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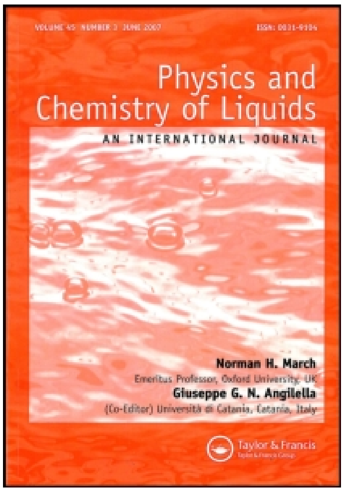

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Quantum simulation on donor and acceptor II calix[4]arene substrate and alkali metal ions: the driven inclusion

A. Amiri[a]; M. Monajjemi[b]; S. Ketabi[c]
[a] Department of Chemistry, Central Tehran Campus, Islamic Azad University, [b] Chemistry Department, Islamic Azad University, [c] Department of Chemistry, Central Tehran Campus(East Tehran - Ghiam Dasht), Islamic Azad University, Tehran, Iran

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Quantum simulation on donor and acceptor II calix[4]arene substrate and alkali metal ions: the driven inclusion

A. AMIRI†, M. MONAJJEMI*‡ and S. KETABI§

†Department of Chemistry, Central Tehran Campus, Islamic Azad University
‡Chemistry Department, Islamic Azad University, Science and Research Campus
§Department of Chemistry, Central Tehran Campus
(East Tehran – Ghiam Dasht), Islamic Azad University, Tehran, Iran

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The energetic and structural optimized of a calix[4]arene with and without alkali-metal cations are presented with performance of various quantum chemical methods such as Hartree–Fock, second order Møller-Plesset perturbation theory, and density functional theory. The geometry optimizations have been carried out with the 3-21G (Li^+–Cs^+) and 3-21G(d,p) (Li^+–K^+) and the 3-21G basis sets for Cs^+ and Rb^+. Additional single-point energy *ab initio* calculations for Li^+–K^+ were carried out at HF/6–31G, HF/6-31G (d,p), HF/6–311G(d,p) for complexes of Li^+ and Na^+. The calculations were carried out to analyze the complexation of calix[4]arene with alkali metal cationic species (Li^+, Na^+, K^+, Rb^+, and Cs^+). Assumption to isolate the effects of the aromatic core and cation-π interactions. Particular emphasis has been on conformational binding selectivity and the structural characterization of the complexes, the smaller cation as Li^+ and Na^+ has been placed in the lower rim's of the calix[4]arene's cavity. The large cations like K^+, Rb^+, and Cs^+ take placed in upper rim and the endo (inclusive) complexation is driven by cation-π interactions, that reflect a superior interaction with two phenol rings. The endo complexation of Cs^+ with calix[4]arene is in agreement with X-ray diffraction data. The binding modes of calixarene-cation systems are studied to involve cooperative effects between cation-π and electrostatic forces.

Keywords: Bonding; Aqueous environments; Molecular recognition

1. Introduction

Numerous attempts have been made to design new host systems, which can selectively interact the target guest and perform intriguing molecular recognition processes [1–3]. Calix[*n*]arenas are cup-like metacyclophanes which derive from the condensation of phenols and formaldehyde in different conditions. From the variety of macro cyclic compounds, calixarenes are preferable for metal extraction because of the easy

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*Corresponding author. Email: m_monajjemi@yahoo.com

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synthesis of a great number of derivatives, which allows to compare the impact of cavity size, conformation, functional groups, and other factors on the extraction behavior, and the flexibility to design a proper ligand to selectively recognize a metal ion [4]. Calixarenes [5, 6] have received much attention recently as one of the most widely employed molecular frameworks for the construction of many versatile supramolecular systems [7, 8].

During the last 25 years, calix[*n*]arenas have received much interest because of their convenient application as receptor molecules for cations, anions, and neutral molecules or as ligands and catalytic systems [9–16].

