1,3-디메톡시-티아캘릭스[4]크라운-5-에테르의 이형체들의 상대적인 안정성과 구조들에 대한 *m*PW1PW91 계산 연구

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*m*PW1PW91 Calculated Relative Stabilities and Structures for the Conformers of 1,3-dimethoxy-*p-tert*-butylthiacalix[4]crown-5-ether

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요 약. 1,3-디메톡시-티아캘릭스[4]크라운-5-에테르 (**3**)의 다양한 이형체들(**cone_oo, cone_oi, pc_oo, pc_io, pc_oi, pc_ii, 13a_oo, 13a_io**)에 대한 구조들이 *DFT* B3LYP/6 - 31 + G(d,p)와 *m*PW1PW91/6 - 31 + G (d,p) (hybrid HF-DF) 계산 방법들에 의하여 최적화 되었다. **13a_oo** (1,3-alternate 이형체에서 두 개의 메톡시기가 모두 밖으로 향해 있는 구조)가 가장 안정하였으며, 기존에 보고된 실험 결과와 잘 일치하였다. *m*PW1PW91/6 - 31 + G(d,p) 계산에 의한 상대적인 안정성은 다음과 같았다: **13a_oo (가장 안정) > 13a_io~ pc_io~cone_oo > cone_oi~pc_oo~pc_oi > pc_ii**.

주제어: 1,3-디메톡시-티아캘릭스[4]크라운-5-에테르, 이형체, *m*PW1PW91, 양자역학.

ABSTRACT. Molecular structures of the various conformers for the 1,3-dimethoxy-*p-tert*-butylthiacalix[4] crown-5-ether (**3**) were optimized by using *DFT* B3LYP/6 - 31 + G(d,p) and *m*PW1PW91/6 - 31 + G(d,p) (hybrid HF-DF) calculation methods. We have analyzed the energy differences and structures of eight in/out orientations (**cone_oo, cone_oi, pc_oo, pc_io, pc_oi, pc_ii, 13a_oo, 13a_io**) of two methoxy groups in three major conformations (cone, partial-cone and 1,3-alternate). The **13a_oo** (out-out orientation of the 1,3-alternate conformer) is calculated to be the most stable among eight different conformations of **3**, and in accord with the experimental result. The ordering of relative stability resulted from the *m*PW1PW91/6 - 31 + G(d,p) calculation method is following: **13a_oo > 13a_io~pc_io~cone_oo > cone_oi~pc_oo~pc_oi > pc_ii**.

Keywords: *DFT* B3LYP, *m*PW1PW91, Conformer, Thiacalix[4]crown-5-ether

INTRODUCTION

Calix[4]arene-crowns are highly selective ionophores for potassium and cesium cations.[1-4] In particular the 1,3-dimethyl ether of *p-tert*-butylcalix[4] crown-5-ether (**1**) has shown a surprisingly high K^+/Na^+ selectivity in extraction.[5]

Thiacalix[4]arenes in the presence of sulfur atoms instead of methylene groups exhibit novel structural and functional features including easy oxidation of sulfur bridges and extra binding sites, which make these compounds very interesting with potential applications such as inclusion of a variety of guest molecules, recognition of metal ions, chiral recognition, novel anion receptors, and novel dendritic-shelled molecular receptors.[6-15]

Therefore, one of the obvious classes of ionophores suitable for selective complexation of alkali metal

cations would be the thiacalix[4]arene-crowns.[16] A number of thiacalix[4]arene-crowns have already been reported by several groups, namely, 1,3-alternate thiacalix[4]arene-biscrowns,[17] bridged thiacalix[4]arene-monocrowns.[18-20] Thiacalix[4]arenes can adopt four different conformations as follows: cone, partial cone, 1,2-alternate, and 1,3-alternate.[21]

We have studied the structures, energies and vibrational frequencies of *p-tert*-butylcalix[4]crown-6-ether and its alkyl ammonium complexes using *ab initio* HF/6-31G method.[22-24] We have also reported the relative stabilities and stable structures of three different (cone, partial cone and 1,3-alternate) conformers for the 1,3-dialkyl ether of *p-tert*-butylcalix[4]crown-5-ether (**1** and **2**) and their potassium-cation complexes using the B3LYP/6 - 31 + G(d,p)// HF/6-31G method.[25,26]

