



Computational study of ion-pair recognition by heteroditopic calix[4]diquinone derivative



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ABSTRACT

The complexation characteristics of isophthalamide diether calix[4]diquinone macrobicycle (**1**) with ion-pairs (alkali metal or ammonium cation and halide anion) were investigated by quantum mechanical calculation methods. The total electronic and Gibbs free energies of the various (monotopic, heteroditopic, and contact motifs) complexes of alkali metal and ammonium cations and/or halide anions with **1** were analyzed and compared. The structures of the endo- or exo-complexes of the various cations and anions with the host (**1**) were optimized using the mPW1PW91/6-31G(d,p) method, followed by DFT B3LYP/6-31G(d,p) calculations. Although the cone conformer is less stable than the partial cone and 1,3-alternate conformers of the free host (**1**), the cone-type complexes are more stable than the partial cone and 1,3-alternate analogues. The contact-complexation efficiencies of the sodium-halide ion-pair inside the cavity of the lower rim of the cone-type hosts were better (~20 kcal/mol) than those of the potassium ion-pair. These calculated outcomes agree with the experimental results of the anion-binding behavior of **1** · M⁺. The contact-complexation efficiencies of the ion-pairs inside the lower rim pocket of the host **1**(cone) were much better (45–50 kcal/mol) than those of its heteroditopic-complexation with host **1**.

The exo-complexation of the cone isomer with the ion-pair could be clearly confirmed by differences in the diagnostic C=O bands in the free host and the infrared spectra of its complexes.

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1. Introduction

Calixarenes [1–4] have a well-defined molecular framework and are attractive as a basic skeleton for constructing new supramolecular systems [5–10]. The complexation properties of these molecules appear to be highly dependent upon the nature and number of donor atoms of the calix[4]aryl receptor [11–17].

Historical developments in the field of cation recognition and sensing [18] have been recently emulated in the emergence of a large number of systems for the recognition and sensing of anions. [19–24] However, the designs of ion receptors studied to date have almost universally focused on the selective recognition of either a cation or an anion, which may be achieved through careful consideration of the size, geometry, and solvation properties of the target guest species. In these systems, the cation can be bound using a number of common motifs, while the anion is coordinated using Lewis acidic, electrostatic, or hydrogen bonding interactions [25–28]. Therefore, this approach implicitly neglects the obviously

important role of the counterion in controlling the strength and selectivity of the recognition process; such a shortcoming is commonly compensated for by making the counterion “non-coordinating”.

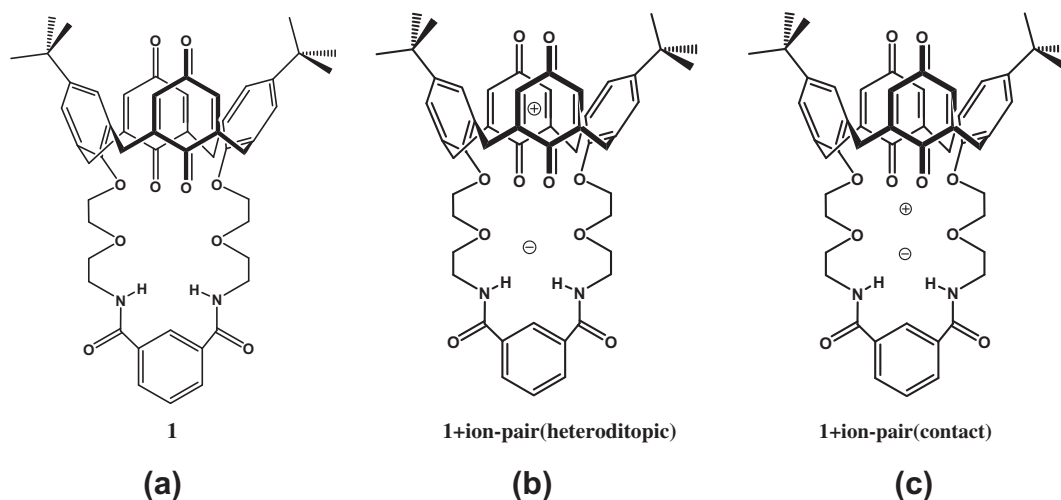
However, an alternative paradigm for ion recognition exists and involves the design of systems wherein the binding of both cation and anion, an ion-pair, can be achieved. The design and application of new heteroditopic receptor systems capable of simultaneous coordination of both anionic and cationic guest species has recently attracted a great deal of interest [29]. Such an approach offers considerable benefits as the overall receptor/ion-pair complex is charge neutral and should prove advantageous for salt solubilization, extraction, detection, and membrane-transport applications [30–39].

Interest in a contact ion-pair binding approach, wherein the anion and cation are bound essentially as one moiety, is particularly noteworthy as this avoids the energetically unfavorable separation of the two ions [40,41]. Importantly, the geometry of the ditopic receptor must be optimized so that the anion and cation binding sites are located in proximity to enhance this interaction, as an incorrect orientation could lead to the ion pair associating outside of the receptor, or solvent-separated ion binding.

Beer's group reported the design, synthesis and binding properties of one such rare system, which demonstrates a dramatic

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Scheme 1. Chemical structures of (a) isophthalamide diether calix[4]diquinone macrobicycle (**1**) and its ion-pair (b) heteroditopic and (c) contact complexes.

Table 1
mPW1PW91/6-31G(d,p) Calculated Energies of the Conformers of the Free Host (**1**).

Conformer ^a	Total electronic energy		Gibbs Free energy	
	E^b (a.u.)	ΔE^c (kcal/mol)	G^d (a.u.)	ΔG^c (kcal/mol)
CONE	-2876.3842	12.9	-2875.4806	8.6
PC	-2876.4025	1.5	-2875.4931	0.8
13ALT	-2876.4049	0.0	-2875.4944	0.0

^a Abbreviations of conformers: PC denotes a partial conformation, one ring inverted out of the two 1,4-benzoquinones of the lower rim of the host; 13ALT is the 1,3-alternate, both the benzoquinones are inverted from the mean plane of the calix[4]aryl skeleton.

^b The error limits of these calculated total electronic energies are about 0.00001 a.u. (0.01 kcal/mol).

^c ΔE or ΔG (kcal/mol) is defined as the energy of the conformer minus the energy of the most stable 13ALT conformation of **1** obtained using 1 a.u. = 627.50955 kcal/mol.

^d Sum of total electronic and thermal Gibbs free energies at 298 K.

enhancement of anion binding by a cobound cation and, in some cases, strong binding with associated ion pairs where no affinity for the free ions is observed [42,43]. A heterotopic receptor (Scheme 1b) relies on the incorporation of distinct anion and cation binding sites within the same molecule to recognize multiple ions [44–49,25,50–59]. The ion-pair recognition process is ideally

cooperative in nature, such that the binding of one ion enhances the binding of the other and vice versa. The design of these heteroditopic receptors commonly relies on separating the two ions, which incurs an unfavorable Coulombic energy penalty. To circumvent this event, it is desirable to coordinate the ion pair such that the components are in contact (Scheme 1c). Such a requirement places severe restrictions on the receptor design that can be employed, and consequently such systems are extremely rare, but recently Smith et al. [60–65] and Rissanen et al. [66] demonstrated the power of such an approach.

The calix[4]diquinone unit has well-documented cation binding properties that may be readily probed by electrochemical and UV-visible spectroscopic methods [67]. The isophthalamide cleft has been widely utilized as an anion binding unit in a variety of systems [68–70]. It was hoped that a considerable enhancement of anion recognition would take place in the presence of a bound cationic guest species by using a combination of these two moieties.

