

캘릭스[n]아렌(n = 4,5,6)의 이형체들의 상대적인 안정성과 수소결합에 대한 양자역학적 계산연구

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mPW1PW91 Calculated Conformational Study of Calix[n]arene (n = 4,5,6): Hydrogen Bond

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요약. 캘릭스[n]아렌 (1-4)의 다양한 이형체들에 대한 구조들이 *DFT* B3LYP/6-31+G(d,p) 와 *mPW1PW91*/6-31+G(d,p) (hybrid HF-DF) 계산 방법들에 의하여 최적화 되었다. 모든 캘릭스[n]아렌 (1-4)의 다양한 이형체들 중에서, 수소결합들의 영향으로, cone 이형체가 가장 안정하였다. 그러나, 이형체들의 상대적인 안정성은 다음과 같이 서로 달랐다.

1. *t*-부틸캘릭스[4]아렌(1): cone > partial-cone > 1,2-alternate > 1,3-alternate.
2. *t*-부틸캘릭스[5]아렌(2): cone > 1,2-alternate > partial-cone > 1,3-alternate.
3. 탈부틸화된 캘릭스[6]아렌(3): cone(*pinched*) > partial-cone > cone(*winged*) ~ 1,2-alternate ~ 1,2,3-alternate > 1,4-alternate > 1,3-alternate > 1,3,5-alternate.
4. *t*-부틸캘릭스[6]아렌(4): cone(*pinched*) > 1,2-alternate > cone(*winged*) > 1,4-alternate ~ partial-cone > 1,2,3-alternate > 1,3,5-alternate > 1,3-alternate.

분자 내부의 수소결합의 개수와 강도들이 캘릭스[n]아렌의 다양한 이형체들의 상대적인 안정성에 가장 영향을 많이 미치는 인자들이었다. 두 가지 서로 다른 계산방법들(B3LYP과 *mPW1PW91*)에 대한 여러 가지 이형체들에서의 수소결합 길이들이 비교되었다.

주제어: 캘릭스[n]아렌, 이형체, 수소결합, *mPW1PW91*, 양자역학

ABSTRACT. We have performed *mPW1PW91* calculations to investigate the conformational characteristics and hydrogen bonds of *p*-*tert*-butylcalix[4]arene (1), *p*-*tert*-butylcalix[5]arene (2), calix[6]arene (3) and *p*-*tert*-butylcalix[6]arene (4). The structures of the different conformers of 1-3 were optimized by using *mPW1PW91*/6-31+G(d,p) method. The relative stability of the four conformers of 1 is in the following order: cone (most stable) > partial-cone > 1,2-alternate > 1,3-alternate. The relative stability of the conformers of 2 is in the following order: cone (most stable) > 1,2-alternate > partial-cone > 1,3-alternate. The relative stability of the various conformers of 3 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 the various conformers of 4 were optimized by using the *mPW1PW91*/6-31G(d,p) method followed by single point calculation of *mPW1PW91*/6-31+G(d,p). The relative stability of the conformers of 4 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 primary factor affecting the relative stabilities of the various conformers of the **1-4** are the number and strength of the intramolecular hydrogen bonds. The hydrogen-bond distances are discussed based on two different calculation methods (B3LYP and *mPW1PW91*).

Keywords: Calix[n]arene, Conformer, *mPW1PW91/6-31+G*, Hydrogen bond

INTRODUCTION

Calix[n]arenes have been receiving much attention as one of the most widely employed molecular frameworks for the construction of many versatile supramolecular systems.¹ The relative stabilities of the various conformations of calix[4]aryl derivatives have been determined by experimental and theoretical methods.²⁻⁸ Pentameric analogue calix[5]arenes^{9,10} have 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. The conformational characteristics of calix[6]arene were studied by using the molecular mechanical method.¹¹ The most stable conformation of calix[6]arenes¹²⁻¹⁴ in the solid state is called a *pinched* cone because two methylene bridges are pointing into the cavity.