Recently, the comparative theoretical study of three parent calix[4]arene analogues (calix[4]arene, thiacalix[4]arene, and homooxacalix[4]arene) has been performed using molecular dynamic simulations and density functional theory (*DFT*) methods.[27]

In this study, we have optimized the conformational isomers of *p-tert*-butylthiacalix[4]crown-5-ether (**3**) by using the *DFT* B3LYP/6 - 31 + G(d,p) and *m*PW1PW91/6 - 31 + G(d,p) (hybrid HF-DF) calculation methods. The primary objective of this research is to determine the relative stability of the different conformational isomers for **3** by using the improved *m*PW1PW91/6 - 31 + G(d,p) calculation method. The secondary objective is to compare the structures (C-S distances) obtained from the B3LYP and *m*PW1PW91 calculation methods.

COMPUTATIONAL METHODS

The initial conformations of 1,3-dimethoxy-*p-tert*-butylthiacalix[4]crown-5-ether (**3**) were constructed by using the molecular mechanics (MM), molecular dynamics (MD), and AM1 semi-empirical calculations of HyperChem.[28] In order to find optimized structures, we executed conformational search by simulated annealing method, which has been described in a previous publication.[29] The conformational isomers of **3** obtained from the MM/MD

and AM1 calculations were fully re-optimized by using the *DFT* B3LYP method to determine the relative energies and the structures of eight distinct conformations. However, better suggestion is new hybrid Hartree-Fock-density functional (HF-DF) models called the modified Perdew-Wang 1-parameter (*m*PW1) calculation method[30-32] such as *m*PW1PW91, which allows obtaining remarkable results both for covalent and noncovalent interactions.[31] The normal mode frequencies of the final structures have been calculated by the *m*PW1PW91/6-31G method. Each vibrational spectrum shows no negative value of frequency, which confirms that the optimized structure exists in the energy minimum. Consecutive *m*PW1PW91/6-31G(d,p) and *m*PW1PW91/6 - 31 + G(d,p) optimizations using Gaussian 03[33] were performed.

RESULTS AND DISCUSSION

Since the 1,3-dimethoxy derivative of *p-tert*-butylthiacalix[4]crown-5-ether (**3**) has *in* or *out* orientation of two methyl groups, we have presented two different cases (out_out and out_in) of *cone* conformer, four kinds (out_out, in_out, out_in and in_in) of partial-cone, and two cases (out_out and in_out) of 1,3-alternate analogue. As one looks at the *Scheme* 1, the 1,2-altenate conformation of **3** is not possible due to the crown-5-ether bridge.

Tables 1 and 2 report the B3LYP/6-31G(d,p) and B3LYP/6 - 31 + G(d,p) optimized energies and dipole moments of the different conformations of **3**, respectively. The *DFT* optimizations of eight conformers of **3** shows that 1,3-alternate(out_out) conformer (**13a_oo**) is the most stable. B3LYP/6 - 31 + G(d,p) calculations suggest that the **13a_oo** is found to be 2.5 and 6.1 kcal/mol more stable than cone(out_out) and partial cone(out_out) analogues, respectively. And **13a_oo** is 2.6 kcal/mol more stable than **13a_io**. Overall, the ordering of relative stability is following: **13a_oo > pc_io ～ cone_oo ～ 13a_io > cone_oi > pc_oo > pc_oi > pc_ii**. This ordering is much different from the relative stability of the conformers of the 1,3-dimethyl ether of *p-tert*-butylcalix[4]crown-5-ether (**1**) of *Table* 3,[11] in

Table 1. *DFT* B3LYP/6-31G(d,p) Optimized Total and Relative Energies and Dipole Moments (Debye)of the various Conformers of **3**.

