The Nature of Lithium Bonding in $C_2H_2Li_2$, C_6Li_6, and Lithium Halide Dimers

Yameng Liu,[a,d] Bin Peng,*[b,d] Xiao Wang,[c,d] Yaoming Xie,[d] and Henry F. Schaefer III*[d]

[a]*State Key Laboratory of Natural and Biomimetic Drugs,*
School of Pharmaceutical Sciences, Peking University. 100191 Beijing, P. R. China

[b]*Center for Computational Quantum Chemistry*
South China Normal University, Guangzhou, Guangdong 510631, China

[c]*Center for Computational Quantum Physics*
Flatiron Institute, New York, New York 10010, USA

[d]*Center for Computational Quantum Chemistry*
University of Georgia, Athens, Georgia 30602, USA

Abstract

Lithium-containing molecules, such as $C_2H_2Li_2$, C_6Li_6, and the lithium halides, have been studied in the present paper, and the nature of lithium bonds in these structures is investigated. In contrast to the hydrogen bond, which features a typical quasi-linear and dicoordinated (X···H-Y) geometry, the ionic lithium bond prefers non-linear and multicoodinated geometrical arrangements. Based on these observations, we have predicted some novel low-lying C_6Li_6 structures. With its unusal features, the Li bond theory should be applied rather widely.

1. Introduction

The idea of a hydrogen kernel held between two atoms as a theory was first proposed by M. L. Huggins in his unpublished thesis, but publicized in a footnote of Latimer and Rodebush's 1920 paper.[1] Based on this proposal, the mono-valent hydrogen can constitute a weak "bond" with two atoms at the same time, i.e., X-H···Y. This idea was not accepted at first because it violates the Lewis theory of bonding, and thus the Latimer-Rodebush paper was almost completely ignored for ten years. However, by the late 1930s, this concept began to be accepted,[2,3] and now the term "hydrogen bond" is a foundamental concept applied to all fields in chemistry.[4,5,6,7]

Similarly, it has been found that the mono-valent lithium atom, which is the closest congener of hydrogen in the periodic table, may be held between two atoms.[8- 11] The existence of dimers and trimers of alkali halides was reported in the 1950s,[8,9] and the term "lithium bonding" was first used by Shigorin in 1959.[10] However, it was soon criticized by West *et al.*, who stated that there is no reason to give a special name for the alkylithium polymers.[11] Nevertheless, a paper titled "The Lithium Bond" was published by Kollman, Liebman, and Allen in 1970.[12] The authors theoretically studied some typical compounds with X-Li···Y bonding, in which the intermolecular interactions were predicted between the Li atom in one molecule and a highly electronegative atom (Y) in another, and this interaction was named a lithium bond, analogous to hydrogen bond. Based on the self-consistent field (SCF) results, the lithium bond was predicted even stronger than the hydrogen bond. For example, Kollman *et al*. reported the hydrogen bond energy for Li-F···H-F to be 16 kcal/mol, while the lithium bond energies for the linear and cyclic Li-F···Li-F dimers are 46 kcal/mol and 66 kcal/mol, respectively.[12] Subsequently, the experimental evidence of lithium bond, where the vibrational frequency shifts similar to hydrogen bond, was provided by Ault and Pimentel.[13] After a brief review by Sannigrahi in 1986,[14] the theory of the Li bond was reexamined by Schleyer, Sannigrahi, and co-workers in 1990,[15] where four types of Li-bonded complexes were extensively studied, and compared to those of hydrogen bonds. In 2011 the definition of the hydrogen bond was proposed by IUPAC,[16] and based on it a analogous definition of the lithium bond can be made.[17]

Recently, a number of studies of Li-containing compounds have been reported, and these are related to many applications, such as lithium batteries,[18] lithium catalysts,[19,20] and organolithium chemistry.[21,22] The lithium bond is found to play important roles in these compounds. For example, the title of the recent *Angewandte* paper[18] by Hou *et al.* is "Lithium Bond Chemistry in Lithium-Sulfur Batteries". One might expect the structure of lithium-containing molecules to be similar to that of the hydrogen analogues. However, the molecular structures have been found to be very different when hydrogen atoms in molecules are completely or partially replaced by lithium atoms. For example, the well-known $(HF)_2$ has a bent chain H-F···H-F structure,[23] whereas the analogous dimer $(LiF)_2$ is cyclic.[4] Other examples include dilithioethylene and hexalithiobenzene, which have have been studied by several researchers.[24,25,26,27] The structures with bridging lithium atoms were found to be significantly lower in energy than their respective ethylene- and benzene-like structures, and furthermore, some anomalous geometries have even lower energies. The peculiar structures of lithium-containing molecules lead us to consider the nature of the lithium bond, where a thorough comparison between the lithium bond and the hydrogen bond will be of significance.