We report herein the computational analysis of a new class of ion-pair receptors reliant on the proximal inclusion of calix[4]diquinone cation binding and isophthalamide-based anion binding fragments within the same macrobicycle. The complexation characteristics of the heteroditopic calix[4]diquinone derivative (**1**) with ion-pairs (alkali metal or ammonium cation and halide anion) were investigated using mPW1PW91 (hybrid HF–DF) and DFT

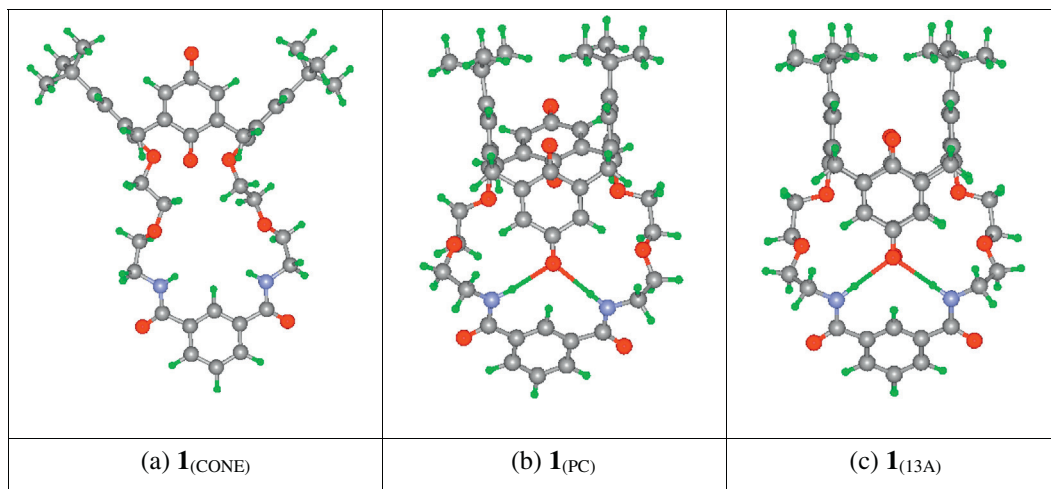


Fig. 1. mPW1PW91/6-31G(d,p) calculated structures of various conformations (cone, PC and 13ALT) for the free host **1**. (a) CONE, (b) PC, and (c) 13ALT.

Table 2
mPW1PW91/6-31G(d,p) calculated energies of isolated ion-pairs.

Cation	K ⁺	Na ⁺	NH ₄ ⁺	Anion	
	–599.7449	–162.0653	–56.8913		
Ion-pair	Total electronic energy ^a				
Salt(Cation ⁺ -Cl ⁻)	–1060.1949	–622.5455	–517.3690	Cl ⁻	–460.2575
Salt(Cation ⁺ -Br ⁻)	–3171.8613	–2734.2141	–2629.0231	Br ⁻	–2571.9182
Complexation energy ^b					
Salt(Cation ⁺ -Cl ⁻)	–120.81	–139.70	–138.18		
Salt(Cation ⁺ -Br ⁻)	–124.38	–144.68	–134.02		

^a The error limit of the calculated total electronic energy is 0.00001 a.u.

^b Complexation energy = $E_{\text{ion-pair}} - E_{\text{cation}} - E_{\text{anion}}$. The error limit is 0.01 kcal/mol.

Table 3
mPW1PW91/6-31G(d,p) calculated energies of Na⁺-anion contact complexes in three different conformations of host (1).

Host (1)	Energy ^a	Guests	Energy ^a	Complexation energy ^b	Guest	Energy ^a
Cone	–2876.38425	Na ⁺ (exo) + Cl ⁻ (exo)	–3499.01447	–192.88	Na ⁺	–162.0653
		Na ⁺ (exo) + Br ⁻ (exo)	–5610.69132	–203.04	Cl ⁻	–460.2575
					Br ⁻	–2571.9182
PC	–2876.40250	Na ⁺ (exo) + Cl ⁻ (exo)	–3499.00056	–184.15		
		Na ⁺ (exo) + Br ⁻ (exo)	–5610.68107	–196.61		
13A	–2876.40486	Na ⁺ (exo) + Cl ⁻ (exo)	–3498.98413	–173.85		
		Na ⁺ (exo) + Br ⁻ (exo)	–5610.66870	–188.85		

^a The Error limit of the calculated total electronic energy is 0.00001 a.u.

^b Complexation energy = $E_{\text{Complex}} - E_{\text{Cone-Host}} - E_{\text{Guests}}$. The error limit is 0.01 kcal/mol.

Table 4
mPW1PW91/6-31G(d,p) calculated total electronic energies^a of the cone-type complexes of host (1) with ions.

	Guest	K ⁺	Na ⁺	NH ₄ ⁺	Cl ⁻	Br ⁻
Monotopic complexes	Endo	–599.7449	–162.0653	–56.8913	–460.2575	–2571.9182
	Exo	–3476.1939	–3038.5590	–2933.3339	–3336.6709	–5448.3469
Ditopic complexes		–3476.2368	–3038.5750	–2933.3694	–3336.7042	–5448.3753
		K ⁺ Halogen ⁻	Na ⁺ Halogen ⁻	NH ₄ ⁺ Halogen ⁻		
Heteroditopic	Cation(endo)+Cl ⁻ (exo)	–3936.5851	–3498.9413	–3393.7385		
Contact	Cation(exo)+Cl ⁻ (exo)	–3936.6634	–3499.0145	–3393.8135		
Heteroditopic	Cation(endo)+Br ⁻ (exo)	–6048.2563	–5610.6134	–5505.3824		
Contact	Cation(exo)+Br ⁻ (exo)	–6048.3292	–5610.6913	–5505.4836		
Complexation energy: ΔE (kcal/mol) ^b						
Monotopic Complexes	Endo	K ⁺	Na ⁺	NH ₄ ⁺	Cl ⁻	Br ⁻
	Exo	–40.7	–68.7	–36.6	–18.3	–27.9
Ditopic complexes		–67.5	–78.7	–58.9	–39.2	–45.8
		K ⁺ Halogen ⁻	Na ⁺ Halogen	NH ₄ ⁺ Halogen ⁻		
Heteroditopic	Cation(endo) + Cl ⁻ (exo)	–124.5	–147.0	–128.9		
Contact	Cation(exo) + Cl ⁻ (exo)	–173.6	–192.9	–176.0		
Heteroditopic	Cation(endo) + Br ⁻ (exo)	–131.2	–154.1	–118.4		
Contact	Cation(exo)+Br ⁻ (exo)	–176.9	–203.0	–181.9		

^a The error limits of these calculated energies are about 0.00001 a.u. (0.01 kcal/mol).

^b ΔE (complexation energy; kcal/mol) is defined as the energy of the complex minus the energies of the guest ion(s) and the CONE conformation of host (1) using 1 a.u. = 627.50955 kcal/mol.

B3LYP calculation methods. The various structures and relative binding affinities of cone-shaped calix[4]diquinone derivative (**1**) toward alkali metal cation and halide anions were studied, focusing on the binding sites (monotopic, heteroditopic, and contact motifs) of host molecules using the quantum mechanical calculation methods.

2. Computational methods

The initial structures of the isophthalamide diether calix[4]diquinone macrobicyclic (**1**) were constructed with HyperChem [71]. Conformational searches were performed using the simulated annealing method to find the optimized structures [72,73]. The

structures of the endo- or exo-complexes [74,75] of the various cations and anions with host **1** were optimized using the mPW1PW91/6-31G(d,p) method, followed by DFT B3LYP/6-31G(d,p) calculations using Gaussian 09 [76]. Modified Perdew-Wang 1-parameter (mPW1) calculations, [77,78] such as mPW1PW91, are hybrid Hartree-Fock-density functional (HF-DF) models that obtain good results both for covalent and non-covalent interactions [79]. The mPW1PW91/6-31G(d,p) method was also used to calculate the normal mode frequencies of the cone, partial-cone, 1,3-alternate, and conformers of **1** and the cone-type complexes of **1** with ions. None of the vibrational spectra showed negative frequencies, confirming that the optimized structures exist at an energy minimum. The calculated vibrational frequencies were scaled by the recommended scale factor for a direct

Table 5
mPW1PW91/6-31G(d,p) calculated gibbs free energies^a of the cone-type complexes of host (**1**) with ions.

