



Probing the influence of solvent effect on the lithium ion binding affinity of 12-crown-O₃N derivatives with unsaturated side arms: A computational study



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ARTICLE INFO

Article history:

Accepted 3 September 2013

Available online 16 September 2013

Keywords:

Aza-crown
Solvent medium
Binding affinity
Complexation
Side-arms

ABSTRACT

Molecular structures of crown ether derivatives play a crucial role in complexing and transporting alkali metal ions such as lithium ion. The complexation of such ions take place in solution, hence it is important to examine the complexation behavior of host systems in solution. We have investigated employing quantum chemical calculations the stable conformations of 12-crown-O₃N derivatives with unsaturated side-arms and its corresponding Li⁺ ion complexation in low polar to high polar solvent medium. The General Gradient Approximation (GGA) using PW91 functional with DNP basis set calculated results show that the side-arms contribute via cation- π interaction in the complexation of lithium ion with the receptor molecules **2** and **3** quite effectively in the gas phase and in low polar solvent medium (CHCl₃). The vinyl and acetylene groups attached to the receptor molecules are away from the cavity of the crown ether, however, orients toward the cavity while complexing with the lithium ion. The auxiliary effect of such side-arms to augment the binding affinity of Li⁺ ion is reduced in the high polar solvent medium. The side-arms also orient away from the complexed Li⁺ ion in relatively more polar solvents. These calculated results indicate that the complexing ability of aza-crowns toward the Li⁺ ion can be enhanced with the unsaturated side-arms in low polar solvent medium, which however, is less effective in more polar mediums.

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1. Introduction

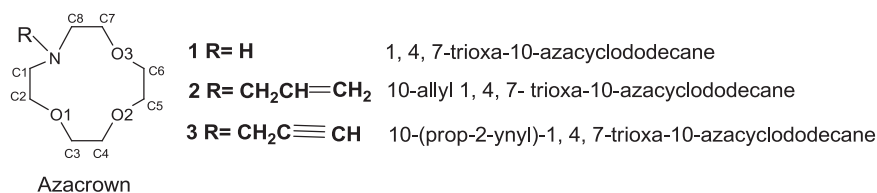
Among alkali metal cations, Lithium is of great importance as it has variety of applications. Academic and industrial research efforts have been made to develop high-power and long-life lithium-ion batteries [1–4]. Rechargeable lithium-ion batteries are now in great use in modern electronic gadgets like digital cameras, mobile telephones and laptops. Lithium is the first choice of the element for metallic alloying to aluminum that provides density reduction and increases modulus to reduce weight of aircraft [5]. Compounds of lithium are mainly useful for nuclear industry e.g. in the production of tritium, as a heat-exchange cooling medium and as a shielding material [6]. Lithium's antimanic efficacy is well known since 1949 and it is robust alternative to the use of typical antipsychotics for the treatment of acute mania [7]. It is used for the production of organolithium compounds (such as butyl lithium and lithium hydride) and as a solution in liquid ammonia for Birch reductions [8]. The four most important lithium mineral sources

are amblygonite, spodumene, petalite, and lepidolite. For such vast applications, the recovery of lithium from different source is one of the prime focuses of research activities. Although its concentration in seawater is 0.17 mg/L, [9] it could be a future source of lithium. Eco-friendly and economically feasible methods are required for its recovery/separation from seawater. Successful extraction requires efficient extractant/carrier molecules. The designing and screening of efficient ionophores/extractant/complexing agent is therefore a promising step. It would be worthy to study the complexation of lithium cation with suitable complexing agents in possible organic solvents, which could be useful to work out the best organic solvent to be employed for its separation from aqueous solution to an immiscible desired solvent.

Crown ethers discovered by C. J. Pedersen are well known as complexing agents for alkali and alkaline earth metal ions [10]. Among several factors that governs the selectivity, perhaps the least explored is the solvent effect in the complexation process. N-pivot lariat ethers are known to have better cation-binding than C-pivot lariat ethers as the nitrogen atom provides a flexible sidearm due to its ability to perform an inversion in space [11]. It is also reported that if sidearms do not interact directly with the ring-bound cation, they may influence the binding by competing with

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Scheme 1. Aza-crown systems examined.

solvent or counter ion [12]. Investigations related to stable structures of 12-crown-0₃N complexes with Li⁺/Na⁺ cation in aqueous and acetonitrile solutions were done by Kenzi Hori et al. [13–15]. Solid-state evidences of cation- π complexation by carbon-carbon double & triple bond and arene systems in sidearms with cation are also known [16–18].