Conformation	Abbreviation[a]	A. U.	ΔE[b]	Dipole Moment
Cone(out_out)	**cone_oo**	-4064.39276	2.64	5.27
Cone(out_in)	**cone_oi**	-4064.38732	6.05	4.90
Partial cone(out_out)	**pc_oo**	-4064.38801	5.62	4.80
Partial cone(in_out)	**pc_io**	-4064.39555	0.88	2.55
Partial cone(out_in)	**pc_oi**	-4064.38205	9.36	5.55
Partial cone(in_in)	**pc_ii**	-4064.37083	16.40	4.65
1,3-Alternate(out_out)	**13a_oo**	-4064.39696	0.00	1.61
1,3-Alternate(in_out)	**13a_io**	-4064.39472	1.41	2.34

[a]See *Figure* 1 for the list of the conformations. Cone(out_out) : **cone_oo** (*Figure* 1(a)) means that both methyl groups are outside of the lower (crown-5-ether) cavities of **3**. Partial cone(in_out): **pc_io** (*Figure* 1(g)) denotes that the upper methyl group is pointing to the inside of three benzene rings and the lower methyl group is toward outside of the crown-5-ether moiety, etc. [b]ΔE is the relative energy (kcal/mol) with respect to the most stable **13a_oo** conformer. Error limit is about 0.01 kcal/mol.

	R	R$_1$
1	te*rt*-Butyl	CH$_3$
2	te*rt*-Butyl	CH$_2$CH$_3$

3
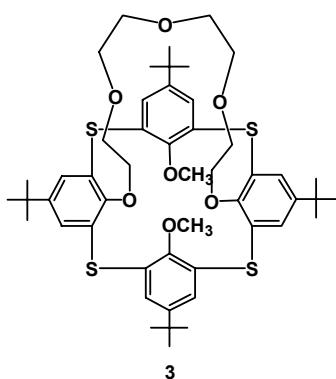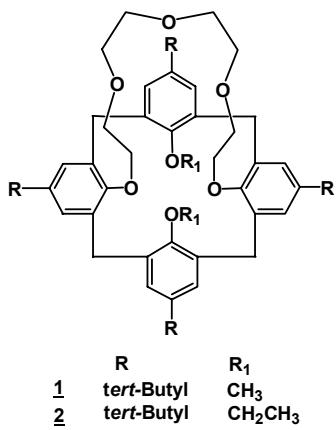
Scheme 1. Chemical drawing of 1,3-dialkoxy-*p-tert*-butylcalix[4]crown-5-ether (**1** and **2**) and 1,3-dimethoxy-*p-tert*-butylthiacalix[4]crown-5-ether (**3**).

Table 2. B3LYP/6-31+G(d,p) Calculated Total and Relative Energies and Dipole Moments (Debye) of the Conformers of **3**.

Conformation	A. U.	ΔE[a]	Dipole Moment
cone_oo	-4064.45848	2.49	6.23
cone_oi	-4064.45272	6.11	4.63
pc_oo	-4064.45267	6.14	5.20
pc_io	-4064.45866	2.38	3.36
pc_oi	-4064.44612	10.25	4.88
pc_ii	-4064.43483	17.34	4.60
13a_oo	-4064.46246	0.00	1.80
13a_io	-4064.45831	2.60	2.99

[a]ΔE is the relative energy (kcal/mol) with respect to the most stable **13a_oo** conformer.

Table 3. B3LYP/6-31+G(d,p) Calculated Total and Relative Energies[a] and Dipole Moments (Debye) of the Conformers of **1**.

Conformation	A. U.	ΔE[b]	Dipole Moment
1(cone_oo)	-2628.9807	0.0	2.00
1(pc_oo)	-2628.9757	3.1	3.55
1(13a_oo)	-2628.9709	6.2	1.54

[a]These data are taken from reference 11, where B3LYP/6-31 + G(d,p) single point calculations are performed after the HF/6-31G optimization. [b]ΔE is the relative energy (kcal/mol) with respect to the most stable **1**(cone_oo) conformer.

Table 4. mPW1PW91/6-31G Optimized Total and Relative Energies and Dipole Moments (Debye) of the Conformers for **3**.