Guest		K ⁺	Na ⁺	NH ₄ ⁺	Cl ⁻	Br ⁻
Monotopic complexes	Endo	-599.7601	-162.0797	-56.8608	-460.2726	-2571.9344
	Exo	-3475.29153	-3037.65235	-2932.3772		
Ditopic complexes					-460.2726	-2571.9344
					-3335.7999	-5447.4712
Heteroditopic	Cation(endo) + Cl ⁻ (exo)	-3935.6808	-3498.0346	-3392.7853		
Contact	Cation(exo) + Cl ⁻ (exo)	-3935.7620	-3498.1134	-3392.8545		
Heteroditopic	Cation(endo) + Br ⁻ (exo)	-6047.3525	-5609.7078	-5504.4301		
Contact	Cation(exo) + Br ⁻ (exo)	-6047.4350	-5609.7900	-5504.5270		
Complexation energy: $\Delta G(\text{kcal/mol})^b$						
Guest		K ⁺	Na ⁺	NH ₄ ⁺	Cl ⁻	Br ⁻
Monotopic complexes	Endo	-31.93	-57.74	-22.51		
	Exo	-57.24	-67.65	-42.42	-29.37	-35.31
Ditopic complexes						
Heteroditopic	Cation(endo) + Cl ⁻ (exo)	-105.16	-126.55	-107.52		
Contact	Cation(exo) + Cl ⁻ (exo)	-156.12	-176.05	-150.95		
Heteroditopic	Cation(endo) + Br ⁻ (exo)	-111.37	-133.75	-96.87		
Contact	Cation(exo) + Br ⁻ (exo)	-163.17	-185.29	-157.68		

^a The error limits of these calculated energies (sum of electronic and thermal Gibbs free energies at 298 K) are about 0.00001. a.u. (0.01 kcal/mol).^b ΔG (complexation energy: kcal/mol) is defined as the Gibbs free energy of the complex minus the energies of the guest ion(s) and the CONE conformation of host (**1**).**Table 6**
DFT B3LYP/6-31G(d,p) calculated total electronic energies^a of the cone-type complexes of host (**1**) with ions.

Guest		K ⁺	Na ⁺	NH ₄ ⁺	Cl ⁻	Br ⁻
Monotopic complexes	Endo	-599.7250	-162.0812	-56.9059	-460.2522	-2571.7613
	Exo	-3476.8366	-3039.2402	-2934.0091	-3337.3278	-5448.8513
Ditopic complexes						
Heteroditopic	Cation(endo) + Cl ⁻ (exo)	-3937.2233	-3499.6170	-3394.4105		
Contact	Cation(exo) + Cl ⁻ (exo)	-3937.3046	-3499.6953	-3394.4812		
Heteroditopic	Cation(endo) + Br ⁻ (exo)	-6048.7424	-5611.1390	-5505.9452		
Contact	Cation(exo) + Br ⁻ (exo)	-6048.8297	-5611.2208	-5506.0045		
Complexation energy: $\Delta E(\text{kcal/mol})^b$						
Guest		K ⁺	Na ⁺	NH ₄ ⁺	Cl ⁻	Br ⁻
Monotopic complexes	Endo	-40.06	-69.77	-34.77	-17.44	-26.46
	Exo	-69.62	-82.04	-60.31	-38.57	-44.84
Ditopic complexes						
Heteroditopic	Cation(endo) + Cl ⁻ (exo)	-124.41	-147.93	-128.39		
Contact	Cation(exo) + Cl ⁻ (exo)	-175.43	-197.06	-172.73		
Heteroditopic	Cation(endo) + Br ⁻ (exo)	-130.68	-155.99	-144.44		
Contact	Cation(exo) + Br ⁻ (exo)	-185.46	-207.33	-181.63		

^a The error limits of these calculated energies are about 0.00001. a.u. (0.01 kcal/mol).^b ΔE (complexation energy: kcal/mol) is defined as the energy of the complex minus the energies of the guest ion(s) and the CONE conformation of host (**1**).**Table 7**
Calculated distances (Å) from cations to the oxygen atoms of the cone-complexes of **1**.

Interaction	M...X		M...O(carbonyl)				M...O(C4ether)				M...O(CRN1)		M...O(CRN2)	
	Cl ⁻ (exo)	Br ⁻ (exo)	Cl ⁻ (exo)	Br ⁻ (exo)	Cl ⁻ (exo)	Br ⁻ (exo)	Cl ⁻ (exo)	Br ⁻ (exo)	Cl ⁻ (exo)	Br ⁻ (exo)	Cl ⁻ (exo)	Br ⁻ (exo)	Cl ⁻ (exo)	Br ⁻ (exo)
Na ^{+(endo)} Heteroditopic	5.62	5.38	3.74	3.65	2.27	2.22	2.28	2.22	3.82	3.66	4.91	4.50	5.23	4.84
Na ^{+(exo)} Contact	2.63	2.74	2.25	2.48	2.24	2.50	2.29	2.26	2.75	2.75	3.14	3.17	5.26	5.33
K ^{+(endo)} Heteroditopic	6.33	6.27	3.99	3.85	4.09	4.04	2.88	2.64	2.89	2.63	5.55	5.61	5.58	5.64
Na ^{+(exo)} Contact	3.01	3.10	2.81	2.61	2.56	2.89	3.02	3.07	2.95	3.13	2.92	2.84	5.44	5.33
NH ₄ ^{+(endo)} Heteroditopic	5.87	5.24	2.68	2.89	2.53	2.78	4.20	4.23	2.78	3.03	6.42	4.77	7.62	6.17
NH ₄ ^{+(exo)} Contact	3.02	3.14	2.72	2.93	2.66	2.92	3.15	3.01	3.07	3.01	3.31	3.00	4.46	5.21

Table 8
Calculated H-bond distances (Å) from halide anions to the hydrogen atoms of the cone-complexes of **1**.

Ditopic complexes	Cation(M ⁺)	X ⁻ · H(amide)			
		Cl _(exo) ⁻	Br _(exo) ⁻	Cl _(endo) ⁻	Br _(endo) ⁻
Heteroditopic Contact	Na ^{+(endo)}	2.29	2.29	2.37	2.46
	Na ^{+(exo)}	2.27	2.67	2.43	2.72
Heteroditopic Contact	K ^{+(endo)}	2.33	2.27	2.37	2.42
	K ^{+(exo)}	2.49	2.27	2.40	2.61
Heteroditopic Contact	NH ₄ ^{+(endo)}	2.42	2.46	2.49	2.50
	NH ₄ ^{+(exo)}	2.38	2.53	2.42	2.61

comparison with the experimental data [80]. Furthermore, the broadened infrared (IR) spectra are presented, assuming a Lorentzian line width of 4 cm⁻¹.

3. Results and discussion

3.1. Conformers of the free host (**1**)

The conformation of calix[4]arenes was analyzed in terms of 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 “cone”, “partial cone”, “1,2-alternate” and “1,3-alternate”, respectively [1–4]. However, the

1,3-bridged crown-ether moiety at the lower rim of **1** prohibited the ‘1,2-alternate’ conformation. Therefore, three conformations (abbreviated CONE, PC, and 13A) are possible in free host **1**. The calculated relative stabilities (ΔE) in Table 1 suggest that the PC (partial cone) or 13A (1,3-alternate) forms are more stable than the CONE conformer of **1**, respectively. Two strong hydrogen bonds between one of the oxygen atoms in the 1,4-benzoquinones at the upper rim and two hydrogen atoms in the isophthalamide group of the lower rim of the host make the PC and 13A conformers very stable. (See Fig. 1)

The ordering of the relative energies (ΔE in kcal/mol) of the conformations of **1** that resulted from the mPW1PW91/6-31G(d,p) calculations in Table 1 is as follows: **1**(PC) ~ **1**(13A) > **1**(CONE: least stable).

3.2. Binding strengths of the individual alkali metal cation interactions:

The cation-oxygen binding energies are reported to be -26.2 (Na⁺) and -18.1 (K⁺) kcal/mol when the cation binds to the O–H group of the phenol based on the HF/6-311G(d,p) calculation [15]. The cation- π interaction energy of the alkali metal ion with a benzene ring and debutylated calix[4]arene was calculated using the mPW1PW91/6-31G(d) method [68–70], in which the Na⁺-benzene binding energy is reported to be -28.5 kcal/mol, and Na⁺-cone-calix[4]arene binding energy in the upper rim is -54.8 kcal/mol, the K⁺-benzene binding energy is -18.7 kcal/mol and the K⁺-cone-calix[4]arene binding energy is -43.3 kcal/mol.

