



Mutual influence between conventional and unconventional lithium bonds



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ABSTRACT

The interplay between conventional and unconventional lithium bonds interactions in $\text{NCLi} \cdots \text{NCLi} \cdots \text{XC} \equiv \text{CX}$ and $\text{CNLi} \cdots \text{CNLi} \cdots \text{XC} \equiv \text{CX}$ ($\text{X} = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{OH}, \text{CH}_3$, and OCH_3) complexes is studied by ab initio calculations. Cooperative effects are observed when $\text{Li} \cdots \text{N}(\text{C})$ and $\text{Li} \cdots \pi$ bonds coexist in the same complex. These effects are analyzed in terms of geometric, energetic and electron charge density properties of the complexes. The cooperative effects are larger in those complexes with shorter intermolecular distances than in those with the longest ones. The electron density at the lithium bond critical points can be regarded as a good descriptor of the degree of cooperative effects. An excellent linear correlation can be obtained between the cooperative energies and the calculated spin–spin coupling constants across the lithium bonds.

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1. Introduction

The study of weak interaction between closed-shell molecules has long been a topic of intensive scientific research due to its relevance in biochemistry, organic chemistry, inorganic chemistry, solid-state physics, and molecular medicine [1–6]. Although research has traditionally focused on the more common hydrogen bond (H-bond) interactions, recently, great progress has been made in the research of different types of intermolecular interactions, such as dihydrogen bonds [7–9] and halogen bonds [10–13]. Due to the similarity of lithium atom with hydrogen atom, the existence of lithium bond was theoretically predicted in 1970 by Kollman et al. [14]. Then, the first experimental evidence for lithium bond (Li-bond) was provided with $\text{X} \cdots \text{Li} - \text{Y}$ ($\text{X} = \text{H}_3\text{N}, \text{Me}_3\text{N}, \text{H}_2\text{O}, \text{Me}_2\text{O}$; $\text{Y} = \text{Cl}, \text{Br}$) systems by Ault and Pimental [15]. To date, Li-bonding has been identified in a variety of systems and the concept of Li-bonding has become important in many fields [16–25], although the study of it is far fewer than that of H-bonding.

Other than conventional Li-bonds, where a lithium donor R-Li group approaches an acceptor atom like O or N, some unconventional Li-bonds such as the Li-hydride bond [26,27] has gained much attention. The single-electron Li-bonds [28] formed between methyl radical and lithium-containing molecules were also suggested with theoretical calculations. A recent ab initio study [29] of

Li-bonded complexes with carbene as an electron donor showed that the electrostatic effect plays a main role in the Li-bonding interactions although the dispersion, polarization and charge transfer contributions are also of importance. Considering the fact that the electron-rich environment of a π bond can readily interact with a proton donor [30], a different type of Li-bonding has been established viz. a so-called $\text{Li} \cdots \pi$ bond [31–34]. The $\text{Li} \cdots \pi$ bonded complexes between LiF and benzene, ethylene, or acetylene have been investigated theoretically [35]. Blue-shifted Li-bonds were also evaluated in a number of Li-bonded systems with F_3CLi or F_3SiLi molecule as the electron acceptor [36]. These studies show that Li-bonds have similar characteristics with H-bonds although the electrostatic force is bigger in the former ones.

Recently, there has been great interest in the cooperativity between different Li-bonds. For example, Solimannejad et al. [37] have investigated the cooperativity effects in linear $(\text{LiCN})_{2-7}$ and $(\text{LiNC})_{2-7}$ clusters. The results indicated that cooperative enhancement stabilizes the average Li-bonding interactions in the $(\text{LiCN})_{2-7}$ and $(\text{LiNC})_{2-7}$ by about -38 kcal/mol, at the MP2/6-311++G** level, which are equivalent to adding -6.6 kcal/mol to the dimer Li-bonding energy. However, the cooperativity of the $\text{Li} \cdots \text{N}$ in the cyclic clusters is more significant than that in the linear ones [38]. The cooperativity between the Li-bond and other types of interactions has been also extensively studied [39,40]. Li et al. [41] found a positive cooperative effect between Li- and H-bond in $\text{HLi} \cdots \text{NCH} \cdots \text{NCH}$ system. Interestingly, their results revealed that the effect of Li-bonding on the properties of H-bonding is larger than that of H-bonding on the properties of Li-bonding.

