

mPW1PW91 Study of Complexation of Alkali Metal Ions with Mixed [2 + 2'] Calix[4]aryl Derivatives

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The complexation characteristics of mixed [2 + 2'] calix[4]aryl derivatives (**3** and **4**) with alkali metal cations were investigated by the mPW1PW91 (hybrid HF-DF) calculation method. The total electronic and Gibbs free energies of the various complexes (cone, partial-cone, 1,2-alternate, and 1,3-alternate) of sodium and potassium cations with **3** and **4** were analyzed and compared. The structures of the *endo*- or *exo*-complexes of the alkali metal cation with the host **3** were optimized using the mPW1PW91/6-31G(d) method, followed by mPW1PW91/6-311+G(d) calculations. The structures of the *endo*- or *exo*-complexes of the alkali metal cation with the host **4** were optimized using the mPW1PW91/6-31G(d,p) method. The mPW1PW91 calculated relative energies of the various conformations of the free hosts (**3** and **4**) suggest that the cone conformers of **3** and **4** are the most stable. The mPW1PW91 calculations also suggest that the complexation efficiencies of the sodium ion with hosts **3** and **4** are about 24 and 27 kcal/mol better than those of the potassium ion, respectively. These trends are in good agreement with the experimental results. The *exo*-complexation efficiencies of the sodium ion toward the conformers of hosts **3** and **4** are roughly 14 and 17 kcal/mol better than those for the *endo*-Na⁺-complexes of **3** and **4**, respectively. The *exo*-complexation of the cone isomer of **3** with cation could be confirmed by the differences of the diagnostic C=O bands in the free host and its complex's IR spectra.

Key Words : Mixed [2 + 2'] calix[4]aryl derivatives, Complexation, Alkali metal ion, mPW1PW91

Introduction

Calixarenes¹ having a well-defined molecular framework are attractive as a basic skeleton for the construction of new supramolecular systems.² The complexation properties of these molecules appear to be highly dependent upon the nature and number of donor atoms and the conformation of the calix[4]arene moiety.³ Several functions have been introduced in the lower rim of calix[4]arene such as ethers, amides, thioamides, ketones and esters.⁴⁻¹⁰ Some of these derivatives have a high potential of encapsulation for metal cations and some selectivities have been reported, for example, *p*-*tert*-butylcalix[4]arene O-substituted by ethyl ester functions (**2**) show a high affinity for sodium and potassium in methanol.¹¹

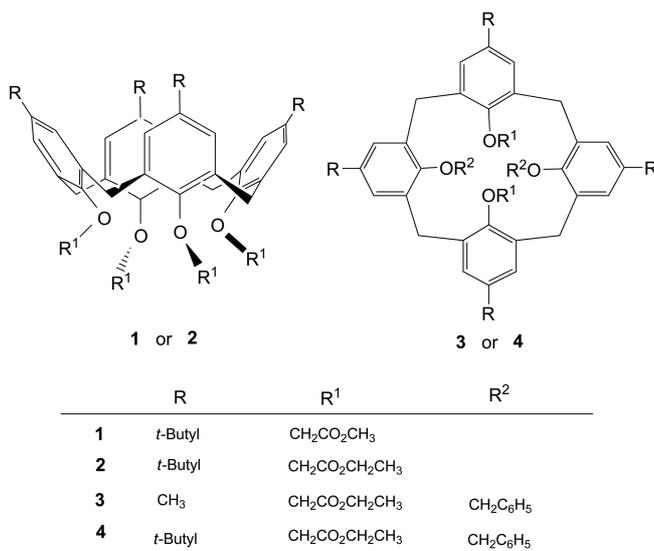
The calculated structures and relative binding affinities of cone-shaped *p*-*tert*-butylcalix[4]aryl tetraesters toward alkali metal cations were studied, focusing on the binding site of the upper or lower-rim pocket of host molecules **1** and **2** using the mPW1PW91/6-31G(d)//HF/6-31G calculation method.¹² The *exo*-complexation efficiencies of the sodium ion inside the cavity of the lower rim of hosts **1** and **2** were much better than those of the potassium ion, and these *exo*-complexation efficiencies of the potassium ion were better than those of its *endo*-complexation inside the upper rim (four aromatic rings).¹²

In order to design calixarene receptors with tunable and thus enhanced selectivities for specific cations, recent interest was taken in the synthesis of calix[4]arene derivatives with mixed functionalities.¹³⁻¹⁷ The complexation and extraction

of alkali cations by mixed [2 + 2'] calix[4]arene derivatives combining ethyl ester and methyl ketone, *tert*-butyl ester or diethylamide arms have been reported.¹⁵ Baklouti *et al.* reported about the complex formation of four dimalonate and one diester calix[4]arene derivatives toward alkali and alkaline earth cations as it was investigated in acetonitrile by means of UV spectrophotometry and supported by ¹H-NMR and FAB+ MS measurements.¹⁸ Recently, the synthesis and binding properties of calix[4]arenes with [2 + 2'] mixed ligating functional groups have been reported for alkali metal ions.^{19,20} They reported the decisive peak selectivity of the sodium ion by [2 + 2'] mixed ethyl ester-benzyl derivative (**4**) compared to other alkali metal cations in acetonitrile by means of UV spectrophotometry and ¹H NMR spectroscopy.

There has been much progress in the development of computational approaches in supramolecular chemistry, which may lead to deeper microscopic insight into the structural and thermodynamical features involved in the processes of molecular recognition and supramolecular organization.²¹

Herein, a computational study of the relative binding affinities of various conformations of mixed [2 + 2'] calix[4]aryl derivatives toward alkali metal cations (Na⁺ and K⁺) is performed. The main objectives of this study are to determine the principal binding site of the upper (*endo*) or lower (*exo*)-rim pocket^{22(a)} of host molecules **3** and **4** with the guest cations and to compare the selectivity of the sodium or potassium ion by the hosts using the mPW1PW91/6-31(d,p) calculation method. The relative stability of the various conformational host-guest complexes and the strengths



Scheme 1. Chemical structures of calix[4]aryl esters and mixed [2+2'] calix[4]aryl derivatives: 5,11,17,23-tetra(*tert*-butyl)-25,26,27,28-tetramethoxycarbonylmethoxycalix[4]arene (**1**). 5,11,17,23-tetra(*tert*-butyl)-25,26,27,28-tetraethoxycarbonylmethoxycalix[4]arene (**2**). 5,11,17,23-tetramethyl-25,27-diethoxycarbonylmethoxy-26,28-diphenylmethoxycalix[4]arene (**3**). 5,11,17,23-tetra(*tert*-butyl)-25,27-diethoxycarbonylmethoxy-26,28-diphenylmethoxycalix[4]arene (**4**).

of the cation-oxygen and cation- π interactions in the complexes will be quantum mechanically analyzed. The comparison of the complexation energies and the distances between the oxygen atoms of the hosts and the alkali metal ions for the alkali-metal-ion complexes of **3** and **4** as well as the calculated IR spectra of the host **4** and its alkali-metal-ion complexes using the *mPW1PW91* method in this paper can contribute to improve our understanding on the structural and thermodynamic properties of the compound **3** and **4**.