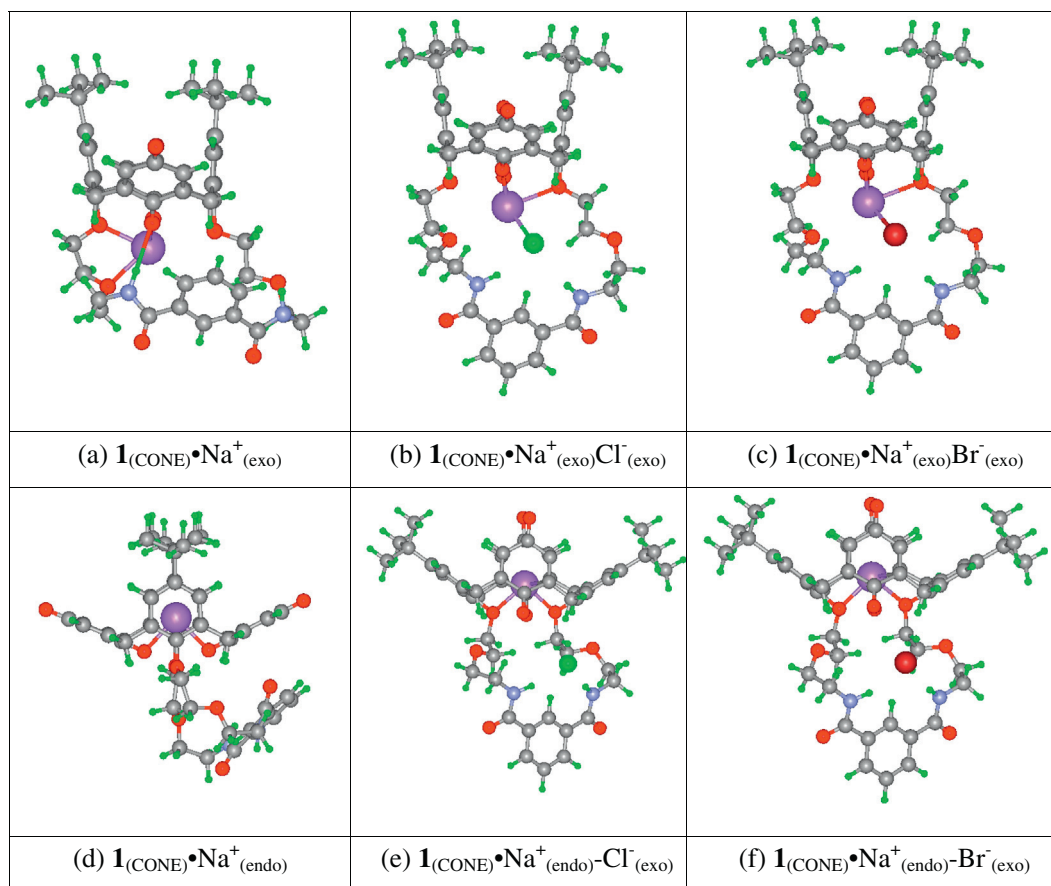


Fig. 2. mPW1PW91/6-31G(d,p) calculated CONE-type Na⁺-complexes of **1**. (a) **1**_(CONE) · Na⁺_(exo), (b) **1**_(CONE) · Na⁺_(exo)Cl_(exo)⁻, (c) **1**_(CONE) · Na⁺_(exo)Br_(exo)⁻, (d) **1**_(CONE) · Na⁺_(endo), (e) **1**_(CONE) · Na⁺_(endo)Cl_(exo)⁻, (f) **1**_(CONE) · Na⁺_(endo)Br_(exo)⁻. Atoms that are within a certain distance (the bond proximate distance) from one another are automatically marked as bonded.²²

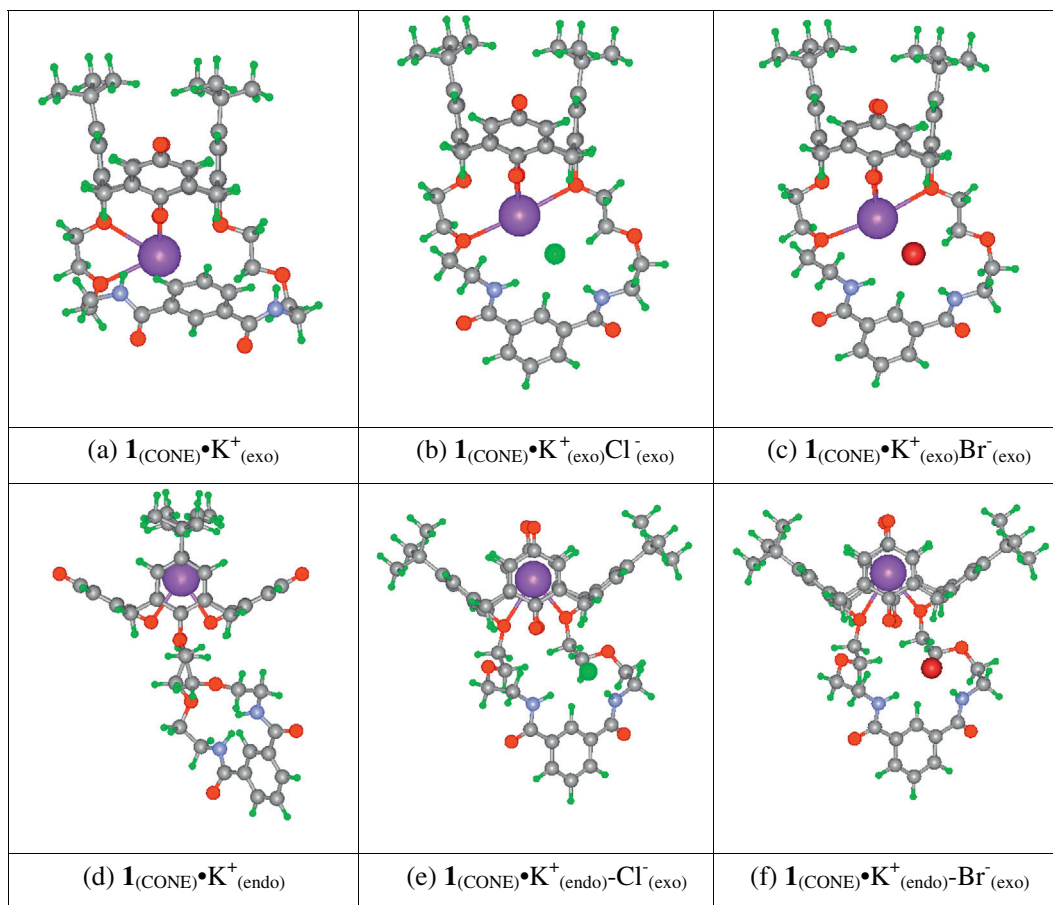


Fig. 3. mPW1PW91/6-31G(d,p) calculated CONE-type K^+ -complexes of **1**. (a) $\mathbf{1}_{(\text{CONE})} \cdot \mathbf{K}_{(\text{exo})}^+$, (b) $\mathbf{1}_{(\text{CONE})} \cdot \mathbf{K}_{(\text{exo})}^+ \text{Cl}_{(\text{exo})}^-$, (c) $\mathbf{1}_{(\text{CONE})} \cdot \mathbf{K}_{(\text{exo})}^+ \text{Br}_{(\text{exo})}^-$, (d) $\mathbf{1}_{(\text{CONE})} \cdot \mathbf{K}_{(\text{endo})}^+$, (e) $\mathbf{1}_{(\text{CONE})} \cdot \mathbf{K}_{(\text{endo})}^+ \text{Cl}_{(\text{exo})}^-$, (f) $\mathbf{1}_{(\text{CONE})} \cdot \mathbf{K}_{(\text{endo})}^+ \text{Br}_{(\text{exo})}^-$.

3.3. Binding strengths of the contact (cation and anion) ion-pair interactions:

The isolated binding strength between cation and halide anion has been calculated for the contact ion-pairs. As shown in Table 2, the sodium (about -142 kcal/mol) and ammonium (-136 kcal/mol) ion-pairs contributed stronger attraction interaction energies than that of the potassium (-122 kcal/mol) ion-pairs.

3.4. Complexation energies of the cone-type host (**1**) with ions:

Although the partial-cone or 1,3-alternate conformers of the free host (**1**) are more stable than the cone conformer as shown in Table 1, the cone-type complexes of host **1** were calculated to be more stable than the partial-cone or 1,3-alternate analogues due to more cation-oxygen and cation- π (heteroditopic case) interactions [67–70]. As one see Table 3 of the preliminary calculations of Na^+ -anion contact complexes, partial-cone (PC) complexes ($\mathbf{1}_{(\text{PC})} \cdot \text{Na}_{(\text{exo})}^+ \text{Cl}_{(\text{exo})}^-$ and $\mathbf{1}_{(\text{PC})} \cdot \text{Na}_{(\text{exo})}^+ \text{Br}_{(\text{exo})}^-$) are 6–8 kcal/mol less stable than cone-type analogues, and 1,3-alternate (13A) complexes ($\mathbf{1}_{13A} \cdot \text{Na}_{(\text{exo})}^+ \text{Cl}_{(\text{exo})}^-$ and $\mathbf{1}_{13A} \cdot \text{Na}_{(\text{exo})}^+ \text{Br}_{(\text{exo})}^-$) were 15–20 kcal/mol less stable than cone-type complexes.

