

Density functional theoretical tailoring of electronic effect through various substituent on Calix[4]arene-crown-6 for efficient Cs⁺ ion encapsulation and extraction

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ABSTRACT

The structure, energetic and quantum chemical descriptors of Cs^+ complexes of calix[4]arene-crown-6 (C4C6) and substituted C4C6 i.e 1,3 alternate-diethoxy C4C6 are reported here based on the analysis of results using density functional theory. Substitution of benzo group to both C4C6 and 1,3 alternate-diethoxy C4C6 resulted in reduction of binding energy (BE). Further substitution on benzo group with methyl, methoxy and amino groups leads to increase in BE and nitro substitution leads to decrease in BE for C4C6, whereas in the case of 1,3 alternate-diethoxy calix[4]arenebenzocrown-6, methoxy substitution leads to highest BE compared to other complexes. The calculated Gibbs free energy, ΔG_{gas} also followed the same order as BE in the case of 1,3 alternate-diethoxy C4C6 and their substituted ligands. Furthermore, the ΔG of complexation were computed using thermodynamic cycle with conductor like screening model (COSMO) in different solvents: toluene, chloroform, octanol and nitrobenzene. The values of ΔG_{ext} are found to be increased with increase in the dielectric constant of the solvent and found to be highest in the nitrobenzene. The Atoms in Molecule (AIM) analysis reveals partial ionic character in Cs-O bond. Among all the studied complexes, 1,3 alternate-diethoxy calix[4]arene 3'-methoxy benzo crown-6 displays highest ΔG_{ext} in nitrobenzene. The calculated value of $\Delta\Delta G_{\text{ext}}$ ($\Delta\Delta G = \Delta G_{\text{Cs}^+} - \Delta G_{\text{Na}^+}$) is found to be -41.82 kcal/mol with 1,3 alternate-diethoxy calix[4]arene 3'-methoxy benzocrown-6 which is higher than that obtained with calix [4] bis-crown-6 (-5.24 kcal/mol). The newly designed ligand might be suitable for the selective extraction of Cs^+ over Na^+ in the reprocessing of nuclear waste and thus invites the experimentalists for testing this DFT finding in the laboratory.

Keywords: Calix[4]arene-crown-6, Cesium, DFT, Free Energy, Binding Energy

I. INTRODUCTION

Calixarenes and the derivatives of Calix[4]arene have drawn considerable interest because of their strong ability to bind Group - I and -II metal cations selectively in comparison to crown ethers¹⁻³. Reprocessing of used nuclear fuel consequences in the long lived Cs-137 fission product, which needs to be selectively separated from waste solutions containing high sodium ion^{4,5}. Still efforts are underway worldwide to devise a molecular system to extract the Cs⁺ ion from spent nuclear waste^{1,6-10}. Crown ethers¹¹ and calix[n]arenes¹² have shown considerable interest for the selective extraction of Cs ion from spent nuclear waste. The calix moiety alone has very weak attraction for cation (dipole-ion interaction) however it can be electronically tailored by suitably functionalization¹³. Previous studies have shown that, for the selective extraction of Cs⁺ extraction, crown ether attached in the 1,3-alternate conformation of calix[4]arene is the most favorable^{14,15}. Several modifications to this calix[4]arene were reported, which includes calix[4]arene-bis-crown ethers⁷, dialkoxy calix[4]arene-mono-crown ethers^{14,15}, benzo and naphtho substituents on the crown ether of calix[4]arene^{7,16,17} and n-octyloxy/n-propyloxy/iso-propyloxy- calix[4]arene monocrown ethers^{14,15}. In order to have a better understanding on the electronic effect of substituents for the selective extraction, Sachleben et.al. reported the Cs ion extraction with 12 different 1,3-alt calix[4]arene crown ethers in 1,2-dichloroethane diluent¹⁸. They have noticed a remarkable increase in the selectivity, when a hybrid calix[4]arene biscrown ether molecule was used¹⁸ and thus encourages for further exploration of new ligands. From the available solvent extraction experimental results¹⁹, the cation-ligand complexation reaction was established to be 1:1 as follows:



The Gibbs free energy of extraction, ΔG_{ext} can be estimated for the above complexation reaction using standard thermodynamical approach. The six ethereal O atoms and benzene rings of the calix structure are responsible for the increase in selectivity of Cs^+ ion.^{15,20} Earlier, several DFT²¹⁻³¹, RI-MP2³² and MD³³⁻³⁵ studies were conducted to understand the Cs^+ ion complex with calix-crown systems. We have also earlier studied the high selectivity of Cs^+ ion over Na^+ with calix[4]arene-bis-crown-6²⁷ using DFT. In the present report we extend our earlier study to investigate the electronic effect of different substituents on the calix[4]arene-crown for their complexation ability towards Cs^+ ion.

In this article, we report the structure and complexation of Cs^+ with calix[4]arene crown-6 and 1,3-diethoxy calix[4]arene crown-6 and their substituents namely benzo, methylbenzo, methoxybenzo, aminobenzo, nitrobenzo respectively using DFT. The COSMO solvation approach was used to account for the solvent effect of water and organic solvent. Details of the computational methodology and results are described in the following sections.

2. COMPUTATIONAL METHODOLOGY

The geometries of different chemical species were optimized and total energies were calculated with B3LYP functional³⁶⁻³⁸ using triple zeta valence plus polarization (TZVP) basis set i.e. C (11s6p1d) / [5s3p1d], O (11s6p1d) / [5s3p1d], H (5s1p) / [3s1p], and Cs (7s6p)/[5s3p]. Effective core potential was used for Cs with 46 core electrons. The hybrid B3LYP functional was better in predicting the energetics of several systems³⁹. All the calculations were performed using Turbomole suite of program⁴⁰. The aqueous and organic solvent effects in the energetics were included using COSMO^{41,42} model which was found to be successful in predicting accurate solvation free energy of the metal ions⁴³. The dielectric constant, ϵ of water and organic solvents namely toluene, chloroform, octanol and nitrobenzene were taken as 80, 2.38, 4.80, 10.38 and 34.82 respectively. It has been observed that the optimized geometries in the solvent phase cause a little effect in the solvation energy compared to single point solvation energy using gas phase geometry^{27,44-50}. Therefore, for the single point energy

calculation in COSMO phase, the geometries obtained from gaseous phase were used. The computation of metal ion solvation energy is described elsewhere²⁷. Furthermore, single point energy calculations were performed from the optimized structures of B3LYP/TZVP with M06 functional⁵¹ using TZ2P basis set for complimentary validation of methodology using ADF package^{42,52}.

3. RESULTS AND DISCUSSION

3.1 Structure of C4C6 and substituted C4C6 and their Cs⁺ ion complexes

The optimized structures of C4C6 and substituted C4C6 are displayed in **Figure 1** and the structural parameters are given in **Table 1**. The ligand of interest hereafter called as **I**, calix[4]arenebenzocrown-6; **II**, calix[4]arene-3'methylbenzocrown-6; **III**, calix[4]arene-3'methoxybenzocrown-6; **IV**, calix[4]arene-3'aminobenzocrown-6; **V**, calix[4]arene-3'nitrobenzocrown-6; **VI** and the corresponding complexes with Cs⁺ metal ion are **Ia**, **Ila**, **IIla**, **IVa**, **Va** and **VIa** respectively.

In the case of **I**, the C_{sp}² and O bond distances are 1.366Å and 1.388Å whereas C_{sp}³ and O bond distances are in the range of 1.414-1.431 Å. The diagonal O-O bond distances are also given in **Table 1**. In the complex, **Ia**, the C_{sp}² and O bond distances are increased to 1.382Å and 1.402 Å whereas the C_{sp}³ and O bond distances are increased to 1.424-1.442Å. The increase in bond lengths between C and O is due to the interaction of O atoms with Cs metal ion. The Cs-O bond lengths are in the range of 3.283-3.429Å respectively with a average distance of 3.347Å. In the case of **II**, the C_{sp}² and O bond distance is 1.361-1.387Å and C_{sp}³ and O bond distances are of 1.414-1.431 Å similar to **I**. From the O-O bond distances of **I** and **II** it is observed that the diagonal O-O distances are shorter in the case of **II** compared to **I**. In the complex **Ila**, the C_{sp}² and O bond distance is increased to 1.373-1.401 Å. The C_{sp}³ and O bond distances are also increased to 1.424-1.442Å. The Cs-O bond length is found to be within 3.204-3.408Å which are smaller than **Ia**. In the case of **III** and **IV**, the benzo group was further substituted

with methyl and methoxy groups. On methyl and methoxy substitution the C_{sp^2} and O bond distances are found to be 1.362-1.387 Å and C_{sp^3} and O bond distances are 1.414-1.432 Å similar to **II**.