Conformation[a]	A. U.	ΔE[b]	Dipole Moment
cone_oo	-4062.97410	2.26	7.49
cone_oi	-4062.97000	4.83	4.94
pc_oo	-4062.96992	4.88	6.23
pc_io	-4062.97770	0.00	4.32
pc_oi	-4062.97229	3.39	6.39
pc_ii	-4062.95515	14.15	5.65
13a_oo	-4062.97481	1.82	2.12
13a_io	-4062.97495	1.73	3.87

[a]See Figure 1 for the list of the conformations. [b]ΔE is the relative energy (kcal/mol) with respect to the most stable **pcio_oo** conformer.

Table 5. mPW1PW91/6-31G Calculated Gibbs Free Energies (A.U.) at 298 K and ΔG (kcal/mol) of the Conformers of **3**.

Conformation	A. U.	ΔG[a]
cone_oo	-4061.98825	0.00
cone_oi	-4061.97744	6.78
pc_oo	-4061.98207	3.87
pc_io	-4061.98774	0.32
pc_oi	-4061.98178	4.06
pc_ii	-4061.96303	15.82
13a_oo	-4061.98728	0.61
13a_io	-4061.98522	1.90

[a]ΔG is the relative Gibbs free energy with respect to the **cone_oo** conformer.

which **1_cone_oo** (most stable) **> 1_pc_oo > 1_13a_oo**.

The primary reason of the instability of 1,3-alternate conformation of **1** is the steric hindrance between two p-tert-butylbenzyl groups and crown-5-ether ring. However, the **13a_oo** conformer of **3** has almost no interference from the p-tert-butylbenzyl groups, since the calculated bond distances (~1.79 angstrom) between the bridging sulfur and carbon atoms of **3** are much longer than the values (~1.52 angstrom)[25] between bridging carbon atoms

of **1**.[27]

Using the DFT B3LYP optimized structures we have performed mPW1PW91 (a hybrid Hartree-Fock-density functional (HF-DF) model) calculations which allow obtaining remarkable results both for covalent and noncovalent interactions.[31]

We have used the mPW1PW91/6-31G method to calculate the vibrational frequencies of the optimized conformer to obtain the zero-point correction and the thermal correction to free energy. Gibbs free energies at 298 K are obtained from the mPW1PW91/6-31G calculations. Tables 4 and 5 report the mPW1PW91/6-31G optimized total electronic and Gibbs free energies of the different conformations of **3**, respectively. The relative stabilities of the eight different conformers calculated from the mPW1PW91/6-31G method is a little different from the ordering (**13_oo** is the most stable one) obtained by using the B3LYP/6-31G(d,p) and B3LYP/6-31+G(d,p). The mPW1PW91/6-31G calculations report that the **pc_io** is slightly more stable than the **13_oo** and **13_io** conformers for the total electronic energy (ΔE) in Table 4, and that the **cone_oo** shows a comparable stability with the **pc_io** and **13a_oo** analogues for the Gibbs free energy (ΔG) in Table 5. Therefore, we have performed the higher level calculations using the mPW1PW91/6-31G(d,p) and mPW1PW91/6-31+G(d,p) methods to compare the relative stabilities with the results from the B3LYP calculations.

Tables 6 and 7 report the mPW1PW91/6-31G(d,p) and mPW1PW91/6-31+G(d,p) calculated energies and dipole moments of the different conformers of **3**, respectively. The mPW1PW91 optimizations of eight conformers of **3** shows that 1,3-alternate(out_out) conformer (**13a_oo**) is again the most stable, which is the same trend as the DFT B3LYP calculated values in Tables 1 and 2. This calculated outcome is in accord with the experimental result, where the 1,3-alternate was the only observed conformation without finding cone or partial-cone conformer.[16] The mPW1PW91/6-31+G(d,p) calculations in Table 7 suggest that the **13a_oo** is found to be 2.4 and 5.9 kcal/mol more stable than the **cone_oo** and **pc_oo** conformers, respectively. And **13a_oo** is 1.4 kcal/mol more stable than **13a_io**.

Table 6. *m*PW1PW91/6-31G(d,p) Calculated Energies and Dipole Moments (Debye) of the Conformer of **3**.