Therefore, we have computed the cone-type complexes only, and Tables 4–6 show the calculated complexation energies of the various (monotopic, heteroditopic, and contact motifs) cone-type complexes of alkali metal and ammonium cations and/or halide anions with **1**.

3.5. Complexation energies of cone-type host (**1**) with monotopic ions:

Alkali metal or ammonium cation was inserted at either endo (calix) or exo (crown-ether) position of the calix[4]diquinone macrocycle (**1**) to analyze the cation- π and cation-oxygen interaction energies of the various monotopic complexes. As you see Table 4, the exo-complexation efficiencies were about 10–27 kcal/mol better than the endo cases. And the sodium ion showed better binding ability than potassium or ammonium ions (the complexation energies in kcal/mol):

Monotopic cation (*exo*): $\text{Na}^+(-79) > \text{K}^+(-68) > \text{NH}_4^+(-59)$,

Monotopic cation (*endo*): $\text{Na}^+(-69) > \text{K}^+(-41) > \text{NH}_4^+(-37)$.

A halide anion was inserted at the exo position to calculate the strength of the hydrogen bonding between the anion and two hydrogen atoms in the isophthalamide moiety of the macrocycle. Bromine ion showed better binding ability than that of chlorine ion:

Monotopic anion (*exo*): $\text{Br}^-(-46) > \text{Cl}^-(-39)$.

3.6. Complexation energies of cone-type host (**1**) with ion-pairs:

The contact-complexation efficiencies of the sodium-halide ion-pair inside the cavity of the lower rim of hosts were better (~ 20 kcal/mol) than those of the potassium or ammonium-halide ion-pair (see Tables 4–6). These calculated outcomes agreed with

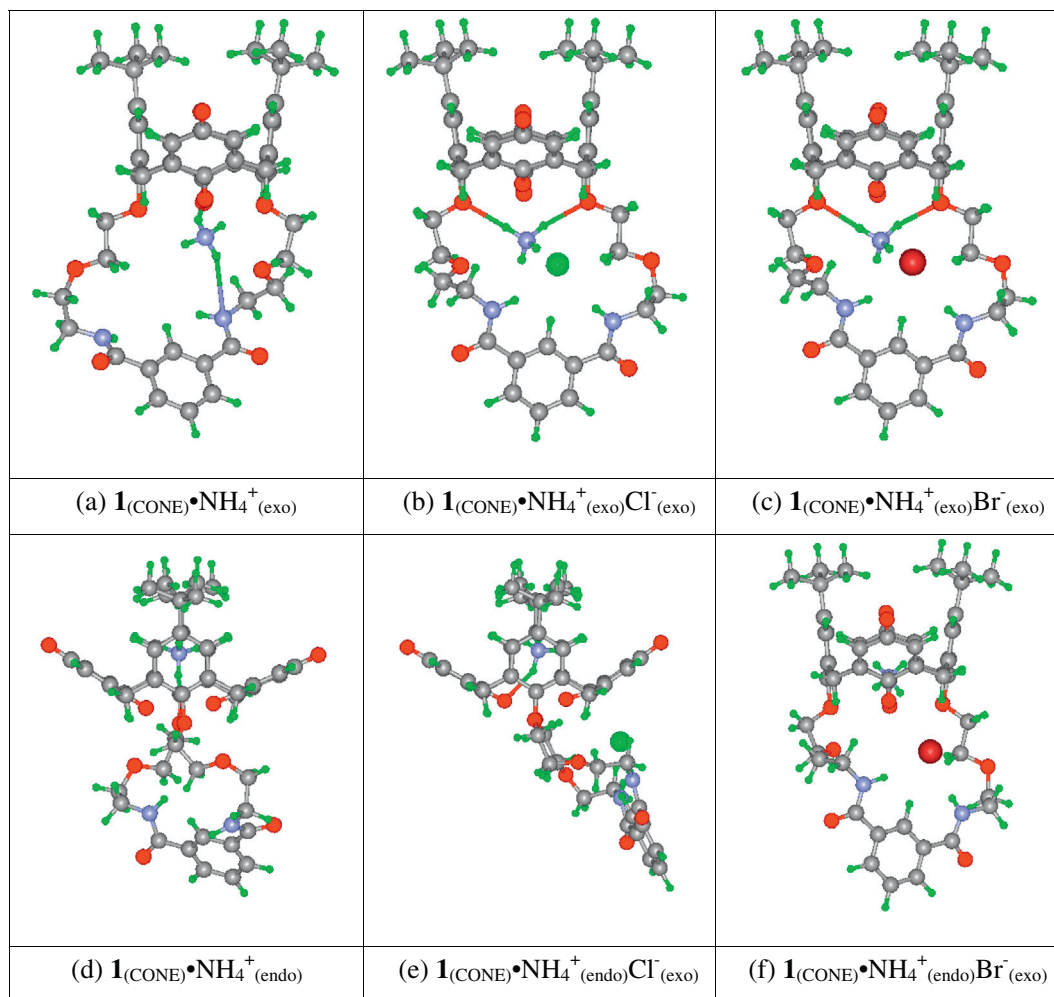


Fig. 4. mPW1PW91/6-31G(d,p) calculated CONE-type NH_4^+ -complexes of **1**. (a) $\mathbf{1}_{(\text{CONE})} \cdot \text{NH}_4^+(\text{exo})$, (b) $\mathbf{1}_{(\text{CONE})} \cdot \text{NH}_4^+(\text{exo}) \text{Cl}^-(\text{exo})$, (c) $\mathbf{1}_{(\text{CONE})} \cdot \text{NH}_4^+(\text{exo}) \text{Br}^-(\text{exo})$, (d) $\mathbf{1}_{(\text{CONE})} \cdot \text{NH}_4^+(\text{endo})$, (e) $\mathbf{1}_{(\text{CONE})} \cdot \text{NH}_4^+(\text{endo}) \text{Cl}^-(\text{exo})$, (f) $\mathbf{1}_{(\text{CONE})} \cdot \text{NH}_4^+(\text{endo}) \text{Br}^-(\text{exo})$.

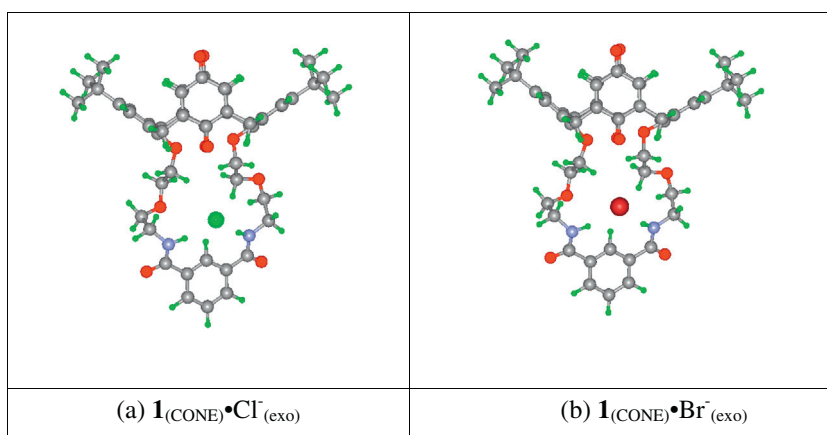


Fig. 5. mPW1PW91/6-31G(d,p) calculated CONE-type Anion-complexes of **1**. (a) $\mathbf{1}_{(\text{CONE})} \cdot \text{Cl}^-(\text{exo})$, (b) $\mathbf{1}_{(\text{CONE})} \cdot \text{Br}^-(\text{exo})$.

the experimental results of the anion-binding behavior of **1** · M^+ . [43] And, the contact-complexation efficiencies of the cation-bromide ion-pair inside the cavity of the lower rim of hosts were better (~7 kcal/mol) than those of the cation-chloride ion-pair. These contact-complexation (Scheme 1c) efficiencies of the ion-pairs were much better (45–50 kcal/mol) than those of the

heteroditopic-complexation (Scheme 1b) of the ion-pairs with the host. The excellent contact-complexation efficiency originated from the fact that the contact (cation and anion) ion-pair attraction interaction is much stronger than the long-distance (6 Å) heteroditopic ion-pair interaction. The calculated distances between interacting atoms are explained in detail below like Table 7 (from

Table 9Infrared (IR) spectra of the **1**(cone) and its stable complexes with sodium cation and halide anion (exo).

