Ab Initio Calculated Structures and Vibrational Spectra of 1,3-Diethoxy-*p-tert*-butylcalix[4]crown-5-ether Complexed with Potassium Cation

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Molecular structures were optimized for the 1,3-diethoxycalix[4]crown-5-ether (**2**) in the various isomers and their potassium-ion complexes by using B3LYP/6-31+G(d,p)//B1LYP/6-31G(d,p) method after *ab initio* RHF/6-31G calculation. The *cone*-shaped isomer of **2** with *cr*-binding mode has shown the strongest binding efficiency among the six different complexes attributed to seven electrostatic interactions between the potassium cation and the oxygen atoms of crown-5-ether and ethoxy groups of the host (**2**). The vibrational spectra of **2** and its K$^+$-complexes were obtained by restricted Hartree-Fock (RHF) calculations with the 6-31G basis set. The characteristic vibrational frequencies of various C-O-C stretching and bending motions are analyzed.

Key Words : 1,3-Diethoxycalix[4]crown-5-ether, Complexation, Potassium cation, *Ab initio* calculation, Vibrational spectrum

Introduction

The selective 1,3-dialkylation of *p-tert*-butylcalix[4]arene followed by the introduction of suitable polyether bridges on the two remaining OH groups has generated a new family of potassium selective ionophores.[1-3] 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.[2] The complexation of alkali metal cations by conformationally rigid calix[4]crown ethers has been studied by ^{1}H NMR experiment, and X-ray crystal structures of 1,3-dialkoxy-calix[4]crown-5-ether were reported.[4] Along with these efforts, a theoretical study of the stereochemical dependence of alkali metal ion complexation and liquid-liquid extraction of alkali cations by 1,3-dimethoxy-calix[4]crown-6-ether has been reported.[5] Recently, *endo-* or *exo*-complexation of calix[4]arene with alkali metal cations has been analyzed by HF, MP2 and DFT calculations.[6]

Great progress for computational facilities provides an opportunity to study the relatively large and complicated supramolecular system.[7] 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* RHF/6-31G method.[8,9] We have also undertaken the relative binding affinity study of cone-shaped *p-tert*-butylcalix[4]aryl esters toward alkali metal cations focusing on the binding site of upper or lower-rim pocket of the host molecule using the B3LYP/6-31G(d)//HF/6-31G method.[10] The B3LYP/6-31G(d) calculation suggested that *exo*-complexation efficiency of potassium ion inside the cavity of lower rim of *p-tert*-butylcalix[4]aryl esters was better than the *endo*-complexation inside the upper rim (four aromatic rings). Recently, we have reported the relative stabilities and stable structures of three different (cone, partial cone and 1,3-alternate) conformers for the 1,3-dimethyl ether of *p-tert*-butylcalix[4]crown-5-ether (**1**) and their potassium-

	R	R$_1$
1	*tert*-Butyl	CH$_3$
2	*tert*-Butyl	CH$_2$CH$_3$
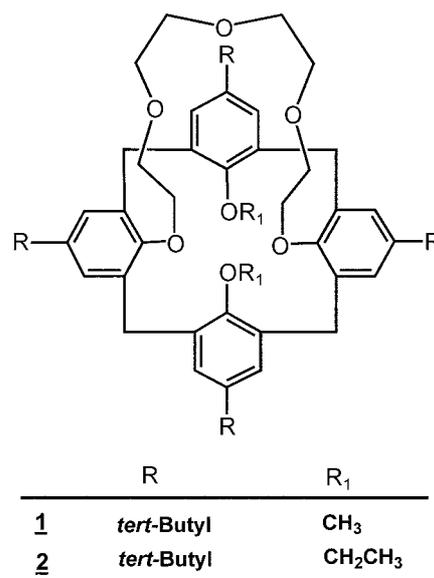
Scheme 1. Chemical drawing of 1,3-dialkoxy-*p-tert*-butylcalix[4]-crown-5-ether.

cation complexes using the B3LYP/6-31+G(d,p)//HF/6-31G method.[11] However, the experimental study[4] suggested that 1,3-diethyl ether derivative (**2**) gave better binding free energy of complexes of host with alkali picrates than the host **1**. Therefore, we have optimized the various isomers of host **2** and their K$^+$-complexes and the vibrational frequencies of the host **2** by using the *ab initio* method in this study.