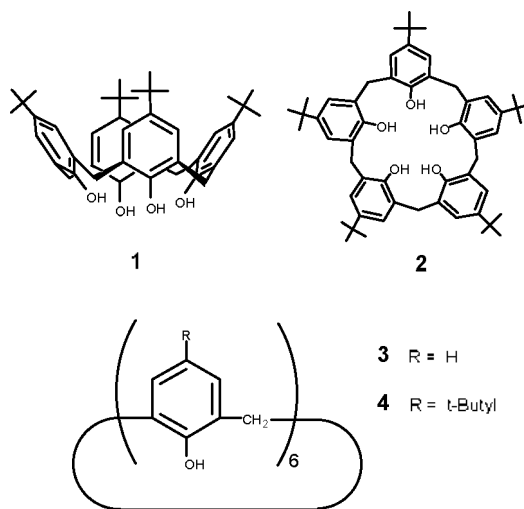
Intramolecular hydrogen bond formation determines the stability of conformations of unsubstituted calix[n]arenes.¹⁵ Recently, we have reported the *DFT* B3LYP optimization results for the conformational study and the hydrogen bonding of calix[n]arene ($n = 4,5$)¹⁶ and the *mPW1PW91* single point calculation of calix[6]arenes.¹⁷ Density functional theory (*DFT*) is very appealing due to its excellent performance-to-cost ratio, and *DFT* methods are widely employed in the computational chemistry community. However, the most popular *DFT* method, B3LYP,^{18,19} cannot successfully describe π hydrogen bonding^{20,21} and B3LYP also fails badly for binding energies dominated by dispersion interactions.²²⁻²⁴ Hydrogen bonding involves not only dispersion but also electrostatic interactions, polarization (induction), and charge transfer.^{25,26} Suggestions are new hybrid Hartree-Fock-density functional (HF-DF) models called the modified Perdew-Wang 1-parameter (*mPW1*) calculation methods,²⁷⁻²⁹ such as *mPW1B95*, *mPW1B1K*, *mPW1-*

PW91, which are suitable for hydrogen bonding. The *mPW1PW91* model allows obtaining remarkable results both for covalent and noncovalent interactions.²⁸

The first objective of this research is to determine the relative stability of the different conformational isomers for calix[n]arene ($n = 4,5,6$) from the total electronic and Gibbs free energies by using the improved *mPW1PW91* calculation method. The second objective is to compare the intramolecular hydrogen bonds by the hydroxyl groups of the **1-4** using two different calculation methods (B3LYP and *mPW1PW91*).

COMPUTATIONAL METHODS

The initial structures of *p-tert*-butylcalix[4]arenes (**1**) and *p-tert*-butylcalix[4]arenes (**2**) were constructed by using HyperChem.³⁰ The initial *pinched* cone-type structures of the calix[6]arene (**3**) and



Scheme 1. ChemDraw structures of *p-tert*-butylcalix[4]arene (**1**), *p-tert*-butylcalix[5]arene (**2**), calix[6]arene (**3**) and *p-tert*-butylcalix[6]arene (**4**)

p-*tert*-butylcalix[6]arene (**4**) were obtained from Cambridge Structure Database (CSD^{31a} entry NOBLEV^{31b} (**3**) and KENBUA^{31c} (**4**)), and other conformations are constructed by using the molecular mechanics (MM), molecular dynamics (MD), and AM1 semi-empirical calculations of HyperChem. 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.³² The conformational isomers of **1-4** obtained from the MM/MD and AM1 calculations were fully re-optimized by using the *DFT* and hybrid HF-DF methods to determine the relative energies and the structures of the distinct conformations. Consecutive B3LYP optimizations followed by *m*PW1PW91 calculations using Gaussian 03³³ were performed. The normal mode frequencies of the *m*PW1PW91/6-31G optimized structures have been calculated. Each vibrational spectrum shows no negative value of frequency, which confirms that the optimized structure exists in the energy minimum. From the zero-point correction by the vibrational analysis and the thermal correction to free energy, Gibbs free energies at 298 K are also calculated by using the *m*PW1PW91/6-31G method.

RESULTS AND DISCUSSION

It is well known that the calix[4]arene and calix[5]arene form strong intramolecular hydrogen

bonds among OH groups and represent the cone conformer as the most stable structure.^{2,9,10} 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.⁴ 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.⁵⁻⁸

The *p*-*tert*-butylcalix[4]arene (**1**) and *p*-*tert*-butylcalix[5]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 the four conformers of the **1** and **2**.

Table 1 reports the *m*PW1PW91/6-31+G(d,p) optimized total electronic and relative energies, and dipole moments of the four conformers of **1**. Sums of total electronic and thermal Gibbs free energies calculated from the *m*PW1PW91/6-31G method are also listed from the zero-point correction by the vibrational analyses and thermal correction to free energy at 298 K. The calculation results suggest that the cone conformer is the most stable among the conformational isomers of **1** in the following order: cone > partial-cone > 1,2-alternate > 1,3-

Table 1. *m*PW1PW91 Optimized Total,^a Gibbs Free and Relative Energies, and Dipole Moments of the Various Conformers^b of **1**