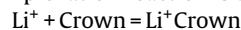
Recently, the structures, energetic and thermodynamic parameters of model crown ethers with different donor, cavity and functional groups have been determined with ab initio MP2 and DFT in gas and solvent phase [19]. DFT study was undertaken to gain insight into the mechanism of the complexation of Cs⁺ and Sr²⁺ ions with crown ether architectures [20]. Wipff et al. have studied molecular mechanics (MM) and molecular dynamics (MD) calculations of solvent effects on free ligand and ionophoric complexes [21]. Theoretical calculations have substantially enhanced the insight into solvent effect on energetics of ion complexation [22]. DFT with B3LYP/6-31G^{*} method offered the fully optimized geometries of lariat crown ethers LCE_s and their complexes with alkali metal ions, nucleophilicity of LCE_s have been investigated by Fukui functions and the sidearm effect had been analyzed with HOMO and LUMO energies [23].

In this present article, we have examined some newly designed Aza-12-crown-4 receptors for Li⁺ cation complexation having unsaturated donor groups i.e. double and triple bond in their sidearm and to predict their cooperativity toward Li⁺ ion encapsulation in different solvent mediums. Among alkali metal cations, Li⁺ is highly acidic and it is expected that it will invite unsaturated residues of sidearm for cation- π interaction, preferably in low polar solvents. Molecular mechanics (MM) and DFT methods have been employed to investigate the binding affinities for Li⁺ with aza-crown receptors in gas phase and different organic solvents of varying polarity.

2. Computational details

An exhaustive conformational search of ligands and their complexes was performed in solvents like chloroform (dielectric constant $\epsilon = 4.80$), dichloromethane ($\epsilon = 9.08$), pyridine ($\epsilon = 12.3$), acetone ($\epsilon = 20.7$), ethanol ($\epsilon = 24.3$), methanol ($\epsilon = 32.63$), acetonitrile ($\epsilon = 37.5$) and the gas phase calculations with molecular modeling program MacroModel [24] within 50 kcal/mol energy window using MM3 force field for 5000 Monte Carlo [25,26] steps. Energy minimizations were performed with the Polak-Ribiere conjugate gradient (PRCG) method, [27] which involves the use of first derivatives with convergence criterion. The resulting conformations were clustered based on torsional RMS using XCluster approach. Filtration and Clusterization offers leading members (conformers) within 5 kcal/mol energy window. Lowest energy conformers were stored for further higher level DFT calculations employing COSMO solvation model. The selected conformers were optimized in solvent with General Gradient Approximation (GGA) using PW91 functional integrated in density functional program Dmol3 in Material Studio (version 4.1.2) of Accelrys Inc [28]. The physical wave functions are expanded in terms of numerical basis set. We used a double numerical polarized DNP basis set which is comparable to the 6-31G^{**} basis set. The minima have been

confirmed by vibrational frequency calculations for all optimized geometries and their complexes at the same level of theory. This level of theory was chosen as the calculated results obtained from it corroborate the experimental results for alkali metal ion complexation with calix-crown hybrid ionophores in solvent medium [29] and was employed for conductor-like screening model (COSMO) for solvent calculations [30]. The Li⁺ cation and crown ether ligand complexation reaction is as follows.



The binding affinity (ΔE) calculated in respective solvent is based on following equation

$$\Delta E = (E_{\text{complex}}) - (E_{\text{crown}} + E_{\text{Li}^+})$$

where E_{Li^+} , E_{crown} , and E_{complex} stands for energy of Li⁺, crown ether and the complex, respectively.

Reliability of the computational method was checked when it is applied to reproduce the crystal structure of N,N'-bis(substituted)-4,13-diaza-18-crown-6 complexes having triple bond residue in its sidearms [31]. Optimized geometries obtained from GGA/PW91/DNP and B3LYP/6-31+G^{*} were compared with the reported crystal structure of 18-Crown-6 derivative (Fig. S1, S2 and table S1). GGA/PW91/DNP calculated bond distances were found to be in good agreement with the crystal structure as compared to that of B3LYP/6-31+G^{*} level of theory. The Li⁺ complexed structural parameters were found to be in good agreement with the observed crystal structure (Figs. S1, S2 and Table S1).