Computational Methods

The initial conformations of 1,3-diethoxy-*p-tert*-butyl-calix[4]crown-5-ether host (**2**) were constructed by Hyper-Chem.[12] In order to find optimized structures, we executed conformational search by simulated annealing method.[13]

Table 1. Calculated energies of the isomers for the 1,3-diethyl ether of *p*-tert-butylcalix[4]crown-5-ether (**2**)

Host	Figure[a]	Method[b]	A.U.	kcal mol^{-1}	ΔE[c]
Cone(out)	Fig. 1(a) and (b)	HF/6-31G	−2688.9071	−1687314.9	3.2
		B1LYP/6-31G(d,p)	−2706.0447	−1698068.9	0.0
		B3LYP/6-31+G(d,p)	−2707.6211	−1699058.1	0.0
Cone(in)	Fig. 1(c) and (d)	HF/6-31G	−2688.8912	−1687304.9	13.1
		B1LYP/6-31G(d,p)	−2706.0365	−1698063.7	5.2
		B3LYP/6-31+G(d,p)	−2707.6115	−1699052.1	6.0
Partial cone	Fig. 1(e) and (f)	HF/6-31G	−2688.9121	−1687318.0	0.1
		B1LYP/6-31G(d,p)	−2706.0380	−1698064.7	4.2
		B3LYP/6-31+G(d,p)	−2707.6179	−1699056.1	2.0
1,3-Alternate	Fig. 1(g) and (h)	HF/6-31G	−2688.9122	−1687318.1	0.0
		B1LYP/6-31G(d,p)	−2706.0419	−1698067.1	1.8
		B3LYP/6-31+G(d,p)	−2707.6182	−1699056.3	1.8

[a]Figure 1(a) is the side view, and Figure 1(b) is the front view of cone isomer, *etc*. [b]HF/6-31G and B1LYP/6-31G(d,p) methods show the optimized energies. However B3LYP/6-31+G(d,p) calculation gives single point energy. [c]ΔE is the relative energy (kcal/mol) with respect to the most stable isomer of free host for each calculation method.

The potassium complexes of **2** were fully re-optimized using *ab initio* methods to estimate the absolute and relative energies for the different complexes after semi-empirical AM1 energy minimization. RHF/6-31G optimizations of various conformers of host **2** and their K$^+$-complexes of **2** by Gaussian 98[14] were done with error limit of less than 0.01 kcal/mol (2×10^{-6} atomic unit(A.U.)) for each structure. Then, B1LYP/6-31G(d,p) optimization and B3LYP/6-31+G (d,p) single point calculation of the final structure were performed. We calculated the normal mode frequencies of the optimized host and complexes using RHF/6-31G method. To directly compare with any future experimental data, the calculated frequencies were scaled following the recommended scale factor of 0.893.[15] Furthermore, the broadened IR spectra were presented assuming a Lorentzian line width of 30 cm^{-1}.

Results and Discussion

Since the ethoxy derivative (**2**) of calix[4]crown-5-ether have more variations on the orientation of ethyl group than the methoxy host (**1**), we have presented two different cases of *cone* isomer. *Cone$_{out}$* of Figure 1(a) means that ethyl group is projecting outward from crown-ether ring. *Cone$_{in}$* of Figure 1(c) denotes that ethyl group is projecting toward inside the ring.

Table 1 reports the HF/6-31G and B1LYP/6-31G(d,p) optimized energies and their B3LYP/6-31+G(d,p) single point energies of the different isomers of the host **2**. These HF and DFT calculations present slightly different energy-orderings for the bare host. HF/6-31G optimization of host **2** shows that *partial-cone* and *1,3-alternate* isomers have a similar stability, and they are 3.2 kcal mol^{-1} more stable than *cone$_{out}$* analogue, which is 9.9 kcal mol^{-1} more stable than the *cone$_{in}$* isomer (*partial cone ~ 1,3-alternate > cone$_{out}$ > cone$_{in}$*). However, B3LYP/6-31+G(d,p) calculation suggests that *cone$_{out}$* isomer of **2** is found to be 2.0 and 1.8 kcal mol^{-1} more stable than *partial cone* and *1,3-alternate* analogues, respectively, and 6.0 kcal mol^{-1} more stable than *cone$_{in}$*

isomer (*cone$_{out}$ > partial cone ~ 1,3-alternate > cone$_{in}$*). Figure 1 shows the front and side views of the stable isomers of the 1,3-diethyl ether of *p-tert*-butylcalix[4]crown-5-ether (**2**).