2. Theoretical Details

In the present study, the "gold standard" coupled-cluster method with the single, double, and perturbative triple excitations, i.e., CCSD(T),[28,29,30] along with Dunning's correlation-consistent polarized valence quadruple-ζ (cc-pVQZ) basis sets[31,32] was adopted to optimize the geometries and perform the vibrational frequency analyses for all the molecules except for C_6Li_6, which is beyond the current capacity of our computational resources. However, the CCSD(T)/cc-pVQZ method is still used for the prediction of the single-point energies for the C_6Li_6 system based on the DFT optimized geometry. All CCSD(T) computations (with the frozen-core approximation) were performed with the MOLPRO software package.[33]

Our high level theoretical predictions were used to test DFT methods. The choice of the DFT functional was validated by a careful benchmark of six popular functionals, namely M06-2X,[34] PBE0,[35] B97-D,[36] B97-D3,[37] MPW1K,[38] and ωB97X-D[39] against the CCSD(T) results for the $C_2H_2Li_2$ molecule (see Section 3.1.2 for details). The ωB97X-D functional was finally chosen for the geometry optimizations of the C_6Li_6 system. The DFT computations were carried out using the Gaussian 09 program package.[40]

The natural atomic charges and the Wiberg bond indices[41] were studied at the ωB97X-D/cc-pVQZ level of thoery with the NBO 6.0 program.[42] In order to further investigate the chemical bonds, we transformed the canonical molecular orbitals (CMOs) into localized molecular orbitals (LMOs) with the Pipek−Mezey scheme,[43] which is a fast intrinsic localization method and weakly depends on the basis sets.

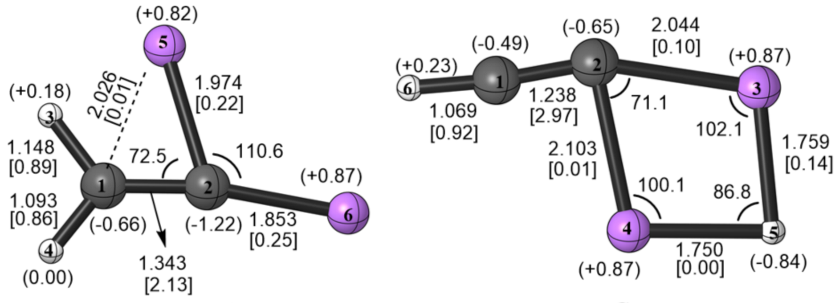
3. Results and Discussions

3.1 $C_2H_2Li_2$

3.1.1 Two Low-Lying Isomers for $C_2H_2Li_2$

The earlier theoretical studies of dilithioethene have been reported by Schleyer, Pople, *et al.* in 1976,[44] then by Schleyer, Schaefer, *et al.* in the 1990s,[45,46] and then by Röthlisberger and

Klein in 1995.[47] Recently, we have studied the possible stationary points of 1,1-dilithioethylene (H_2CCLi_2) at the CCSD(T)/cc-pVQZ level of theory, and predicted the energetics at the CCSDT(Q)/CBS level.[24] The singlet ethylene-like H_2CCLi_2 structure (C_{2v}) is actually a transition state, rather than a minimum, with one imaginary vibrational frequency that corresponds to the CCLi bending mode. Along the direction of this mode, one finds a local minimum (C_s) with one lithium atom bridging the C-C bond (**1**, Figure 1). The local minimum **1** has its energy lower than the ethylene-like structure by ~10 kcal/mol, and other possible $H_2C=CLi_2$ structures have energies above structure **1** by 5 - 32 kcal/mol at either singlet or triplet states (Figure 1 in ref. 24). In isomer **1** (1,1-dilithioethylene), the predicted C–C distance of 1.343 Å is very close to that of the typical C=C double bond in ethylene (1.334 Å).[48] The terminal C-Li distance is predicted to be 1.853 Å, and the bridging C-Li distances are somewhat longer, i.e., 1.974 and 2.026 Å, respectively.



