

알칼리금속 양이온과 착물을 형성한 캘릭스[4]아릴에스터의 진동스펙트럼에 대한 순수양자역학적 연구

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Ab Initio Study of Vibrational Spectra of *p-tert*-Butylcalix[4]aryl Ester Complexed with Alkali Metal Cation

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요 약. 콘-이형체 모양의 캘릭스[4]아릴에스터 호스트(1)와 그것의 알칼리 금속 양이온과의 착물에 대하여 이론적인 적외선 흡수 스펙트럼들이 계산되었다. 진동 스펙트럼들은 RHF/6-31G 방법으로 최적화된 후에 얻어졌다. 1+Na⁺ 착물의 여러 가지 C-O와 C=O 신축 운동들의 특징적인 진동수들은 C_{2v} 형태의 분자 모양을 입증하여 주는 데에 반하여, 1+K⁺ 착물의 구조는 C_{4v}에 가깝다는 것을 보여 주었다. 호스트 분자(1)와 1+Na⁺ 착물에 대한 이론적인 결과와 실험 스펙트럼들을 비교하였을 때, 계산된 진동수들이 실험 데이터와 잘 일치하는 것을 알 수 있었다.

주제어: 캘릭스[4]아릴 에스터, 알칼리 금속 이온, 적외선 스펙트럼, RHF/6-31G 양자역학

ABSTRACT. Theoretical infrared(IR) absorption spectra were calculated for the ethyl ester of *p-tert*-butylcalix[4]arene (1) in the cone conformer and its alkali-metal-ion complex. The vibrational spectra were obtained by restricted Hartree-Fock (RHF) calculations with the 6-31G basis set. The characteristic vibrational frequencies of various C-O and C=O stretching motions of the complexes show that the structure of 1+K⁺ complex is almost of C_{4v} symmetry compared to 1+Na⁺ (C_{2v}) analogue. The theoretical results for the host molecule 1 and complex (1+Na⁺) were compared with the experimental results, and the calculated vibrational frequencies agree well with the features of the experimental spectra.

Keywords: Calix[4]aryl Ester, Complexation, Alkali Metal ion, *Ab initio* Calculation, Vibrational spectra

INTRODUCTION

The calixarenes having well-defined molecular framework are particularly attractive as a basic skeleton for the construction of new supramolecular systems.¹ The alkali metal ions have received much attention as guests due to the selectivity shown by particular calixarenes² in alkali cation coordination. The most extensively studied properties of calixarenes are the recognition of metal ions in the hydrophilic and polar region created after functionalization of the lower rim, and the inclusion of neutral molecules in the apolar cavity by the interaction with the aromatic nuclei.²⁻⁴ Earlier, Chang *et al.*⁵ as well as McKervey group⁶ suggested the possibility of introducing carbonyl containing substituents, expecting that ester moiety might be able to act cooperatively as efficient ligating groups attached to the calixarene substructure. They reported the decisive peak selectivity of

sodium ion among alkali metal cations by the calix[4]aryl esters. Wipff group has performed molecular dynamics studies on complexation characteristics of alkali metal cations with a series of important ionophores derived from calix [4]arenes.⁷ Kinetics and mechanism of the sodium ion complexation by tetramethoxy derivative of *p*-*tert*-butylcalix[4]arene have been reported experimentally.⁸

Hay *et al.* calculated the complexation behaviors of sodium and cesium cations with tetramethoxycalix[4]arene using a combined density-functional theory and second-order perturbation theory.⁹ Recently, *endo*- or *exo*-complexation of calix[4]arene with alkali metal cations has been analyzed by HF, MP2 and DFT calculations.¹⁰

Great progress for computational facilities provides us an opportunity to study the relatively large and complicated supramolecular system. We have studied the structures and energies of the cone-shaped *p*-*tert*-butylcalix[4]crown-6-ether and its alkyl ammonium complexes using *ab initio* RHF/6-31G method.¹¹ By a series of calculations the central part of the crown moiety is confirmed to be the primary binding site of *p*-*tert*-butylcalix[4]crown-6-ether for the recognition of alkyl ammonium guests in the cone conformation. We have also reported the calculated vibrational spectra for the cone conformation of *p*-*tert*-butylcalix[4]crown-6-ether and its ethyl ammonium complex using *ab initio* RHF/6-31G method.¹²