3. Results and discussion

Chemical properties of a molecule are largely governed by the structure of the molecule. To get information about variation in molecular structure of Aza-crowns and their Li⁺ complexes in different solvents and gas phase, the molecular structures of free ligands and their 1:1 complexes were optimized. We have examined three Aza-crowns and their corresponding Li⁺ complex (Scheme 1).

Compounds **2** and **3** are mono-brachial lariat ethers having a single carbon spacer while **1** is parent system and all these offer a suitable cavity and binding sites for Li⁺ complexation [19]. Sidearms were designed to be sufficiently flexible depending on systems demand to further enhance the encapsulation of Li⁺. The structure of ligand **1** is modified by adding double bond for **2** and triple bond for **3** which are unsaturated against the traditional one which generally bears the heteroatoms for additional binding support. The double and triple bonded sidearm attachment may reduce the solubility of the ligands in water and hence could enhance the extraction capability in organic solvent phase as most of the metal ion extraction takes place from aqueous phase to organic phase. As the complexation takes place in solvent phase, therefore, consideration of solvent effect on the structure and complexation of the host with metal ion is important.

In host **1**, all three O donor remains above the plane of crown ring before and after complexation for almost all phases except in gas phase and chloroform where two oxygen remains above the plane while third one changes its position from bottom to up on complexation (Fig. 1). There is no change in the orientation of N