1. C_s 39.6 *

2. C_s 0.0

Figure 1. Geometries (bond distances in Å, angles in degree) and relative energies including ZPVE (kcal/mol) predicted by the CCSD(T)/cc-pVQZ method for the two $C_2H_2Li_2$ isomers (**1** and **2**). Carbon, hydrogen, and lithium atoms are denoted by black, white, and purple spheres, respectively. The natural atomic charges are shown in parentheses, and the Wiberg bond indices are shown in square brackets. (*Structure **1** was earlier reported in Ref [24].)

As proposed by the previous studies,[44-47] the global minimum of $C_2H_2Li_2$ has been confirmed in the present paper to be structure **2** (Figure 1). Despite the absence of a hydrogen analogue, structure **2** features a surprisingly low energy (almost 40 kcal/mol lower than **1)**. The optimized geometry of isomer **2** at the CCSD(T)/cc-pVQZ level of theory is shown in Figure 1. It is a planar structure with C_s symmetry, which can be regarded as a complex between the HC–C$^-$ anion and the Li_2H^+ cation. The predicted length of the C–C bond (1.238 Å) is much shorter than that in structure **1**, indicating a C≡C triple bond, like that (1.203 Å) in acetylene.[49] The quasi-linear H–C–C moity (174.6°) also largely resembles that of acetylene. However, in isomer **2** there is an uncommon four-membered ring, with the Li-C distances of 2.044 Å and 2.103 Å and the Li–H distances of 1.759 Å and 1.750 Å (Figure 1). For comparison the bond distance in diatomic LiH is significantly shorter, 1.607 Å predicted at the same level of theory. The peculiar geometries of **1** and **2** are related to an uncommon electronic structure, and we will study the nature of the chemical bonding for these structures with the DFT method below.

3.1.2 DFT Methods Benchmark

In addition, six DFT functionals, namely M06-2X, PBE0, B97-D, B97-D3, MPW1K and ωB97X-D, combined with the cc-pVQZ basis set, were employed to optimize the geometries and compute ZPVE-corrected energies for structures **1** and **2**. The relative energies ΔE between **1** and **2**, i.e., $\Delta E = E_1 - E_2$, and the deviations of them from those of CCSD(T), are listed in Table 1. It is shown that all the DFT functionals predict the qualitatively reasonable results, and among them, the ωB97X-D method has the least deviation (-0.12 kcal/mol). The ωB97X-D predicted geometry is also close to the CCSD(T) one. For structure **2**, the deviation of bond distances is in the range 0.002 – 0.016 Å. Thus, the ωB97X-D method will be employed for the subsequent chemical bond analyses in the present paper.

Table 1. Relative Energies (*ΔE*, kcal/mol) including ZPVE between isomers **1** and **2** obtained with six DFT methods with cc-pVQZ basis sets. The deviations from the CCSD(T)/cc-pVQZ results are also listed.

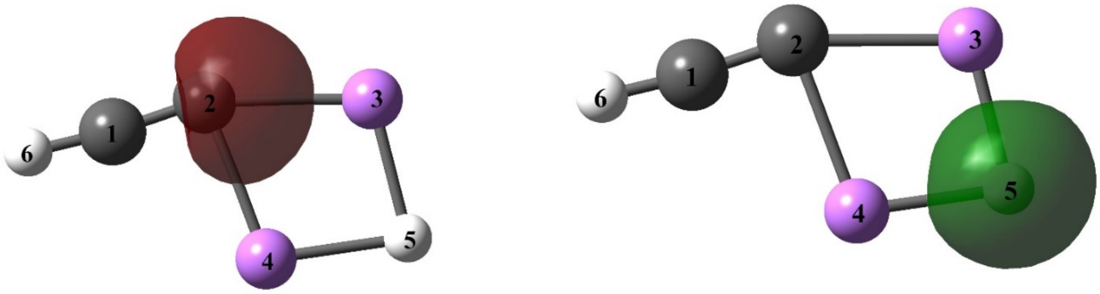
	CCSD(T)	M06-2X	PBE0	B97-D	B97-D3	MPW1K	ωB97X-D
ΔE	39.60	37.20	33.19	40.69	35.61	35.26	39.48
deviation	0.00	-2.40	-6.41	1.09	-3.99	-4.34	-0.12

3.1.3 Lithium Bonds in $C_2H_2Li_2$ Isomers

It is known that for closed-shell systems localized molecular orbitals (LMOs) represent the same physical state as the canonical molecular orbitals (CMOs), while the former are generally corresponding to traditional chemical bonds.[50] Therefore, we can use LMO analysis as a useful tool to study the nature of lithium bonds.