Computational Methods

The initial structures of the mixed [2 + 2'] calix[4]aryl derivatives were constructed by HyperChem.²³ In order to find the optimized structures, conformational searches were performed by the simulated annealing method.²⁴ The alkali metal ion complexes of the *para*-tetramethyl (**3**) and *para*-tetra-*tert*-butyl (**4**) mixed [2 + 2'] calix[4]aryl derivatives obtained from MM/MD and semi-empirical AM1 calculations were fully re-optimized using the *mPW1PW91/6-31G(d)* method using *Gaussian 09*,²⁵ in order to estimate the absolute and relative energies for the different complexes. Modified Perdew-Wang 1-parameter (*mPW1*) calculations,^{26,27} such as *mPW1PW91*, are hybrid Hartree-Fock-density functional (HF-DF) models that obtain good results both for covalent and non-covalent interactions.²⁸

After these preliminary calculations, additional *mPW1PW91/6-311+G(d)* optimizations of the final structures of **3** and their complexes, and *mPW1PW91/6-31G(d,p)* optimizations of the various conformers of **4** and their complexes were

performed to include the effect of the electron correlation and the basis set with polarization function, as well as to reduce the basis sets superposition error (BSSE²⁹).

The *mPW1PW91/6-31G(d)* method was also used to calculate the normal mode frequencies of the various conformers of **3** and their complexes. None of the vibrational spectra showed negative frequencies, confirming that the optimized structures exist at an energy minimum. For direct comparison with the experimental data, the calculated vibrational frequencies were scaled by the recommended scale factor.³⁰ Furthermore, the broadened IR spectra are presented, assuming a Lorentzian line width of 10 cm⁻¹. The calculations of the vibrational frequencies and Gibbs free energies of the various complexes of the bigger *p-tert*-butyl analogue **4** were not performed due to the limited computational resources available.

Results and Discussion

Full *mPW1PW91* optimizations without any constraints were carried out for the *exo/endo*-complexes²² of the sodium or potassium ion with the calix[4]aryl derivatives (**3** and **4**) containing [2+2'] mixed ligating functional groups. The *mPW1PW91* optimized total electronic and Gibbs free energies of the possible conformers (cone, partial-cone, 1,2-alternate, and 1,3-alternate) of **3** and the differences between them are reported in Table 1. The *mPW1PW91/6-31G(d,p)* optimized total electronic of the various conformations of **4** and the differences between them are reported in Table 2.

Table 1. *mPW1PW91* Calculated Energies of the Various Conformers of the Free Host (**3**)

| Conformer ^a | Basis set | <i>E</i> (a.u.) ^b | ΔE (kcal/mol) ^c |
|------------------------|-----------------------------|------------------------------|------------------------------------|
| CONE | /6-31G(d) | -2692.66280 | 0.00 |
| | 6-31G(d) Gibbs ^d | -2691.77282 | 0.00 |
| | /6-311+G(d) | -2693.23767 | 0.00 |
| PC1 | /6-31G(d) | -2692.66194 | 0.54 |
| | /6-31G(d) Gibbs | -2691.77243 | 0.24 |
| | /6-311+G(d) | -2693.23627 | 0.88 |
| PC2 | /6-31G(d) | -2692.65973 | 1.93 |
| | /6-31G(d) Gibbs | -2691.76978 | 1.91 |
| | /6-311+G(d) | -2693.23518 | 1.57 |
| 12ALT | /6-31G(d) | -2692.65783 | 3.12 |
| | /6-31G(d) Gibbs | -2691.76538 | 4.67 |
| | /6-311+G(d) | -2693.23336 | 2.70 |
| 13ALT | /6-31G(d) | -2692.65968 | 1.96 |
| | /6-31G(d) Gibbs | -2691.76818 | 2.91 |
| | /6-311+G(d) | -2693.23294 | 2.97 |

^aAbbreviations of conformers: PC1, the first one out of the two kinds of partial cone conformer, has one aryl ether ring inverted out of the two aryl ether branches of the lower rim of **3**. PC2 is the second partial cone conformer which has one ester group inverted out of the two ester chains of **3**. 12ALT is the 1,2-alternate form. 13ALT is the 1,3-alternate. ^bThe error limits of these calculated total electronic energies are about 0.00001 a.u. (0.01 kcal/mol). ^c ΔE (kcal/mol) is defined as the energy of the conformer minus the energy of the most stable CONE conformation of **3** obtained by using 1 a.u. = 627.50955 kcal/mol. ^dSum of electronic and thermal Gibbs free energies at 298 K.

Table 2. mPW1PW91/6-31G(d,p) Calculated Energies of the Various Conformers of the Free Host (**4**)

| Conformer ^a | <i>E</i> (a.u.) ^b | <i>E</i> (kcal/mol) | ΔE (kcal/mol) ^c |
|------------------------|------------------------------|---------------------|------------------------------------|
| CONE | -3164.41972 | -1985703.59451 | 0.00 |
| PC1 | -3164.41790 | -1985702.45244 | 1.14 |
| PC2 | -3164.41451 | -1985700.32518 | 3.27 |
| 12ALT | -3164.41314 | -1985699.46550 | 4.13 |
| 13ALT | -3164.41091 | -1985698.06615 | 5.53 |

^{a,b,c}See the footnotes of Table 1.

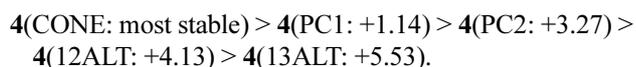
The mPW1PW91 calculated relative complexation efficiencies for the various complexes of **3** are listed in Table 3, and the mPW1PW91/6-31G(d,p) calculated relative complexation efficiencies for the various complexes of **4** are listed in Table 4.

Conformers of Calix[4]aryl Derivatives with [2+2'] Mixed Ligating Functional Groups. In general, the conformation of calix[4]arenes is analyzed in terms of the four basic arrangements resulting from the different 'up' or 'down' orientations of the phenol rings relative to the mean macrocyclic plane passing through the four methylene carbons. These arrangements are usually designated as 'cone', 'partial cone', '1,2-alternate' and '1,3-alternate', respectively.¹ The [2+2'] mixed ligating functional groups at the lower rim of **3** or **4** can make two kinds of 'partial cone' conformation. The first one (PC1: see Figures 1(b) and 2(b)) has one aryl ring inverted out of the two aryl ether branches of the lower rim of the cone-type host, and the other (PC2: see Figures 1(c) and 2(c)) has one ester group inverted out of the two ester chains of the host.

