**1**) and *p*-*tert*-butylcalix[4]arene⁴ (**2**) by using *DFT* calculation. The second objective is to investigate the intramolecular hydrogen bonds by the

hydroxyl groups of the **1** and **2** using different calculation methods.

Computational Methods

The initial structures of *p*-*tert*-butylcalixarenes (**1** and **2**) were constructed by using HyperChem.¹³ 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.¹⁴ The conformational isomers of **1** and **2** obtained from MM/MD and AM1 semi-empirical calculations were fully re-optimized by using the HF and *DFT* methods to estimate the total and relative energies of the different conformations. *DFT* B3LYP/6-31G(d,p) and B3LYP/6-31+G(d,p) optimizations using Gaussian 98¹⁵ were performed.

Results and Discussion

It is well known that the calix[5]arene and calix[4]arene form strong intramolecular hydrogen bonds among OH groups and represent the cone conformer as the most stable structure.²⁻⁴ Substitution of all the phenolic protons of a *p*-*tert*-butylcalix[4]arene by a bulky alkyl group generally leads to conformationally rigid structures like the tetraethyl ester of *p*-*tert*-butylcalix[4]arene.⁶ However, when the substituent is small enough such as a methyl group, the resulting tetramethyl ether of *p*-*tert*-butylcalix[4]arene is no longer rigid, and any anisole ring can rotate via oxygen-through-the-annulus to give a mixture of the four possible conformers.⁷⁻¹⁰

The *p*-*tert*-butylcalix[5]arene (**1**) and *p*-*tert*-butylcalix[4]arene (**2**) are identical with respect to the numbers of up/down conformations that are possible, and for convenience the same descriptive names are used for both: cone, partial cone, 1,2-alternate or 1,3-alternate. The *DFT* optimizations without any constraint were carried out for four conformers of the **1** and **2**.

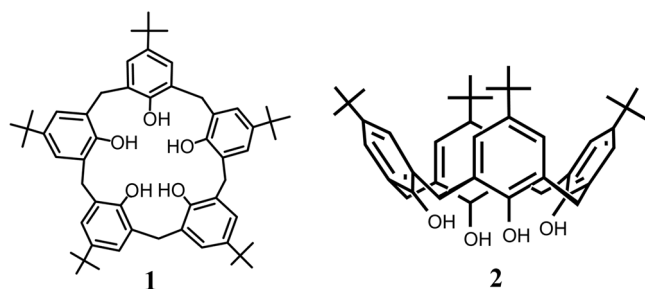


Chart 1. ChemDraw Structures of *p*-*tert*-Butylcalix[5]arene (**1**) and the cone conformer of *p*-*tert*-Butylcalix[4]arene (**2**).

Table 1. DFT B3LYP Optimized Relative Energies^a of the Various Conformers of **1** (*t*-Butylcalix[5]arene)

Calculation Method	DFT B3LYP		HF	AM1
	6-31+G(d,p)	6-31G(d,p)	6-31G	Semi-empirical
Conformer	ΔE	ΔE	ΔE	ΔE
1 (cone)	0.00	0.00	0.00	0.00
1 (partial cone)	9.70	11.07	16.03	7.36
1 (1,2-alternate)	5.09	8.38	5.22	4.59
1 (1,3-alternate)	15.15	16.58	22.59	9.76

^a ΔE is the relative energy (kcal/mol) with respect to the most stable cone conformation of the free host. Error limits in these calculations are about 0.01 kcal/mol.

Table 2. DFT B3LYP Optimized Relative Energies^a of the Various Conformers of **2** (*t*-Butylcalix[4]arene)

Calculation Method	DFT B3LYP		HF	AM1
	6-31+G(d,p)	6-31G(d,p)	6-31G	Semi-empirical
Conformer	ΔE	ΔE	ΔE	ΔE
2 (cone)	0.00	0.00	0.00	0.00
2 (partial cone)	8.45	10.35	12.13	6.64
2 (1,2-alternate)	11.59	13.34	16.02	9.03
2 (1,3-alternate)	14.21	17.31	22.35	11.11

^aSee the footnote of the Table 1.