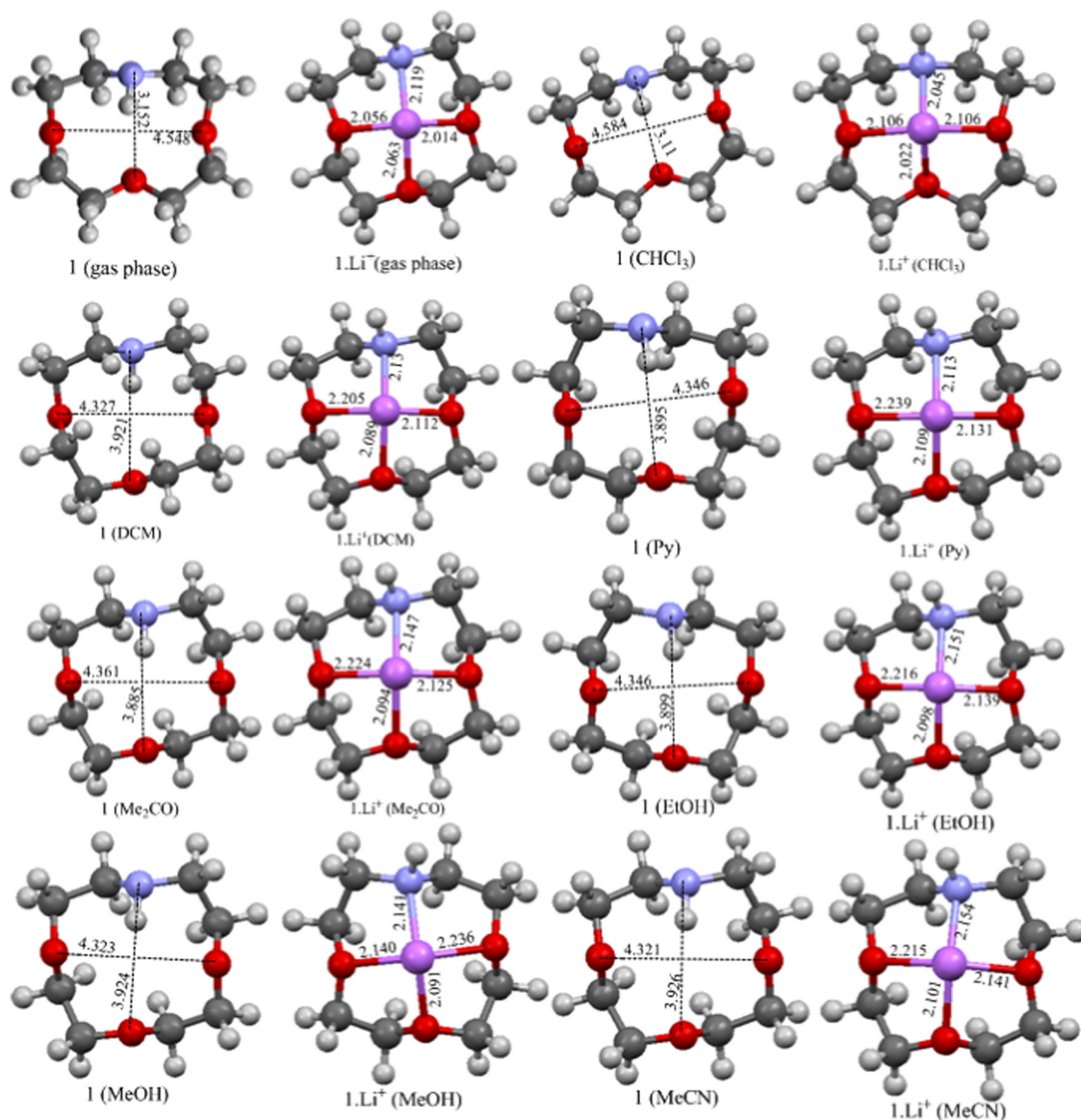


Fig. 1. GGA/PW91/DNP optimized geometries of free ligand **1** and its complexes in different solvents. (Red = oxygen; blue = nitrogen; gray = carbon; purple = lithium. Color indication is same for all rest of figures). Distances are given in Å.

donor before and after complexation, which remains above the plane of crown ring for all phases except in dichloromethane where it turns from bottom to up during complexation. On complexation of **1**, the diagonally center to center O1–O3 distance decreases in almost all phases. However, its major variation occurs in gas phase and chloroform. On complexation, the diagonally center to center O1–O3 distance decreases by 0.727 Å from 4.584 Å to 3.821 Å

and 0.437 Å from 4.584 Å to 4.147 Å respectively in gas phase and chloroform while for rest of the solvent phases it bears minimum difference of about 0.3 Å between free host and complexed state (Fig. 1). It suggests that with respect to the diagonally center to center oxygen, on complexation of **1** the crown ring has been perturbed highly in gas phase and chloroform while for rest of the solvent phases it makes a moderate perturbation. On the contrary

Table 1
The calculated O–Li⁺–O Angle (°) for the complexes of host **1**–**3**.

Geometry	Gas Phase	CHCl ₃	DCM	Py	Me ₂ CO	EtOH	MeOH	MeCN
1. Li⁺								
O1–Li ⁺ –O3	139.6	159.8	134.7	134.3	133.5	133.1	133.4	133.1
N–Li ⁺ –O2	143.1	108.6	134.6	133.5	133.3	132.9	132.4	133.0
2. Li⁺								
O1–Li ⁺ –O3	135.1	121.0	132.0	132.8	131.9	132.2	130.1	131.7
N–Li ⁺ –O2	141.0	153.2	138.8	138.2	137.8	137.6	136.6	137.9
3. Li⁺								
O1–Li ⁺ –O3	133.3	149.5	132.0	132.5	131.7	131.8	132.0	131.3
N–Li ⁺ –O2	139.2	129.2	137.8	137.5	137.1	137.1	137.2	136.4