The calculated relative stabilities (ΔE) in Tables 1 and 2 suggest that the cone forms are the most stable of the various conformers of **3** and **4**, respectively. The ordering of the relative energies (ΔE in kcal/mol) of the conformations of **3** that resulted from the mPW1PW91/6-311+G(d) calculations is as follows:



The configurations of the various conformers of **3** are very similar to those of **4**. Therefore, the calculated structures of the **4** are presented in this paper. Figure 1 shows the optimized conformations (CONE, PC1, PC2, 12ALT and 13ALT) of the free host **4**. The ordering (in kcal/mol) of the relative stability (ΔE) of **4** that resulted from the mPW1PW91/6-31G(d,p) calculations is as follows:



The CONE conformer of the **4** is calculated to be the most stable, similar as in the host **3**, and it has 5.53 kcal/mol lower energy than the 13ALT form of **4**.

Complexation Energies of Mixed [2 + 2'] Calix[4]aryl Derivative **3.** Table 3 shows the mPW1PW91 calculated complexation energies of the various conformations (CONE, PC1, PC2, 12ALT and 13ALT) for the host **3** with alkali

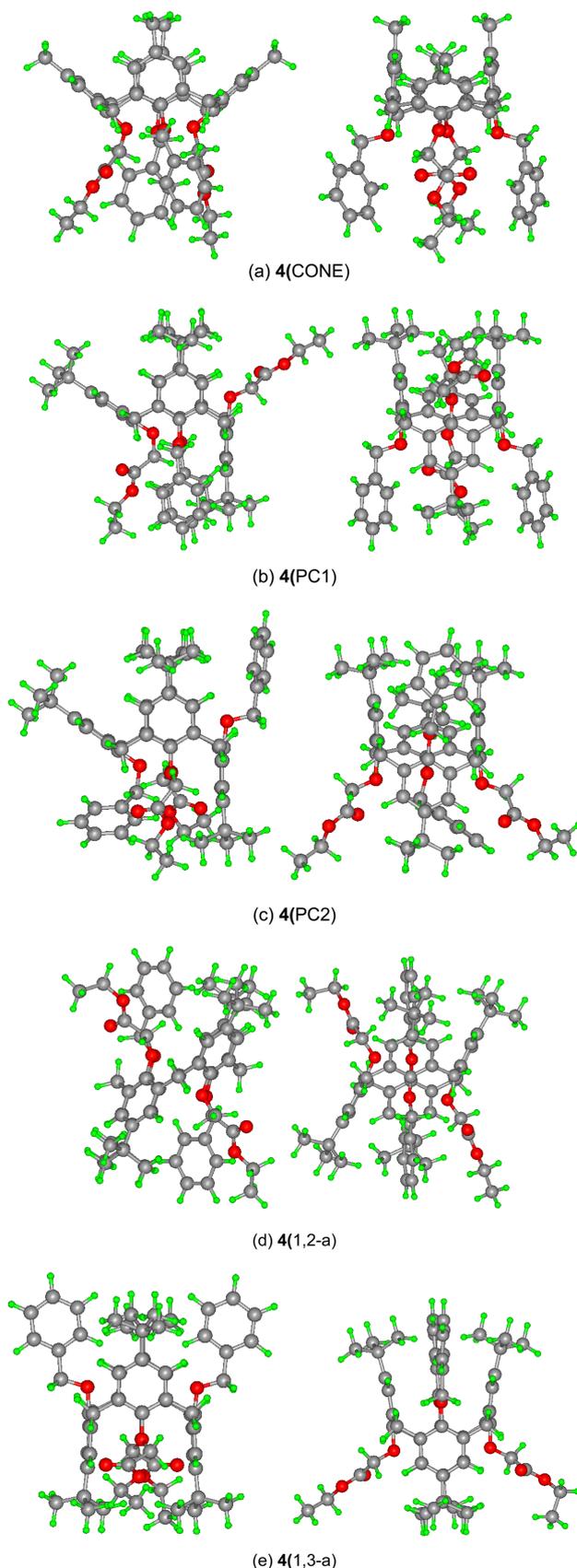


Figure 1. mPW1PW91/6-31G(d,p) calculated structures (front and side views) of various conformations (cone, PC1, PC2, 12ALT and 13ALT) for the free host **4**. (a) CONE, (b) PC1, (c) PC2, (d) 12ALT, and (e) 13ALT.

Table 3. *mPW1PW91* Calculated Complexation Energies ($\Delta E_{\text{complex}}$: kcal/mol)^a of the Various Complexes of Host **3** with Alkali Metal Cation

| | Conformer: Binding mode ^c | Basis set | 3·Na ⁺ -complex | 3·K ⁺ -complex | |
|--|--|---|----------------------------|---------------------------|--------|
| <i>exo</i> ^b | CONE: 4O _{ether} +2O _{carbonyl} | /6-31G(d) | -98.96 | -72.38 | |
| | | 6-31G(d) Gibbs | -85.23 | -61.78 | |
| | | /6-311+G(d) | -91.43 | -67.25 | |
| | PC1: 3O _{ether} +1O _{carbonyl} +1A | /6-31G(d) | -91.16 | -68.23 | |
| | | /6-31G(d) Gibbs | -78.84 | -57.67 | |
| | | /6-311+G(d) | -83.95 | -62.49 | |
| | PC2: 3O _{ether} +2O _{carbonyl} +1A | /6-31G(d) | -99.34 | -75.22 | |
| | | /6-31G(d) Gibbs | -88.35 | -65.27 | |
| | | /6-311+G(d) | -92.28 | -57.39 | |
| | 12ALT: 2O _{ether} +1O _{carbonyl} +2A | /6-31G(d) | -89.50 | -65.89 | |
| | | /6-31G(d) Gibbs | -79.29 | -57.73 | |
| | | /6-311+G(d) | -81.88 | -61.08 | |
| | 13ALT: 2O _{ether} +2O _{carbonyl} +2A | /6-31G(d) | -97.05 | -76.86 | |
| | | /6-31G(d) Gibbs | -87.48 | -65.24 | |
| | | /6-311+G(d) | -88.70 | -69.99 | |
| | <i>endo</i> ^b | CONE: 2O _{ether} +2A _{strong} | /6-31G(d) | -84.51 | -62.51 |
| | | | /6-31G(d) Gibbs | -71.85 | -50.50 |
| | | | /6-311+G(d) | -77.71 | -58.02 |
| PC1: 2O _{ether} +1O _{carbonyl} +2A | | /6-31G(d) | -84.52 | -67.14 | |
| | | /6-31G(d) Gibbs | -72.85 | -55.81 | |
| | | /6-311+G(d) | -76.74 | -61.43 | |
| PC2: 2O _{ether} +2A _{strong} | | /6-31G(d) | -82.62 | -63.25 | |
| | | /6-31G(d) Gibbs | -71.39 | -50.49 | |
| | | /6-311+G(d) | -74.54 | -57.39 | |