For structure **1**, besides the C=C double bond and two C-H single bonds, there should be four valence electrons (two occupied orbitals) to describe the bonding among the three atoms: C(2) and the two Li atoms. There are no valence LMOs on either Li atom in structure **1** (Figure 2). The two LMOs are on the C(2) atom, except one of them slightly shared by the other carbon C(1) atom. One should expect that both lithium atoms Li(5) and Li(6) are positively charged, and the C(2) and C(1) atoms are negatively charged. This is indeed in agreement with the natural atomic charges shown in Figure 1, i.e., +0.82 and +0.87 for the two Li atoms, respectively, and -1.22 and -0.66 for the C(2) and C(1) atoms, respectively. Thus, there exist only ionic C-Li bonds in structure **1**. The WBI values are 0.22 for the C(2)-Li(5) bond, 0.25 for C(2)-Li(6), and 0.01 for C(1)-Li(5) (Figure 1), indicating very small covalent character for these bonds and supporting the ionic bond nature. It should be noted that the LMO for the C=C double bond (in Supporting Information) is polarized, migrating some electron density from C(2) to C(1), facilating the Li(5) atom in the favorable bridging position between the two C atoms.

LMO on C(2) atom in **1**. Another LMO on C(2) atom in **1**.



LMO on C(2) atom in **2**. LMO on H(5) atom in **2**.

Figure 2. The localized molecular orbitals (LMOs) related to Li atoms in structures **1** and **2**. (The atoms were numbered in Figure 1.) Carbon, hydrogen, and lithium atoms are denoted by black, white, and purple spheres, respectively.

Let us now turn to $C_2H_2Li_2$ structure **2**. In addition to a C(1)-H(6) single bond and a C≡C triple bond, which do not involve the Li atoms, there is a four-membered ring (Figure 1), consisting of two lithium atoms that bridge the carbon atom C(2) and hydrogen atom H(5). For the four-membered ring there are four valence electrons provided by the four atoms (one electron from each atom in the ring). Figure 2 shows the two LMOs occupied by the four electrons. One LMO is mainly on the C(2) atom, the other on the H(5) atom, but no valence LMOs on either Li atom, just like in structure **1**, suggesting each of the Li atoms loses one electron and each of C(2) and H(5) gains one. This is indeed consistent with the natural atomic charges in Figure 1, i.e., +0.87

for each Li atom, -0.84 for the H atom, and -0.65 for the C(2) atom. Furthermore, the negligibly small WBI values (0.01 and 0.10, Figure 1) for the two C(2)-Li bonds and those (0.00 and 0.14, Figure 1) for the two H(5)-Li bonds also indicate that there are no covalent bonds involving the Li atoms. We conclude that the lithium bond in structure **2** is essentially ionic. The other LMOs (not related to the Li atoms) are shown in Figure S1 (Supporting Information).