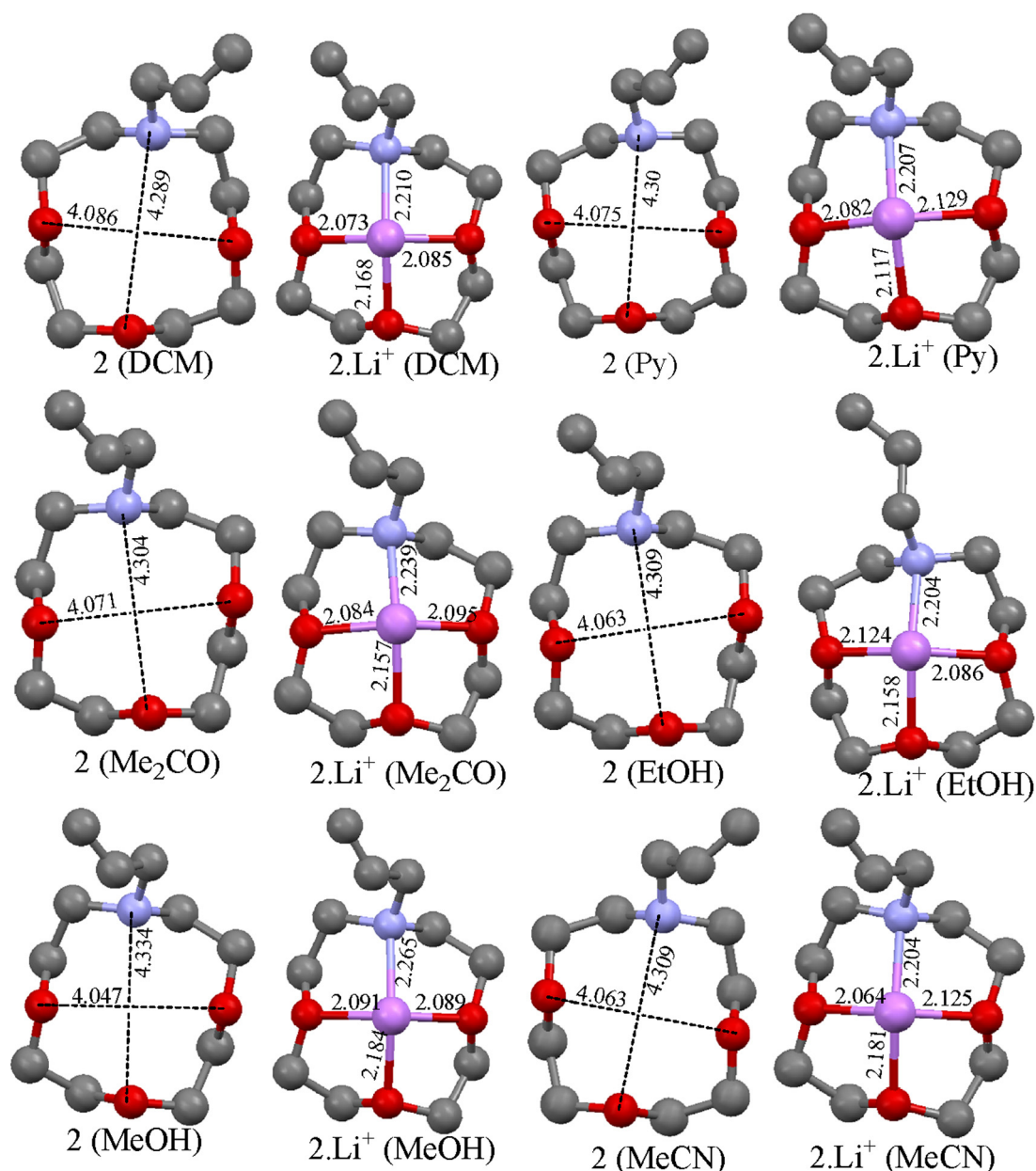


Fig. 2. GGA/PW91/DNP optimized geometries of free ligand **2** and its complexes in different solvents showing non cooperation of side arm toward Li^+ encapsulation. Red = oxygen; blue = nitrogen; gray = carbon; purple = lithium. Distances are given in Å.

to this, on its complexation the diagonally center to center N–O2 distance expand by 0.816 Å from 3.152 Å to 3.968 Å and 0.193 Å from 3.11 Å to 3.303 respectively in gas phase and chloroform but for rest of the solvent phases this expansion is negligible. However, it is to note that the compression (0.727 Å) of diagonally center to center O1–O3 distance is nearly same to the expansion (0.816 Å) of the diagonally center to center N–O2 distance in gas phase while in chloroform compression of just mention parameters is higher than expansion. This folding of the molecular structure leads to suffice the coordination number of Li^+ (which is generally 4), which occurs due to electrostatic interaction of the positive charge of the metal ion with the dipole of the donor atom of the host. In the complexed state of **1–3**, Li^+ sits above the center of crown cavity which can be gauge from O–Li–O/O–Li–N angles (Table 1). For all solvent phase including gas phase in each complex of **1–3**, almost all Li–O bond lengths is shorter than the Li–N bond lengths (except **1.Li⁺** in chloroform and dichloromethane) which may be due to high electrostatic interaction between Li^+ and O donor atom compared

to the interaction between Li^+ and N atom. Li^+ induction causes variation in the geometrical parameters of the hosts essentially in gas phase and chloroform. As the chloroform is a low polar solvent, the degree of desolvation of ion is high and hence strong complexation may occur which causes measurable geometrical changes.