^a $\Delta E_{\text{complex}}$ (kcal/mol) 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 (CONE). ^b*exo* indicates the binding site of the lower-rim cavity of the calix[4]arylene skeleton, and *endo* means benzene-rings pocket mode.²² ^cThe total number of strong binding modes of the cation-oxygen (O_{ether}: between an alkali metal cation and the oxygen atoms of the ether moiety; O_{carbonyl}: between an alkali metal cation and the oxygen atoms of the carbonyl moiety) and cation- π (A: between an alkali metal cation and the electrons of the aromatic rings) interactions.

metal ions. The *exo*-complexation of the sodium ion to the cavity of the lower rim of the various conformations of host **3** shows the best efficiency (around -90 kcal/mol), and is roughly 24 kcal/mol better than that of the potassium ion, which is in line with the experimental observations (see next section). These *exo*-complexation efficiencies of the sodium ion toward the conformers of host **3** are approximately 14 kcal/mol better than those of the *endo*-Na⁺-complexes of **3**. The CONE, PC2, and 13ALT *exo*-complexes showed very

Table 4. *mPW1PW91/6-31G(d,p)* Calculated Complexation Energies ($\Delta E_{\text{complex}}$: kcal/mol)^a of the Various Complexes of Host **4** with Alkali Metal Cation

| | Conformer: Binding mode ^c | # ^c | 4·Na ⁺ -complex | 4·K ⁺ -complex |
|--------------------------|--|----------------|----------------------------|---------------------------|
| <i>exo</i> ^b | CONE: 4O _{ether} +2O _{carbonyl} | 6 | -100.38 | -73.32 |
| | PC1: 3O _{ether} +1O _{carbonyl} +1A | 5 | -93.49 | -70.27 |
| | PC2: 3O _{ether} +2O _{carbonyl} +1A | 6 | -98.62 | -73.71 |
| | 12ALT: 2O _{ether} +1O _{carbonyl} +2A | 5 | -87.90 | -66.93 |
| | 13ALT: 2O _{ether} +2O _{carbonyl} +2A | 6 | -95.24 | -73.84 |
| <i>endo</i> ^b | CONE: 2O _{ether} +2A _{strong} | 4 | -83.50 | -65.09 |
| | PC1: 2O _{ether} +1O _{carbonyl} +2A | 5 | -84.90 | -70.15 |
| | PC2: 2O _{ether} +2A _{strong} | 4 | -81.58 | -65.25 |

^{a,b,c}See the footnotes of Table 3.

similar efficiencies and are calculated to be the most efficient among the eight kinds of *exo*- and *endo*-complexes. The principal contributions of these different complexation efficiencies come from both the cation-oxygen and cation- π interactions, which will be discussed in the following section.

Complexation Energies of Mixed [2+2'] Calix[4]arylene Derivative **4.** Table 4 shows the *mPW1PW91* calculated complexation energies of the various conformations for host **4** with the alkali metal ions. Figures 2-6 show the optimized stable complexes (CONE, PC1, PC2, 12ALT and 13ALT) of host **4** with the alkali metal ions. The *exo*-complexation of the sodium ion (Figure 2(a)) to the cavity of the lower rim of the cone-type host **4** shows the best efficiency ($-\Delta E_{\text{complex}} = 100$ kcal/mol), and is about 27 kcal/mol better than that of the potassium ion (Figure 2(b)), which trend is in line with the experimental observations like followings.¹⁶ The observed stability constant ($\log \beta_{11}$) for alkali metal ion complex of host **4** in acetonitrile at 25 °C (ionic strength = 0.01 M using Et₄NClO₄) was 4.84 for Na⁺ and 2.90 for K⁺, respectively. And the extraction percentage (%*E*) of alkali metal picrates by host **4** was 15.9% for Na⁺ and 12.3 for K⁺, respectively. Experimentally, the host **4** formed only 1:1 species from Li⁺ to Rb⁺ with peak selectivity with Na⁺.¹⁶

The calculated *exo*-complexation efficiency of the sodium ion is about 17 kcal/mol better than the *endo*-complexation