It was revealed that in calixarene selectivity the alkali-metal cations (except Li^+) prefer to bind to the oxygen rather than to the phenyl by approximately $1\,\mathrm{kcal\,mol^{-1}}$ [17]. The high complexity of host-guest interactions in calixarenes was illustrated by theoretical studies on the binding of Na^+ and Cs^+ to conformers of tetramethoxycalix [4]arene [18]. In several conformations, formed stronger complexes when more cation-π interactions with the cations were possible. In a recent theoretical study of calix[4]arene, Li^+ and Na^+ bound closely to the oxygen while K^+, Cs^+, and Rb^+ bound within the aromatic cavity of the cone conformation [19]. Due to the nature of calixarene complexes previously reported, little is known concerning the influence of cation-π interactions upon conformational stability and selective binding of ligands cleanly separated from electrostatic and hydrogen-bonding effects.

Experimental evidence suggests a role for multiple cation-π interactions in biological and supramolecular systems. While the binding strength of most single noncovalent bonds is relatively weak ($-2.6\,\mathrm{kcal\,mol^{-1}}$) in aqueous environments, multiple bonds increase the total binding strength and selectivity [20].

Macrocyclic hosts synthesized to investigate the cation-π interaction by Dougherty and co-workers contained multiple aromatic binding sites [21]. In biological systems, there are cationic binding sites rich in aromatic amino acids. 1H NMR binding studies reveal that the presence of additional double bonds in vinyl-substituted calixarene derivatives enhances the binding of cations, suggesting that additional cation-π interactions improve complexation [22].

The X-ray structure of the synthetic receptor resorcin[4]arene complexed with acetylcholine trimethylammonium reveals the presence of multiple cation-π interactions [23], since the three methyl groups are in close contact (<3.8) with the aromatic ring centroids.

Consequently, the calixarene aromatic core provides an excellent model for studying the relationship between binding strength and the number and geometry of cation-π interactions, since the different conformations provide a variety of aromatic binding motifs. A majority of computational studies on calixarene conformations and binding of ligands have been reported using molecular mechanical force fields [24–26]. The cone conformation is found to be the most stable in the majority of cases.

The large computational resources required to evaluate the energy and structure of calix[*n*]arenas have prevented extensive *ab initio* and density functional treatments until recently. To clarify the role of the aromatic core and cation-π interactions in determining the conformations and energies of calix[4]arenas and their complexes.

In this investigation undertaken *ab initio* study at the Hartree–Fock (HF) level of a dehydroxylated calix[4]arene or parent calix[4]arene (figure 1) with alkali-metal cations Li^+, Na^+, K^+, Rb^+ and Cs^+ semiempirical methods usually cannot be applied successfully and the small size of the guest molecule limiting the computation effort [27].

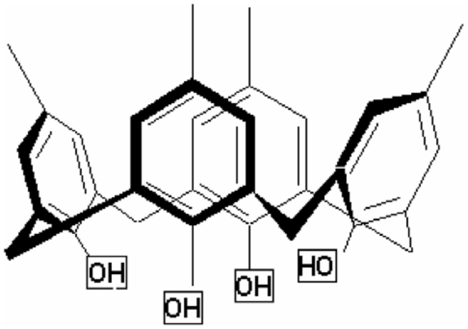

Figure 1. The calix[4]arene molecule.

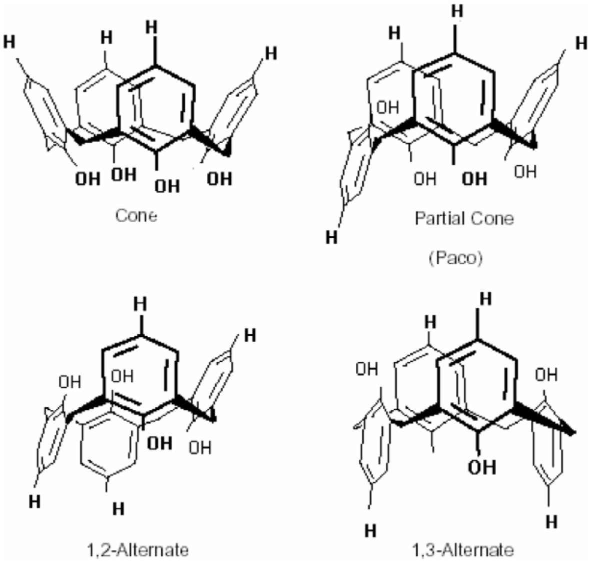

Figure 2. The four extreme conformations of calix[4]arenes.