Calculation Method	Total (a.u.) ^a Cone	ΔE (kcal/mol) ^c		
		Partial-cone	1,2-Alternate	1,3-Alternate
<i>m</i> PW1PW91/6-31+G(d,p) ^c	-2011.0784	7.53	10.85	12.25
<i>m</i> PW1PW91/6-31G(d,p) ^c	-2011.0373	9.22	12.38	15.15
<i>m</i> PW1PW91/6-31G ^c	-2010.4597	15.16	19.08	27.01
<i>m</i> PW1PW91/6-31G (298 K) ^d (Gibbs Free Energy)	-2009.6141	13.99	17.17	24.73
Dipole Moment ^e	2.72	1.25	0.06	0.05

^aThe unit of total energy is in a.u. Error limits in these calculations are about 0.01 kcal/mol. ^bConformer: "pc" denotes partial-cone, "12a" means 1,2-alternate, etc. ^cTotal electronic energies (a.u.) at 0 K. ΔE (kcal/mol) is the relative energy with respect to the most stable cone conformation. ^dSum of electronic and thermal Gibbs free energies at 298 K. ΔG (kcal/mol) is the relative free energy. ^eTotal Dipole moment in Debye calculated from the final structure by using *m*PW1PW91/6-31-G(d,p) method.

Table 2. *mPW1PW91* Optimized Total,^a Gibbs Free and Relative Energies, and Dipole moments of the Various Conformers^b of **2**

Calculation Method	Total (a.u.) ^a Cone	ΔE (kcal/mol) ^f		
		Partial-cone	1,2-Alternate	1,3-Alternate
<i>mPW1PW91/6-31+G(d,p)</i> ^c	-2513.8457	8.49	4.23	13.48
<i>mPW1PW91/6-31G(d,p)</i> ^c	-2513.7924	9.69	4.13	14.69
<i>mPW1PW91/6-31G</i> ^c	-2513.0723	17.66	7.83	27.59
<i>mPW1PW91/6-31G (298 K)</i> ^d (Gibbs Free Energy)	-2512.0114	17.42	8.59	26.40
Dipole Moment ^e	2.13	3.96	1.16	3.79

^{a-b}See the footnotes of *Table 1*

Table 3. *mPW1PW91* Optimized Total^a, Gibbs Free and Relative Energies, and Dipole moments of the Various Conformers^b of **3**

<i>mPW1PW91</i>	Total (a.u.) ^a cone (<i>pinched</i>)	ΔE (kcal/mol) ^f						
		cone (<i>winged</i>)	pc	12a	13a	14a	123a	135a
<i>/6-31+G(d,p)</i> ^c	-2073.2231	13.05	9.38	12.89	17.22	17.03	12.96	20.48
<i>/6-31G(d,p)</i> ^c	-2073.1685	14.13	10.72	14.65	20.42	18.72	15.25	24.34
<i>/6-31G</i> ^c	-2072.6008	26.56	17.81	27.39	35.08	33.06	26.86	47.99
<i>/6-31G (298 K)</i> ^d (Gibbs Free Energy)	-2071.9703	13.05	15.35	26.70	31.52	31.14	25.94	43.93
Dipole Moment ^e	0.95	1.59	1.40	6.79	1.11	1.98	1.49	4.46

^{a-e}See the footnotes of *Table 1*

alternate.

The *mPW1PW91/6-31+G(d,p)* calculated relative stabilities of the conformations of **1** in *Table 1* suggest that the cone conformer is 7.53 kcal/mol more stable than partial-cone, 10.85 kcal/mol more stable than 1,2-alternate, and 12.25 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.^{5d}

Table 2 shows the total electronic, Gibbs free and relative energies, and dipole moments of the four distinct conformers of *p-tert*-butylcalix[5]arene (**2**) optimized by the *mPW1PW91* calculations. The cone conformer is the most stable one among the conformational isomers of **2**. However, the order (cone > 1,2-alternate > partial-cone > 1,3-alternate) of the relative stability for the conformers of **2** is

different from **1**. The *mPW1PW91/6-31+G(d,p)* calculated relative stabilities of the conformations of **2** in *Table 2* suggest that the cone conformer is 4.23 kcal/mol more stable than 1,2-alternate, 8.49 kcal/mol more stable than partial-cone, and 13.48 kcal/mol more stable than 1,3-alternate analogue, respectively.

Table 3 shows the total electronic, Gibbs free and relative energies, and dipole moments of the conformers of calix[6]arene (**3**) calculated by the *mPW1PW91* calculations. During the 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 3* and *4*. The relative stabilities of *mPW1PW91/6-31+G(d,p)* optimization results of **3** are in the following order: cone (*pinched*: most stable) > partial-cone > 1,2-alternate ~ 1,2,3-alternate ~ cone (*winged*) > 1,4-alternate ~ 1,3-alternate > 1,3,5-alternate. The calculated

Table 4. *mPW1PW91* Optimized Total^a and Relative Energies and Dipole Moment^b of the Various Conformers^b of **4**