1 (cone) Free host Energy (cm ⁻¹)	1 · Na ⁺ (exo) Cl ⁻ Contact Energy (cm ⁻¹)	1 · Na ⁺ (endo)Cl ⁻ Heteroditopic Energy (cm ⁻¹)	Complexes Complex motif Vibrational modes	1 · Na ⁺ (exo)Br ⁻ Contact Energy (cm ⁻¹)	1 · Na ⁺ (endo)Br ⁻ Heteroditopic Energy (cm ⁻¹)
–	204	–	Na ⁺ -Anion stretching <i>exo</i> -complexed	188	–
523	544	679	N–H waggings	573	722,731
1109	1114	1111,1140	C _{aromatic} –O _{ether} stretching	1117	1112,1140
1242	1234	1228,1270	C–C stretching	1234	1270
1460	1435,1494	1430,1492	C–N stretching	1435,1485	1486
1653–1678	1644–1663	1641–1679	C=O stretching	1648–1669	1645–1668
2848–2942	2837–2933	2835–2931	C _{tb} –H stretching	2833–2933	2833–2935
3427,3444	3260,3352	3188,3203	N–H stretching	3285,3343	3188,3203

Table 10Main characteristic features of the mPW1PW91 calculated vibrational modes of the partial-cone conformer of **1** and cone-type complexes with potassium cation and halide anion (exo).

1 (partial-cone) Energy (cm ⁻¹)	1 · K ⁺ (exo) Cl ⁻ Energy (cm ⁻¹)	1 · K ⁺ (endo) Cl ⁻ Energy (cm ⁻¹)	Vibrational modes Description	1 · K ⁺ (exo)Br ⁻ Energy (cm ⁻¹)	1 · K ⁺ (endo)Br ⁻ Energy (cm ⁻¹)
–	163	–	K ⁺ -Anion stretching <i>exo</i> -complexed	146	–
523	599,655	679	N–H wagging	599,655	680
1112	1117	1111,1147	C–O stretching	1117	995,1111
1264	1234	1225,1271	C–C stretching	1234	1270
1489	1436,1485	1492	C–N stretching	1436,1485	1488
1630–1662	1644–1669	1646–1679	C=O stretching	1644–1669	1648–1673
2826–2950	2835–2933	2835–2931	C–H stretching	2835–2933	2835–2933
3356,3370	3204,3306	3188,3203	N–H stretching	3204,3306	3158,3180

Table 11Main characteristic features of the mPW1PW91 calculated vibrational modes of cone-type complexes of **1** with ammonium cation and halide anion (exo).

1 · NH ₄ ⁺ (exo) Cl ⁻ Energy (cm ⁻¹)	1 · NH ₄ ⁺ (endo) Cl ⁻ Energy (cm ⁻¹)	Vibrational modes Description	1 · NH ₄ ⁺ (exo) Br ⁻ Energy (cm ⁻¹)	1 · NH ₄ ⁺ (endo) Br ⁻ Energy (cm ⁻¹)
562,593	565,573	N–H wagging	594,614	590,663
1121	1117	C–O stretching	1122	1116
1232	1242	C–C stretching	1233	1238
1435,1494	1394,1494	C–N stretching	1481,1489	1485,1496
1646–1665	1651	C=O stretching	1648–1668	1629–1669
2582	–	N–H (H-bond with halide anion)	2580	–
2841–2933	2841–2937	C–H stretching	2837–2942	2824–2942
3180–3385	3109–3402	N–H stretching	3168–3382	3144–3315

cations to the oxygen atoms) and Table 8 (H-bond distances from halide anions to the hydrogen atoms).

Tables 7 and 8 report the calculated distances between the ions and the ligating atoms of **1**. In Figs. 2–5, 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. Alkali metal cations cannot have this high a coordination number. The cation complexed at the *exo*-position of **1**(cone) (Figs. 2 and 3) show electrostatic interactions with a cation and some of the ether- and diquinone-oxygen atoms of the lower rim of **1**. The Na⁺···Br⁻ (2.74 Å) and Na⁺···O distances (~2.50 Å) in **1**·Na⁺(exo)·Br⁻(exo) contact-complex (Fig. 2c) shows strong attractions. Experimental cation–anion distances of Na⁺···Br⁻ (2.79 Å) and K⁺···Br⁻ (3.23 Å) of a different cation–anion contact-complex [63] shows very similar values with our calculated distances (2.74 Å (Fig. 2c) and 3.10 Å (Fig. 3c)) of host **1** in Table 5, respectively. And our calculated N–H···Cl⁻ distance (3.02 Å) of **1**(cone) · NH₄⁺(exo) Cl⁻(exo) contact-complex (Fig. 4b) is comparable with experimental value (3.24 Å) [43].

Table 8 reports that the anion complexed at the *exo*-position of **1**(cone) shows very short H-bond distances, therefore, strong hydrogen bondings between an anion and two of the hydrogen atoms in the isophthalamide moiety of the lower rim of **1**. (See also Fig. 5.)

It can be clearly seen that the complexation efficiencies of these hosts with the ion-pairs were proportional to the total number of multiple attractive interactions such as cation–oxygen, cation–π, and hydrogen bonding interactions.

3.7. Calculated IR spectra

The IR spectra of the free host **1** and its contact and heteroditopic complexes were calculated at the mPW1PW91/6-31G(d,p) level (Tables 9–11 and Figs. 6–9). The spectra of the complexes from two alkali metal ions (Na⁺: Table 9, K⁺: Table 10) were very similar; therefore, only the sodium- and ammonium-complexes are described in the following:

1(cone) · Na⁺–Cl⁻ complexes: A weak peak at 204 cm⁻¹ of the contact-complex (**1**(cone) · Na⁺(exo) – Cl⁻(exo)) was caused by the complexed Na⁺–Cl⁻ stretching vibration. Compare this with the isolated Na⁺–Cl⁻ vibrational frequency (333 cm⁻¹). The medium intensity peaks at 544 (contact) and 679 (heteroditopic) were attributed to N–H wagging motions. The strong intensity peaks at ~1114 cm⁻¹ were due to various C_{aromatic}–O bond stretching vibrations. The strong peaks at about 1230 cm⁻¹ were due to C–C–C anti-symmetric stretching vibrations. The peaks at about 1430 and 1490 cm⁻¹ were due to C–C–N anti-symmetric stretching vibrations. The peaks at about 1650 cm⁻¹ were due to two

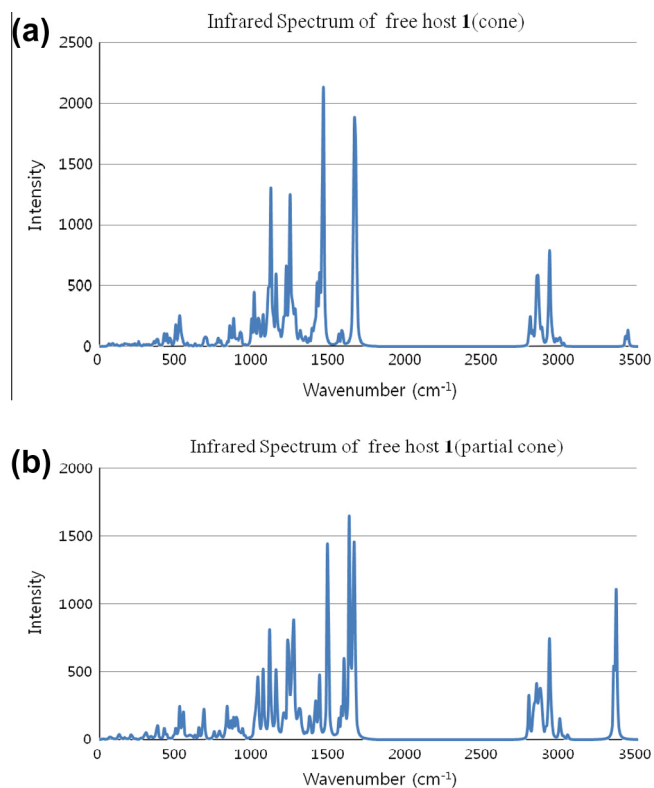


Fig. 6. mPW1PW91/6-31G(d,p) calculated IR spectra of (a) CONE, (b) PC. The broadened infrared (IR) spectra assume a Lorentzian line width of 4 cm^{-1} . The calculated vibrational frequencies were scaled by the recommended scale factor (0.93) to directly compare with the experimental data, [14].

kinds of C=O (from amide and diquinone) stretching vibrations. A series of peaks ($2837\text{--}2933\text{ cm}^{-1}$) were attributable to various C–H stretching vibrations.