Table 1 shows the relative energies of the four distinct conformers of *p*-*tert*-butylcalix[5]arene (**1**) optimized by the DFT calculations as well as other methods. All of the calculation results suggest that the cone conformer is the most stable among the conformational isomers of **1** in the following order: cone > 1,2-alternate > partial-cone > 1,3-alternate. For completeness and in order to keep in touch with other theoretical studies of related systems, we also report the results based on DFT, HF and AM1 optimizations for the conformers of *p*-*tert*-butylcalix[4]arene (**2**). Table 2 shows the relative energies of the four conformers of **2**. All of the calculation results also suggest that the cone conformer is the most stable one among the conformational isomers of **2**. However, the order of relative stability (cone > partial-cone > 1,2-alternate > 1,3-alternate) is different from **1**.

The primary factors affecting the relative stabilities of the various conformers of the *t*-butylcalix[4 or 5]arene are the number and strength of the intramolecular hydrogen bonds. The good stability of 1,2-alternate conformer of *t*-butylcalix[5]arene (**1**) among less stable conformers can be explained by the four hydrogen bonds in **1** (1,2-alternate), whereas **1** (partial-cone) has three H-bonds and **2** (1,2-alternate) has only two H-bonds. We will explain the characteristics of the hydrogen bonds in various conformers later in this section.

The B3LYP/6-31+G(d,p) calculated relative stabilities of the conformations of **1** in Table 1 suggest that the cone conformer is 5.09 kcal/mol more stable than 1,2-alternate, 9.70 kcal/mol more stable than partial-cone, and 15.15 kcal/mol more stable than 1,3-alternate analogue, respectively. However, The B3LYP/6-31+G(d,p) calculated relative stabilities of the conformations of **2** in Table 2 suggest that the