From the O-O bond distances of **III** and **IV**, it is observed that the shorter value of O-O bond distance of **III** is increased to 6.239Å and **IV** is increased to 6.247Å compared to **II** (6.237Å). Similarly the longer O-O bond distance is also increased compared to **II**. The shorter and longer Cs-O bond distances of **IIIa** and **IVa** are 3.204Å, 3.205 Å and 3.408Å, 3.420Å respectively. The Cs-O bond distances of **IVa** are longer compared to **II**. In the case of **V** and **VI**, the benzo group is substituted with amino and nitro groups respectively. In the complexes **V** and **VI**, the C_{sp^2} and O bond distance and the C_{sp^3} and O bond distances are similar to that of **II**. From the O-O bond distances of **V** and **VI**, it is observed that the shorter value of O-O bond distance of **V** is decreased to 6.232Å and **VI** is increased to 6.239Å compared to **II** i.e. 6.237Å. Similarly, the longer O-O bond distance of **V** is increased to 6.924 Å and is decreased to 6.836 Å compared to **II**. The shorter and longer Cs-O bond distances of **Va** and **VIa** are 3.211, 3.185 Å and 3.420, 3.396Å respectively. The Cs-O bond distances of **Va** are higher compared to **II** whereas for **VIa** it is shorter compared to **II**.

Table 1 Structural parameters of optimized free calix[4]arene crown-6 and substituted calix[4]arene crown-6 and Cs^+ complexes at the B3LYP/TZVP level of theory

S.No	Complex	Free Ligand			Cs-Complex				
		C-O (Å ⁰)			O-O (Å ⁰)		C-O (Å ⁰)		
1	I	1.388, 1.418, 1.415, 1.409,	1.428, 1.419, 1.415, 1.431,	1.417, 1.412, 1.414, 1.366	6.375, 6.547, 7.094		1.402, 1.423, 1.422, 1.419,	1.438, 1.4242, 1.421, 1.441,	1.423, 1.422, 1.423, 1.382
2	II	1.387, 1.414, 1.363, 1.414,	1.427, 1.423, 1.425, 1.431,	1.418, 1.361, 1.418, 1.378	6.237, 6.486, 6.887		1.401, 1.424, 1.374, 1.420,	1.437, 1.430, 1.430, 1.442,	1.424, 1.373, 1.425, 1.389
3	III	1.378, 1.418, 1.362, 1.418,	1.431, 1.424, 1.423, 1.427,	1.414, 1.365, 1.415, 1.387	6.239, 6.480, 6.899		1.389, 1.425, 1.374, 1.424,	1.442, 1.429, 1.429, 1.437,	1.420, 1.376, 1.424, 1.401
									3.283, 3.325, 3.384, 3.429, 3.300, 3.363
									3.345, 3.386, 3.307, 3.364, 3.408, 3.204
									3.204, 3.408, 3.364, 3.302, 3.386, 3.348

4	IV	1.378, 1.432, 1.414, 1.418, 1.423, 1.369, 1.362, 1.422, 1.414, 1.418, 1.426, 1.387	6.247, 6.469, 6.894	1.401, 1.437, 1.425, 1.424, 1.428, 1.373, 1.380, 1.428, 1.425, 1.420, 1.442, 1.389	3.354, 3.383, 3.263, 3.397, 3.420, 3.205
5	V	1.387, 1.426, 1.418, 1.414, 1.422, 1.361, 1.370, 1.421, 1.419, 1.414, 1.432, 1.378	6.232, 6.471, 6.924	1.401, 1.437, 1.424, 1.424, 1.428, 1.373, 1.383, 1.426, 1.426, 1.419, 1.442, 1.388	3.359, 3.385, 3.253, 3.378, 3.420, 3.211
6	VI	1.388, 1.427, 1.419, 1.413, 1.429, 1.353, 1.350, 1.432, 1.415, 1.416, 1.431, 1.379	6.239, 6.513, 6.836	1.402, 1.437, 1.426, 1.424, 1.436, 1.365, 1.362, 1.435, 1.423, 1.422, 1.441, 1.390	3.306, 3.396, 3.388, 3.408, 3.393, 3.180

3.2 Structure of 1,3-alternate diethoxy C4C6 and substituted 1,3-alternate diethoxy C4C6 and Cs⁺ complexes

The structure of 1,3-alternate diethoxy C4C6 and their substituents are displayed in **Figure 2**. Structural parameters are given in **Table 2**. As the objectives of investigation, we have chosen 1,3-alternate diethoxycalix[4]arene-crown-6 here after called as **VII**, 1,3-alternatediethoxycalix[4]arenebenzo-crown-6; **VIII**, 1,3-alternatediethoxycalix[4]arene-3'methylbenzo-crown-6; **IX**, 1,3-alternatediethoxycalix[4]arene-3'methoxybenzo-crown-6; **X**, 1,3-alternatediethoxycalix[4]arene-3'aminobenzo-crown-6; **XI**, 1,3-alternatediethoxycalix[4]arene-3'nitrobenzo-crown-6; **XII** and their complexes with Cs⁺ metal ion are **VIIa**, **VIIIa**, **IXa**, **Xa**, **XIa** and **XIIa** respectively.

In the case of **VII**, the C_{sp}² and O bond distances are 1.383 and 1.386 Å and C_{sp}³ and O bond distances are ranging from 1.414-1.427 Å. The diagonal O-O bond distances are also given in **Table 2**.

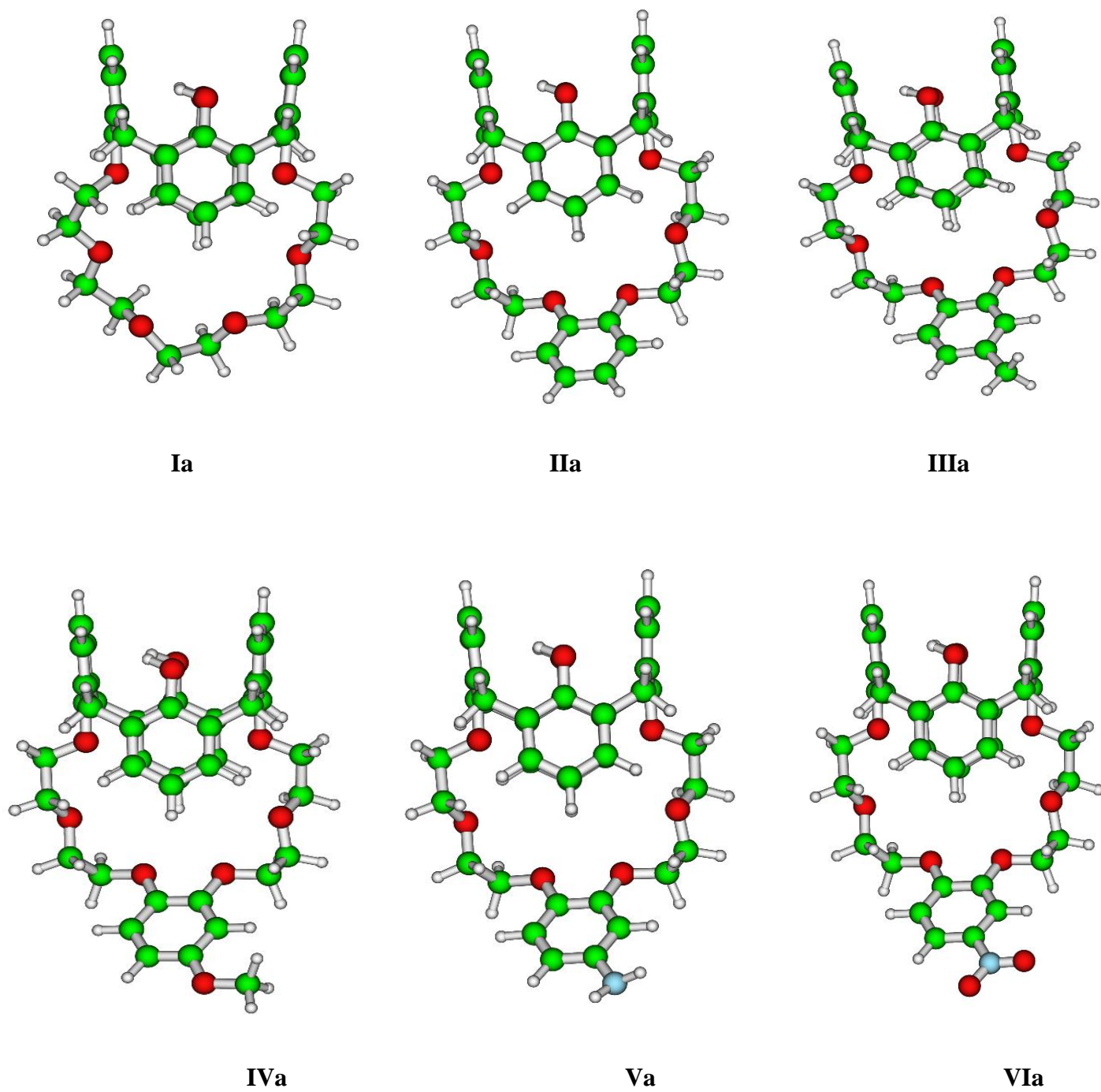
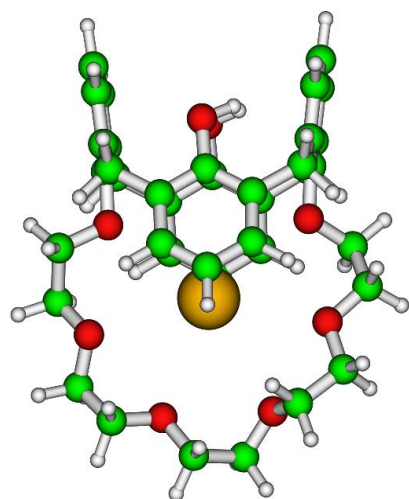
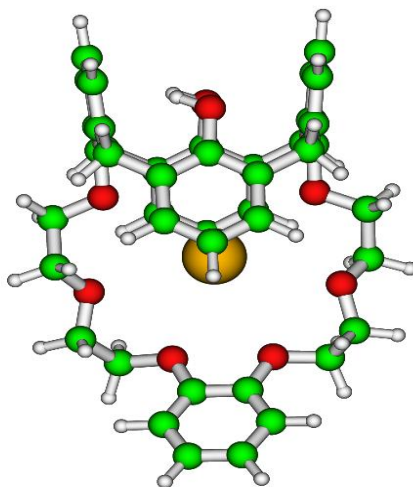