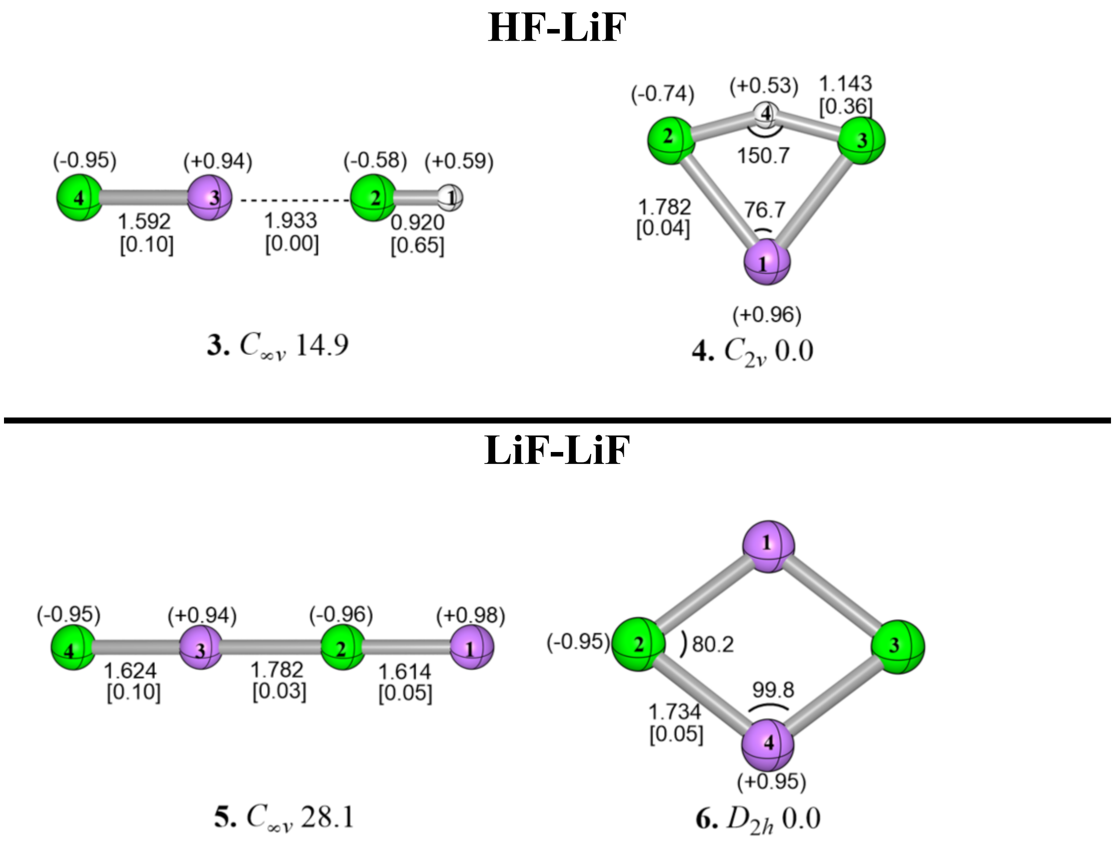
3.2 The HF-LiF and LiF-LiF Dimers

3.2.1 Structures for HF-LiF and LiF-LiF

As early as the 1950s, lithium halides (e.g., LiCl and LiBr) were prepared in the vapor phase, and their dimers were observed predominantly.[8,9,51] Following the experimental discovery, Kollman and Allen theoretically studied these molecules in the 1970s.[4,12] They reported the cyclic structure for the $(LiF)_2$ dimer, which is significantly different from the bent chain structure for $(HF)_2$ dimer,[23] and they attributed such difference to the ionic character for LiF.

In the present research we have optimized both cyclic and linear structures for HF-LiF at the CCSD(T)/cc-pVQZ level of theory. The linear structure HF-LiF (**3**, $C_{\infty v}$, Figure 3) is predicted to lie 15 kcal/mol higher than the cyclic structure (**4**, C_{2v}, Figure 3) . Structure **3** has a degenerate imaginary vibrational frequency (218*i* cm^{-1} from CCSD(T)/cc-pVQZ), corresponding to the bending vibrational modes, while structure **4** is a minimum. For the linear structure **3** the Li–F(4) bond distance is 1.592 Å, and the distance of the weak Li···F(2) bond is 1.933 Å, compared to 1.577 Å for diatomic LiF. The H–F bond distance is normal, 0.920 Å. For the cyclic structure **4** (C_{2v} symmetry) the two identical Li–F bonds are 1.782 Å, and the F–Li–F angle is 76.7°. The two H–F bonds are 1.143 Å, and the F–H–F angle is 150.7°.

For the LiF-LiF system, the cyclic structure (**6**, D_{2h}, Figure 3) is 28 kcal/mol lower in energy than the linear structure (**5**, $C_{\infty v}$, Figure 3). For the linear structure **5** the two Li−F bonds are 1.624 Å and 1.614 Å respectively, and the weaker Li···F bond is 1.782 Å in length. For the rhombus structure **6** the four identical Li−F bonds are 1.734 Å, and the F−Li−F angle is 99.8°.