<i>mPW1PW91</i>	Total (a.u.) ^a cone (<i>pinched</i>)	ΔE (kcal/mol) ^c						
		cone (<i>winged</i>)	pc	12a	13a	14a	123a	135a
/6-31+G(d,p) (0 K) ^d	-3016.6188	12.94	15.20	7.86	21.48	13.32	19.10	20.11
/6-31G(d,p) (0 K) ^e	-3016.5581	13.26	16.63	9.36	25.23	16.34	19.53	23.55
Dipole Moment ^e	1.98	2.77	4.69	1.64	3.91	0.48	3.48	4.66

^{a,b,c,e}See the footnotes of Table 1. ^d*mPW1PW91*/6-31+G(d,p) single point calculation energy from the *mPW1PW91*/6-31G(d,p) optimized structure.

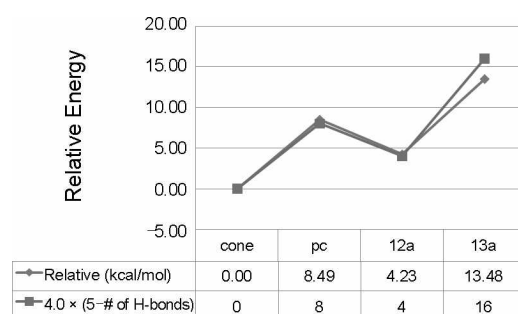
relative stabilities of the conformations of **3** in Table 3 suggest that the cone (*pinched*) conformer is 9.38 kcal/mol more stable than partial-cone, about 13 kcal/mol more stable than cone (*winged*), 1.2-alternate and 1.2,3-alternate analogues, about 17 kcal/mol more stable than 1.3-alternate and 1.4-alternate, and 20.48 kcal/mol more stable than 1.3,5-alternate, respectively.

The *mPW1PW91* calculations from three different basis sets are compared. For the relative stabilities of four different conformer in the Tables 1-3, ΔE 's calculated from 6-31+G(d,p) basis set are smaller than the values obtained from the 6-31G(d,p) and 6-31G basis sets in following order: 6-31+G(d,p) < 6-31G(d,p) < 6-31G. The higher level calculation shows less energy gap between the most stable cone conformer and the less stable analogues.

We also report the calculated results of the *mPW1PW91* calculations for the conformers of *p*-*tert*-butylcalix[6]arene (**4**). Since the molecule **4** (156 atoms) is much bigger than the debutylated calix[6]arene **3** (84 atoms), only *mPW1PW91*/6-31+G(d,p) single point calculation following the *mPW1PW91*/6-31G(d,p) optimization of **4** was allowed with our computing resources. Table 4 shows the total and relative energies of the various conformers of **4**. The relative stabilities of the *mPW1PW91*/6-31+G(d,p) calculation results of **4** 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. The *mPW1PW91*/6-31+G(d,p) calculated relative stabilities of the conformations of **4** in Table 4 suggest that the cone conformer is 7.86 kcal/mol

more stable than 1.2-alternate, about 13.1 kcal/mol more stable than cone (*winged*) and 1.4-alternate, 15.20 kcal/mol more stable than partial-cone, 19.10 kcal/mol more stable than 1,2,3-alternate conformers, respectively.

One of the important factors affecting the relative stabilities of the various conformers of the calix[n]arenes is the number and strength of the intramolecular hydrogen bonds. The good stability of 1.2-alternate conformer of *p*-*tert*-butylcalix[5]arene **2** among the less stable conformers can be explained by the four hydrogen bonds, whereas **2** (partial cone) has three and **2** (1.3-alternate) has one H-bonds. In Chart 1, we have compared the *mPW1PW91*/6-31+G(d,p) calculated relative energies of the conformers of **2** and the number of H-bonds to prove an excellent proportionality between two values.



(Chart 1. Comparison of the *mPW1PW91*/6-31+G(d,p) optimized relative stabilities of the conformers of *p*-*tert*-butylcalix[5]arene **2** and the number of H-bonds. The relative energies of **2** is proportional to the value which is obtained by one H-bond energy (~4.0 kcal/mol)¹⁶ multiplied by the scaled number (5 (the number of H-bonds in the most stable cone conformer) - the number of H-bonds).