The *ab initio* HF/6-31G and B1LYP/6-31G(d,p) full optimizations without any constraint were carried out for six kinds of complexation mode: combining cone, partial-cone, or 1,3-alternate isomer of host **2** with potassium cation in two different locations (the crown-5-ether (*cr*) and benzene-rings (*bz*) pocket) of the calix[4]crown-5-ether.

Table 2 reports the HF/6-31G and B1LYP/6-31G(d,p) optimized energies and their B3LYP/6-31+G(d,p) single point energies of the complexes obtained from three isomers with two different binding modes. The potassium cation in the crown-5-ether moiety (*cr*) has much better complexation efficiency than in the benzene-rings pocket (*bz*) for the three kinds of isomers of host **2**.

Figures 2 and 3 show the side and front views of the optimized structures of **2** complexed in crown-ether moiety (*cr*-mode) and in aromatic rings (*bz*-mode) with potassium ion, respectively. The binding energies in the complexation of K$^+$ with the host **2** are coming from the multiple electrostatic interactions between the potassium cation and the oxygen atoms in crown-5-ether ring and ethoxy groups, and from the cation-π interactions between K$^+$ and the aromatic rings. The *cr*-binding complexes are 20-30 kcal/mol more stable than the *bz*-binding modes for most cases of the isomers in Table 2. The weaker *bz*-complexation efficiency is originated from the fewer number of electrostatic inter-actions of potassium cation with the ligand sites of oxygen atoms in host. The strongest binding efficiency among the six different complexes is obtained for the cone-shaped isomer with *cr*-binding mode, attributed to seven electrostatic interactions between the potassium cation and the oxygen atoms of crown-5-ether and ethoxy groups. Table 2 presents the six kinds of binding modes explicitly. We will omit other detailed discussions, since the analyses of the relative strengths of the interactions in the various *cr*- and *bz*-complexes are already reported in the previous publication of the methoxy-host (**1**).[11] Instead, we will focus on the
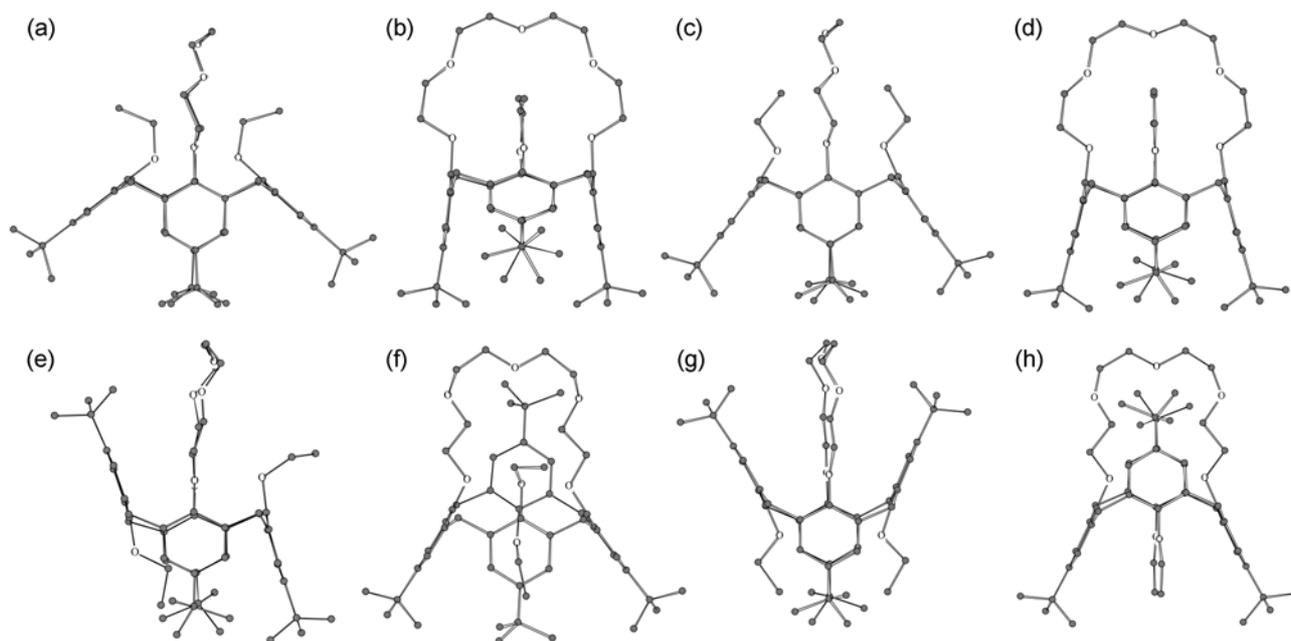
Figure 1. *Ab initio* calculated structures of host **1**. (a) Side view and (b) front view of *cone_out* conformer, (c) side view and (d) front view of *cone_in* conformer, (e) side view and (f) front view of partial-cone conformer, (g) side view and (h) front view of 1,3-alternate conformer.