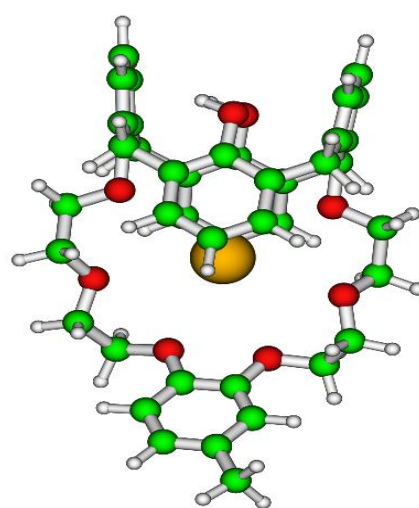
Figure 1a. Optimized structures of calix[4]arene-crown-6 and substituted calix[4]arene-crown-6 at the B3LYP/TZVP level of theory.



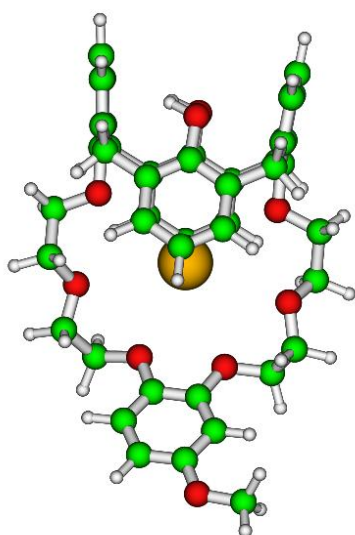
Ia



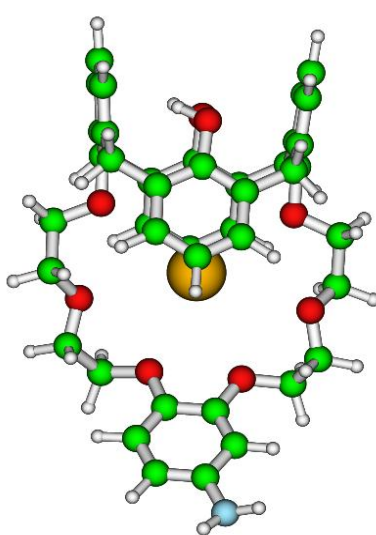
IIa



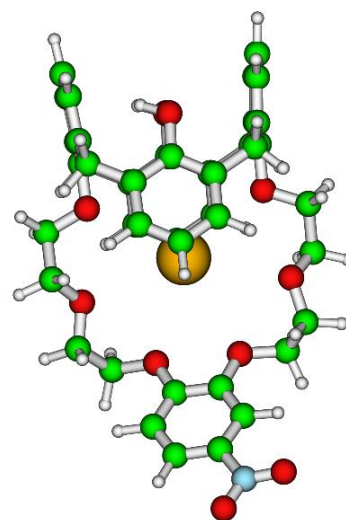
IIIa



IVa



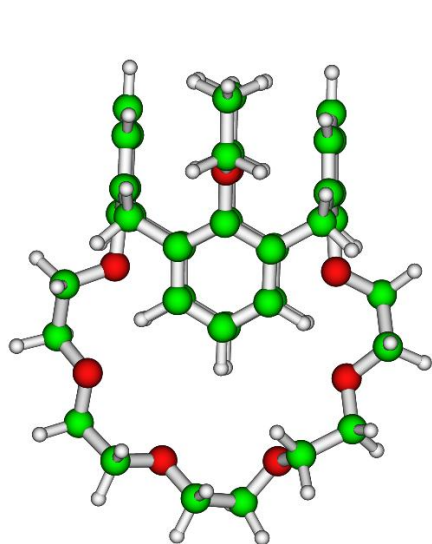
Va



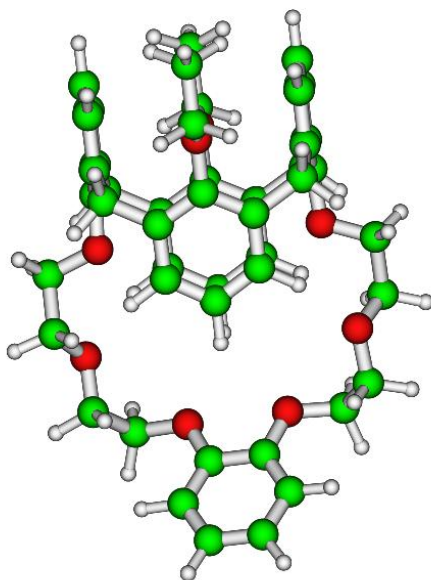
VIa

Figure 1b. Optimized Cesium complexes of calix[4]arene-crown-6 and substituted calix[4]arene-crown-6 at the B3LYP/TZVP level of theory.

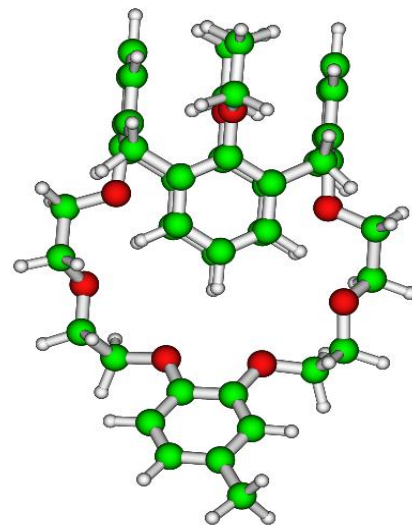
In complex **VIIa**, the C_{sp}^2 and O bond distance is increased to 1.395 and 1.401 Å whereas C_{sp}^3 and O bond distances are increased to 1.421 Å -1.439Å due to the interaction of O atoms with Cs metal ion. The shorter and longer Cs-O bond lengths are 3.266 Å and 3.439 Å respectively. In the case of **VIII**, the C_{sp}^2 and O bond distance is 1.363 Å -1.387Å which is shorter than **VII** whereas C_{sp}^3 and O bond distances are ranging from 1.416 Å -1.427 Å similar to **VII**. The diagonal O-O bond distances are displayed in **Table 2**. From the O-O bond distances of **VII** and **VIII**, it is observed that the shorter O-O bond distance is further shortened and longer O-O bond distance is lengthened compared to **VII**. In the complex **VIIIa**, the C_{sp}^2 and O bond distance is increased to 1.373 Å -1.401 Å and the C_{sp}^3 and O bond distances are increased to 1.422 Å -1.438Å. The Cs-O bond length is shorter (3.211 Å) than **VIIa** and is longer (3.419 Å) than **VIIa**. In the case of **IX** and **X**, the benzo group further substituted with methyl and methoxy groups. On methyl substitution the C_{sp}^2 and O bond distance are changed to 1.363 Å -1.387 Å and C_{sp}^3 and O bond distances are elongated to 1.416 Å -1.426 Å similar to **VIII**. On methoxy substitution, the C_{sp}^2 and O bond distance are 1.368 Å -1.387 Å and C_{sp}^3 and O bond distances are of 1.415 Å -1.431 Å. From the O-O bond distances of **IX** and **X**, it is observed that the shorter O-O bond distance of **IX** and **X** is decreased to 6.255Å and 6.229Å respectively compared to **VIII** (6.260Å). Similarly, the longer O-O bond distance is increased for **IX** and decreased for **X** compared to **VIII**. The shorter and longer Cs-O bond distances of **IXa** and **Xa** are 3.213Å, 3.222 Å and 3.416Å, 3.419Å respectively. In the case of **XI** and **XII**, the benzo group is substituted with amino and nitro groups respectively. From the O-O bond distances of **XI** and **XII**, it is observed that the shorter O-O bond distance of **XI** is decreased to 6.235Å and **XII** is increased to 6.265Å compared to **VIII** (6.260Å). Similarly the longer O-O bond distance of **XI** is increased to 7.139 Å and **XII** is decreased to 7.045Å compared to **VIII**. The shorter and longer Cs-O bond distances of **XIa** and **XIIa** are 3.226 Å, 3.188 Å and 3.420 Å, 3.441Å respectively. The Cs-O bond distances of **XIa** are longer compared to **VIII** and **XIIa** and are shorter compared to **VIII**.