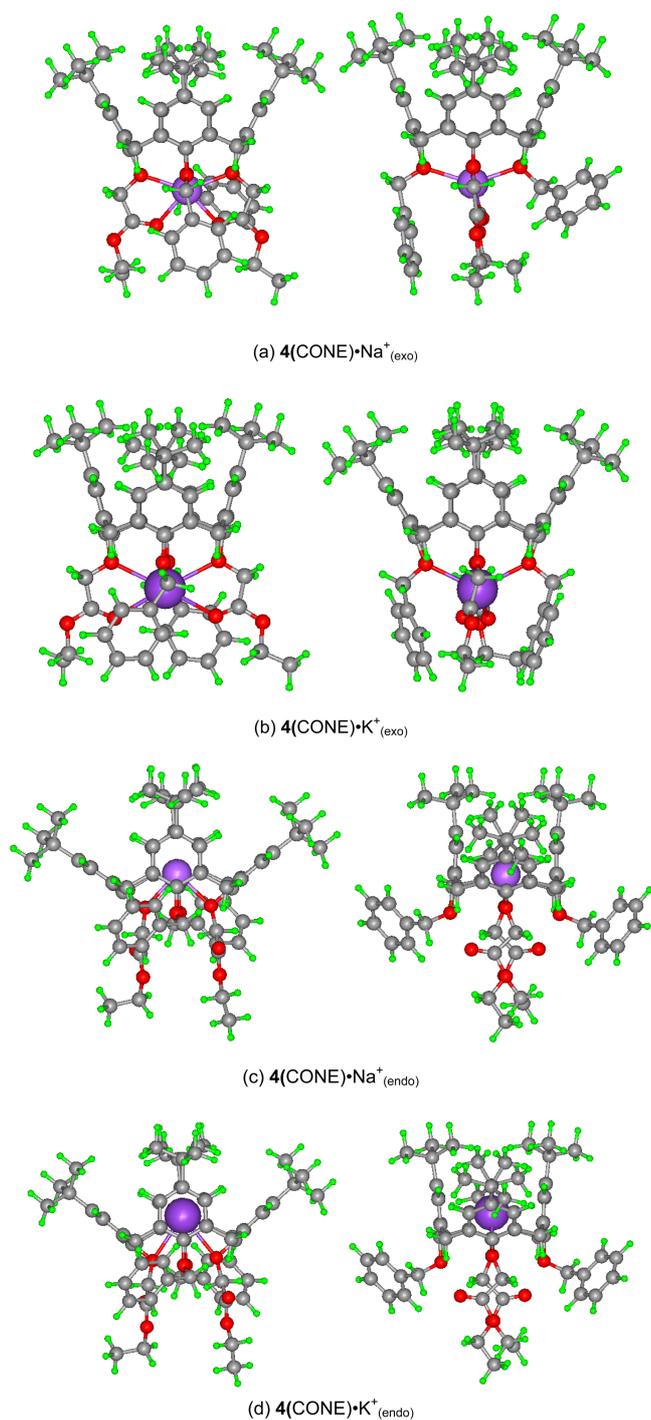


Figure 2. mPW1PW91/6-31G(d,p) calculated CONE conformers of **4** (a) *exo*-complexed with sodium ion, (b) *exo*-complexed with potassium ion, (c) *endo*-complexed with sodium ion, and (d) *endo*-complexed with potassium ion. Atoms that are within a certain distance (the bond proximate distance) from one another were automatically marked as bonded.³¹

of Na^+ inside the upper rim (four aromatic rings in Figure 2(c)) of **4**. This relative *exo/endo*-complexation efficiency originates from the fact that the cation- π interactions in the upper rim differ from the number and strength of the electrostatic interactions of the metal ionic guest with the efficient ligand site of the ether and ester carbonyl functions

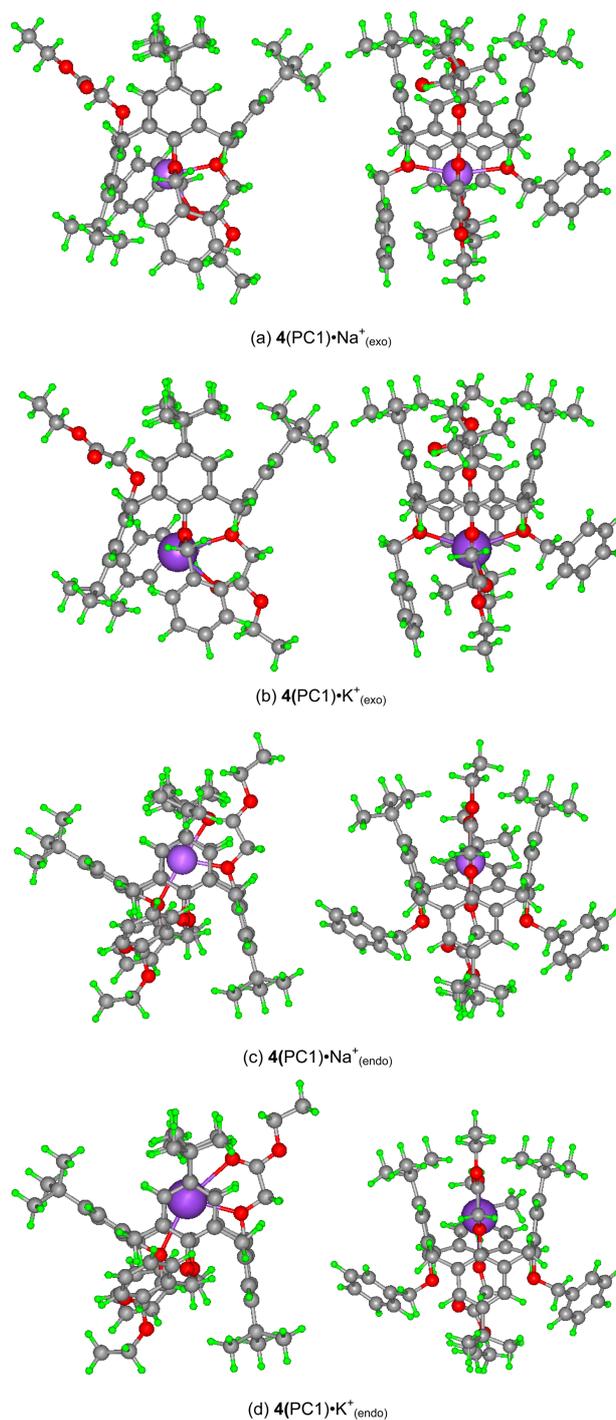


Figure 3. mPW1PW91/6-31G(d,p) calculated PC1 conformers of **4** (a) *exo*-complexed with sodium ion, (b) *exo*-complexed with potassium ion, (c) *endo*-complexed with sodium ion, and (d) *endo*-complexed with potassium ion.

in the lower rim. The calculated binding strengths of sodium and potassium ions in the cation-oxygen and cation- π interactions were already described in the previous publications of calix[4]aryl derivatives.^{12,22}

An interesting observation regarding the *endo*-position structure (Figure 1(c)) of $4_{(\text{cone})}\cdot\text{Na}^+$ is that the planes of the four benzene rings show significantly different dihedral