Recently our conformational study of tetraethyl ester (**1**) of the *p*-*tert*-butylcalix[4]arene using B3LYP/6-311+G(d,p)//HF/6-31G calculations suggests that cone conformational isomer is slightly more stable than partial-cone analogue.¹³ We have also undertaken the relative binding affinity study of cone-shaped *tert*-butylcalix[4]aryl esters toward alkali metal cations focusing on the binding site of upper or lower-rim pocket of the host molecule **1** using the B3LYP/6-31G(d)//HF/6-31G method.¹⁴ It was suggested that *exo*-complexation efficiency of potassium ion inside the cavity of lower rim of hosts **1** is better by 31.5 kcal/mol than the *endo*-complexation inside the upper rim (four aromatic rings).

In the present work, we report the vibrational spectra for the cone conformation of host **1** and its alkali-metal-ion *exo*-complexes using *ab initio* molecular orbital method, and provide the theoretical information for the infrared (IR) absorption spectra in order to distinguish the complexed state from the isolated host molecule. *Scheme 1* shows the simplified structure of *p*-*tert*-butylcalix[4]aryl ethyl ester (**1**), and *Scheme 2* displays RHF/6-31G optimized structures of host (**1**) and complexes (**1**+Na⁺ and **1**+K⁺).¹⁴

Ab initio CALCULATIONS

Restricted Hartree-Fock (RHF) calculations on the host molecule, guest cations, and complexes were carried out using 6-31G basis set. Molecular geometries were fully optimized, and vibrational frequencies without imaginary value were obtained by using analytic second derivative technique. To directly compare with the experimental data, the calculated frequencies were also 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. All calculations were performed with the Gaussian 98 program package.¹⁶ The geometry optimizations were done with Fujitsu VPP5000 supercomputer owned by the Research Center for Computational Science at Okazaki. The frequency analysis was quite time-consuming step in the calculations because there are 153 nuclei for the complex conformation, and the number of vibrational modes is 453 (153×3-6).

RESULT AND DISCUSSIONS

The theoretical IR spectrum for the host-molecule in cone conformer (*Scheme 2(a)*) is shown in *Fig. 1(a)*. The spectrum is characterized with several vibrational groups, consisting of the vibrational frequencies below

1300 cm^{-1} , the middle vibrational frequencies around 1450 and 1700 cm^{-1} , and the high frequencies of the non-interacting CH stretching above 2900 cm^{-1} . The lower vibrational frequencies were mainly assigned to the various C-O stretching motions of the four branches of $-\text{OCH}_2\text{CO}_2\text{CH}_2\text{CH}_3$ attached to four benzene rings. On the other hand, the frequencies around 1450 cm^{-1} correspond to the CC stretching motions of the ethyl groups and benzene rings, and the two strong peaks (1684 and 1702 cm^{-1}) correspond to the two kinds of C=O stretching motions in the C_{2v} -Host. 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 broad spectrum is not completely same as the bar spectrum, because some peaks overlapped each other due to the degenerate or almost degenerate vibrational modes; for example, although there are lots of small peaks 1000~1500 cm^{-1} , the corresponding peak becomes intense after broadening the bar spectrum using the assumption of a Lorentzian line shape.

The corresponding experimental spectrum for the host-molecule is shown in *Fig. 2(a)*. Our theoretical spectrum could almost reproduce the features of the experimental results; there are several vibrational groups, and the strong and broad peak around 1200 cm^{-1} corresponds to the two groups of C-O stretching motions. However, the spectral structure of middle frequency region is slightly different from the calculated result although the general appearance duplicates relatively well.