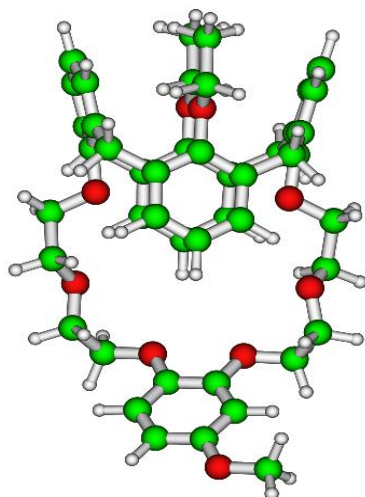
VII



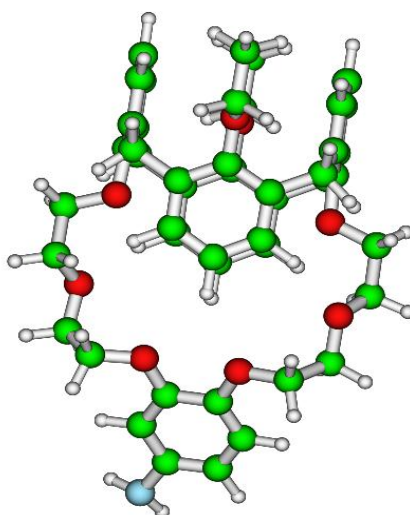
VIII



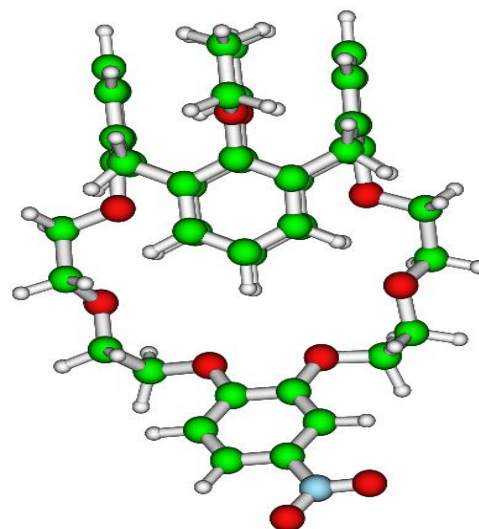
IX



X

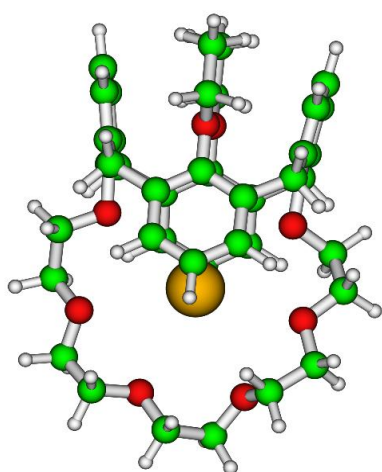


XI

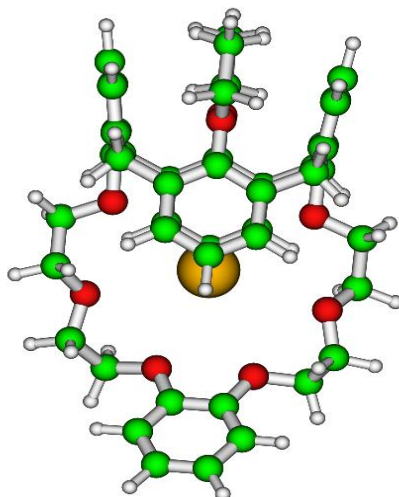


XII

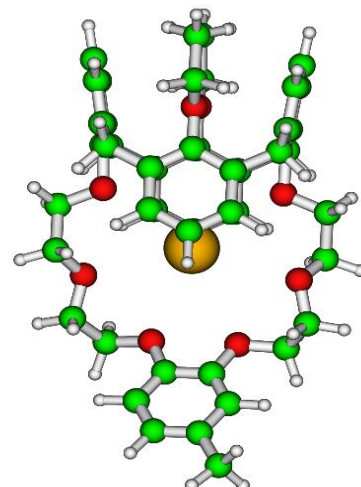
Figure 2a. Optimized structures of 1,3-alternate diethoxycalix[4]arene-crown-6 and substituted 1,3-alternate diethoxycalix[4]arene-crown-6 at the B3LYP/TZVP level of theory.



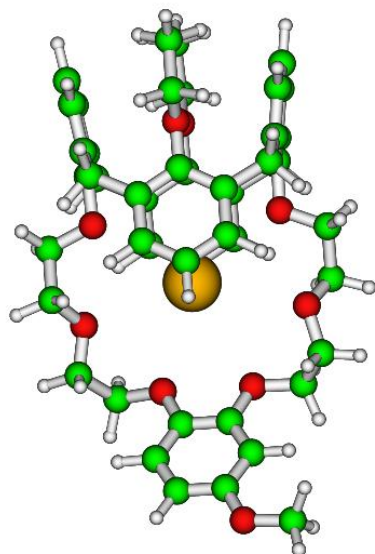
VIIa



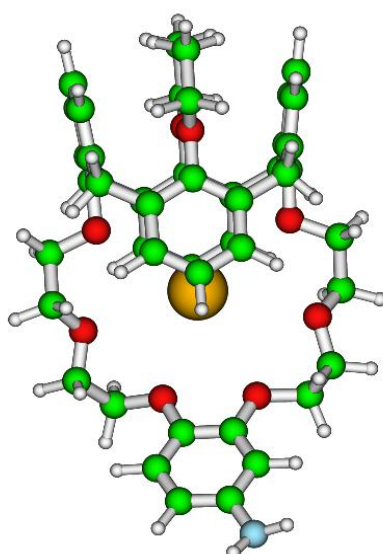
VIIIa



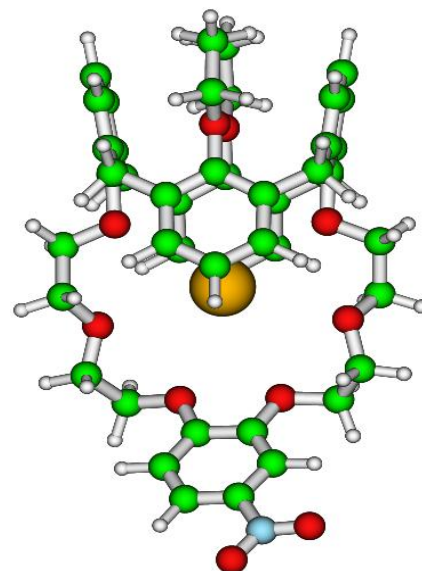
IXa



Xa



XIa



XIIa

Figure 2b. Optimized Cesium ion complexes 1,3-alternate diethoxycalix[4]arene-crown-6 and substituted 1,3-alternate diethoxycalix[4]arene-crown-6 at the B3LYP/TZVP level of theory.

Table 2. Structural parameters of optimized free 1,3-alternate diethoxycalix[4]arene-crown-6 and substituted 1,3-alternate diethoxycalix[4]arene-crown-6 and Cs⁺ complexes at the B3LYP/TZVP level of theory.

S.No	Complex	Free Calix		Cs-Complex	
		C-O	O-O	C-O (Å ⁰)	Cs ⁺ -O (Å ⁰)
1	VII	1.386, 1.427,1.415, 1.417, 1.419,1.414, 1.416, 1.417,1.415, 1.414, 1.425,1.383	6.721, 6.768, 6.825	1.401, 1.439,1.423, 1.424, 1.423,1.422, 1.422, 1.422, 1.421, 1.422, 1.438,1.395	3.266, 3.261, 3.439, 3.411, 3.321, 3.299
2	VIII	1.387, 1.426,1.417, 1.416, 1.424,1.363, 1.363, 1.427, .416, 1.416, 1.426,1.387	6.260, 6.381, 7.107	1.400, 1.438,1.423, 1.424, 1.429,1.373, 1.373, 1.430, 1.423, 1.422, 1.438,1.400	3.244, 3.351, 3.323, 3.401, 3.419, 3.211
3	IX	1.387, 1.426,1.416, 1.416, 1.426,1.365, 1.363, 1.424,1.416, 1.417, 1.426,1.387	6.255, 6.379, 7.114	1.400, 1.438,1.423, 1.424, 1.429,1.374, 1.375, 1.429, 1.423, 1.422, 1.438,1.400	3.248, 3.348, 3.315, 3.395, 3.416, 3.213
4	X	1.386, 1.431,1.420, 1.415, 1.421,1.362, 1.368, 1.423, .417, 1.416, 1.432,1.384	6.229, 6.631, 6.690	1.438, 1.400,1.424, 1.424, 1.428,1.374, 1.379, 1.429, 1.423, 1.421, 1.438,1.400	3.258, 3.346, 3.266, 3.419, 3.415, 3.222
5	XI	1.387, 1.426,1.417, 1.416, 1.424,1.363, 1.371, 1.423, .417, 1.415, 1.426,1.387	6.235, 6.382, 7.139	1.400, 1.438,1.423, 1.424, 1.428,1.374, 1.382, 1.427, 1.424, 1.421, 1.438,1.400	3.259, 3.351, 3.261, 3.396, 3.420, 3.226
6	XII	1.387, 1.426,1.418, 1.414, 1.430,1.355, 1.350, 1.434, .413, 1.418, 1.426,1.388	6.265, 6.408, 7.045	1.401, 1.438,1.425, 1.424, 1.435,1.365, 1.361, 1.435, 1.422, 1.425, 1.437,1.402	3.213, 3.346, 3.416, 3.441, 3.391, 3.188