**Table 2**. Energetic data (kcal mol^{-1}) of different complexes of host (**2**) with potassium cation

	Binding mode^a		Method	$\Delta E_{complex}{}^b$	$\Delta E_{rel}{}^c$	$\Delta E_{comp}{}^d$
cr	CONE	$5O_{ether}+2O_{methoxy}$	HF/6-31G	−88.4	0.0	0.0
			B1LYP/6-31G(d,p)	−80.6	0.0	1.0
			B3LYP/6-31+G(d,p)	−74.2	0.0	0.1
	PACO	$5O_{ether}+1O_{methoxy}+1A_{weak}$	HF/6-31G	−82.7	5.7	8.8
			B1LYP/6-31G(d,p)	−76.3	4.3	1.0
			B3LYP/6-31+G(d,p)	−68.0	6.2	4.3
	13ALT	$5O_{ether}+2A_{weak}$	HF/6-31G	−82.7	5.7	8.9
			B1LYP/6-31G(d,p)	−79.8	0.8	0.0
			B3LYP/6-31+G(d,p)	−72.5	1.7	0.0
bz	CONE	$2O_{ether}+2A_{strong}+2A_{weak}$	HF/6-31G	−59.6	28.7	28.7
			B1LYP/6-31G(d,p)	−57.5	23.1	24.1
			B3LYP/6-31+G(d,p)	−51.7	22.5	22.6
	PACO	$2O_{ether}+2A_{strong}+1A_{weak}$	HF/6-31G	−55.2	33.2	36.3
			B1LYP/6-31G(d,p)	−55.3	25.3	22.0
			B3LYP/6-31+G(d,p)	−48.5	25.8	23.9
	13ALT	$2O_{methoxy}+2A_{medium}$	HF/6-31G	−68.3	20.0	23.2
			B1LYP/6-31G(d,p)	−61.4	19.2	18.3
			B3LYP/6-31+G(d,p)	−55.1	19.1	17.4

^{a}*cr* indicates crown-5-ether pocket binding, and *bz* means benzene-rings pocket mode. PACO is partial cone, and 13ALT is 1,3-alternate isomer. O_{ether} indicates that the complex has a strong cation-oxygen (of crown-ether) interaction. $O_{methoxy}$ means strong cation-oxygen (of methoxy group) interaction. A_{strong} indicates that the complex has a strong cation-π (of arene) interaction between potassium ion and benzene-ring with ~3.0 Angstrom which is similar to the distance between K$^+$ and the centroid of anisole ring reported in reference 16. $^b\Delta E_{complex}$ is defined as the total energy of the complex minus the sum of the total energies of the cation and the most stable free ligand conformation. HF ΔE values are given with respect to the 13ALT conformation of the bare host (the lowest-energy HF structure). B1LYP and B3LYP ΔE values are with respect to the CONE conformation of the bare host. $^c\Delta E_{rel}$ is defined as the binding energies relative to that of the most strongly bound complex. $^d\Delta E_{comp}$ is defined as the total energy of the complex minus the sum of the total energies of the cation and the binding conformer of the free ligand and reported relative to the most strongly bound complex. These values provide a quantitative measure of the degree of cation *complementarity* associated with each binding mode.[17]

calculated vibrational modes of the cone-shaped host **2** and some of the *cr*-complexes of the different isomers.