For free host **2** and **3**, the sidearms are observed to be greatly relaxed in the gas phase as well as in solvent phases i.e. turned away from macrocyclic cavity (Figs. 2 and 3). For free host **2**, in the gas phase only one O donor is lying above the plane of crown ring and two oxygen's at the bottom of the plane and both these turned above the molecular plane of crown ring on complexation. In all phases, for host **2** and **3**, upward position of N donor remains unaltered on complexation. For **2.Li⁺** and **3.Li⁺** in chloroform the observations related with O donors position are same to that of **1.Li⁺**. On complexation in host **2** and **3**, the diagonally center to center O1–O3 distance decreases at least about 0.2 Å almost in all solvent phases (except for **2.Li⁺** in chloroform where it is 0.754 Å

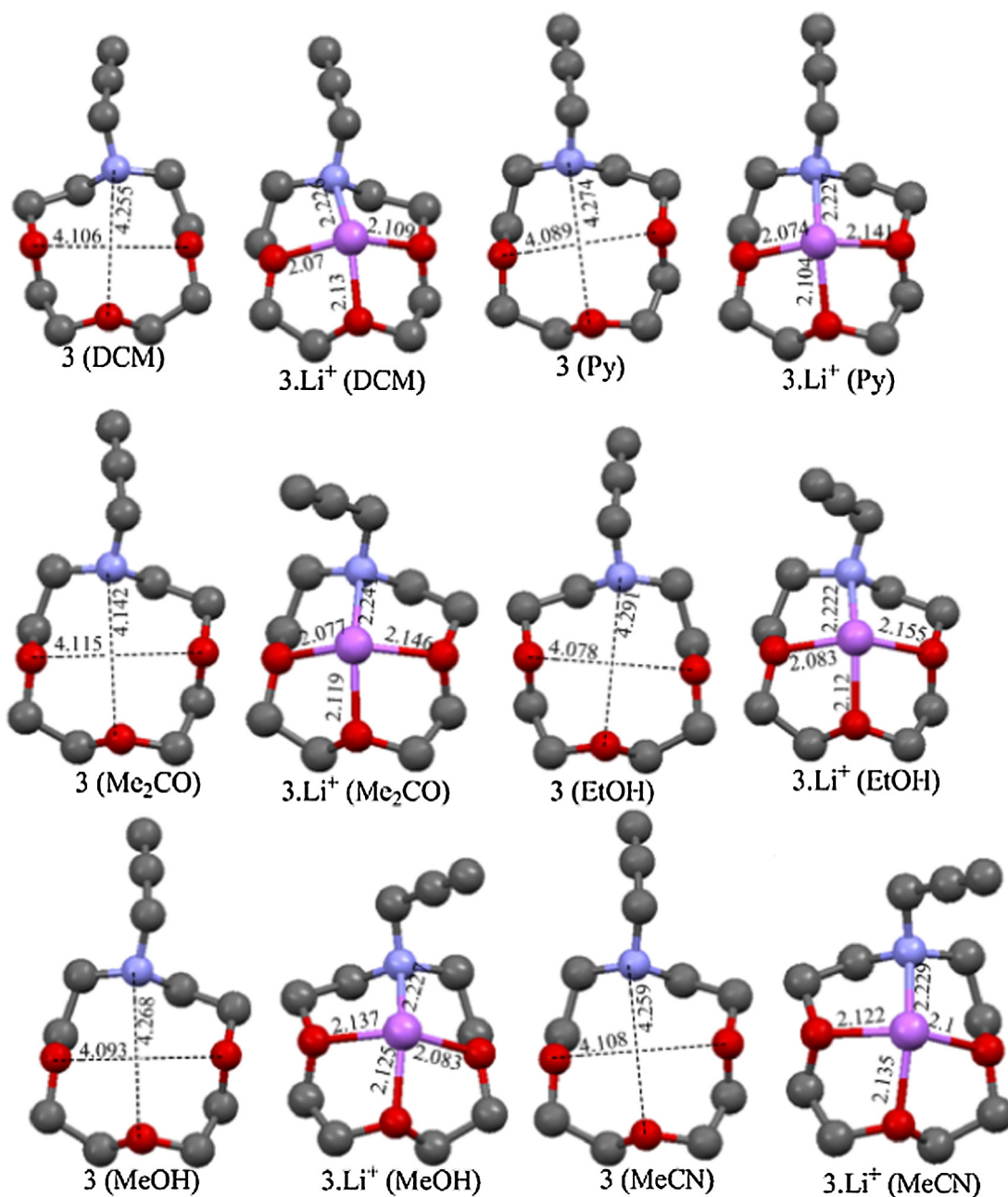


Fig. 3. GGA/PW91/DNP optimized geometries of free ligand **3** and its complexes in different solvents showing non cooperation of side arm toward Li^+ encapsulation. Distances are given in Å.

and negligible in gas phase) while diagonally center to center O–N distance decreases negligibly for all phases (except for $3.\text{Li}^+$ in chloroform where it is 0.643 Å). It is to note that on complexation, expansion of diagonally center to center N–O distance as noted for **1** has not been observed for **2** and **3** in any other solvent phases.