3.3 Metal ion-ligand binding energy

The gas phase binding energy (BE) of a metal ion (M⁺) with a ligand (L) can be expressed for the complexation reaction:



as

$$\Delta E = E_{M+L} - (E_{M^+} + E_L) \quad (3)$$

Where E_{M+L} , E_L and E_{M+} , represent the total energy of the complex, ligand and the metal ion respectively. The calculated BE values are given in **Table 3**. From the table it is seen that BE of ligand **I** is -57.12kcal/mol which is reduced to -54.55kcal/mol when **I** is substituted with benzo group (**II**) due to electron withdrawing effect of benzo group. This can be well explained by natural bond order (NBO) analysis. From the NBO analysis it is observed that the residual partial charge on Cs^+ in case of **IIa** is 0.9387 which is higher compared to **Ia** (0.9318). This is indicating that less amount of charge is transferred from calixarene O atoms to Cs^+ in the case of **IIa**. Addition of methyl group to benzene ring (**III**) and methoxy group addition (**IV**) leads to the increase in BE slightly by 0.5kcal/mol. Similarly addition of amino and nitro group resulted to **V** and **VI** ligands and the corresponding complexes are **Va** and **VIa**. In the case of **Va**, the BE is increased by 1.37kcal/mol compared to **IIa**. The BE was decreased by 5.22kcal/mol in the case of **VIa** compared to **IIa** because of electron withdrawing effect of nitro group.

The BE of ligand **VII** is -56.34kcal/mol, which on substitution with benzo group (**VIII**), was reduced to -53.24kcal/mol due to the electron withdrawing effect of benzo group. It is seen from the NBO analysis that the residual charge on Cs^+ in case **VIIIa** is 0.9377 which is more compared to **VIIa** (0.9316). This is indicating that less amount of charge is transferred from Cs^+ to calixarene O atoms in the case of **VIIa**. Addition of methyl group to benzene ring (**IX**) and methoxy group (X), the BE is increased by 0.42 kcal/mol for **IX** compared to **VIII** and 6.89kcal/mol for **X** compared to **VIII**. Similarly, addition of amino and nitro group lead to **XI** and **XII** ligands and the corresponding complexes are **XIa** and **XIIa**. In the case of **XIa**, the BE is increased by 1.26kcal/mol compared to **VIIIa**. The BE was decreased by 4.98kcal/mol in the case of **XIIa** compared to **VIIIa** because of electron withdrawing effect of nitro group.

Table 3 The calculated binding energies of Cs⁺ ion with different calix systems. * indicates the binding energy value corresponding to Na⁺ ion.

S.No	System	BE (B3LYP/TZVP)	Partial charge (a.u)	BE (MO6/TZ2P)
1	I	-57.12	0.9318	-75.45
2	II	-54.55	0.9387	-72.04
3	III	-55.02	0.9388	-72.16
4	IV	-55.07	0.9390	-72.63
5	V	-55.92	0.9390	-73.71
6	VI	-49.46	0.9386	-67.30
7	VII	-56.34	0.9316	-79.14
8	VIII	-53.24	0.9377	-73.06
9	IX	-53.66	0.9378	-73.56
10	X	-60.13(-89.96)*	0.9380	-77.19
11	XI	-54.50	0.9379	-74.34
12	XII	-48.26	0.9376	-67.72

3.4 Charge Transfer

Electronic structure calculations are very useful to describe the host (C4C6) guest (metal ion) type interaction and thus helps in the design of tailor made ion selective ligands. Electronic chemical potential, μ and absolute hardness, η are generally used to characterize the chemical systems⁵³ where,

$$-\mu = \frac{(I + A)}{2} = \chi \quad \eta = \frac{(I - A)}{2} \quad (4)$$

Here I, A and χ represent the ionization potential, electron affinity and absolute electronegativity respectively. According to Koopmans' theorem⁵⁴, I and A can be obtained as

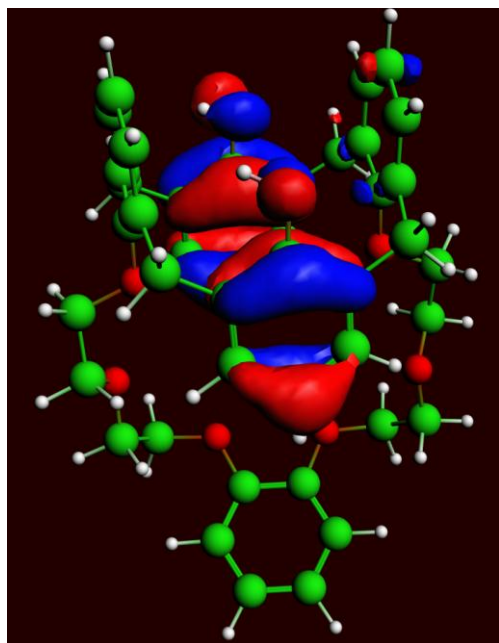
$$I = -E_{\text{HOMO}} \quad A = -E_{\text{LUMO}} \quad (5)$$

The charge transfer amount, ΔN can be calculated using⁵³

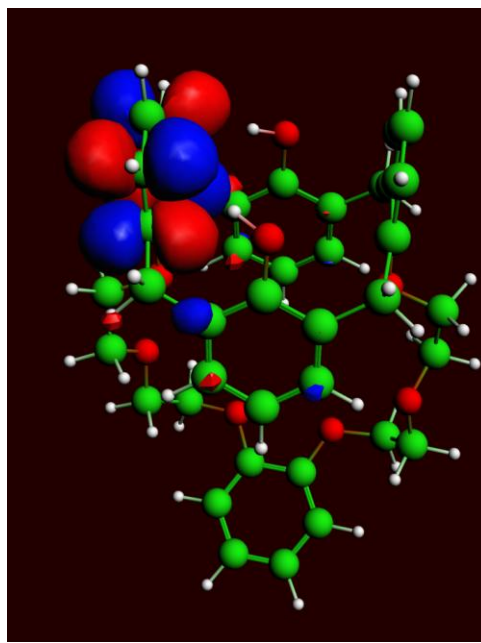
$$\Delta N = \frac{(\chi^M - \chi^L)}{2(\eta^M + \eta^L)} \quad (6)$$

Here, M stands for metal ion (acceptor), and L stands for ligand i.e. C4C6 (donor). The difference in energy of LUMO and HOMO, $\Delta E_{HL} = E_{LUMO} - E_{HOMO}$, provides the reactivity of a chemical systems. Lower values of ΔE_{HL} , represent higher reactivity and vice versa.

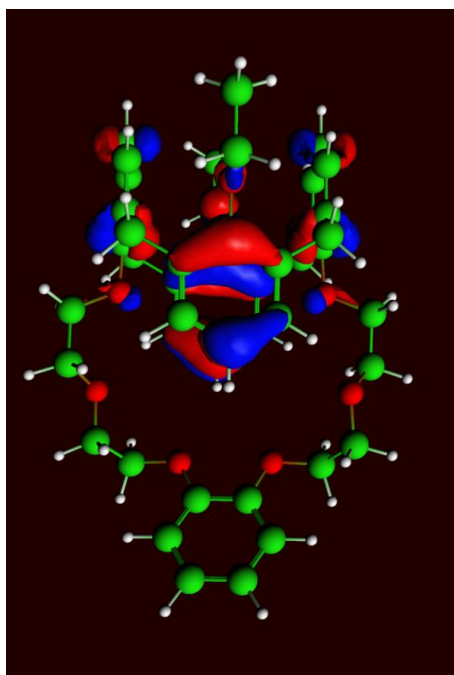
The calculated Quantum chemical descriptors values are presented in **Table 4, 5** and the HOMO, LUMO picture are given in **Figure 3**. In **Table 4**, the descriptors of C4C6 and their substituents were provided. From the table it is found that the charge transfer is highest for **V** and lowest for **VI**. The charge transfer in **I** is greater than **II** and the same has been reflected in the higher BE of **I** than **II**. The values of ΔN on substitution by methyl and methoxy and amino group were increased and on nitro substitution was decreased compared to **II**. The same trend was observed in the BEs. The BE order was **V>IV>III>II>VI** whereas ΔN order was **V<IV<III<II<VI**. From the table it is seen that the ΔE_{HL} value is highest for **II** and lowest for **VI**. The ΔE_{HL} value of **I** is smaller than **II** and the same has been reflected in the BE. i.e the BE of **I** is greater than **II**. By substituting methyl and methoxy and amino group the ΔE_{HL} values were decreased compared to **II**. The same trend was observed in the BEs. The BE order was **V>IV>III>II** whereas ΔE_{HL} order was **V<IV<III<II**. On nitro substitution ΔE_{HL} was further decreased compared to **II** and the BE was also decreased compared to **II**. Hence, no coorelation can be drawn using the value of ΔE_{HL} on nitro substitution.