The final two peaks above 3100 cm^{-1} were attributable to various N–H stretching vibrations: The N–H stretching peaks at 3427 and 3444 cm^{-1} of the free host **1** (cone) were down-shifted to 3260 and 3352 cm^{-1} of the $\mathbf{1} \cdot \text{Na}^+_{(\text{exo})}\text{Cl}^-_{(\text{exo})}$ contact-complex due to strong hydrogen bonding between the chlorine anion and two hydrogen atoms in the isophthalamide moiety of the lower rim of **1**, and the N–H peaks of the free host (**1**) were further down-shifted to 3188 and 3203 cm^{-1} of the $\mathbf{1} \cdot \text{Na}^+_{(\text{endo})}\text{Cl}^-_{(\text{exo})}$ heteroditopic-complex due to stronger hydrogen bonding from the non-ion-pair anion and two hydrogen atoms.

$\mathbf{1}_{(\text{cone})} \cdot \text{Na}^+ \text{--} \text{Br}^-$ contact complex: The weak peak at 188 cm^{-1} of $\text{Na}^+(\text{exo})\text{--}\text{Br}^-(\text{exo})$ contact-complex was caused by the complexed $\text{Na}^+ \text{--} \text{Br}^-$ stretching vibration. (Compare this with the $\text{Na}^+ \text{--} \text{Br}^-$ vibrational frequency [284 cm^{-1}] when the $\text{Na}^+ \text{--} \text{Br}^-$ salt was isolated). The remaining peaks were similar to the $\mathbf{1}_{(\text{cone})} \cdot \text{Na}^+ \text{--} \text{Cl}^-$ complexes.

$\mathbf{1}_{(\text{cone})} \cdot \text{NH}_4^+ \text{--} \text{Cl}^-$ complex: A very strong new peak at 2582 cm^{-1} was attributable to N–H stretching vibration between a hydrogen atom of the ammonium ion and a chloride anion connected through strong hydrogen bonding, which is displayed not in alkali-metal-ion complexes but in the ammonium contact-complex.

Peaks above 3100 cm^{-1} were attributable to various N–H stretching vibrations: The N–H stretching peaks at 3427 and 3444 cm^{-1} of the free host **1** (cone) were down-shifted to $3180\text{--}3385\text{ cm}^{-1}$ of the $\mathbf{1} \cdot \text{NH}_4^+_{(\text{exo})}\text{Cl}^-_{(\text{exo})}$ contact-complex due to strong hydrogen bonding between the chlorine anion and two hydrogen atoms in the isophthalamide moiety of the lower rim of **1**, and the N–H peaks of the free host (**1**) are further down-shifted to $3109\text{--}3402\text{ cm}^{-1}$ of the $\mathbf{1} \cdot \text{NH}_4^+_{(\text{endo})}\text{Cl}^-_{(\text{exo})}$ heteroditopic-complex

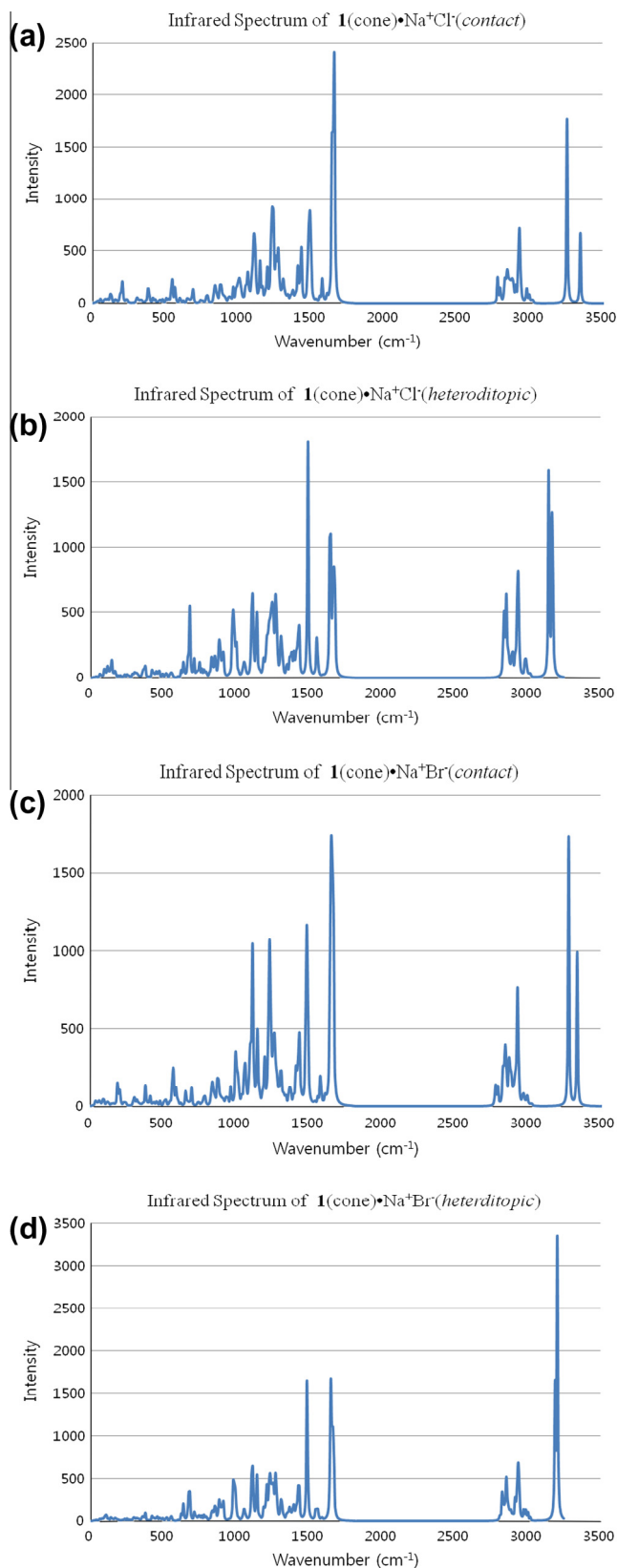


Fig. 7. mPW1PW91/6-31G(d,p) calculated infrared (IR) spectra of (a) $\mathbf{1}_{(\text{cone})} \cdot \text{Na}^+_{(\text{exo})}\text{Cl}^-_{(\text{exo})}$ (contact), (b) $\mathbf{1}_{(\text{cone})} \cdot \text{Na}^+_{(\text{endo})}\text{Cl}^-_{(\text{exo})}$ (heteroditopic), (c) $\mathbf{1}_{(\text{cone})} \cdot \text{Na}^+_{(\text{exo})}\text{Br}^-_{(\text{exo})}$ (contact), (d) $\mathbf{1}_{(\text{cone})} \cdot \text{Na}^+_{(\text{endo})}\text{Br}^-_{(\text{exo})}$ (heteroditopic).

due to stronger hydrogen bonding from the non-ion-pair anion and two hydrogen atoms. Thus, the complexation of the cone iso-