The theoretical IR spectrum for the host-molecule in *cone_in* isomer (Figure 1(c)) is shown in Figure 4(a). The *cone_in* isomer is chosen instead of the *cone_out* isomer, since

the *cone_in* K$^+$-complex is more stable than the *cone_out* K$^+$-complex. The spectrum is characterized with several vibrational groups, which consist of the lower vibrational frequencies than 1300 cm^{-1}, the middle vibrational frequencies around 1450 and 1700 cm^{-1}, and the high frequencies of the
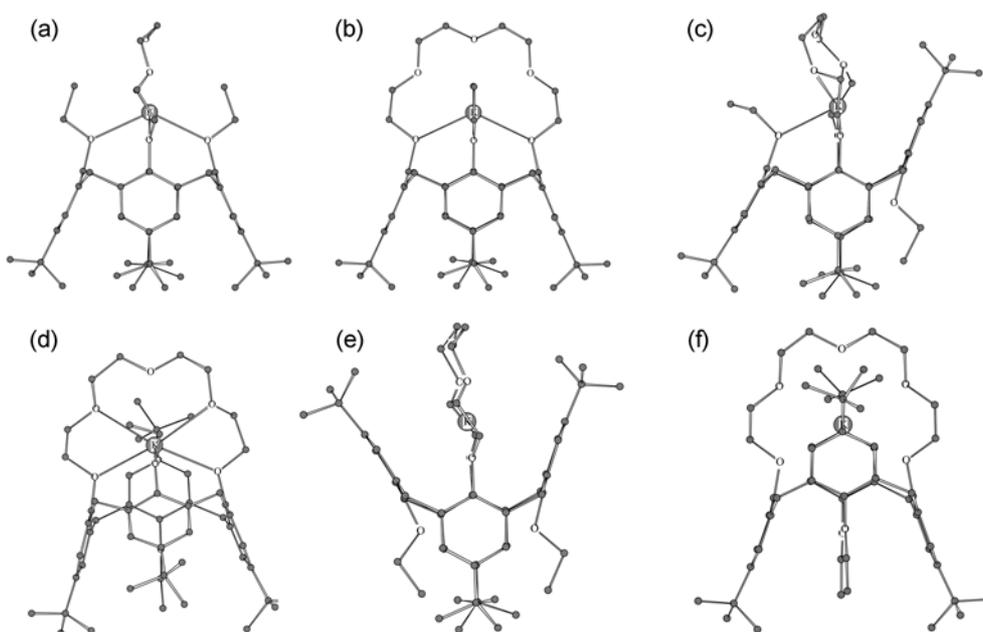
Figure 2. *Ab initio* calculated structures of *cr*-complex **2**+K^{+}. (a) Side view and (b) front view of *cone_in* conformer, (c) side view and (d) front view of *partial-cone* conformer, (e) side view and (f) front view of *1,3-alternate* conformer. Atoms that are within a certain distance (the bond proximate distance) from one another were automatically marked as bonded.[18]
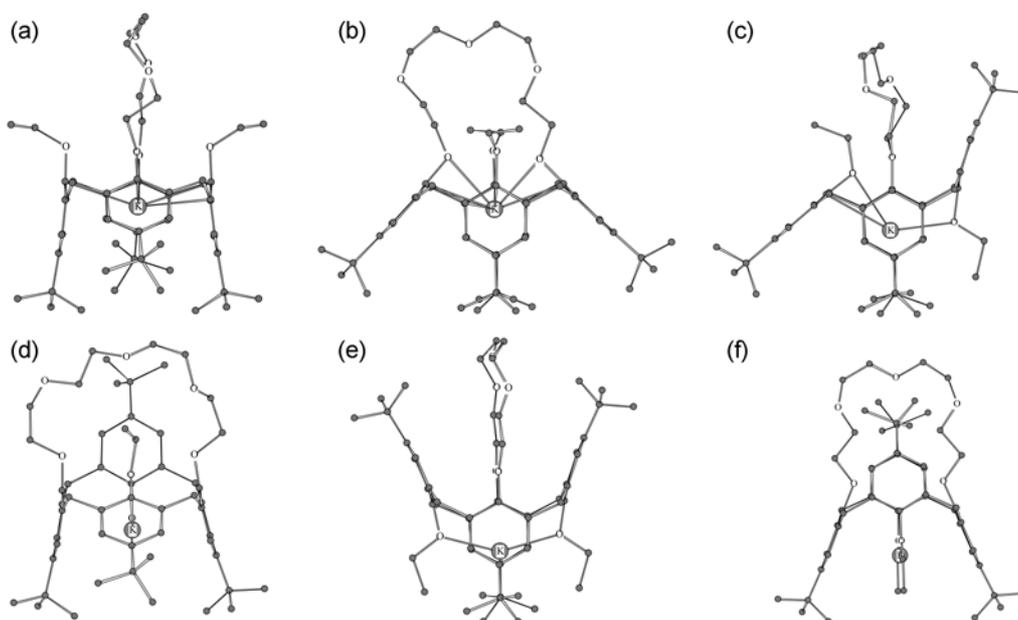