For $2.\text{Li}^+$ in the gas phase and chloroform, the angle at Li^+ from the double bond carbon atoms are 26° and 9° respectively while for $3.\text{Li}^+$ these are 26° and 18° from triple bonded carbon atoms respectively, indicates that the unsaturated part of the sidearm is obliquely placed onto the macrocyclic otherwise these angles would have been high. The unsaturated part has partially enveloped the Li^+ and there is certain degree of cation– π interaction observed for the complexes of **2** and **3** in the gas phase geometries. Such interaction is more effective in chloroform with the acetylene unit (Figs. 4 and 5) [16–18]. The binding energy

of Li^+ ion is relatively higher for $2.\text{Li}^+$ and $3.\text{Li}^+$ compared to $1.\text{Li}^+$ clearly shows the influence of cation– π interaction in these cases (Table 2).

In general, there is a considerable variation in the binding affinity from solvent of low dielectric constant to relatively high dielectric constant (Table 2). For all three complexes, the binding affinity decreases with increasing polarity of the solvent. The binding affinity predicted in solvent medium for all the three hosts to the lithium ion is highest in chloroform. The side arms of **2** and **3** are not acting as an auxiliary group to augment the binding of Li^+ ion with these receptor molecules in more polar medium. The optimized structures show that in strong polar environment, the vinyl and acetylene groups are away from the complexed Li^+ ion (Fig. 2 and 3). It appears that the side-arms destabilize the complexation behavior of the receptor molecules with Li^+ in polar solvent medium. However, generally the unsaturated side-arms enhance

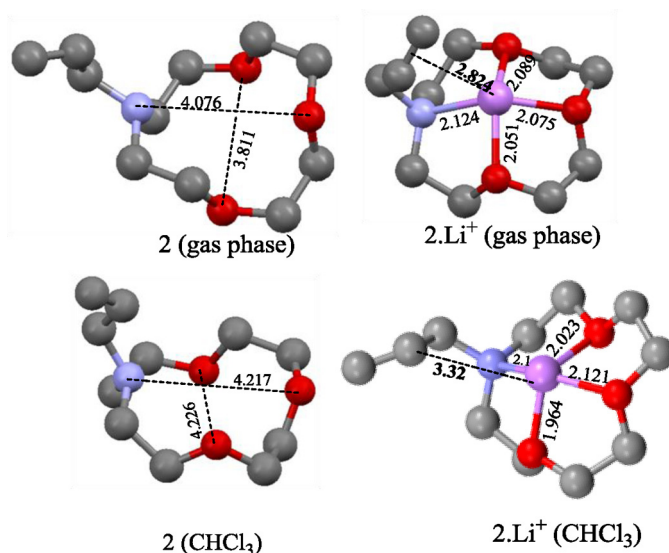


Fig. 4. GGA/PW91/DNP optimized geometries of free ligand **2** and its complexes showing cation-pi interaction. Distances are given in Å.