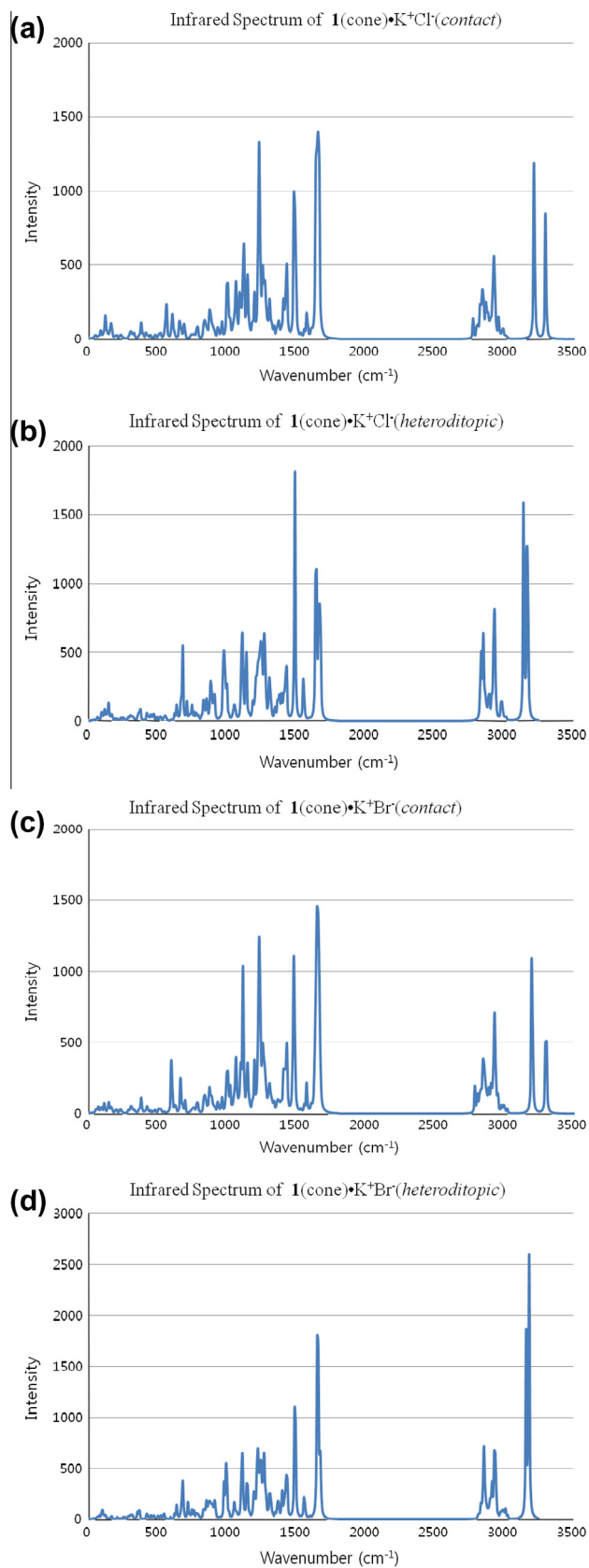


Fig. 8. mPW1PW91/6-31G(d,p) calculated infrared (IR) spectra of (a) $\mathbf{1}_{(\text{CONE})} \cdot \text{K}_{(\text{exo})}^+ \text{Cl}_{(\text{exo})}^-$ (contact), (b) $\mathbf{1}_{(\text{CONE})} \cdot \text{K}_{(\text{endo})}^+ - \text{Cl}_{(\text{exo})}^-$ (heteroditopic), (c) $\mathbf{1}_{(\text{CONE})} \cdot \text{K}_{(\text{exo})}^+ \text{Br}_{(\text{exo})}^-$ (contact), (d) $\mathbf{1}_{(\text{CONE})} \cdot \text{K}_{(\text{endo})}^+ - \text{Br}_{(\text{exo})}^-$ (heteroditopic).

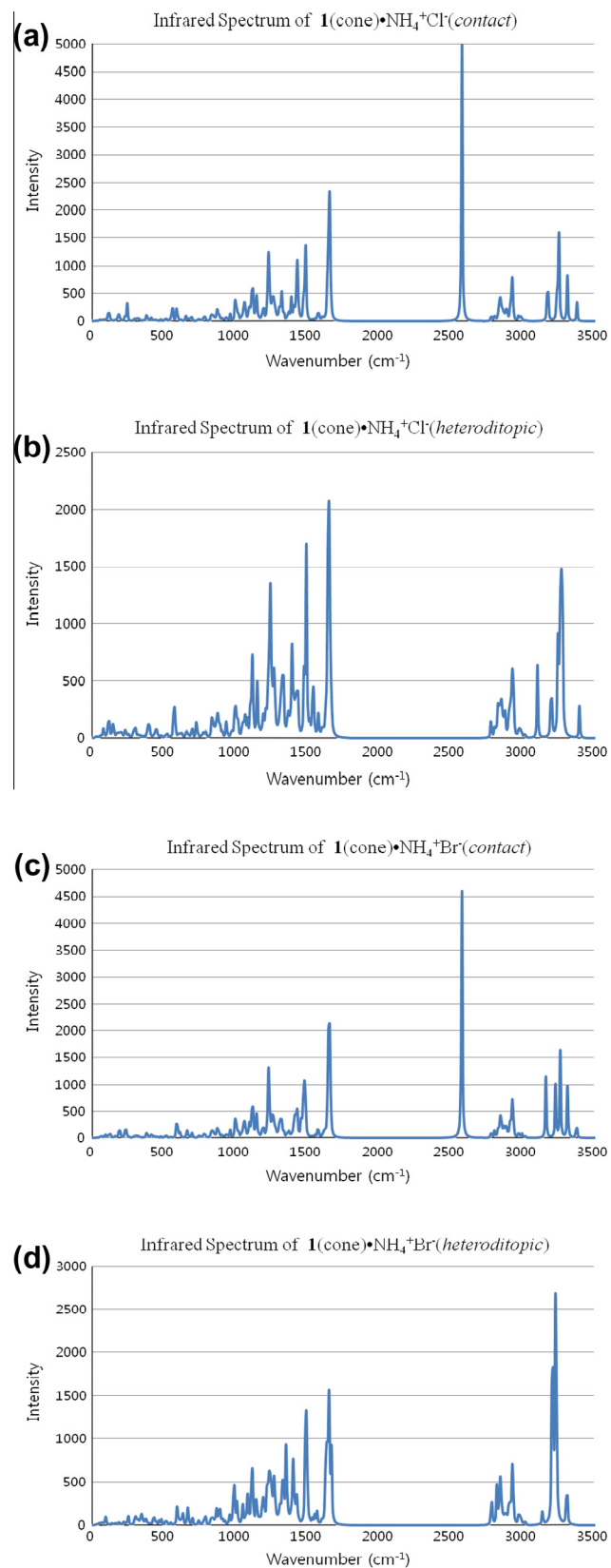


Fig. 9. mPW1PW91/6-31G(d,p) calculated infrared (IR) spectra of (a) $\mathbf{1}_{(\text{CONE})} \cdot \text{NH}_{4(\text{exo})}^+ \text{Cl}_{(\text{exo})}^-$ (contact), (b) $\mathbf{1}_{(\text{CONE})} \cdot \text{NH}_{4(\text{endo})}^+ - \text{Cl}_{(\text{exo})}^-$ (heteroditopic), (c) $\mathbf{1}_{(\text{CONE})} \cdot \text{NH}_{4(\text{exo})}^+ \text{Br}_{(\text{exo})}^-$ (contact), (d) $\mathbf{1}_{(\text{CONE})} \cdot \text{NH}_{4(\text{endo})}^+ - \text{Br}_{(\text{exo})}^-$ (heteroditopic).

mer with the cation-anion pair could be clearly confirmed by differences in these diagnostic N–H bands in the free host and the IR spectra of the complexes.

4. Conclusion

The ordering of the relative energies (ΔE in kcal/mol) of the conformations of **1** that resulted from the mPW1PW91/6-31G(d,p) calculations in Table 1 is as follows: **1**(PC) \sim **1**(13A) $>$ **1**(CONE: least stable).

Monotopic cation exo-complexation efficiencies of cone-type complexes were 10–27 kcal/mol better than the endo cases. The sodium ion showed better binding ability than either potassium or ammonium ion (the complexation energies in kcal/mol):

Monotopic cation (*exo*) : $\text{Na}^+(-79) > \text{K}^+(-68) > \text{NH}_4^+(-59)$,

Monotopic cation (*endo*) : $\text{Na}^+(-69) > \text{K}^+(-41) > \text{NH}_4^+(-37)$.

Monotopic anion(*exo*) : $\text{Br}^-(-46) > \text{Cl}^-(-39)$.

The contact-complexation efficiencies of the sodium ion-pair inside the cavity of the lower rim of cone-type hosts were better (~ 20 kcal/mol) than those of the potassium or ammonium ion-pairs. These contact-complexation efficiencies of the ion-pairs were much better (45–50 kcal/mol) than those of the heteroditopic-complexation of the ion-pairs with the cone-type host.

The complexation of the cone isomer with the cation-anion pair could be clearly confirmed by differences in the diagnostic N–H bands in the free host and the IR spectra of complexes.

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