Figure 3. *Ab initio* calculated structures of *bz*-complex **2**+K^{+}. (a) Side view and (b) front view of *cone_in* conformer, (c) side view and (d) front view of *partial-cone* conformer, (e) side view and (f) front view of *1,3-alternate* conformer.

non-interacting CH stretching above 2900 cm^{-1}. The lower vibrational frequencies were mainly assigned to the various C-O-C stretching motions of the 1,3-diethoxy-*p-tert*-butyl-calix[4]crown-5-ether. On the other hand, the frequencies around 1450 cm^{-1} correspond to the CC stretching motions of the ethyl groups and benzene rings. The high frequencies above 2900 cm^{-1} consists of lots of small peaks from numerous CH stretching motions. Thus, the IR spectrum of the host-molecule is well characterized with these vibrational groups. Note that the broadened spectrum has a little differ-

ent shape from the bar spectrum, since some peaks over-lapped each other due to the degenerate or almost degenerate vibrational states. For example, although there are lots of small peaks around 1100 cm^{-1}, the corresponding peak becomes strong after broadening the bar spectrum using the assumption of a Lorentzian line shape.

Figure 4(b) shows the theoretical IR spectrum of the range between 900 and 1300 cm^{-1} for the *cone_in*-shaped host **2** (Figure 1(c)). Figure 4(c) and 4(d) show the IR spectra calculated for the **2**+K^{+} *cone_in*-complex (Figure 2(a)) and
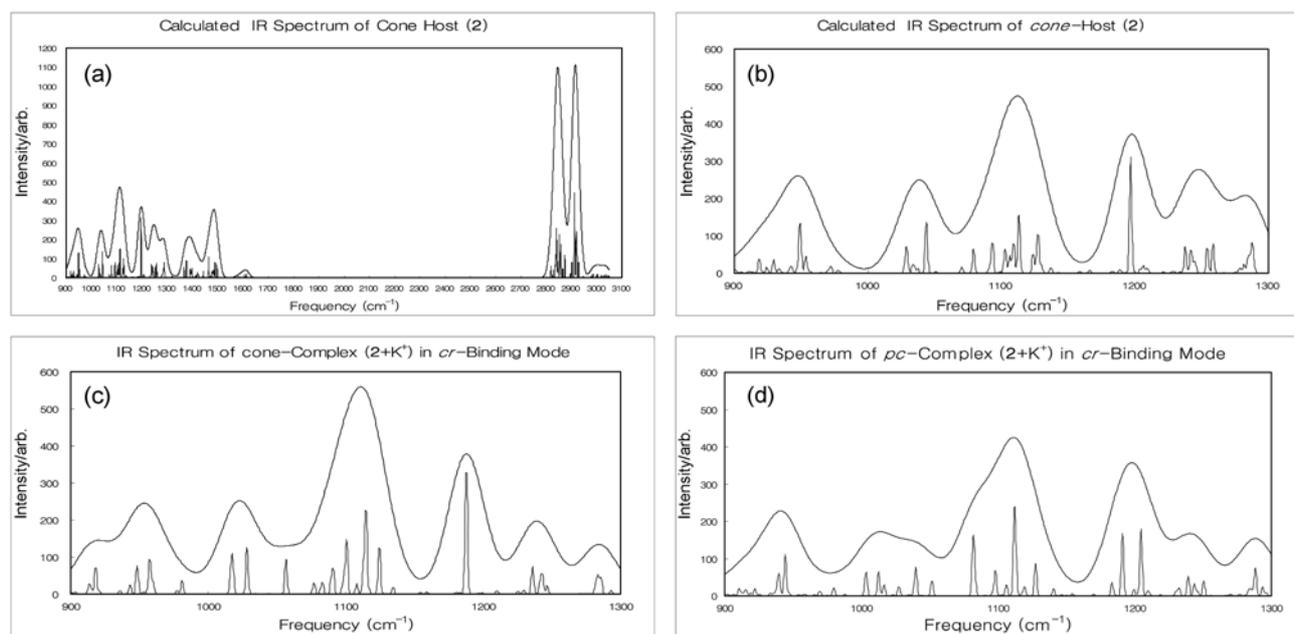
Figure 4. Calculated IR spectra of (a) the range between 900 and 3100 cm^{-1} and (b) the range between 900-1300 cm^{-1} of *cone$_{in}$*-shaped 1,3-diethoxy-*p-tert*-butylcalix[4]crown-5-ether **2** as the host molecule, and (c) **2$_{cone}$**+K$^+$ complex and (d) **2$_{pc}$**+K$^+$ complex in *cr*-binding mode. In each figure, the upper trace is presented as the broadened IR spectrum assuming a Lorentzian line width of 30 cm^{-1} to simulate the experimental spectrum, and the lower spectrum as line width of 2 cm^{-1} to show the vibrational frequencies.