Fig. 1(b) shows the theoretical IR spectrum calculated for the $1+\text{Na}^+(\text{C}_{2v})$ *exo*-complex (*Scheme 2(b)*) comprising the cone-conformer and sodium ion. The two strong peaks consisting of 1189 and 1255 cm^{-1} for various C-O stretching motions are more separated than the free-host peak in the frequency region around 1210 cm^{-1} shown in *Fig. 1(a)*, and these peaks could be evidence of the complex formation. That is because the strong peaks located at 1196 and 1222 cm^{-1} shown in *Fig. 1(a)* should be split further into two peaks (1189 and 1255 cm^{-1}) due to the complex formation, and the double shoulders at the higher frequency could appear. Moreover, another strong peak around 1690 cm^{-1} for four kinds of C=O stretching motions shown in the host spectrum should be moved down by 20 cm^{-1} (around 1670 cm^{-1}) due to the bridging of sodium ion upon formation of the complex. Thus, the complexation of cone-conformer and sodium ion could be confirmed by the presence of these diagnostic bands in the IR spectra.

The corresponding experimental spectrum for the sodium ion complex is shown in *Fig. 2(b)*. As expected in the theoretical spectrum, the new two peaks appear in 1207 and 1215 cm^{-1} ; the $\text{C}_{\text{C=O}}-\text{O}_{\text{ester}}$ stretching peaks are clearly shown on the double shoulders of 1191 cm^{-1} because of the condensed phase, and C=O stretching peak around 1763 cm^{-1} for four kinds of motions shown in the host spectrum should be moved down by 20 cm^{-1} (around 1742 cm^{-1}) due to the bridging of sodium ion upon formation of the complex. However, the spectral structure of middle frequency region is slightly different from the calculated result although the general appearance duplicates relatively well.

Fig. 1(c) shows the theoretical IR spectrum calculated for $1+\text{K}^+(\text{C}_{4v})$ *exo*-complex (*Scheme 2(c)*) comprising the cone-conformer and potassium ion. The two strong peaks consisting of 1188 and 1250 cm^{-1} for various C-O stretching motions are very similar to $1+\text{Na}^+$ complex. However, another strong peak around 1690 cm^{-1} for four kinds of C=O stretching motions shown in the host spectrum should be moved down by 20 cm^{-1} (around 1670 cm^{-1}) with more closely degenerate bands (1668~1672 cm^{-1}) than $1+\text{Na}^+$ complex (1664~1681 cm^{-1}) due to the bridging of bigger potassium ion upon formation of the C_{4v} complex rather than C_{2v} symmetry.

The calculated main features for the host and complex systems of sodium and potassium ions are summarized in *Table 1*, and the experimental spectral features for the host and complex system of sodium ion are summarized in *Table 2*. Since the complex should be formed from the interaction between the alkali-metal-ion and the non-bonding orbitals of the oxygen atoms of four branches ($-\text{OCH}_2\text{CO}_2\text{CH}_2\text{CH}_3$), the vibrational motions related with the complex are confined in the lower rim. Therefore,

we have omitted the peaks at $\sim 2900\text{ cm}^{-1}$ for the CH stretching motions in alkyl groups and benzene rings, since those exhibit no prominent difference in host and complex systems.

Specifically, the $\text{C}_{\text{C=O}}\text{-O}_{\text{ester}}$ anti-symmetric stretching motions were significantly affected, while the $\text{C}_{\text{bz}}\text{-C}_{\text{butyl}}$ and $\text{C}_{\text{C=O}}\text{-O}_{\text{ester}}$ symmetric stretching motions were not. The degenerate vibrational modes consisting of the concerted anti-symmetric stretching motions of $4(\text{C}_{\text{bz}}\text{-C}_{\text{bz}}) + 4(\text{C}_{\text{bz}}\text{-O}_{\text{ether}}) + 2(\text{C}_{\text{C=O}}\text{-O}_{\text{ester}})$ (one of the degenerate peaks number 3: 1193 cm^{-1}) should be shifted to higher frequencies due to larger force constant from the strong electrostatic interactions with sodium cation, and split into the several peaks ($1228\sim 1248\text{ cm}^{-1}$) with larger intensities. The calculated energy shift is about 45 cm^{-1} . However, another vibrational mode consisting of the symmetric stretching motions of $4(\text{C}_{\text{bz}}\text{-C}_{\text{bz}}) + 4(\text{C}_{\text{bz}}\text{-O}_{\text{ether}}) + 2(\text{C}_{\text{C=O}}\text{-O}_{\text{ester}})$ (1196 cm^{-1}) stays in similar region ($\sim 1189\text{ cm}^{-1}$) without splitting with weaker intensity than host. This situation is a little different in strong C=O stretching states for the host and complex molecules.