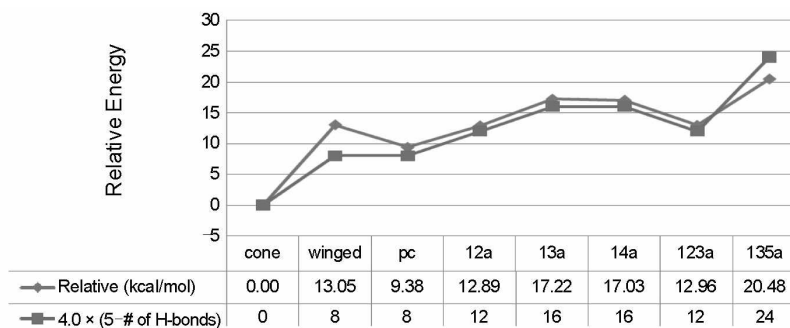


Chart 2. Comparison of the *mPW1PW91/6-31+G(d,p)* optimized relative stabilities of the conformers of calix[6]arene **3** and the number of H-bonds. The relative energies of **3** is proportional to the value which is obtained by one H-bond energy (~4.0 kcal/mol) multiplied by the scaled number (6 (the number of H-bonds in the most stable cone conformer) - the number of H-bonds).

Again, the good stability of 1,2,3-alternate conformer among the less stable conformers of **3** can be explained by the four hydrogen bonds, whereas **3** (1,3-alternate) has three H-bonds and **3** (1,3,5-alternate) has none. In Chart 2, we have compared the *mPW1PW91/6-31+G(d,p)* calculated relative energies of the conformers of **2** and the number of H-bonds to prove the proportionality between two values.

Table 5 lists the *mPW1PW91/6-31+G(d,p)* calculated distances and angles of intramolecular hydrogen bonds of *p-tert*-butylcalix[4]arene (**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.³¹ The

O...O distances of 2.645 ~ 2.777 Å in Table 5 suggest that our calculated distances of **1** are in accord with the experimental distances (2.727 ~ 2.779 Å in Table 8) of the intramolecular hydrogen bonds (O...O) of the *p-tert*-butylcalix[4]arene and calix[4]crown-5-ether obtained from Cambridge Structure Database.³¹

In order to compare our calculated H-bond distances of *t*-butylcalix[4]arene (**2**) with the values of the strong intramolecular hydrogen bonds of *t*-butylcalix[4]arene (**1**), we have tabulated the *mPW1PW91/6-31+G(d,p)* calculated H-bond distances of **2** in Table 6. The average calculated distances (2.753 ~ 2.846 Å in Table 6) of the intramolecular hydrogen bonds of *t*-butylcalix[5]arene (**2**) are long-

Table 5. *mPW1PW91/6-31+G(d,p)* Optimized Distances (Å) and Angles of Hydrogen Bonds of **1**

Conformer	H-bond	1	2	3	4	Average
1 (cone)	O...O	2.664	2.640	2.638	2.640	2.645
	H...O	1.672	1.683	1.683	1.683	1.680
	O-H	0.988	0.988	0.988	0.988	0.988
	Angle(°)	164.6	165.3	164.6	165.3	165.0
1 (partial-cone)	O...O	2.709	2.702			2.706
	H...O	1.787	1.73			1.759
	O-H	0.976	0.981			0.979
	Angle(°)	156.3	170.7			163.5
1 (1,2-alternate)	O...O	2.778	2.776			2.777
	H...O	1.827	1.824			1.826
	O-H	0.976	0.976			0.976
	Angle(°)	164.0	164.5			164.3
1 (1,3-alternate)	none					

Table 6. *mPW1PW91/6-31+(d,p)* Optimized Distances (Å) and Angles of Hydrogen Bonds of **2**

Conformer	H-bond	1	2	3	4	5	Average
2 (cone)	O...O	2.753	2.754	2.754	2.753	2.757	2.754
	H...O	1.775	1.774	1.776	1.774	1.777	1.775
	O-H	0.983	0.983	0.982	0.983	0.983	0.983
	Angle(°)	172.8	175.1	173.2	174.4	174.3	174.0
2 (partial-cone)	O...O	2.753	2.769	2.882			2.801
	H...O	1.795	1.798	1.908			1.834
	O-H	0.974	0.979	0.976			0.976
	Angle(°)	170.0	170.9	176.0			172.3
2 (1,2-alteranate)	O...O	2.717	2.754	2.786	2.756		2.753
	H...O	1.802	1.838	1.828	1.782		1.813
	O-H	0.976	0.977	0.977	0.979		0.977
	Angle(°)	154.5	154.7	165.9	173.3		162.1
2 (1,3-alteranate)	O...O	2.846					2.846
	H...O	1.878					1.878
	O-H	0.972					0.972
	Angle(°)	173.2					173.2

Table 7. *mPW1PW91* Optimized Distances (Å) and Angles (°) of Intramolecular Hydrogen Bonds of **3**