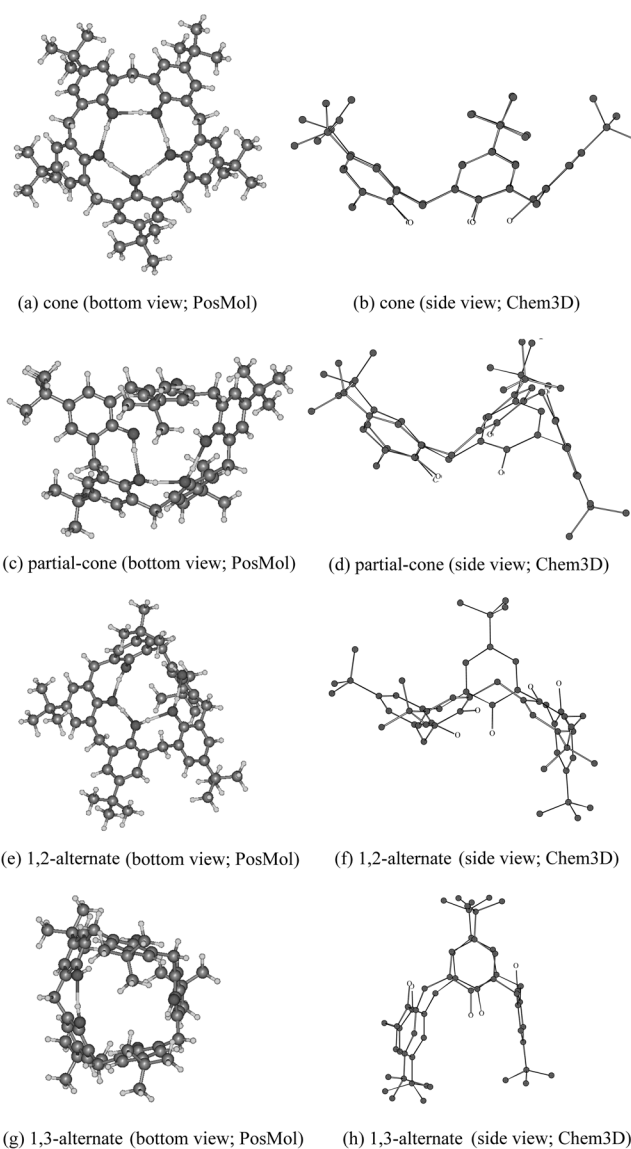


Figure 1. DFT B3LYP/6-31+G(d,p) optimized molecular structures of the conformers of **1** (*p*-*tert*-butylcalix[5]arene). (a) Bottom view of the cone conformer by PosMol²² with hydrogen bonds shown, (b) side view of the cone conformer by Chem3D²³ without hydrogen atoms, (c) bottom view of the partial-cone conformer, (d) side view of the partial-cone conformer, (e) bottom view of the 1,2-alternate conformer, (f) side view of the 1,2-alternate conformer, (g) bottom view of the 1,3-alternate conformer, and (h) side view of the 1,3-alternate conformer. Atoms that are within a certain distance (the bond proximate distance) from one another were automatically marked as bonded.²²

cone conformer is 8.45 kcal/mol more stable than partial-cone, 11.59 kcal/mol more stable than 1,2-alternate, and 14.21 kcal/mol more stable than 1,3-alternate analogue, respectively. In the case of the original calix[4]arene without *p*-*tert*-butyl group, the relative stability was calculated in different order, where 1,3-alternate conformer had slightly better stability than the 1,2-alternate analogue.^{7d} For the calix[4]hydroquinone (CHQ), the order in stability is as follows: cone > partial cone > 1,2-alternative > 1,3-alternative, where the cone conformer is 11.6 kcal/mol more

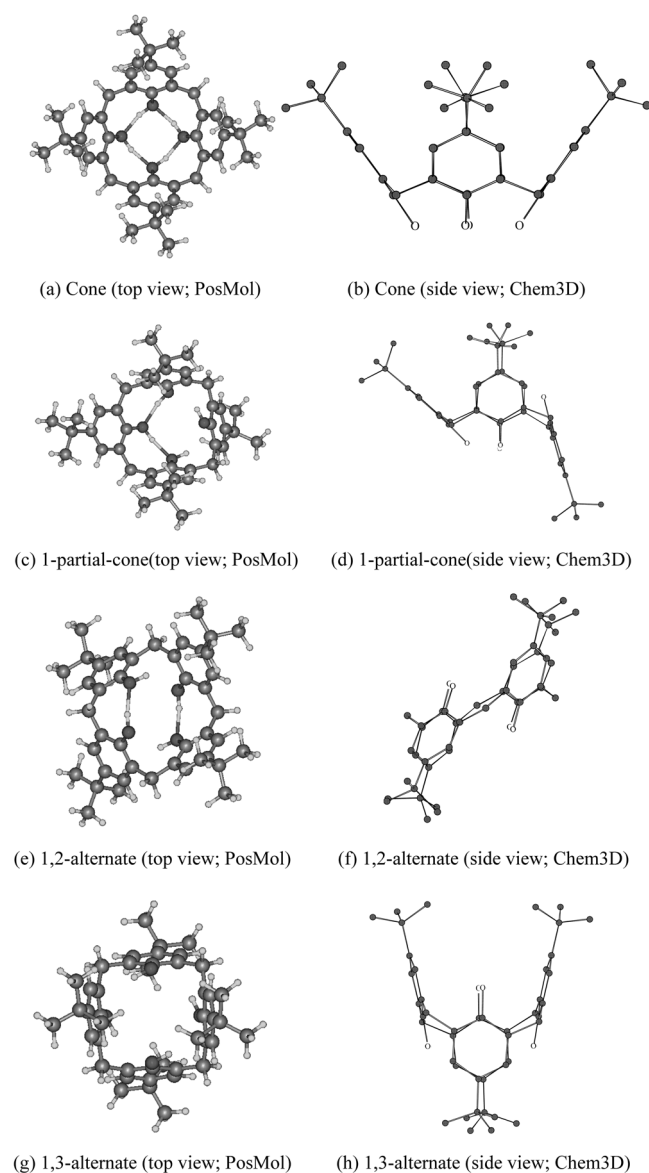


Figure 2. DFT B3LYP/6-31+G(d,p) optimized molecular structures of the conformers of **2** (*p*-*tert*-butylcalix[4]arene). (a) Top view of the cone conformer by PosMol²² with hydrogen bonds shown, (b) side view of the cone conformer by Chem3D²³ without hydrogen atoms, (c) top view of the partial-cone conformer, (d) side view of the partial-cone conformer, (e) top view of the 1,2-alternate conformer, (f) side view of the 1,2-alternate conformer, (g) top view of the 1,3-alternate conformer, and (h) side view of the 1,3-alternate conformer.