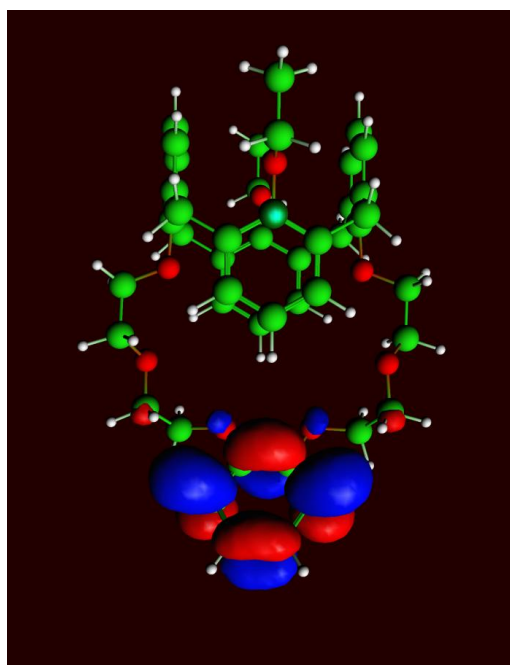
II-HOMO



II-LUMO



VIII-HOMO



VIII-LUMO

Figure 3. Picture of HOMO and LUMO of calix[4]arenebenzo-crown-6 and 1,3-alternate diethoxycalix[4]arenebenzo-crown-6.

Table 4 Quantum chemical descriptors of calix[4]arene-crown-6 and substituted calix[4]arene-crown-6 at the B3LYP/TZVP level of theory .

S.No	Complex	Charge on Cs(a.u)	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	χ (eV)	η (eV)	ΔN
1	I	0.9318	-5.5788	-0.7343	4.84458	3.15654	2.42229	0.4836
2	II	0.9387	-5.6087	-0.7588	4.84994	3.18376	2.42497	0.4821
3	III	0.9388	-5.5662	-0.7465	4.81971	3.15630	2.40985	0.4842
4	IV	0.9390	-5.3006	-0.7479	4.55268	3.02424	2.27634	0.4979
5	V	0.9390	-5.07915	-0.7309	4.34824	2.90503	2.17412	0.5096
6	VI	0.9386	-5.76589	-2.4465	3.31938	4.1062	1.65969	0.4717

Table 5 Quantum chemical descriptors of 1,3 alternate diethoxy calix[4]arene-crown-6 and substituted 1,3 alternate diethoxy calix[4]arene-crown-6 at the B3LYP/TZVP level of theory

S.No	Complex	Charge on Cs(a.u)	E _{HOMO} (eV)	E _{LUMO} (eV)	ΔE (eV)	χ (eV)	η (eV)	ΔN
1	VII	0.9316	-5.69462	-0.0710	5.62357	2.882835	2.811785	0.4785
2	VIII	0.9377	-5.70857	-0.1677	5.54087	2.938135	2.770435	0.4777
3	IX	0.9378	-5.5913	-0.1828	5.40842	2.88709	2.70421	0.4834
4	X	0.9380	-5.30564	-0.2644	5.04115	2.785065	2.520575	0.4977
5	XI	0.9379	-5.09667	-0.1083	4.98828	2.60253	2.49414	0.5084
6	XII	0.9376	-5.90243	-2.4568	3.44557	4.179645	1.722785	0.4643

In the **Table 5**, the descriptors of 1,3 alternate diethoxy C4C6 and their substituents were provided. From the table it is found that the charge transfer is highest for **V** and lowest for **VI**. The charge transfer in **I** is greater than **II** and the same has been reflected in the BE i.e the BE of **I** is greater than **II**. By substituting methyl and methoxy and amino group the values of ΔN were increased compared to **II** and on nitro substitution ΔN was decreased compared to **II**. The trend observed in the BE was

IV>V>III>II>VI whereas trend in ΔN was **V<IV<III<II<VI**. The order in ΔE_{HL} was **VI<V<IV<III<II<I**. We could not find any correlation for methoxy substitution from ΔN and ΔE_{HL} .

3.5 Atoms In Molecule (AIM) calculations

In AIM calculations, the charge density (ρ_c) and lapalcian ($\nabla^2\rho_c$) at bond critical point (BCP), where $\nabla\rho(r)=0$ is used to describe the strength and charecterization of bond^{55,56}. The bigger ρ_c values describe the stronger bonds. On the other hand, $\nabla^2\rho_c < 0$, represnts covalent bond; while $\nabla^2\rho_c > 0$, represnts closed shell interaction (ionic bond, coordination bond, Hydrogen bond, or Van der Waals interaction).

The calculated values of charge density (ρ_c) and lapalcian ($\nabla^2\rho_c$) at bond critical point were listed in **Table 6** and **7**. From the calculated values of $\nabla^2\rho_c$, the interactions between donor atoms and metal ion were found to be closed-shell interactions because of their positive $\nabla^2\rho_c$ values. Further, these interactions were stronger than hydrogen bond from their ρ_c and $\nabla^2\rho_c$ values which are bigger than that of hydrogen bond for which $\rho_c = 0.002\text{--}0.035 \text{ e/au}^3$ and $\nabla^2\rho_c = 0.024\text{--}0.139 \text{ e/au}^5$ ⁵⁷. On the contrary, the ellipticity value ε of BCP, reflects the characteristics of σ bond⁵⁸. A large value of ε indicates a large deviation from the σ bond. The AIM parameters of complexes of C4C6 and substituted C4C6 are given in **Table 6** and complexes of 1,3 alternate- diethoxy C4C6 and substituted 1,3 alternate- diethoxy C4C6 are given in **Table 7**. The BCP graphics are displayed in **Figure 4**. The calculated values shows that the interaction between metal ion and donor atoms were closed shell interactions because of their positive values of $\nabla^2\rho_c$. On the contrary, the large value of ε indicates that the Cs^+ and O bonds have partial ionic character. In the case of Cs^+ -complexes of substituted C4C6, it is observed that the average value of $\nabla^2\rho_c$ is more for the complex **Va** (i.e 0.0340 e/au^5) compared to other complexes. This may be the reason for selectivity for Cs^+ with **Va** compared to other complexes. Similarly, in the case of complexes of 1,3 alternate-diethoxyC4C6 and substituted 1,3 alternate-diethoxyC4C6, the calculated values of $\nabla^2\rho_c$ is more for **X** and **XIa** complexes i.e 0.0351 e/au^5 . Further, the calculated value of ε indicates more ionic chracter in the **Xa** (0.0983) compared to **XIa** complex (0.0968). This may be the reason for the

selectivity for Cs^+ with **Xa** complex compared to all other studied complexes of substituted C4C6 and substituted 1,3 alternate- diethoxy C4C6.

Table 6 AIM parameters of Cs^+ complexes of calix[4]arene-crown-6 and substituted calix[4]arene-crown-6 at the B3LYP/TZVP level of theory.