Conformer	H-bond	1	2	3	4	5	6	Average
3 (cone: <i>pinched</i>)	O...O	2.613	2.624	2.606	2.612	2.622	2.605	2.614
	H...O	1.653	1.658	1.633	1.652	1.657	1.633	1.648
	O-H	0.987	0.987	0.987	0.986	0.987	0.987	0.987
	Angle(°)	163.4	164.9	167.7	163.5	164.6	167.4	165.3
3 (cone: <i>winged</i>)	O...O	2.755	2.728	2.755	2.729			2.742
	H...O	1.836	1.812	1.836	1.813			1.824
	O-H	0.975	0.975	0.975	0.975			0.975
	Angle(°)	156.0	155.1	156.0	155.1			155.6
3 (partial-cone)	O...O	2.793	2.665	2.665	2.690			2.703
	H...O	1.852	1.701	1.687	1.709			1.737
	O-H	0.976	0.981	0.984	0.982			0.981
	Angle(°)	160.9	166.6	171.7	176.2			168.9
3 (1,2-alteranate)	O...O	2.689	2.645	2.726				2.687
	H...O	1.729	1.686	1.764				1.726
	O-H	0.976	0.980	0.976				0.977
	Angle(°)	167.2	165.3	167.9				166.8
3 (1,3-alteranate)	O...O	2.690	2.738					2.714
	H...O	1.741	1.777					1.759
	O-H	0.978	0.976					0.977
	Angle(°)	162.8	167.9					165.4
3 (1,4-alteranate)	O...O	2.717	2.736					2.727
	H...O	1.748	1.775					1.762
	O-H	0.979	0.977					0.978
	Angle(°)	169.7	167.0					168.4
3 (1,2,3-alteranate)	O...O	2.710	2.830	2.830				2.790
	H...O	1.741	1.859	1.892				1.831
	O-H	0.978	0.976	0.973				0.976
	Angle(°)	170.3	172.6	160.9				167.9
3 (1,3,5-alteranate)	none							

er than the values (2.645 ~ 2.777 Å in Table 5) of *p*-tert-butylcalix[4]arene (**1**). FTIR studies already confirmed the intramolecular character of the H-bonding and showed that it is strongest for the cyclic tetramer (**1**) and weakest for the cyclic pentamer (**2**).³⁹

Table 7 lists the *m*PW1PW91/6-31+G(d,p) optimized distances and angles of intramolecular hydrogen bonds of **3**. The O...O distances of 2.614 ~ 2.790 Å in Table 7 suggest that these calculated values in the calix[6]arene (**3**) display strong hydrogen bonds. The calculated O...O

distances (2.687 ~ 2.790 Å) of the less stable conformations of **3** are 0.07 ~ 0.15 Å longer than the value (2.614 Å) of the most stable cone conformer.

Since the *m*PW1PW91/6-31+G(d,p) optimization of the bigger *t*-butylcalix[6]arene (**4**) was not possible due to our limited computational resources, the distances and angles of the intramolecular hydrogen bonds of **4** are not listed in this publication. The average calculated O...O distances (2.614 Å of calix[6]arene (**3**) in Table 7 and 2.640 Å of *t*-butylcalix[6]arene (**4**) from the B3LYP optimization in reference 17) of the intramolecular hydrogen bonds of the cone conformers are slightly longer than the experimental crystal structure values (2.585 and 2.597 Å, respectively) in Table 8.

We have compared the *m*PW1PW91 optimized hydrogen-bond distances of **1**, **2** and **3** with the values obtained from previous B3LYP calculation method. Table 9 shows the *m*PW1PW91 optimized average O...O distances (2.645 ~ 2.777 Å) in **1** are about 0.015 Å shorter than the values (2.650 ~ 2.796 Å) of B3LYP method. The *m*PW1PW91 optimized average O...O distances (2.754 ~ 2.846 Å) in **2** are also shorter than the values (2.765 ~

Table 8. Experimental Distances(O...O) of Intramolecular Hydrogen Bonds of the Cone Conformers of Calix-[n]arenes

Molecule (CSD entry) ³¹	Average (Å)
<i>p</i> -tert-Butylcalix[4]arene 1 (XAHMOI) ³⁵	2.779
<i>p</i> -tert-Butylcalix[5]arene 2 (VETXUO) ³⁶	2.894
Calix[5]arene (UKAGIW) ³⁷	2.764
Calix[5]arene (VETYAV) ³⁶	2.780
Calix[6]arene 3 (NOBLEV) ^{31b}	2.585
<i>p</i> -tert-Butylcalix[6]arene 4 (KENBUA) ^{31b}	2.597
Calix[4]crown-5-ether (VERLUA) ³⁸	2.727

Table 9. *m*PW1PW91 Optimized Average O...O Distances (Å) of Intramolecular (O-H...O) Hydrogen Bonds of **1**, **2** and **3**