The two degenerate vibrational modes (the concerted symmetric and anti-symmetric stretching motions of two carbonyl groups (the degenerate peak number 8: 1684 cm^{-1})) of host should be shifted to lower frequency due to the hindrance of the sodium cation in complex and split into the unresolved peaks (1664 (stronger intensity of anti-symmetric stretching) and 1670 cm^{-1} (weaker intensity of symmetric stretching)). Another vibrational state (the degenerate peak number 9: around 1702 cm^{-1}) is similarly shifted to 1681 cm^{-1} without splitting for sodium ion. However, for potassium ion, two degenerate vibrational states of two carbonyl groups (the degenerate peak number 8: around 1684 cm^{-1}) is shifted to a less degree to $\sim 1669\text{ cm}^{-1}$ and two degenerate vibrational states of another two carbonyl groups (the degenerate peak number 9: around 1684 cm^{-1}) is shifted more to ~ 1670 . Thus, four vibrational states of two carbonyl groups (two from peak number 8 and other two from peak 9) are converged to almost the same frequency (1670 cm^{-1}), indicating that the $\mathbf{1}+\text{K}^+$ complex is almost of C_{4v} symmetry compared to $\mathbf{1}+\text{Na}^+$ (C_{2v}) for the interacting region of the cation and carbonyl groups.

CONCLUSIONS

We found the characteristic of the vibrational modes of the host molecule and complexes. Theoretical infrared absorption spectra were calculated for the ethyl ester of *p-tert*-butylcalix[4]arene (**1**) in the cone conformer and its alkali-metal-ion complexes. The theoretical results for the host molecule **1** and complex ($\mathbf{1}+\text{Na}^+$) were compared with the experimental results, and we found that the calculated results agree well with the features of the experimental spectra. The structure of $\mathbf{1}+\text{K}^+$ complex is almost of C_{4v} symmetry compared to $\mathbf{1}+\text{Na}^+$ (C_{2v}) for the interacting region of the cation and carbonyl groups. The diagnostic differences in the IR spectra should provide us the key to understanding more deeply the host-guest molecular structures.

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Table 1. Main features of calculated vibrational modes

Host 1 (C _{2v})		1+Na ⁺ (C _{2v})		1+K ⁺ (C _{4v})				
Peak Energy No.	Vibrations	Int. ^a	Vibrational modes Description	Energy/cm ⁻¹	Int.	Vibrations	Energy/cm ⁻¹	Int.
1047	2(CH ₂ -O _{ether}) +2(CH ₂ -O _{ester})	112	CH ₂ -O anti-symmetric stretching	1037	28	2(CH ₂ -O _{ether}) +2(CH ₂ -O _{ester})	1038	69
1056	2(CH ₂ -O _{ether}) +2(CH ₂ -O _{ester})	146	CH ₂ -O anti-symmetric stretching	1040	55	2(CH ₂ -O _{ether}) +2(CH ₂ -O _{ester})	1038	86
1058	4(CH ₂ -O _{ether}) +2(CH ₂ -O _{ester})	328	CH ₂ -O stretching	1045	455	4(CH ₂ -O _{ether}) +4(CH ₂ -O _{ester})	1044	643
2	4(C _{bz} -O _{ether})	261	C _{bz} -O _{ether} stretching	1123	301	4(C _{bz} -O _{ether})	1126	287
1196	4(C _{bz} -C _{bz}) +4(C _{bz} -O _{ether}) +2(C _{c=O} -O _{ester})	1004	C _{bz} -C _{bz} stretching +C-O stretching	1189	698	4(C _{bz} -C _{bz}) +4(C _{bz} -O _{ether})	1188	657
				1228	120	4(C _{bz} -O _{ether}) +2(C _{c=O} -O _{ester})	1229	36
3	4(C _{bz} -C _{bz})			1230	179	4(C _{bz} -O _{ether}) +2(C _{c=O} -O _{ester})	1232	90
1193	+4(C _{bz} -O _{ether}) +2(C _{c=O} -O _{ester})	34	anti-symmetric stretchings of C _{bz} -C _{bz} and C-O	1234	121	4(C _{bz} -C _{bz}) +4(C _{bz} -O _{ether}) +4(C _{c=O} -O _{ester})	1234	240
				1248	229	4(C _{bz} -O _{ether}) +4(C _{c=O} -O _{ester})	1239	202
1211	4(C _{c=O} -O _{ester})	312	C _{c=O} -O _{ester}	1251	26	2(C _{c=O} -O _{ester})	1244	122
4	4(C _{c=O} -O _{ester})	245	anti-symmetric stretching	1255	887	4(C _{c=O} -O _{ester})	1250	1204
1222	4(C _{c=O} -O _{ester})	1173	C _{c=O} -O _{ester} stretching	1258	451	4(C _{c=O} -O _{ester})	1260	561
5	4(C _{bz} -C _{butyl})	84	C _{bz} -C _{butyl} stretching	1297	304	4(C _{bz} -C _{butyl})	1295	111
6	4(CH ₂ -CH ₂) +4(C _{bz} -C _{bz})	68	CH ₂ -CH ₂ stretching	1420	159	4(CH ₂ -CH ₂) +4(C _{c=O} -O _{ester})	1415	92