Conformation	A. U.	ΔE[a]	Dipole Moment
cone_oo	-4063.85323	2.70	6.10
cone_oi	-4063.84750	6.30	4.65
pc_oo	-4063.84817	5.88	5.17
pc_io	-4063.85525	1.43	3.29
pc_oi	-4063.84804	5.96	4.93
pc_ii	-4063.83202	16.01	4.41
13a_oo	-4063.85754	0.00	1.77
13a_io	-4063.85607	0.92	3.07

[a]ΔE is the relative energy (kcal/mol) with respect to the most stable **13a_oo** conformer.

Table 7. *m*PW1PW91/6 - 31 + G(d,p) Calculated Energies[a] and Dipole Moments (Debye) of the Conformers of **3**.

Conformation	A. U.	ΔE[a]	Dipole Moment
cone_oo	-4063.90433	2.40	6.38
cone_oi	-4063.89877	5.89	4.70
pc_oo	-4063.89871	5.93	5.28
pc_io	-4063.90464	2.21	3.32
pc_oi	-4063.89854	6.03	5.05
pc_ii	-4063.88235	16.20	4.60
13a_oo	-4063.90815	0.00	1.81
13a_io	-4063.90600	1.35	3.07

[a]*m*PW1PW91/6 - 31 + G(d,p) single point calculation energy from the *m*PW1PW91/6 - 31G(d,p) optimized structure. [b]ΔE is the relative energy (kcal/mol) with respect to the most stable **13a_oo** conformer.

Overall, the ordering of relative stability is following: **13a_oo** (most stable) **> 13a_io ～ pc_io ～ cone_oo > cone_oi ～ pc_oo ～ pc_oi > pc_ii**.

When we connect the relative stabilities of the various conformers of **3** with the dipole moments in the *Tables* 1-7, the most stable **13a_oo** has the smallest dipole moment (1.81 Debye), which is much different from the **cone_oo** (6.38 Debye) and **pc_oo** (5.28 Debye). Two methoxy oxygen atoms of **13a_oo** are toward to the other side from the five oxygen atoms of the crown-5-ether bridge. These opposite directions of the oxygen atoms in the **13a_**

oo make the smallest dipole moment of this conformer, and the delocalized negative charges may contribute a reason for the good stability of **13a_oo**, compared with other conformations of **3**.

Figure 1 shows the front and side views of the various conformers of the 1,3-dimethyl ether of *p-tert*-butylthiacalix[4]crown-5-ether (**3**). The experimental structure of **3** is not reported yet. However our *m*PW1PW91/6 - 31 + G(d,p) calculated distance (1.789 Å) between the bridging sulfur and carbon atoms of **cone_oo** of **3** is very close to the experimental C-S distance (1.784 Å) of the cone conformer of unsubstituted *p-tert*-butylthiacalix[4]arene.[35] The calculated C-S distance of **cone_oo** conformer is 0.010 Å longer than the value (1.779 Å) of **13a_oo**.

The *m*PW1PW91 calculated C-S distance (1.789 Å) of **cone_oo** of **3** is about 0.014 Å shorter than the value (1.803 Å) from the B3LYP calculation. And the *m*PW1PW91 calculated value (1.779 Å) of **13a_oo** of **3** is about 0.017 Å shorter than the average C-S values (1.796 Å) from the B3LYP calculation. Therefore, the *m*PW1PW91 calculated C-S distances of **3** are normally shorter than the values obtained from B3LYP and closer to the experimental value (1.784 Å).