Conformer	<i>m</i> PW1PW91/6-31+(d,p)	B3LYP/6-31+(d,p) ^a	Difference ^b
1 (cone)	2.645	2.650	-0.005
1 (partial-cone)	2.706	2.718	-0.012
1 (1,2-alternate)	2.777	2.796	-0.019
2 (cone)	2.754	2.765	-0.011
2 (partial-cone)	2.801	2.810	-0.009
2 (1,2-alternate)	2.753	2.768	-0.015
2 (1,3-alternate)	2.846	2.861	-0.015
3 (cone: <i>pinched</i>)	2.614	2.640	-0.026
3 (cone: <i>winged</i>)	2.742	2.762	-0.020
3 (partial-cone)	2.703	2.712	-0.009
3 (1,2-alternate)	2.687	2.760	-0.073
3 (1,3-alternate)	2.714	2.782	-0.068
3 (1,4-alternate)	2.727	2.748	-0.021
3 (1,2,3-alternate)	2.790	2.795	-0.005
Average	2.733	2.755	-0.022

^aB3LYP calculated O...O distances are obtained from references 16 and 17. ^bDifference: *m*PW1PW91 optimized distance minus B3LYP calculated value.

Table 10. Comparison between *mPW1PW91*^a and B3LYP^b methods for the Calculated Relative Energies of the conformers of **1-4**

Conformer	<i>mPW1PW91/6-31+(d,p)</i>	B3LYP/6-31+(d,p)	Difference ^c
1 (cone)	0.00	0.00	0.00
1 (partial-cone)	7.53	8.45	-0.91
1 (1,2-alteranate)	10.85	11.59	-0.74
1 (1,3-alteranate)	12.25	14.21	-1.96
2 (cone)	0.00	0.00	0.00
2 (partial-cone)	8.49	9.70	-1.22
2 (1,2-alteranate)	4.23	5.09	-0.87
2 (1,3-alteranate)	13.48	15.15	-1.67
3 (cone: <i>pinched</i>)	0.00	0.00	0.00
3 (cone: <i>winged</i>)	13.05	13.80	-0.75
3 (partial-cone)	9.38	10.37	-0.99
3 (1,2-alteranate)	12.89	13.87	-0.98
3 (1,3-alteranate)	17.22	18.55	-1.33
3 (1,4-alteranate)	17.03	17.81	-0.77
3 (1,2,3-alteranate)	12.96	13.59	-0.62
3 (1,3,5-alteranate)	20.48	23.44	-2.96
4 (cone: <i>pinched</i>)	0.00	0.00	0.00
4 (cone: <i>winged</i>)	12.94	14.48	-1.54
4 (partial-cone)	15.20	18.03	-2.83
4 (1,2-alteranate)	7.86	10.72	-2.86
4 (1,3-alteranate)	21.48	23.58	-2.11
4 (1,4-alteranate)	13.32	13.77	-0.44
4 (1,2,3-alteranate)	19.10	20.99	-1.89
4 (1,3,5-alteranate)	20.11	27.12	-7.01

^a*mPW1PW91/6-31+(d,p)* calculated relative energies are copied from Tables 1-4. ^bB3LYP calculated relative energies are obtained from references 16 and 17. ^cDifference: *mPW1PW91* optimized relative energy minus B3LYP calculated value.

2.861 Å) of B3LYP method. The *mPW1PW91* optimized average O...O distances (2.614 ~ 2.790 Å) in **3** are about 0.022 Å shorter than the values (2.640 ~ 2.795 Å) of B3LYP method. Those *mPW1PW91* optimized distances in **3** are closer to the experimental results (2.585 Å in Table 8).

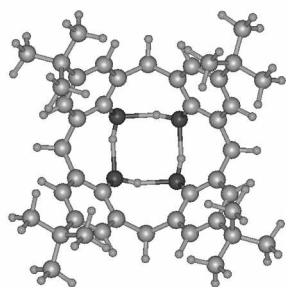
In Table 10, we have compared the relative energies of *mPW1PW91* calculations of the various conformers of **1-4** with the values obtained from previous B3LYP method. The differences in Table 10 tell us that the relative energies obtained from the *mPW1PW91* method always give smaller gap than the B3LYP calculated values. The range is -0.44 ~ -2.96 kcal/mol (average -1.2 kcal/mol) except one case (-7.01 kcal/mol) of **4** (1,3,5-alteranate).

Since the *mPW1PW91* optimized low-resolution figures of the various conformers of **1-4** are very

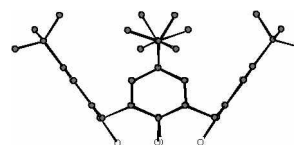
similar to the structures obtained from previously published B3LYP calculations,^{16,17} we report the structures of the most stable cone conformers for the respective molecules of **1-4** in Fig. 1. The cone conformer (**1**(cone): Fig. 1(a)) having four hydrogen bonds and **2**(cone) (Fig. 1(c)) having five hydrogen bonds are the most stable, as shown in experimental studies.^{2h,18,19} The *pinched* cone conformations of calix[6]arene (Figures 1(e) and 1(g)) having six hydrogen bonds are the most stable conformers of **3** and **4**, respectively.