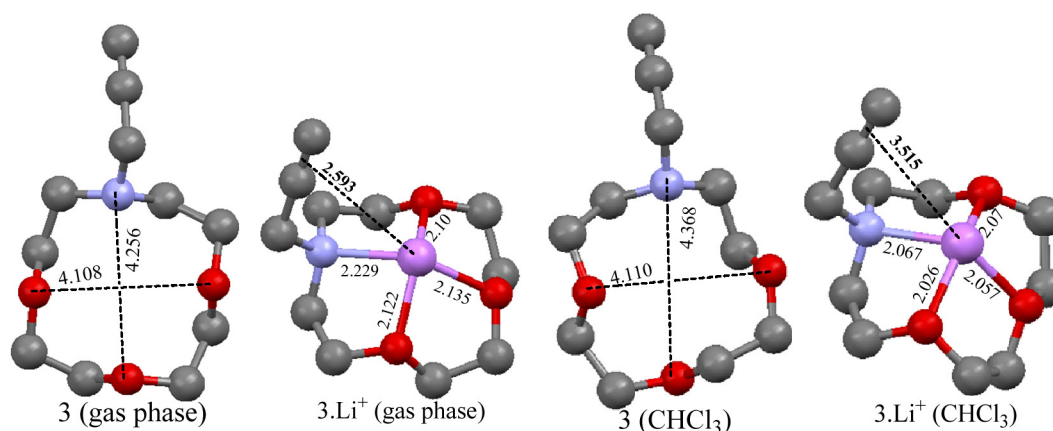


Fig. 5. GGA/PW91/DNP optimized geometries of free ligand **3** and its complexes showing cation-pi interaction. Red = oxygen; blue = nitrogen; gray = carbon; purple = lithium. Distances are given in Å.

Table 2

Binding affinity (kJ/mol) of Li^+ with host **1–3** in the gas phase and in different solvent phase.

Complex	Gas phase	$\text{CHCl}_3 \epsilon = 4.80$	$\text{DCM} \epsilon = 9.08$	$\text{Py} \epsilon = 12.3$	$\text{Me}_2\text{CO} \epsilon = 20.7$	$\text{EtOH} \epsilon = 24.3$	$\text{MeOH} \epsilon = 32.63$	$\text{MeCN} \epsilon = 37.5$
1. Li^+	–564.56	–156.04	–118.62	–104.94	–87.80	–83.55	–77.53	–76.10
2. Li^+	–457.74	–173.26	–142.47	–126.90	–109.26	–105.96	–101.31	–95.32
3. Li^+	–460.75	–165.27	–143.09	–126.82	–89.00	–100.17	–94.54	–93.09

ϵ = dielectric constant.

the binding affinity of Li^+ ion with **2** and **3** compared to **1** in respective solvent medium. The role of solution thermodynamics has been observed beside the auxiliary effect of such side-arms in the receptor molecules [12].

4. Conclusions

In the present study, the side arm effect was investigated with new Aza-crown systems in different solvent medium computationally. The General Gradient Approximation (GGA) using PW91 functional with DNP basis set shows that the side-arms contribute via cation- π interaction in the complexation of lithium ion with the receptor molecules **2** and **3** quite effectively in the gas phase and low polar solvent medium (CHCl_3). The vinyl and acetylene groups attached to the receptor molecules are away

from the complexation site, however, orients toward the cavity while complexing with the lithium ion. The auxiliary effect of such side-arms to augment the binding affinity of Li^+ ion is reduced in the high polar solvent medium. The side-arms also orient away from the complexed Li^+ ion in relatively more polar solvents. These calculated results indicate that the complexing ability of aza-crowns toward the Li^+ ion can be enhanced with the side-arms in low polar solvent medium, which however, is less important in strong polar mediums. This study would help the researcher to design the systems for the possible extraction of Li^+ ion in solution.

Acknowledgements

Authors thank SIP CSIR, New Delhi, India for financial support to this work. Authors thank Dr. P.K. Ghosh (Director), CSMCRI for his

keen interest in the work. We thank the anonymous reviewer for suggestions/comments that have helped us to improve the paper.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jmngm.2013.09.004>.

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