stable than partial-cone, 18.3 kcal/mol more stable than 1,2-alternate, and 19.8 kcal/mol more stable than 1,3-alternate analogue, respectively.^{10a}

Figure 1 shows the DFT B3LYP/6-31+G(d,p) optimized stable structures showing hydrogen bondings of the various conformers of the *p*-*tert*-butylcalix[5]arene (**1**). **1** (cone) (Figure 1(a)) having five hydrogen bonds is the most stable, and **1** (1,2-alternate) (Figure 1(e)) having four hydrogen bonds is next in the order. Experimental studies show that it also exists in a cone conformation.^{2h,18,19} The ordering of less stable conformers is a kind of unusual outcome, since the

adjacent *t*-butylbenzene rings of 1,2-alternate conformer may produce more steric hindrance than other cases such as partial-cone and 1,3-alternate. However, four hydrogen bondings of the 1,2-alternate conformer overcome the more interferences.

Figure 2 shows the DFT B3LYP/6-31+G(d,p) optimized stable structures showing hydrogen bondings of the various conformers of the *tert*-butylcalix[4]arene (**2**). The cone conformer (**2** (cone): Figure 1(a)) having four hydrogen bonds is the most stable, and **2** (partial-cone: Figure 1(e)) having two hydrogen bonds is next in the order.

In order to show the relationship between the stability and the hydrogen bonds, we have listed the number of H-bonds and the B3LYP/6-31+G(d,p) calculated relative energies of the conformers of **1** and **2** in the Table 3. Each additional hydrogen bond contributes 4-5 kcal/mol better stability of the conformers of **1** and **2**, if we ignore other effects such as steric hindrances.

Table 4 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.¹⁶ The O...O distances of 2.76-2.86 Å in Table 4 sug-

Table 3. The Number of the H-bonds and DFT B3LYP/6-31+G(d,p) Relative Energies^a of the Various Conformers of **1** and **2**

Conformer	# of H-bond	ΔE	Conformer	# of H-bond	ΔE
1 (cone)	5	0.00	2 (cone)	4	0.00
1 (partial cone)	3	9.70	2 (partial cone)	2	8.45
1 (1,2-alternate)	4	5.09	2 (1,2-alternate)	2	11.59
1 (1,3-alternate)	1	15.15	2 (1,3-alternate)	0	14.21

^aSee Tables 1 and 2.

Table 4. Calculated^a Average Distances (Å) and Angles of Intra-molecular (O-H...O) Hydrogen Bonds of **1** (*t*-Butylcalix[5]arene)

Conformer	H-bond	AM1	HF	B3LYP	B3LYP+
1 _(cone)	O...O	3.071	2.753	2.762	2.765
	H...O	2.120	1.800	1.780	1.783
	O-H	0.972	0.966	0.986	0.986
	Angle(°)	166.1	168.1	174.5	173.1
1 _(partial cone)	O...O	3.111	2.791	2.808	2.810
	H...O	2.159	1.847	1.837	1.841
	O-H	0.971	0.960	0.979	0.979
	Angle(°)	168.7	166.9	171.6	170.1
1 _(1,2-alternate)	O...O	3.066	2.748	2.765	2.768
	H...O	2.160	1.835	1.816	1.823
	O-H	0.972	0.962	0.981	0.982
	Angle(°)	158.1	158.8	163.0	162.3
1 _(1,3-alternate)	O...O	3.196	2.884	2.859	2.861
	H...O	2.228	1.949	1.887	1.890
	O-H	0.972	0.958	0.976	0.976
	Angle(°)	173.0	165.2	173.0	172.6

^aAM1 semi-empirical, HF/6-31G, DFT B3LYP/6-31G(d,p) and B3LYP/6-31G+(d,p).