CONCLUSION

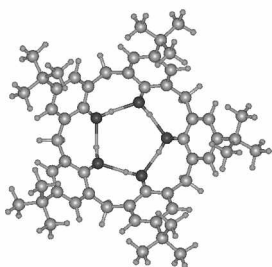
The relative stabilities of the conformers of *p*-*tert*-butylcalix[4]arene (**1**), *p*-*tert*-butylcalix[5]-arene (**2**), calix[6]arene (**3**) and *p*-*tert*-butylcalix[6]arene (**4**) were calculated by using *mPW1PW91*/



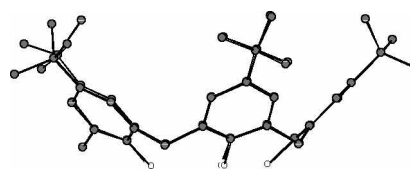
(a) 1_cone (bottom view; PosMol)



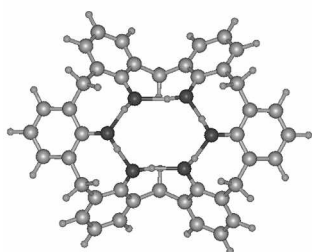
(b) 1_cone (side view; Chem3D)



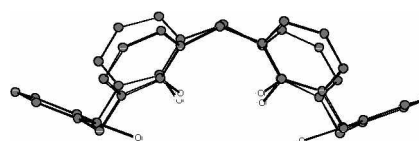
(c) 2_cone (bottom view; PosMol)



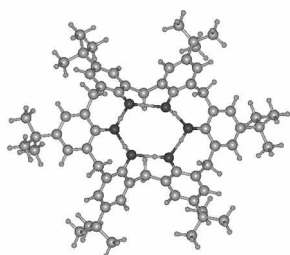
(d) 2_cone (side view; Chem3D)



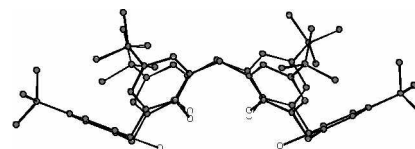
(e) 3_cone (pinched; bottom view; PosMol)



(f) 3_cone (pinched; side view; Chem3D)



(g) 4_cone (pinched; PosMol)



(h) 4_cone (pinched; Chem3D)

Fig. 1. *mPW1PW91/6-31+G(d,p)* optimized molecular structures of the cone conformers of **1-3**. (a) Bottom view of **1** (*p*-*tert*-butylcalix[4]arene) by PosMol⁴⁰ with hydrogen bonds shown, (b) side view of **1** (*p*-*tert*-butylcalix[4]arene) by Chem3D⁴¹ without hydrogen atoms, (c) bottom view of **2** (*p*-*tert*-butylcalix[5]arene) by PosMol, (d) side view of **2** (*p*-*tert*-butylcalix[5]arene), (e) bottom view of **3** *pinched* cone (calix[6]arene) by PosMol, (f) side view of **3** *pinched* cone (calix[6]arene) by Chem3D. (g) *mPW1PW91/6-31+G(d,p)* optimized molecular structures of bottom view of **4** *pinched* cone (*p*-*tert*-butylcalix[6]arene) by PosMol and (h) side view of **4** *pinched* cone (*p*-*tert*-butylcalix[6]arene) by Chem3D. Atoms that are within a certain distance (the bond proximate distance) from one another were automatically marked as bonded.⁴⁰

6-31+G(d,p) method. The relative stability of four conformers of **1** is in the following order: cone (most stable) > partial-cone > 1,2-alternate > 1,3-alternate. The relative stability of the various conformers of **2** is in the following order: cone (most stable) > 1,2-alternate > partial-cone > 1,3-alternate. The relative stability of the conformers of **3** 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 **4** were optimized by using the *mPW1PW91/6-31G(d,p)* method followed by single point calculation of *mPW1PW91/6-31+G(d,p)*. The relative stability of the conformers of **4** 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 primary factor affecting the relative stabilities of the various conformers of the **1-4** are the number and strength of the intramolecular hydrogen bonds. Each hydrogen bond contributes about 4 kcal/mol for the stability of the conformers of these calix[n]arenes.

The *mPW1PW91* optimized average H-bond distances (2.645 ~ 2.846 Å) in **1-4** are slightly shorter than the values (2.640 ~ 2.861 Å) calculated from B3LYP method.

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