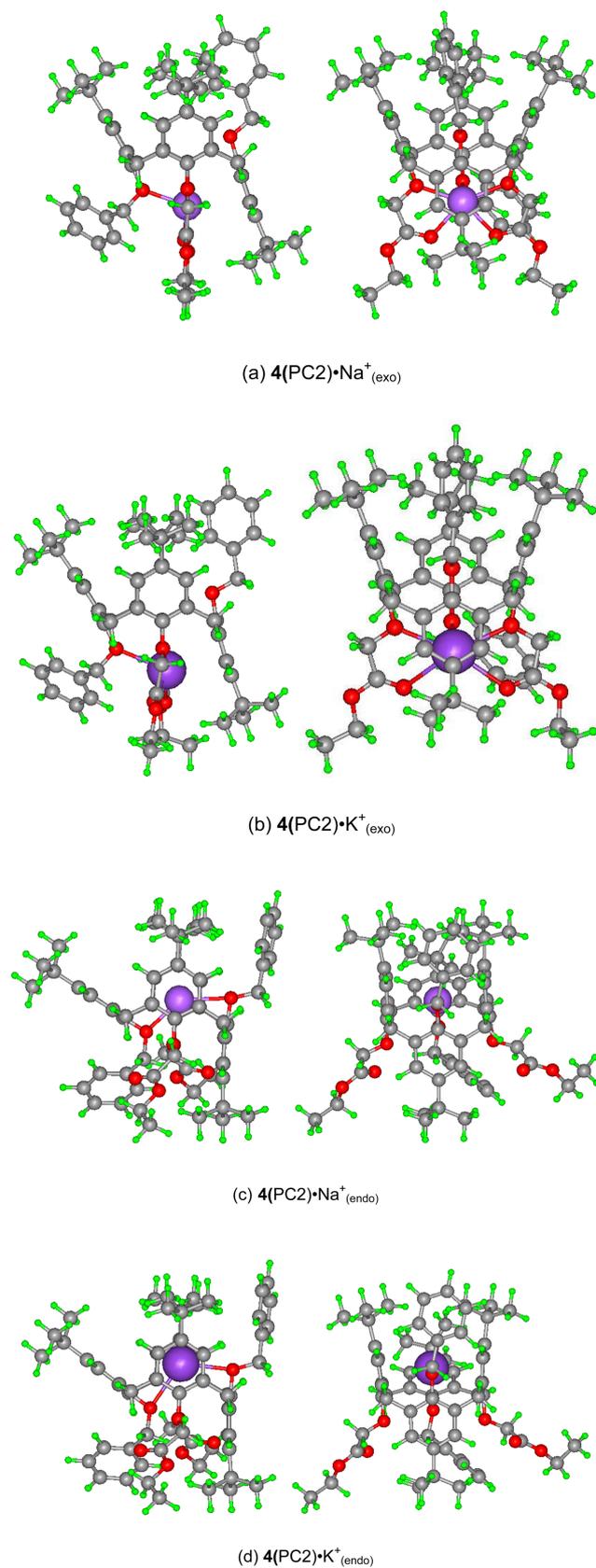


Figure 4. *mPW1PW91/6-31G(d,p)* calculated PC2 conformers of **4** (a) *exo*-complexed with sodium ion, (b) *exo*-complexed with potassium ion, (c) *endo*-complexed with sodium ion, and (d) *endo*-complexed with potassium ion.

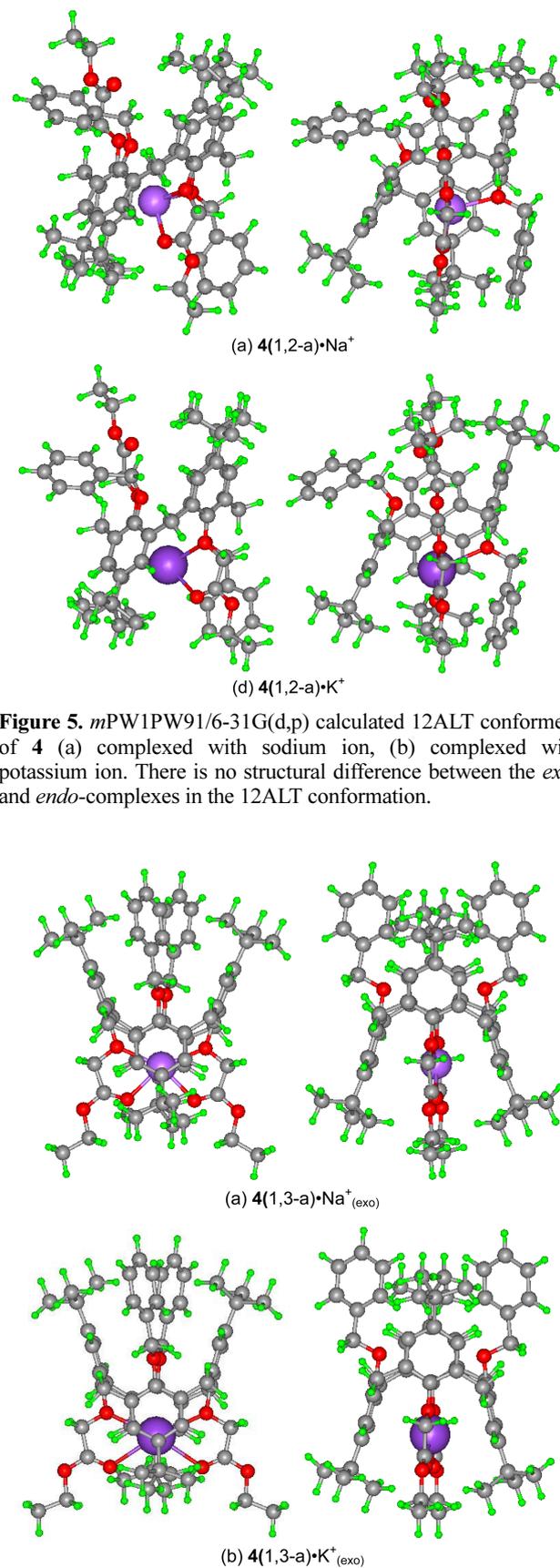


Figure 5. *mPW1PW91/6-31G(d,p)* calculated 12ALT conformers of **4** (a) complexed with sodium ion, (b) complexed with potassium ion. There is no structural difference between the *exo*- and *endo*-complexes in the 12ALT conformation.

Figure 6. *mPW1PW91/6-31G(d,p)* calculated 13ALT conformers of **4** (a) *exo*-complexed with sodium ion, (b) *exo*-complexed with potassium ion.

angles for the opposite rings. The two opposite rings are almost parallel to each other and the other opposite planes are almost perpendicular, whereas the *exo*-position skeleton (Figure 1(b)) of $4(\text{cone})\cdot\text{Na}^+$ displays almost C_{4v} symmetry. Therefore, the major portion of the binding energy for the *endo*-complexation of the cation inside the aromatic rings of **4** comes from the two cation- π interactions. However, the binding energy of the alkali metal ion to the cavity of the lower rim of host **4** originates from the four ether-oxygens and two carbonyl oxygens of the ester groups. Both the individual binding strength and the different number of

electrostatic interactions explain the better binding of the *exo*-complexation than its *endo*-analogue.