When one methyl moiety of two methoxy groups of the partial cone conformer of **3** is pointing to the inside of either benzene rings or crown-5-ether ring, the structure of in_out (**pc_io**) or out_in (**pc_oi**) variation of partial cone conformation is less stable than out_out analogue (**pc_oo**) of **3**. The relative stability in two cases of the **pc_io** and **pc_oi** conformers is much different. When we compare two ΔE values (2.2 and 6.0 kcal/mol of **pc_io** and **pc_oi**, respectively) in *Table* 4, the **pc_io** conformer is 3.8 kcal/mol more stable than the **pc_oi** analogue. When one look at the *Figure* 1(g), the **pc_io** has one methyl moiety pointing to the cavity of benzene rings and the other methyl group toward outside of the crown-5-ether moiety. *Figure* 1(i) of the **pc_oi** shows that one methyl moiety is outside of the benzene rings and the other methyl group points to the inside of the crown-5-ether moiety. The wider cavity of benzene rings of *Figure* 1(h) of the **pc_io** shows one of the reasons of the better stability of **pc_io** than **pc_oi**. However,
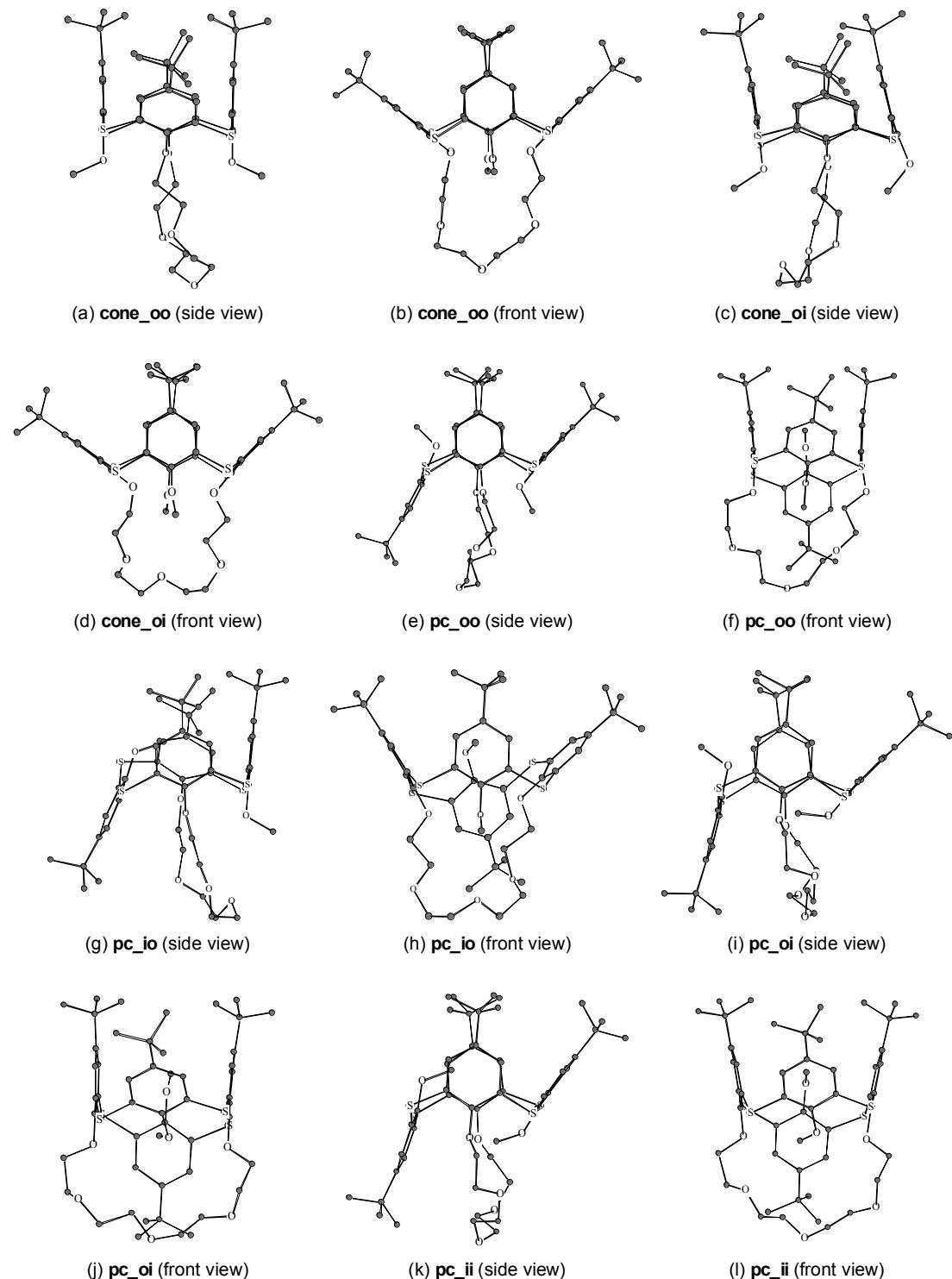
(a) **cone_oo** (side view)