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For the model trimer systems $\text{FX} \cdots \text{FH}/\text{Li} \cdots \text{OH}_2$ ($X = \text{H}, \text{Li}$ and Cl), McDowell and Yarde [42] indicated that the intermolecular properties of the H- and Li-bonded $\text{FH}/\text{Li} \cdots \text{OH}_2$ subunits are enhanced by the noncovalent interactions introduced by the FX ($X = \text{H}, \text{Li}, \text{Cl}$) molecule in the order $\text{Li-bond} > \text{H-bond} > \text{halogen-bond}$. To the best of our knowledge, neither a theoretical nor an experimental study has thus far been reported to examine the cooperativity between conventional and unconventional Li-bonded complexes. Herein, we report our theoretical study on $\text{NCLi} \cdots \text{NCLi} \cdots \text{XC}\equiv\text{CX}$ and $\text{CNLi} \cdots \text{CNLi} \cdots \text{XC}\equiv\text{CX}$ complexes where $X = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{OH}, \text{CH}_3$, and OCH_3 . A detailed analysis of the binding distances and interaction energies has been performed on these complexes. Our aim in this study is to explore how the conventional $\text{Li} \cdots \text{N}(\text{C})$ and the unconventional $\text{Li} \cdots \pi$ Li-bonding interactions influence each other in the complexes where both interactions are present. The study of the interplay between both interactions is beneficial in preparation of crystal materials where both interactions may coexist. In order to unveil the mechanism of the cooperativity, quantum theory of atoms in molecules (QTAIM) and interaction energy decomposition analyses are also described. We have also calculated nuclear magnetic resonance (NMR) properties for these systems.

2. Computational details

All quantum chemical calculations were carried out using the GAMESS electronic structure package [43]. Geometries were optimized at the MP2 level with the 6-311++G** basis set. Then corresponding frequency calculations were carried out at the same level to ensure that the optimized structures are true minima. Recent studies [23,37,39] suggest that this method is reliable for estimating the interaction energy of the Li-bonds. The interaction energies were calculated at the MP2/6-311++G** and CCSD(T)/6-311++G** levels of theory with correction for the basis set superposition error (BSSE) by the Boys–Bernardi method [44]. The topological analysis of the electron charge density performed for all complexes was performed using QTAIM [45]. The QTAIM analysis was performed with the help of AIM 2000 software [46] using the wave functions generated at the MP2/6-311++G** level. The interaction energy was decomposed according to the following scheme [47]:

$$E_{\text{int}} = E_{\text{elst}} + E_{\text{exch-rep}} + E_{\text{pol}} + E_{\text{disp}} \quad (1)$$

where E_{elst} , $E_{\text{exch-rep}}$, E_{pol} and E_{disp} correspond to electrostatic, exchange-repulsion, polarization and dispersion terms, respectively.

^{15}N and ^{13}C chemical shielding tensors as well as spin–spin coupling constants across the Li-bonds for complexes were computed using the gauge-including atomic orbital (GIAO) approach [48]. In the principal axis system (PAS), the chemical shielding tensor is converted to a diagonal matrix with σ_{11} , σ_{22} and σ_{33} components where $\sigma_{33} > \sigma_{22} > \sigma_{11}$. The isotropic (σ_{iso}) and anisotropic ($\Delta\sigma$) chemical shielding are related to the principal components by the following equation, respectively [49]:

$$\sigma_{\text{iso}} = (\sigma_{11} + \sigma_{22} + \sigma_{33})/3 \quad (2)$$

$$\Delta\sigma = \sigma_{33} - (\sigma_{11} + \sigma_{22})/2 \quad (3)$$

3. Results and discussion

Geometries. Fig. 1 shows a sketch of the $\text{NCLi} \cdots \text{NCLi} \cdots \text{XC}\equiv\text{CX}$ and $\text{CNLi} \cdots \text{CNLi} \cdots \text{XC}\equiv\text{CX}$ trimers, where $X = \text{H}, \text{F}, \text{Cl}, \text{Br}, \text{OH}, \text{CH}_3$ and OCH_3 . It should be noted that no symmetry constraints were introduced in the optimization of the complexes. All these species are true minima on the potential energy surface, as the vibrational analysis proved a posteriori. Two bond lengths (r_{AB} and

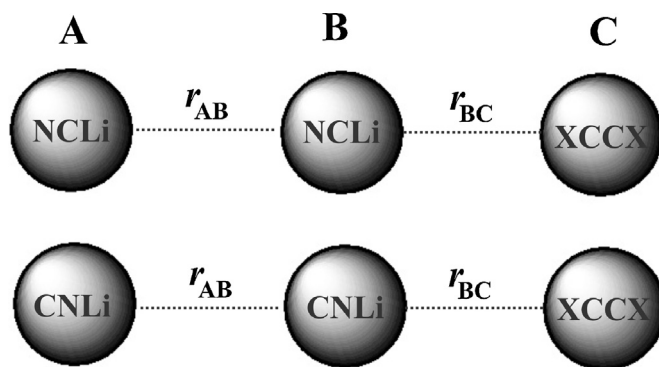


Fig. 1. Disposition of the monomers within the complexes.