Table 5 reports the calculated distances between the alkali metal ion and the ether-oxygens and carbonyl-oxygens of **3** and **4**. In Figures 2-6, the guest ion and the ligating atoms of the host in the optimized structure, which are within a certain distance (the bond proximate distance) from one another, were automatically indicated as bonded. However, these are not real coordinations or bonds. For the Na^+ complex, the distances of less than ~ 2.60 Å are such cases. For the K^+ complex, all such cases have distances of less

Table 5. Calculated Distances (Å) from Alkali Metal Cation to the Oxygen Atoms of the Various Complexes of **4**

| Distance from cation to oxygen atom | O _{ether} (1) | O _{ether} (2) | O _{ether} (3) | O _{ether} (4) | O _{carbonyl} (1) | O _{carbonyl} (2) |
|---|------------------------|------------------------|------------------------|------------------------|---------------------------|---------------------------|
| $4(\text{cone})\cdot\text{Na}^+(\text{exo})$ | 2.402 | 2.423 | 2.493 | 2.409 | 2.362 | 2.387 |
| $4(\text{cone})\cdot\text{Na}^+(\text{endo})$ | 2.389 | 2.367 | | | | |
| $4(\text{PC1})\cdot\text{Na}^+(\text{exo})$ | 2.392 | 2.458 | 2.499 | | 2.300 | |
| $4(\text{PC1})\cdot\text{Na}^+(\text{endo})$ | 2.289 | 2.562 | | | 2.427 | |
| $4(\text{PC2})\cdot\text{Na}^+(\text{exo})$ | 2.400 | 2.390 | 2.374 | | 2.381 | 2.369 |
| $4(\text{PC2})\cdot\text{Na}^+(\text{endo})$ | 2.673 | 2.390 | | | | |
| $4(1,2\text{-a})\cdot\text{Na}^+$ | 2.346 | 2.348 | | | | |
| $4(1,3\text{-a})\cdot\text{Na}^+(\text{exo})$ | 2.413 | 2.392 | | | 2.344 | 2.358 |
| Average Distance from Na^+ | 2.413 | 2.416 | 2.455 | 2.409 | 2.363 | 2.371 |
| $4(\text{cone})\cdot\text{K}^+(\text{exo})$ | 2.873 | 2.798 | 2.915 | 2.824 | 2.705 | 2.720 |
| $4(\text{cone})\cdot\text{K}^+(\text{endo})$ | 2.883 | 2.859 | | | | |
| $4(\text{PC1})\cdot\text{K}^+(\text{exo})$ | 2.679 | 2.687 | 2.753 | | 2.656 | |
| $4(\text{PC1})\cdot\text{K}^+(\text{endo})$ | 2.647 | 2.969 | | | 2.894 | |
| $4(\text{PC2})\cdot\text{K}^+(\text{exo})$ | 2.712 | 2.673 | 2.683 | | 2.736 | 2.750 |
| $4(\text{PC2})\cdot\text{K}^+(\text{endo})$ | 2.750 | 2.845 | | | | |
| $4(1,2\text{-a})\cdot\text{K}^+$ | 2.724 | 2.744 | | | | |
| $4(1,3\text{-a})\cdot\text{K}^+(\text{exo})$ | 2.714 | 2.714 | | | 2.758 | 2.758 |
| Average Distance from K^+ | 2.748 | 2.786 | 2.784 | 2.824 | 2.750 | 2.743 |

Table 6. Main characteristic features of the mPW1PW91 calculated vibrational modes of the free host of **3** and its stable complexes with alkali metal ion

| 3 (cone) | 3 (cone) $\cdot\text{Na}^+(\text{exo})$ | 3 (cone) $\cdot\text{Na}^+(\text{endo})$ | Vibrational modes | 3 (cone) $\cdot\text{K}^+(\text{exo})$ | 3 (1,3-a) $\cdot\text{Na}^+(\text{exo})$ |
|-------------------------|--|---|---|---|---|
| Energy/cm ⁻¹ | Energy/cm ⁻¹ | Energy/cm ⁻¹ | Description | Energy/cm ⁻¹ | Intensity ^a |
| 665-713 | 665 | 674 | C-C-C bending | 703 | 703 |
| 941 | 949 | 941 | C _{methylene} -O _{ether} stretching | 949 | 994 |
| 1053 | 1060 | 1038 | | 1053 | 1060 |
| 1112 | 1105 | 1105 | C _{aromatic} -O _{ether} stretchings | 1105 | 1112 |
| 1164 | 1172 | 1164 | | 1172 | 1172 |
| 1172 | 1224 | 1202 | C _{methylene} -O _{ester} stretching | 1216 | 1224 |
| 1425,1432 | 1410 | 1403, 1425 | C-C _{aromatic} stretchings | 1417, 1424 | 1425 |
| 1730 | 1700 | 1733 | C=O stretchings | 1700 | 1692 |
| 1737 | 1715 | 1737 | | 1715 | 1700 |
| $\sim 2854^b$ | $\sim 2831^b$ | $\sim 2861^b$ | C _{methyl} -H stretchings | $\sim 2861^b$ | $\sim 2861^b$ |
| $\sim 2958^b$ | $\sim 2950^b$ | $\sim 2950^b$ | C _{methylene} -H stretchings | $\sim 2958^b$ | $\sim 2972^b$ |

^aCalculated absorption bands obtained by the mPW1PW91/6-31G(d) method using the broadened IR spectra assuming a Lorentzian line width of 10 cm⁻¹. For direct comparison with experimental data, the calculated vibrational frequencies were scaled by the recommended scale factor (0.93).²⁴

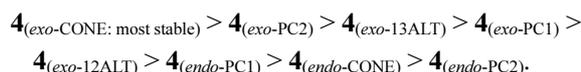
^bThese peaks were made using the broadened IR spectra of the numerous peaks of the C-H stretching vibrations.

than ~ 2.90 Å and are marked as bonded. The cation complexed at the *exo*-position of **4**_(cone) shows electrostatic interactions with all of the ether- and carbonyl-oxygens of the four branches of **4** (see Figures 2(a) and 2(b)).

In Tables 3 and 4, the numbers of strong binding modes of the cation-oxygen (between an alkali metal cation and the oxygen atoms) and cation- π (between an alkali metal cation and the π electrons of aromatic rings) interactions are explicitly reported. It can be clearly seen that the complexation

efficiencies of these hosts with the alkali metal cations are proportional to the total number of the two kinds of attractive interactions. The cone, PC2, and 13ALT *exo*-complexes are calculated to be the most efficient and show the maximum number (6) of interactions compared with those (4 or 5) of the other less efficient complexes.

The ordering of the relative complexation efficiencies ($-\Delta E_{\text{complex}}$) of **4**·Na⁺ complexes that resulted from the *mPW1PW91/6-31G(d,p)* calculations is as follows:



Calculated Infrared Spectra. The IR spectra of the free host **3**(cone) and its stable complexes, **3**(cone)·Na⁺(*endo*), **3**(cone)·Na⁺(*exo*), **3**(cone)·K⁺(*exo*), and **3**(1,3-a)·Na⁺(*exo*) were calculated at the *mPW1PW91/6-31G(d)* level (Table 6 and Figure 7).