The flexibility and lack of substituents can provide a better understanding of the cation-π interaction strength and induced structural variations of biochemical and supramolecular systems. The computations provide deeper insight into the nature of the cation-π interactions in the absence of competing forces and supplement a more complete understanding of the experimental binding of calix[4]arenes, in which electrostatic interactions and solvent effects are well-known.

2. Computational details

Geometry optimizations for the four calix[4] arenes conformers (figure 2) and their complexes with alkali metal cations have been carried out at the Hartree–Fock (HF) level. The structures were determined by complete optimizations without any symmetry constraint.

However it was shown that due to the strong intermolecular H bonding the conformation definitely is the cone conformer [28].

To confirm that the final structure is in the local minimum point we have calculated the normal mode frequency of the optimized complex. Each vibrational spectrum shows no negative value of frequency, which suggests that the optimized structure is really in minimum point. Zero point vibrational energies were not included in the calculation of the complexation energies.

The geometry optimizations have been carried out with the 3-21G (Li^+–Cs^+ and 3-21G(d,p) (Li^+–K^+) and the 3-21G basis sets for Cs^+ and Rb^+.

Additional single-point energy *ab initio* calculations for Li^+–K^+ were carried out at HF/6-31G, HF/6-31G(d,p), HF/6-311G(d,p) for complexes of Li^+ and Na^+ using Becke's three parameter hybrid method [29], and the Lee, Yang and Parr correlation functional(LYP) [30].

The calculations have been carried out using the Gaussian 98 Molecular-modeling package running on a 75 MHz Pentium PC [31, 32].

3. Results and discussion

In this research study the complexation of calix[4]arenas with alkali metal cations has been investigated by using *ab initio* calculations with different basis sets in HF method and also the results compared with the second order Møller-Plesset [41] perturbation theory MP2/6-31G(d,p) Single-point energy B3LYP/6-31G(d,p) density functional calculations and additionally it has been compared with the Charmm simulation [42] and the experimental results [43].

In table 1 the energy differences in kcal mol^{-1} between the free calix[4]arene conformers, partial-cone (PC), l,2-alternate (l,2-A) and l,3-alternate (l,3-A) with the more established conformer, cone (C) in different methods reports.

It is known that the calix[4]arene cone conformer is energetically stabilized due to the formation of a hydrogen bond cyclic array in the lower rim. It has been found that this feature is also present in the complexes of calix[4]arene with cationic species. In table 2 Energy differences between host–guest complexes of calixarene and alkali metal ions against at the free calixarenes are reported.

However, some basis set dependence is observed and HF/3-21G calculations seem to overestimate the energy difference between the conformers and also when polarization functions are included although the results at HF/3-21G(d,p) are still higher than the experimental data. HF/6-31G(d,p) single-point calculations with geometries optimized at HF3-21G(d,p) are in much better agreement with experiment [43] and other theoretical predictions. In addition, MP2/6-31G(d,p) calculations with HF/3-21G(d,p) geometries predict energy differences between the conformers in excellent agreement with density functional optimizations at BLYP/6-31G(d) level [38].

So HF/3-21G(d,p) optimizations are adequate procedure to study the conformational equilibrium of calix[4]arene and also it is currently the method of choice weighing accuracy against CPU time.

Cation-π interactions play an important role in the complexation of alkali metal cations with benzene and with an extensive series of aromatic structures [33, 34] and several studies suggest a strong correlation between the total binding energy and the electrostatic contribution to the interaction energy [33, 35].