Table 5. Experimental Distances (O···O) of Intramolecular Hydrogen Bonds of Calixarenes

Molecule (CSD entry) ¹⁷	Average (Å)
Calix[5]arene (UKAGIW) ¹⁸	2.764
Calix[5]arene (VETYAV) ¹⁹	2.780
1 (VETXUO) ¹⁹	2.894
2 (XAHMOI) ²⁰	2.779
Calix[4]crown-5-ether (VERLUA) ²¹	2.727

Table 6. Calculated^a Average Distances (Å) and Angles of Intramolecular (O-H···O) Hydrogen Bonds of **2** (*t*-Butylcalix[4]arene)

Conformer	H-bond	AM1	HF	B3LYP	B3LYP+
2 _(cone)	O···O	2.918	2.654	2.647	2.650
	H···O	2.055	1.740	1.677	1.683
	O-H	0.970	0.965	0.991	0.991
	Angle(°)	147.3	156.6	164.7	164.0
2 _(partial-cone)	O···O	3.015	2.728	2.711	2.718
	H···O	2.121	1.819	1.758	1.767
	O-H	0.971	0.961	0.982	0.982
	Angle(°)	155.9	158.4	164.0	163.5
2 _(1,2-alternate)	O···O	3.082	2.766	2.783	2.796
	H···O	2.137	1.849	1.825	1.842
	O-H	0.972	0.960	0.979	0.978
	Angle(°)	163.6	158.9	165.6	164.2
2 _(1,3-alternate)	none				

^aSee the footnote of the Table 4.

gest that our calculated values in the *p*-*tert*-butylcalix[5]arene (**1**) are in accord with the experimental distances (2.76–2.89 Å in Table 5) of the intramolecular hydrogen bonds (O···O) of the calixarenes obtained from Cambridge Structure Database.¹⁷ Also, one recognizes that the (O-H···O) hydrogen bond is stronger if the (O-H···O) angle is closer to 180°. Our calculated (O-H···O) angles of 154°–175° in Table 4 tell that the hydrogen bondings in the molecule (**1**) are pretty strong.

In order to compare our calculated H-bond distances of **1** with the values of the strong intramolecular hydrogen bonds of *t*-butylcalix[4]arene (**2**), we have tabulated the *DFT* calculated H-bond distances of **2** (Table 6). The average calculated distances (2.65–2.80 Å in Table 6) of the intramolecular hydrogen bonds of *t*-butylcalix[4]arene (**2**) are shorter than the values (2.76–2.86 Å in Table 4) of *p*-*tert*-butylcalix[5]arene (**1**). FTIR studies already confirmed the intramolecular character of the bonding and showed that it is strongest for the cyclic tetramer (**2**) and weakest for the cyclic pentamer (**1**).²⁴

We have also tabulated the hydrogen-bond distances of lower level calculation methods (see Table 4 for **1** and Table 6 for **2**), and found an interesting outcome. The semi-empirical AM1 optimized average H-bond distances (2.92–3.20 Å) in **1** and **2** are always ~0.30 longer than the values of *ab initio* HF (2.75–2.88 Å) and *DFT* (2.76–2.86 Å) methods which are much closer to the experimental results (2.76–2.89 Å in Table 5). These calculation results suggest us that the

AM1 optimized H-bond distances are too long and that one should be careful for the discussion of the hydrogen bonding using the semi-empirical calculation method.²⁵

Conclusion

The relative stabilities of the conformers of the *t*-butylcalix[5]arene (**1**) and *t*-butylcalix[4]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 (most stable) > 1,2-alternate > partial-cone > 1,3-alternate. The relative stability of the different conformers of **2** is in the following order: cone (most stable) > partial-cone > 1,2-alternate > 1,3-alternate.

Each hydrogen bond contributes 4–5 kcal/mol for the stability of the conformers of **1** and **2**. The O···O distances of 2.76–2.86 Å suggest that the *DFT* optimized values in the molecule **1** are in accord with the experimental distances (2.76–2.89 Å) of the intramolecular hydrogen bonds (O···O) of the calix[5]arenes.

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