(b) **cone_oo** (front view)

(c) **cone_oi** (side view)

(d) **cone_oi** (front view)

(e) **pc_oo** (side view)

(f) **pc_oo** (front view)

(g) **pc_io** (side view)

(h) **pc_io** (front view)

(i) **pc_oi** (side view)

(j) **pc_oi** (front view)

(k) **pc_ii** (side view)

(l) **pc_ii** (front view)

Figure 1. *m*PW1PW91 calculated structures (side and front views) drawn by Chem3D[34] of eight conformers of **3.**

(m) **13a_oo** (side view)

(n) **13a_oo** (front view)

(o) **13a_io** (side view)

(p) **13a_io** (front view)
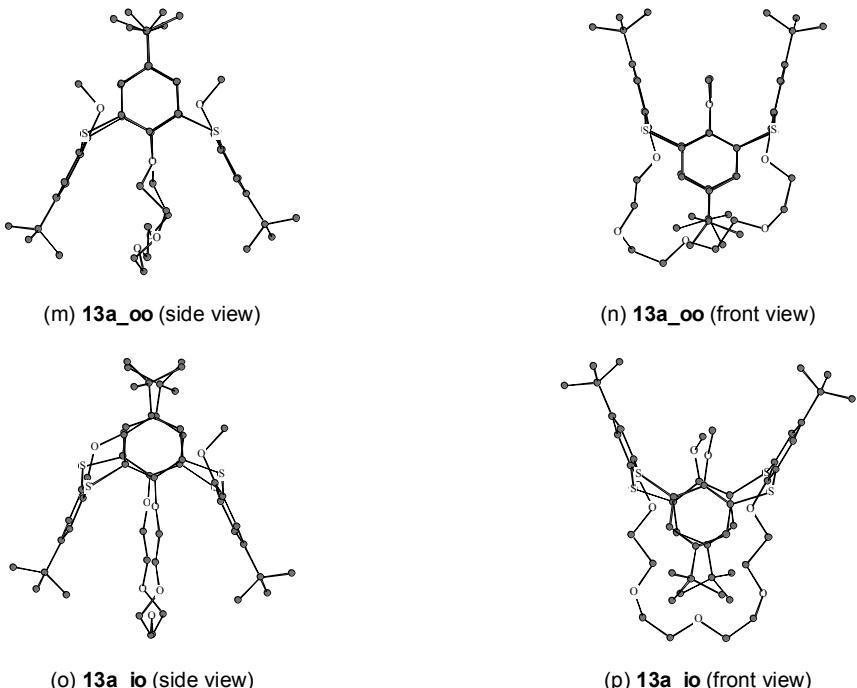
Figure 1. *m*PW1PW91 calculated structures (side and front views) drawn by Chem3D[34] of eight conformers of **3** (continued).

Figures 1(k) and 1(l) of **pc_ii** show one of the reasons of the worst stability due to the steric hindrances between the two methyl groups and both of the benzene rings and the crown-5-ether moiety.

CONCLUSION

*m*PW1PW91/6 - 31 + G(d,p) optimizations for the 1,3-dimethyl ether of *p-tert*-butylthiacalix[4]crown-5-ether (**3**) suggest that the **13a_oo** (out-out orientation of the 1,3-alternate conformer) is calculated to be the most stable among eight different conformations of **3.** The ordering of relative stability is following: **13a_oo** (most stable) **> 13a_io ～ pc_io ～ cone_oo > cone_oi ～ pc_oo ～ pc_oi > pc_ii**. This ordering is different from the 1,3-dimethyl ether of *p-tert*-butylcalix[4]crown-5-ether (**1**), in which **1**(cone_oo: most stable) **> 1**(pc_oo) **> 1** (13a_oo).

The *m*PW1PW91/6 - 31 + G(d,p) calculated bond distances (1.789 Å) between the bridging sulfur and carbon atoms of **3** is 0.014 Å shorter than the average C-S values (1.803 Å) from the B3LYP calculations of **3** and closer to the experimental value (1.784 Å) of the cone conformer of *p-tert*-butylthiacalix[4]arene.

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