Table 1. Energy difference (in kcal mol^{-1}) between the calix[4]arene conformers partial-cone (PC), l,2-alternate (l,2-A) and l,3-alternate (l,3-A) and the cone (C).

Method	PC-C (kcal mol^{-1})	1,2-A-C (kcal mol^{-1})	1,3-A-C (kcal mol^{-1})
AM1	16.2	21.9	31.9
HF/6-31G	11.6	20.9	23.1
HF/3-21G(d,p)	16	26.3	28.1
HF/6-31G(d,p)	7	14.7	13.6
MP2/6-31G(d,p)	9.4	18.9	17.1
BLYP/6-31G(d)	10.7	18.6	18.1
BLYP/6-31G(d,p)	10.7	18.3	17.7
B3LYP/6-31G(d,p)	10.5	18.4	17.6
CHARMM	9.6	11.8	17.2
Experiment	14.3		

Table 2. Energy differences between calix-metal and free calix (kcal mol^{-1}).

Method	Free calix	Calix–Li^{+}	Calix–Na^{+}	Calix–K^{+}	Calix–Rb^{+}	Calix–Cs^{+}
AM1						
C	−1368.22478	−95.8	−62.7	−43.8	−36.7	−24.9
PC	−1368.79472	−104.5	−78.6	−38.4	−31.5	−19.5
1,2-A	−1368.48719	−111.9	−86.7	−41.2	−32.3	−16.2
1,3-A	−1368.75367	−124.8	−90.7	−42.7	−36.6	−13.4
HF/6-31G						
C	−1371.57891	−81.4	−50.7	−33.4	−27.2	−15.2
PC	−1371.44789	−85.4	−61.7	−36.1	−23.8	14.7
1,2-A	−1371.14782	−90.7	−61.8	−30.2	−21.9	−11.8
1,3-A	−1371.47812	−97.8	−61.9	−26.6	−21.7	−11.4
HF/3-21G(d,p)						
C	−1375.6662	−97.8	−71.8	−59.7	−53.4	−46.5
PC	−1375.12152	−100.8	−86.8	−53.8	−49.8	−44.1
1,2-A	−1375.80632	−113.8	−95.1	−55.9	−52.3	−47
1,3-A	−1375.79832	−117.1	−98.6	−62	−55.4	−50.4
HF/6-31G(d,p)						
C	−1374.25647	−74.9	−47.2	−40.2	−28.5	−27.5
PC	−1374.53179	−73.8	−51.8	−32.4	−23.7	−25.8
1,2-A	−1374.22365	−81.7	−56.7	−23.6	−13.5	−24.6
1,3-A	−1374.55427	−83.1	−53.9	−25.3	−15.7	−26.3
HF/6-311G(d,p)						
C	−1374.78441	−71.9	−32.4	−32.9	−24.3	−23.8
PC	−1374.47818	−72.5	−51.9	−27.3	−19.7	−28.6
1,2-A	−1374.65471	−77.7	−57.7	−20.1	−11.6	−23.9
1,3-A	−1376.80147	−78.9	−58.4	−21.8	−13.8	−25.3
MP2/6-31G(d,p)						
C	−1378.26662	−73.8	−33.4	–	−26.5	−28.5
PC	−1378.25121	−76.5	−51.9	–	−24.7	−26.2
1,2-A	−1378.23608	−89.1	−58.5	–	−23.9	−24.3
1,3-A	−1378.23897	−19.1	−58.9	–	−25.8	−27.4
B3LYP/6-31G(d,p)						
C	−1382.40441	−70.8	−37.9	−36.6	−24.2	−22.9
PC	−1382.38654	−77.4	−51.4	−27.5	−22.5	−19.6
1,2-A	−1382.37305	−86	−59.3	−21	−19.8	−18.5
1,3-A	−1382.36888	−92.1	−63.6	−29.9	−23.7	−21.2

In the complexation of alkali metal cations with benzene [36, 37] binding energies are according to the trend Li^+, Na^+, K^+, Rb^+ which is a normal electrostatic sequence. In most cases, the complexation energies of the 1,3-alternate calix[4]arene with Na^+ are about 30 kcal mol^{-1} lower than those calculated for the smaller cation Li^+. This finding is in accordance with the general selectivity $Li^+ > Na^+ > K^+ > Rb^+$. It is graphically shown in figure 3.