7	1469	$4(C_{\text{bz}}-C_{\text{bz}})$ $+4(C_{\text{bz}}-O_{\text{ether}})$	123	$C_{\text{bz}}-C_{\text{bz}}$ stretching	1463	90	$4(C_{\text{bz}}-C_{\text{bz}})$ $+4(C_{\text{bz}}-O_{\text{ether}})$	1461	100
	1684 ^b	2(C=O)	124	C=O stretching	1664	631	2(C=O)	1668 ^d	443
8	1684 ^b	2(C=O)	506	C=O anti-symmetric stretching	1670	30	2(C=O)	1669 ^d	546
	1701 ^c	2(C=O)	412	C=O anti-symmetric stretching	1681	472	2(C=O)	1670 ^d	213
9	1703 ^c	2(C=O)	49	C=O stretching	1681	205	2(C=O)	1672 ^d	115

^aCalculated Infrared Intensity from RHF/6-31G.

^bTwo degenerate vibrational states of two carbonyl groups attached to two parallel benzene-rings of opposite side in Host **1** (C_{2v}).

^cTwo degenerate vibrational states of two other carbonyl groups attached to two perpendicular benzene-rings of opposite side in Host **1** (C_{2v}).

^dFour degenerate vibrational states of four carbonyl groups attached to four benzene-rings of complex **1**+K⁺ (C_{4v}).

Table 2. Main features of experimental vibrational modes

Host 1				1 +Na ⁺	
Peak No.	Energy/cm ⁻¹	Int.	Vibrational mode Assignments	Energy/cm ⁻¹	Int.
1	1056	medium	CH ₂ -O _{ether} anti-symmetric stretching and CH ₂ -O _{ether} stretching	1068	medium
2	1128	medium	C _{bz} -O _{ether} stretching	1128	medium
3	1191 ^a	strong	C _{bz} -C _{bz} stretching +C _{bz} -O _{ether} stretching	1192	strong
4	1191 ^a	strong	C _{c=O} -O _{ether} anti-symmetric stretching	1207 ^b	medium
			C _{c=O} -O _{ether} stretching	1215 ^b	medium
5	1302	weak	C _{bz} -C _{butyl} stretching	1302	weak
6	1366	weak	No Assignment	1366	weak
7	1480	medium	$4(C_{\text{bz}}-C_{\text{bz}})$ + $4(C_{\text{bz}}-O_{\text{ether}})$	1481	medium
8	1742	medium	C=O stretching and C=O anti-symmetric stretching	1730 ^c	shoulder
9	1763	strong	C=O anti-symmetric stretching and C=O stretching	1742 ^c	strong

^aPeak #4 was unresolved with peak #3 at 1191 cm⁻¹ in free Host **1**.

^bPeak #4 is resolved to two more medium peaks (1207 and 1215 cm⁻¹) on the shoulder of one strong peak #3 (1191 cm⁻¹) in complex (**1**+Na⁺).

^cPeaks #8 and #9 of complex (**1**+Na⁺) are shifted to lower frequency (~20 cm⁻¹) region from Host **1**.