complex	BCP	λ_1	λ_2	λ_3	ρ_c	$\nabla^2\rho_c$	$\varepsilon = (\lambda_1/\lambda_2) - 1$
Ia							
	Cs-O1	-0.0059	-0.0052	0.0422	0.0074	0.0312	0.1346
	Cs-O2	-0.0072	-0.0063	0.0508	0.0088	0.0374	0.1429
	Cs-O3	-0.0067	-0.0063	0.0475	0.0085	0.0345	0.0635
	Cs-O4	-0.0056	-0.0053	0.0411	0.0074	0.0302	0.0566
	Cs-O5	-0.0051	-0.0049	0.0375	0.0069	0.0275	0.0408
	Cs-O6	-0.0067	-0.0060	0.0490	0.0085	0.0363	0.1167
IIa							
	Cs-O1	-0.0061	-0.0053	0.0440	0.0077	0.0326	0.1509
	Cs-O2	-0.0086	-0.0076	0.0607	0.0104	0.0445	0.1316
	Cs-O3	-0.0054	-0.0051	0.0392	0.0072	0.0287	0.0588
	Cs-O4	-0.0059	-0.0053	0.0426	0.0076	0.0314	0.1132
	Cs-O5	-0.0068	-0.0062	0.0486	0.0086	0.0355	0.0968
	Cs-O6	-0.0057	-0.0055	0.0413	0.0075	0.0302	0.0364
IIIa							
	Cs-O1	-0.0086	-0.0076	0.0607	0.0104	0.0445	0.1316
	Cs-O2	-0.0060	-0.0053	0.0437	0.0076	0.0324	0.1321
	Cs-O3	-0.0057	-0.0055	0.0413	0.0075	0.0302	0.0364
	Cs-O4	-0.0069	-0.0063	0.0491	0.0087	0.0359	0.0952
	Cs-O5	-0.0058	-0.0053	0.0426	0.0076	0.0314	0.0943
	Cs-O6	-0.0054	-0.0051	0.0392	0.0072	0.0287	0.0588
IVa							
	Cs-O1	-0.0086	-0.0076	0.0605	0.0104	0.0443	0.1316
	Cs-O2	-0.0059	-0.0052	0.0431	0.0075	0.0319	0.1346
	Cs-O3	-0.0058	-0.0055	0.0416	0.0076	0.0304	0.0545
	Cs-O4	-0.0076	-0.0069	0.0537	0.0094	0.0391	0.1014
	Cs-O5	-0.0054	-0.0049	0.0394	0.0071	0.0292	0.1020
	Cs-O6	-0.0052	-0.0050	0.0381	0.0070	0.0279	0.0400
Va							
	Cs-O1	-0.0059	-0.0051	0.0426	0.0074	0.0316	0.1569
	Cs-O2	-0.0085	-0.0075	0.0598	0.0102	0.0439	0.1333
	Cs-O3	-0.0052	-0.0050	0.0382	0.0070	0.0280	0.0400
	Cs-O4	-0.0056	-0.0051	0.0412	0.0074	0.0305	0.0980
	Cs-O5	-0.0078	-0.0071	0.0549	0.0096	0.0400	0.0986
	Cs-O6	-0.0057	-0.0055	0.0414	0.0075	0.0302	0.0364
Via							
	Cs-O1	-0.0067	-0.0058	0.0480	0.0083	0.0352	0.1552
	Cs-O2	-0.0090	-0.0079	0.0633	0.0107	0.0468	0.1392
	Cs-O3	-0.0056	-0.0053	0.0405	0.0073	0.0296	0.0566
	Cs-O4	-0.0052	-0.0048	0.0385	0.0069	0.0285	0.0833
	Cs-O5	-0.0054	-0.0049	0.0393	0.0071	0.0297	0.1020
	Cs-O6	-0.0056	-0.0053	0.0410	0.0074	0.0295	0.0566

Table 7 AIM parameters of Cs⁺ complexes of 1,3alternate diethoxycalix[4]arene-crown-6 and 1,3 alternatediethoxy calix[4]arene-crown-6 at the B3LYP/TZVP level of theory.

complex	BCP	λ_1	λ_2	λ_3	ρ_c	$\nabla^2 \rho_c$	$\varepsilon = (\lambda_1/\lambda_2) - 1$
VIIa							
	Cs-O1	-0.0075	-0.0066	0.0527	0.0091	0.0386	0.1364
	Cs-O2	-0.0069	-0.0060	0.0490	0.0085	0.0361	0.1500
	Cs-O3	-0.0068	-0.0064	0.0479	0.0086	0.0348	0.0625
	Cs-O4	-0.0053	-0.0050	0.0387	0.0070	0.0285	0.0600
	Cs-O5	-0.0050	-0.0047	0.0366	0.0067	0.0269	0.0638
	Cs-O6	-0.0074	-0.0066	0.0535	0.0092	0.0395	0.1212
VIIIa							
	Cs-O1	-0.0079	-0.0069	0.0554	0.0095	0.0407	0.1449
	Cs-O2	-0.0085	-0.0075	0.0597	0.0102	0.0438	0.1333
	Cs-O3	-0.0053	-0.0050	0.0383	0.0070	0.0281	0.0600
	Cs-O4	-0.0054	-0.0049	0.0392	0.0071	0.0289	0.1020
	Cs-O5	-0.0065	-0.0060	0.0468	0.0083	0.0343	0.0833
	Cs-O6	-0.0062	-0.0059	0.0447	0.0081	0.0325	0.0508
IXa							
	Cs-O1	-0.0078	-0.0068	0.0550	0.0095	0.0403	0.1471
	Cs-O2	-0.0084	-0.0074	0.0594	0.0102	0.0436	0.1351
	Cs-O3	-0.0053	-0.0050	0.0385	0.0071	0.0282	0.0600
	Cs-O4	-0.0054	-0.0049	0.0397	0.0072	0.0294	0.1020
	Cs-O5	-0.0067	-0.0061	0.0477	0.0084	0.0350	0.0984
	Cs-O6	-0.0063	-0.0060	0.0450	0.0081	0.0328	0.0500
Xa							
	Cs-O1	-0.0076	-0.0067	0.0537	0.0093	0.0395	0.1343
	Cs-O2	-0.0082	-0.0072	0.0582	0.0100	0.0427	0.1389
	Cs-O3	-0.0053	-0.0050	0.0386	0.0071	0.0283	0.0600
	Cs-O4	-0.0051	-0.0046	0.0375	0.0068	0.0278	0.1087
	Cs-O5	-0.0076	-0.0069	0.0533	0.0093	0.0389	0.1014
	Cs-O6	-0.0063	-0.0060	0.0453	0.0081	0.0330	0.0500
XIa							
	Cs-O1	-0.0076	-0.0066	0.0535	0.0092	0.0393	0.1515
	Cs-O2	-0.0082	-0.0072	0.0577	0.0099	0.0423	0.1389
	Cs-O3	-0.0052	-0.0050	0.0382	0.0070	0.0280	0.0400
	Cs-O4	-0.0054	-0.0049	0.0396	0.0071	0.0293	0.1020
	Cs-O5	-0.0076	-0.0070	0.0539	0.0094	0.0393	0.0857
	Cs-O6	-0.0062	-0.0059	0.0448	0.0081	0.0326	0.0508
XIIa							
	Cs-O1	-0.0067	-0.0058	0.0477	0.0083	0.0352	0.1552
	Cs-O2	-0.0092	-0.0080	0.0641	0.0109	0.0468	0.1500
	Cs-O3	-0.0056	-0.0053	0.0405	0.0074	0.0296	0.0566
	Cs-O4	-0.0052	-0.0048	0.0385	0.0069	0.0285	0.0833
	Cs-O5	-0.0055	-0.0050	0.0403	0.0072	0.0297	0.1000
	Cs-O6	-0.0056	-0.0053	0.0405	0.0074	0.0295	0.0566

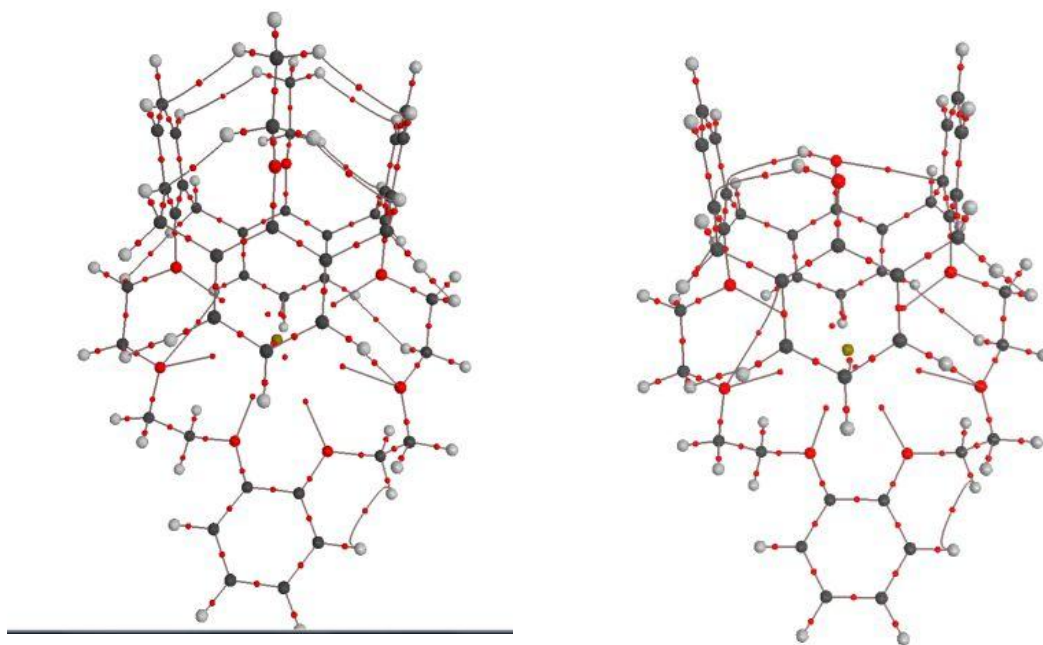


Figure 4. BCP of Cs^+ complex of calix[4]arenebenzo-crown-6 and 1,3-alternate diethoxycalix[4]arenebenzo-crown-6

3.6 Gibbs Free energies of complexes in gas phase and different solvents

The Gibbs free energy (G) of the optimized metal-calix[4]arene complexes has been performed using earlier reported procedure²⁷. The free energy of complex are computed using thermodynamic cycle given in **Figure 5**.