The electrostatic sequence suggests that dispersion interactions or polarization effects may be not of much relevance and that the cation could be represented by a charged "hard-sphere" of larger diameter for the bigger ones leading to a smaller elctrostatic interaction with the molecular structure.

The structures of the binding modes of cationic species with benzene [39] reflect the strong binding of the cations to the π face of the aromatics. Recently, density functional theory calculations on the complexation of the methyl cation with benzene [40] suggested that the stabilization of carbocation intermediates in biochemical reactions via cation-π interactions can be correctly afforded to carbocations over different parts of a benzene ring and at distances greater than typical covalent bonding distances.

In figure 4 the distance between the alkali metal ions and nearest oxygen atom in the optimized calix[4]arene complexes has been compared.

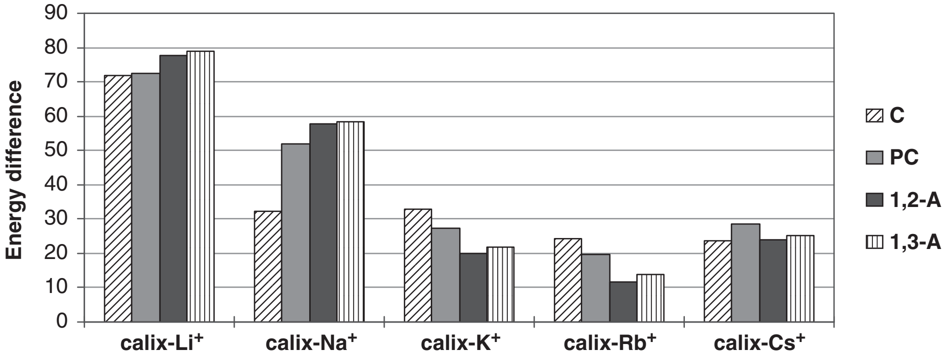

Figure 3. Energy differences between calix-metal complex and free calix[4]arene (kcal mol^{-1}) HF/6-311G(d,p).

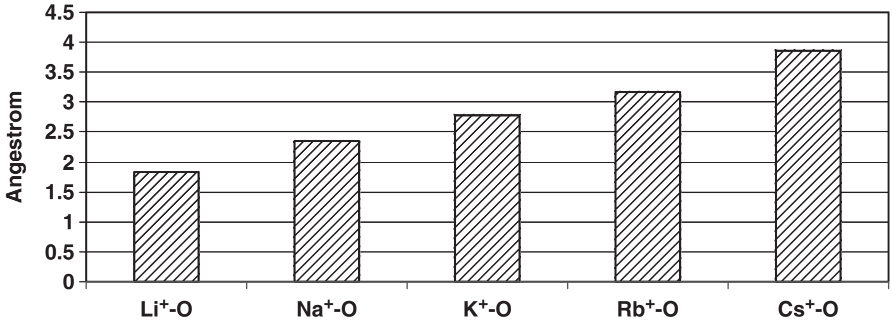

Figure 4. Comparison of the distance between the alkali metal ions and nearest oxygen atom in the optimized calix[4]arene complexes.

As it is shown the distance between the Li^+ and nearest oxygen atom in the optimized calix[4]arene complex is 1.83 Å and resemble distance in Na^+ complexes is 2.35 Å and in K^+, Rb^+ and Cs^+ is 2.78, 3.24 and 3.87 Å.

In the complexation of cations with calix[4] arenes, two aspects are worth referring to: the interactions between a charged species and the calix[4]arene depends on the specific conformation of the host; and cation-π interactions can be certainly enchanced by a cooperative effect due to the simultaneous presence of several aromatic structures. Thus, we can anticipate that the complexation of calix[4]arene with alkali metal cations involves a competition between different factors, including the interactions of the cation with the O–H groups and with the π faces of phenol, hydrogen bonding interactions in the calix[4]arene lower rim, and size effects.