The weak peaks at 665–713 cm⁻¹ were caused by C–C_{aromatic} bending vibrations. The medium intensity peaks at around 941 and 1053 cm⁻¹ were attributed to C_{methylene}–O bond stretching vibrations. The medium intensity peaks at 1112 and 1164 cm⁻¹ were due to various C_{aromatic}–O bond stretching vibrations. The strong peaks at around 1172 cm⁻¹ were due to another C_{methylene}–O bond stretching vibration.

Several spectral features (frequencies and intensities) of the complexes are a little different from the free host **3** due to the anchored cation. The strong peak located at 1172 cm⁻¹ of cone-type free host **3** for the concerted symmetric stretching motions of C_{aromatic}–O bonds in the calix[4]arene skeleton moved up at 1224 cm⁻¹ for **3**(cone)·Na⁺(*exo*) and **3**(1,3-a)·Na⁺(*exo*) with weaker intensity hindered by the sodium cation.

The peaks at around 1425 cm⁻¹ were due to C–C_{aromatic} stretching vibrations. The peaks at around 1730 cm⁻¹ were due to two kinds of C=O stretching vibrations. The almost degenerate peaks which consist of 1730 and 1737 cm⁻¹ for the C=O stretching vibrations of free host **3**(cone) are moved down to lower frequencies and split further into two peaks (1700 and 1715 cm⁻¹) for **3**(cone)·Na⁺(*exo*) and **3**(cone)·K⁺(*exo*) due to the anchoring of the alkali-metal cation. Thus, the *exo*-complexation of the *cone* isomer with cation could be clearly confirmed by these differences of these diagnostic C=O bands in the free host and its complexes' IR spectra.

The final series of peaks (2854–2958 cm⁻¹) are attributable to various C–H stretching vibrations:

2854 cm⁻¹: C_{methoxy}–H (the bond between the methoxy carbon and hydrogen atom) stretching;

2958 cm⁻¹: C_{methylene}–H (the bond between the methylene carbon and hydrogen atom) antisymmetric stretching.

Conclusion

The complexation characteristics of mixed [2 + 2']calix[4]aryl derivatives with alkali metal cations were investigated by the *mPW1PW91* (hybrid HF-DF) calculation method. The total electronic and Gibbs free energies of the various complexes (cone, partial-cone, 1,2-alternate, and 1,3-alter-

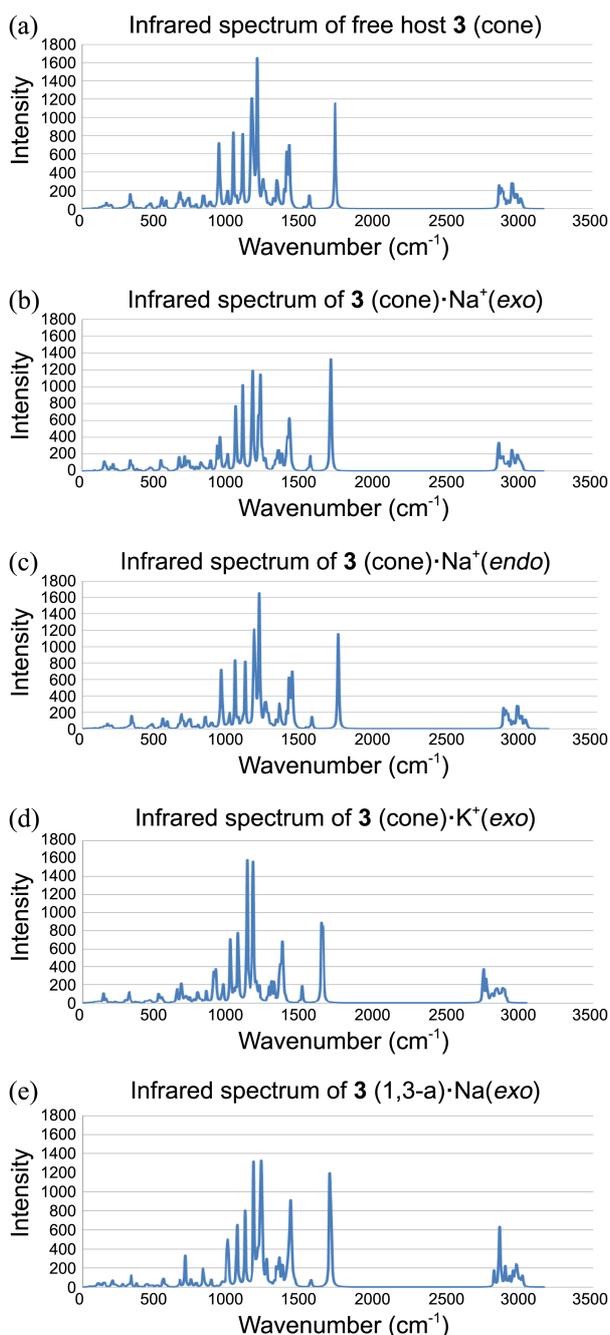


Figure 7. Calculated IR spectra of (a) free host **3**(cone), (b) **3**(cone)·Na⁺(*endo*), (c) **3**(cone)·Na⁺(*exo*), (d) **3**(cone)·K⁺(*exo*), and (e) **3**(1,3-a)·Na⁺(*exo*). The broadened IR spectra are assuming a Lorentzian line width of 4 cm⁻¹. For direct comparison with experimental data, the calculated vibrational frequencies were scaled by the recommended scale factor (0.93).²⁴

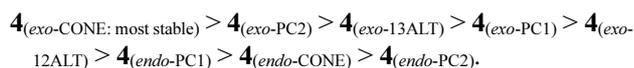
nate) of the sodium and potassium cations with **3** and **4** and the differences between them were reported.

The orderings of the relative energies (ΔE in kcal/mol) of the conformations of the free hosts **3** and **4** that resulted from the mPW1PW91 calculations are as follows:



The mPW1PW91 calculations suggest that the *exo*-complexation efficiencies of the sodium ion with hosts **3** and **4** are excellent (around 90-100 kcal/mol) and are 24-27 kcal/mol better than those of the potassium ion, respectively. These trends are in accord with the experimental results. These *exo*-complexation efficiencies of the sodium ion inside the cavity of the lower rim of the cone-type hosts **3** and **4** are *ca.* 14-17 kcal/mol better than those of the *endo*-complexation inside the upper rim, respectively.

The ordering of the relative complexation efficiencies ($-\Delta E_{\text{complex}}$) of 4-Na^+ complexes that resulted from the mPW1PW91/6-31G(d,p) calculations is as follows:



The *exo*-complexation of the *cone* isomer of **3** with cation could be clearly confirmed by the differences of the diagnostic C=O bands in the free host and its complex's IR spectra.

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