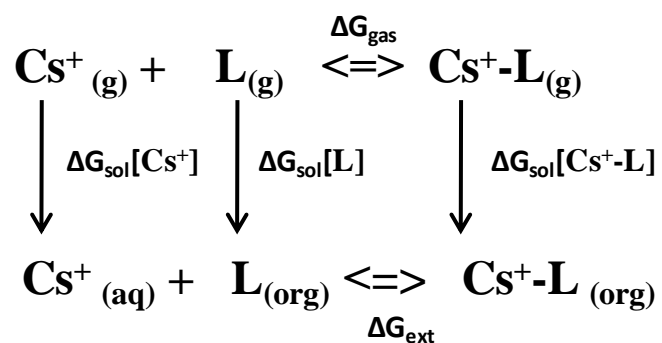


Figure 5. Thermodynamic cycle for the computation of free energy in the solvent

3.6.1 Gibbs Free energies of Cs^+ complexes of C4C6 and substituted C4C6

The free energy of Cs^+ complex with C4C6 and substituted C4C6 are calculated in the gas phase and solvents such as: toluene, chloroform, octanol and nitrobenzene are calculated and given in **Table 8**. The ΔG_{Cs} value was taken from our previous study²⁷. The gas phase free energy of complexation was found to be smaller than the gas phase BE. This is due to structure making process of the complex formation. The gas phase free energy of **IIa** is greater than **Ia**, but the BE is in the reverse order. This is due to the rigidity imparted to the C4C6 by the addition of benzene ring resulting more positive ΔS of complex **Ia** than **IIa** (given in the supplementary Table, **Table S1**) leading less free energy. The gas phase free energy of **IIIa** and **IVa** are also lower than **IIa** due to their large entropy difference compared to **IIa**. The free energy of **VIa** is lower than **IIa** in the gas phase. The free energy value of **Va** in the gas phase is higher compared to all studied complexes (6) here. The free energy in the solvent phase, ΔG_{ext} of all the complexes were found to be positive in the toluene solvent. The ΔG_{ext} of **IIa** is found to be higher in the chloroform solvent compared to all other complexes and the value was found to be negative except **Ia**. The ΔG_{ext} value of **IIa** is found to be higher in octanol and nitrobenzene. Also all the free energy values were found to be negative. The ΔG_{ext} value of all the complexes found to be increased with increase in the dielectric constant of the solvent. The free energy values in the solvent phase were found to be smaller than the gas phase values because of decrease in the interaction of Cs^+ ion with ligand due to the occurrence of metal ion-solvent interactions.

Table 8 Free energies of Cs^+ complexes (kcal/mol) of calix[4]arene-crown-6 and substituted calix[4]arene-crown-6 at the B3LYP/TZVP level of theory.

S.No	Complex	Gas phase	Toluene	Chloroform	Octanol	Nitrobenzene
1	Ia	-46.75	6.16	2.00	-0.40	-1.91
2	IIa	-46.87	3.59	-2.10	-5.56	-7.82
3	IIIa	-45.46	5.17	-0.44	-3.84	-6.07
4	IVa	-45.13	5.56	-0.03	-3.43	-5.67
5	Va	-47.03	3.91	-1.50	-4.78	-6.92
6	VIa	-39.36	9.69	3.16	-0.88	-3.55

3.6.2 Free energies of Cs⁺ complexes of 1,3-alternate diethoxy C4C6 and substituted 1,3-alternate diethoxy C4C6

The free energy of Cs⁺ complex with 1,3-alternate diethoxy C4C6 and substituted 1,3-alternate diethoxy C4C6 in the gas phase and solvents: toluene, chloroform, octanol and nitrobenzene are calculated and given in **Table 9**. The free energy values in the solvent phase were found to be smaller than the gas phase. The gas phase free energy followed the similar trend as BE. The solvent phase free energy, ΔG_{ext} of all the complexes were found to be positive in toluene similar to C4C6 and their substituents. The ΔG_{ext} of **Xa** is found to be higher in chloroform compared to all other complexes and the values were found to be negative except **VIIIa**. The ΔG_{ext} values of **Xa** is not only found to be high in octanol and nitrobenzene but all the values were found to be negative also. The ΔG_{ext} value of all the complexes are increased with increase in the dielectric constant of the solvent for C4C6 and their substituents. The free energy value of **Xa** (Cs⁺ complex of 1,3-alternatediethoxycalix[4]arene-3'methoxybenzo-crown-6) in nitrobenzene found to be higher compared to all studied complexes here including C4C6 and substituted C4C6. Therefore, methoxy substitution on 1,3-alternatediethoxycalix[4]arenebenzo-crown-6 in nitrobenzene is found to be better ligand for Cs⁺ extraction of all studied complexes in this study.

In order to study the selectivity of Cs⁺ over Na⁺ ion, the Na⁺ complex of screened ligand i.e with 1,3-alternatediethoxycalix[4]arene-3'methoxybenzo-crown-6 was optimized and the value of ΔG_{ext} was calculated in 1,2-dichloro ethane solvent and found to be 34.10 kcal/mol. This is indicating that the complexation with Na⁺ ion is not favourable and the value of $\Delta\Delta G_{\text{ext}}$ ($\Delta\Delta G = \Delta G_{\text{Cs}^+} - \Delta G_{\text{Na}^+}$) is found to be -41.82 kcal/mol which is superior than the value obtained with calix [4] bis-crown-6 i.e -5.24 kcal/mol from our previous study²⁷. Hence, the newly designed ligand might be useful for the selective extraction of Cs⁺ over Na⁺ in the nuclear waste reprocessing.

Table 9 Gibbs Free energies of Cs⁺ complexes (kcal/mol) 1,3-alternate diethoxycalix[4]arene-crown-6 and substituted 1,3-alternate diethoxycalix[4]arene-crown-6 at the B3LYP/TZVP level of theory. The value with the '*' represents free energy of Na⁺ complex.

S.No	Complex	Gas phase	Toluene	chloroform	octanol	Nitrobenzene
1	VIIa	-47.35	3.77	-1.50	-4.67	-6.72
2	VIIIa	-45.22	5.73	0.31	-2.96	-5.10
3	IXa	-46.60	4.51	-0.83	-4.06	-6.17
4	Xa	-51.04 (-44.63)*	0.50	-4.63	-7.72	-9.74
5	XIa	-46.70	4.71	-0.45	-3.56	-5.58
6	XIIa	-41.03	8.52	2.26	-1.61	-4.17

4. CONCLUSION

We have reported here the effect of substituents on the structure, energetic, thermodynamics, and quantum chemical descriptors of the Cs^+ ion complexes of C4C6. Substitution of electron withdrawing group (benzo group) to both C4C6 and 1,3 alternate-diethoxy C4C6 resulted in reduction of binding energy (BE). Further substitution on benzo group with electron donating groups like methyl, methoxy and amino groups leads to increase in BE and electron withdrawing group(nitro) substitution leads to decrease in BE for C4C6 and 1,3 alternate-diethoxy C4C6. In the present study, 1,3 alternate-diethoxy calix[4]arene3'-methoxy benzo-crown-6 has the highest BE compared to all other complexes. The substitution of benzo group to both C4C6 and 1,3 alternate-diethoxy C4C6 decreased the complexation free energy. Further substitution of methyl, methoxy and amino groups leads to increase in the ΔG_{gas} and nitro substitution leads to decrease in the ΔG_{gas} in the case of calix[4]arenebenzo-crown-6. But in the case of 1,3 alternate-diethoxy calix[4]arenebenzo-crown-6, methoxy substitution leads to highest ΔG_{gas} compared to all studied complexes here. The values of free energy of complexation were computed using thermodynamic cycle in the polar solvents like toluene, octanol, chloroform, and nitrobenzene. The values of ΔG_{ext} are found to be increased with increase in the dielectric constant of the solvents and found to be highest in the nitrobenzene solvent. Among all the studied complexes here 1,3 alternate-diethoxy calix[4]arene3'-methoxy benzo-crown-6 displays highest ΔG_{ext} value in nitrobenzene solvent. Further from AIM calculations, the calculated $\nabla^2 \rho_c$ and ϵ values showed that the selectivity for Cs^+ with **Xa** complex is more compared to all other studied complexes of substituted C4C6 and substituted 1,3 alternate-diethoxyC4C6. The calculated value of $\Delta \Delta G_{\text{ext}}$ ($\Delta \Delta G = \Delta G_{\text{Cs}^+}$ -

ΔG_{Na^+}) is found to be -41.82 kcal/mol with 1,3 alternate-diethoxy calix[4]arene3'-methoxy benzo-crown-6 which is much higher than that obtained with calix [4] bis-crown-6 i.e -5.24 kcal/mol. The selectivity origin of Cs^+ over Na^+ is mainly due to higher solvation free energy of Na^+ metal ion in the aqueous phase and lower free energy of complexation with the 1,3 alternate-diethoxy calix[4]arene3'-methoxy benzocrown-6 compared to Cs^+ ion. Hence, the newly designed ligand might be suitable for the selective extraction of Cs^+ over Na^+ in the reprocessing of nuclear waste. The present DFT study will help in the revelation of the complex metal ion extraction and will add to the design and screening of selective ligands for real applications.

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Declaration of Competing Interest

The authors declare no competing financial interest.

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Additional supporting information may be found online in the Supporting Information section at the end of this article. Optimized coordinates of the chemical species studied here can be provided on reasonable request.