In figure 5 a three dimensional graph of optimized HF/6-311 G(d,p) energy level against the distance between the alkali metal ions and nearest oxygen atom (Å) and ionic radius (Å) [44] is plotted and as also it is shown in figure 6. The graph shown as a Contour diagram and it is specified that at 1.83 Å distance between the cation and nearest oxygen atom and 0.585 Å ionic radius the optimized energy is in least amount (−71.9 kca/mol).

For smaller cations, such as Li^+ and K^+, the complexation with calix[4]arene is mainly due to electrostatic interactions with the oxygen atoms of the narrow rim of the calix[4]arene adopting an 1,2- or 1,3-alternate conformation thus complexation means binding to the oxygen atoms in the lower rim and in for Li^+ and Na^+

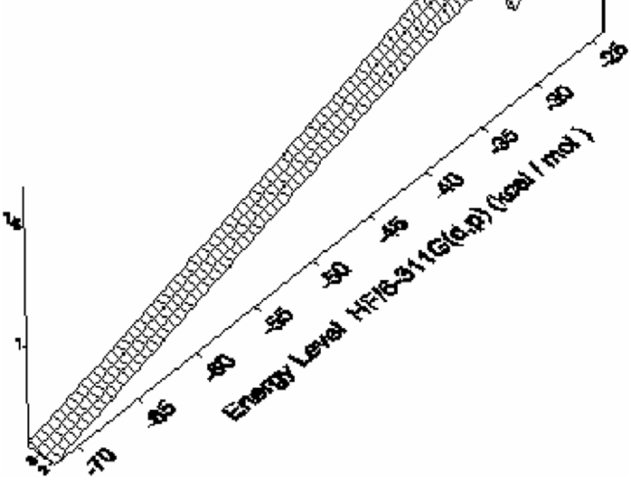

Figure 5. A three dimensional graph of optimized HF/6-311G(d,p) energy against the distance between 7cation and nearest oxygen atom (Å) and ionic radius (Å).

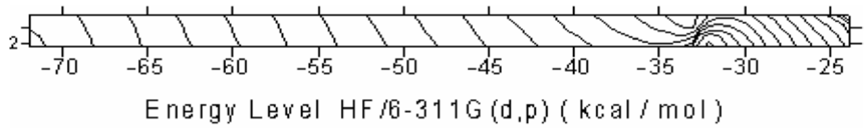

Figure 6. The contour diagram of optimized HF/6-311G(d,p) energy against the distance between cation and nearest oxygen atom (Å) and ionic radius (Å).

suggests a strong charge reorganization in the complexed calix[4]arene relative to the free macrocycle. The bigger cations (K^+, Rb^+ and Cs^+) are enclosed in the π-rich cavity of the macrocycle in the cone conformation. Inclusion of the larger cations preserves the array of cyclic hydrogen bonding in the lower rim and does not modify in a very significant way the electrostatic potential in this region. However, the interaction of the larger cations with the phenol faces induces some modification of the electrostatic potential over these surfaces. This is well illustrated for K^+, Rb^+ and Cs^+.

In general, the use of high-level *ab initio* quantum chemical calculations in calixarene chemistry seems to be somewhat in its infancy. The systems of interest are quite big; this is a fact that sometimes might hamper the use of a reasonably high level of theory. However, useful contributions have been already made studying all aspects of the supramolecular chemistry of calixarenes.

In future, computational resources will be getting cheaper and cheaper and high level calculations for all problems in structure elucidation of supramolecular systems will be routinely available. In particular the methods that are based on a combination of experiment and theory will make it easier for the non-computational expert to rely on computer chemistry results because of the common basis.

Furthermore, novel computational methods such as linear scaling DFT, ONIOM models, effective solvent models or calculations using periodic boundary conditions will have a serious impact on the applicability of quantum chemical calculation in the field of calixarene chemistry.

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