Table 3. Main features of calculated vibrational modes of the host (**2**)^a and the complexes with potassium cation

Peak No.	Host **2$_{cone}$**			**2$_{cone}$**+K$^+$		**2$_{pc}$**+K$^+$		
	Energy/ cm^{-1}	Int.^{b}	Main Vibrational modes	Energy/ cm^{-1}	Int.	Main Vibrational modes	Energy/ cm^{-1}	Int.
1	918	31	CH$_2$-CH$_2$ + anti-symmetric stretchings of C-O$_{ether1,5}$-C + C-O$_{ethoxy1,2}$-C	918	77	anti-symmetric stretchings of C-O$_{ether1,5}$-C	922	19
	930	39	CH$_2$-CH$_2$ anti-symmetric Stretching + C-O$_{ether2,4}$-C bending	914	15	Same as host	940	56
	949	121	anti-symmetric stretchings of C-O$_{ether1,2,4,5}$-C + C-O$_{ether3}$-C bending	958	61	Same as host	944	112
	954	38	O$_{ether}$-C-C bending	948	77	weak		
2	1028 1029	43 46	O$_{ethoxy}$-C-C anti-symmetric stretching	1017 1018	67 79	O$_{ethoxy1}$-CH$_2$-CH$_3$ anti-symmetric stretching	1004	66
						O$_{ethoxy2}$-CH$_2$-CH$_3$ anti-symmetric stretching	1013	66
	1043 1045	82 49	C-O$_{ether}$-C stretching + CH$_2$-CH$_2$ stretching	1028	126	C-O$_{ether2,4}$-C stretchings + CH$_2$-CH$_2$ stretchings	1040	82
				1056	94	stretchings of C-O$_{ether1,3,5}$-C	1052	40
3	1093	86	anti-symmetric stretchings of C-O$_{ether2,3,4}$-C + C$_{bz}$-C$_{bz}$ stretching	1101	147	Same as host	1082	160
							1098	69
	1113	163	anti-symmetric stretchings of C-O$_{ether2}$-C + C-O$_{ether4}$-C	1114	239	anti-symmetric stretchings of all C-O-C + C$_{bz}$-O$_{ethoxy3}$	1113	255
	1127	97	anti-symmetric stretchings of all C-O-C	1124	133	Same as host	1127	82
4	1197	314	C$_{bz}$-O$_{ethoxy}$ stretching + C-C$_{bz}$-C bending	1188	361	C$_{bz}$-O$_{ether2,3,4}$ stretching + C-C$_{bz}$-C bending	1191	167
						C$_{bz}$-O$_{ethoxy1}$ stretching + C-C$_{bz}$-C bending	1205	181

^{a}**2$_{cone}$** means the cone conformation of Host **2**, and **2$_{pc}$** means the partial cone conformation of Host **2**. ^{b}Calculated Infrared Intensity from RHF/6-31G method

partial-cone-complex (Figure 2(c)), respectively.