r_{BC}) are marked explicitly in Fig. 1. Table S1 (Supporting Information) lists the optimized binding distances and the corresponding bond length changes of the Li-bonds in the 14 trimers. Some interesting points can be extracted from the geometrical results. The equilibrium distances r_{AB} in the binary $(\text{LiCN})_2$ and $(\text{LiNC})_2$ systems are calculated to be 1.978 and 2.111 Å, respectively. These are shorter than the sums of the van der Waals (vdW) radii of the atoms involved ($r_{\text{vdw,Li}} = 1.82$ Å, $r_{\text{vdw,N}} = 1.55$ Å and $r_{\text{vdw,C}} = 1.70$ Å) [50], which implies that there is an attractive force between the two subunits. It is seen also from Table S1 that the bond distances for the $\text{Li} \cdots \pi$ interactions of dimers are within a range of 2.233–2.432 Å, that is, the interaction distances of $\text{Li} \cdots \pi$ bonds are generally longer than those of $\text{Li} \cdots \text{N}$ and $\text{Li} \cdots \text{C}$ bonds. The equilibrium binding distances r_{AB} and r_{BC} in the ternary systems are always shorter than that in the respective dimers. This trend can be interpreted as a mutual influence between the conventional $\text{Li} \cdots \text{N}(\text{C})$ and unconventional $\text{Li} \cdots \pi$ Li-bonds. The shortening of the r_{AB} distance varies from 0.004 Å in the $\text{CNLi} \cdots \text{CNLi} \cdots \text{FC}\equiv\text{CF}$ trimer to 0.014 Å in the $\text{NCLi} \cdots \text{NCLi} \cdots \text{CH}_3\text{OC}\equiv\text{CCH}_3\text{O}$ complex, while the shortening of the $\text{Li} \cdots \pi$ distance is in a range of 0.015–0.055 Å. Evidently, the effect is larger in those complexes with shorter intermolecular distances than in those with the longest ones (Table S1). In each trimer, the decrease in the $\text{Li} \cdots \pi$ length is larger than that of the $\text{Li} \cdots \text{N}(\text{C})$ length. This reveals that the effect of a $\text{Li} \cdots \text{N}(\text{C})$ on a $\text{Li} \cdots \pi$ is more pronounced than that of a $\text{Li} \cdots \pi$ on a $\text{Li} \cdots \text{N}(\text{C})$.

Interaction energies. The interaction energy is a powerful method of estimating the cooperative effects between the non-covalent interactions. The interaction energies in the binary and ternary complexes are obtained as the energy difference between the complex and sum of the isolated monomers. All MP2 and CCSD(T) interaction energies have been corrected for the BSSE using the counterpoise method (Table 1). The contribution of BSSE to the uncorrected interaction energy ranges from 10 to 18% for the $\text{Li} \cdots \pi$, and it varies from 8 to 14% for $\text{Li} \cdots \text{N}(\text{C})$. From Table 1 results, it is seen that the MP2 interaction energies overestimate the attraction slightly in comparison with the more reliable CCSD(T) ones. The calculated CCSD(T) interaction energies of $\text{NCLi} \cdots \text{XC}\equiv\text{CX}$ and $\text{CNLi} \cdots \text{XC}\equiv\text{CX}$ dimers are estimated to lie in the range from -2.82 to -13.66 kcal/mol and from -2.72 to -13.51 kcal/mol, respectively, which compare favorably with the results of previous calculations [31–34]. The interaction energies of $\text{Li} \cdots \text{N}(\text{C})$ bonds are generally much larger (more negative) than those of $\text{Li} \cdots \pi$ bonds. The data in Table 2 also demonstrate that the $\text{NCLi} \cdots \text{XC}\equiv\text{CX}$ and $\text{CNLi} \cdots \text{XC}\equiv\text{CX}$ interactions become stronger when the electron-donating ability of the X group increases. An interesting aspect of the results presented in Table 1 is the fact that the interaction energies of the systems tend to increase as the size of the halogen increases, which corresponds to a decreasing value of the halogen atom electronegativity.

The cooperative energy E_{coop} is calculated by subtracting the sum of the interaction energies of the corresponding dimers from

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