Table 3 summarized the calculated vibrational frequencies and intensities of several strong IR peaks of the host **2** and two different complexes with potassium cation. The small peak located at 918 cm^{-1} of *cone*$_{in}$-host **2** is assigned for a concerted vibration of four anti-symmetric stretching modes of C-O$_{ether1,5}$-C and C-O$_{ethoxy1,2}$-C moieties and CH$_2$-CH$_2$ stretchings in the crown-ether. The same peak gets stronger in the **2**+K$^+$ *cone*-complex due to a synchronized vibration anchored by the potassium guest. However, the intensity in **2**+K$^+$ *partial-cone*-complex becomes much weaker in the less-symmetric isomer. The peak located at 930 cm^{-1} for four CH$_2$-CH$_2$ anti-symmetric stretching and C-O$_{ether2,4}$-C bending motions in the crown-ether moiety of *cone*-host **2** should be moved down to 16 cm^{-1} lower frequency (914 cm^{-1}) and weaker for the **2**+K$^+$ *cone*-complex due to the bridging of the potassium ion upon formation of the complex. The medium peak located at 949 cm^{-1} of host **2** for the concerted anti-symmetric stretchings of C-O$_{ether1,2,4,5}$-C and C-O$_{ether3}$-C bending motions in the crown-ether moiety moved up at 958 cm^{-1} with weaker intensity hindered by the guest cation.

The almost degenerate peaks at 1028 and 1029 cm^{-1} for two kinds of the O$_{ethoxy1-or-2}$-CH$_2$-CH$_3$ anti-symmetric stretching vibration of cone-host **2** are moved down to 11 cm^{-1} lower frequencies (1017 and 1018 cm^{-1}) for **2**+K$^+$ *cone*-complex due to the anchoring of the potassium cation, and should be moved down and split further into two peaks (1004 and 1013 cm^{-1}) for **2**+K$^+$ *partial-cone* analogue due to the less-symmetric structure.

The strong peak at 1197 cm^{-1} for four kinds of C$_{bz}$-O$_{ethoxy}$ stretching + C-C$_{bz}$-C bending motions shown in the host spectrum should be moved down to 9 cm^{-1} lower frequency (around 1188 cm^{-1}) due to the bridging of potassium ion upon formation of the *cone*-complex, and should be moved down and split further into two peaks (1191 and 1205 cm^{-1}) for **2**+K$^+$ *partial-cone* analogue. The peak at 1191 cm^{-1} of the **2**+K$^+$ *partial-cone* complex represent the three kinds of C$_{bz}$-O$_{ethoxy2,3,4}$ stretching modes and the peak at 1205 cm^{-1} represent the C$_{bz}$-O$_{ethoxy1}$ stretching mode of the partial-cone isomer. Thus, the complexation of the *partial-cone* isomer and potassium ion could be confirmed by the presence of this broader diagnostic band in the IR spectra.

Conclusion

B3LYP/6-31+G(d,p) calculations suggest that the relative stability of the different isomers of 1,3-diethoxy-*p-tert*-butylcalix[4]crown-6-ether (**2**) is in following order: cone (out, most stable) > partial cone ~ 1,3-alternate > cone (in). The potassium cation in the crown-5-ether moiety (*cr*) has much better complexation efficiency than in the benzene-rings (*bz*) pocket for all kinds of conformation of host **2**. The relative stability of three conformations for *cr*-complex (**2**+K$^+$) is: cone > 1,3-alternate ~ partial-cone isomer. The number of cation-oxygen interactions in crown-5-ether ring and ethoxy groups with potassium cation was crucial to the

stability of the different conformation of **2**+K$^+$ complex.

Theoretical infrared (IR) absorption spectra were calculated for the 1,3-diethoxy-*p-tert*-butylcalix[4]crown-5-ether (**2**) in the cone isomer and its alkali-metal-ion complexes. The vibrational frequencies for the host molecule **2**$_{cone}$ are compared with those of its complexes (**2**$_{cone}$+K$^+$ and **2**$_{pc}$+K$^+$), and found that the calculated results agree well with the structural features of the complexes. The diagnostic differences in the IR spectra should provide us the key to understand more deeply the host-guest molecular structures by enabling to assign and distinguish the individual and complexed molecular states.

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