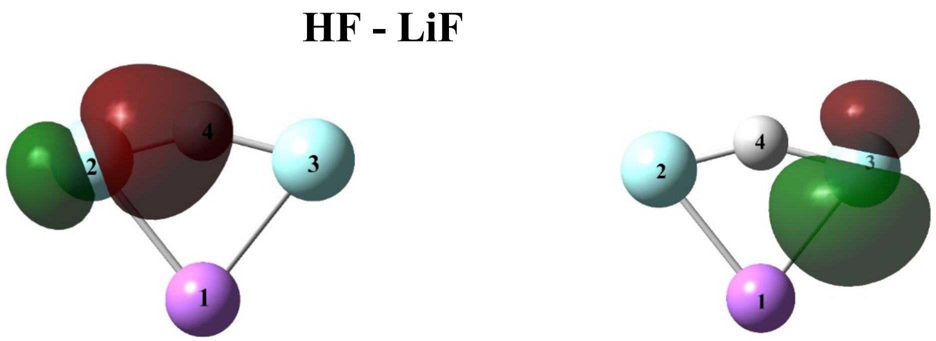
3. $C_{\infty v}$ 14.9 **4.** C_{2v} 0.0

5. $C_{\infty v}$ 28.1 **6.** D_{2h} 0.0

Figure 3. Geometries (bond in Å, angle in degree) and relative energies including ZPVE (kcal/mol) predicted by the CCSD(T)/cc-pVQZ method for HF-LiF (**3** and **4**) and LiF-LiF (**5** and **6**). Fluorine, hydrogen, and lithium atoms are denoted by green, white, and purple spheres, respectively. The natural atomic charges are shown in parentheses and the Wiberg bond indices shown in square brackets.

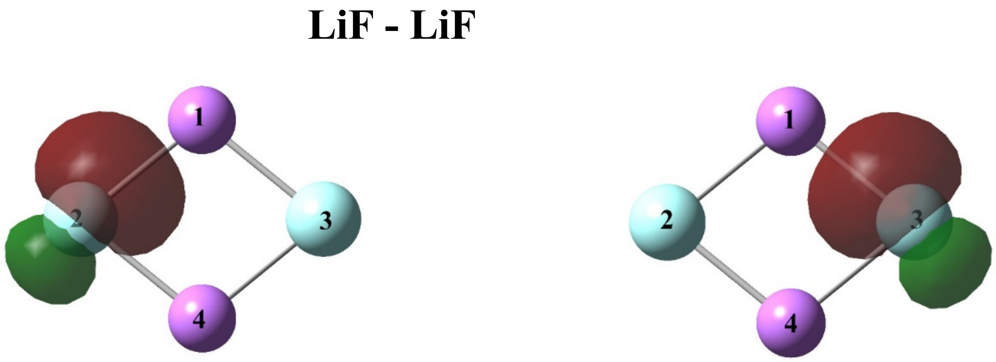
3.2.2 Lithium Bonds in HF-LiF and LiF-LiF

For the cyclic HF-LiF structure **4**, besides the lone pairs on the F atoms, there are two H−F bonds and two Li-F bonds, and thus, this system serves as a good reference to compare the H-F and Li-F bonds. The LMO related to one H-F bond consists of contribution from both H and F atoms though it is polarized, while the Li-F bond LMO (with the same contour value) electron density is essentially only provided by the F atom, suggesting that the former has certain covalent components and the latter is mainly ionic. The NBO analysis results are consistent with this finding. The natural atomic charges of lithium atom is +0.96 (Figure 3), and that of the hydrogen atom is only +0.53, while the atomic charges for the two F atoms are -0.74. The WBI value of the noncovalent Li-F bond is 0.04 (Figure 3) and that of the H···F bond is 0.36, supporting the conclusion that the Li bond is significantly more ionic than the H bond.


HF - LiF

H–F σ bond LMO in HF-LiF (**4**)

LMO related to a Li-F bond in (**4**)


LiF - LiF

LMO related to a Li-F bond in LiF-LiF (**6**)

LMO related to another Li-F atom (**6**)

Figure 4. Selected LMOs for the HF-LiF (**4**) and LiF-LiF (**6**) systems**.** Fluorine, hydrogen, and lithium atoms are denoted by light blue, white, and purple spheres, respectively. The complete valence LMOs are shown in Supporting Information.

For the cyclic $(LiF)_2$ structure **6**, there are four LMOs related to the Li-F bonds, two of which are shown in Figure 4 (the other two are equivalent by symmetry), and it is seen that all these LMOs are essentially on the F atoms. The natural atomic charge of each lithium atom is predicted to be +0.95, and that of each fluorine atom is -0.95. The WBI value of each Li-F bond is as small as 0.05. All these theoretical results indicate that the Li-F bonds are ionic. Note that for a perfectly ionic bond, the Wiberg Bond Index should approach zero.

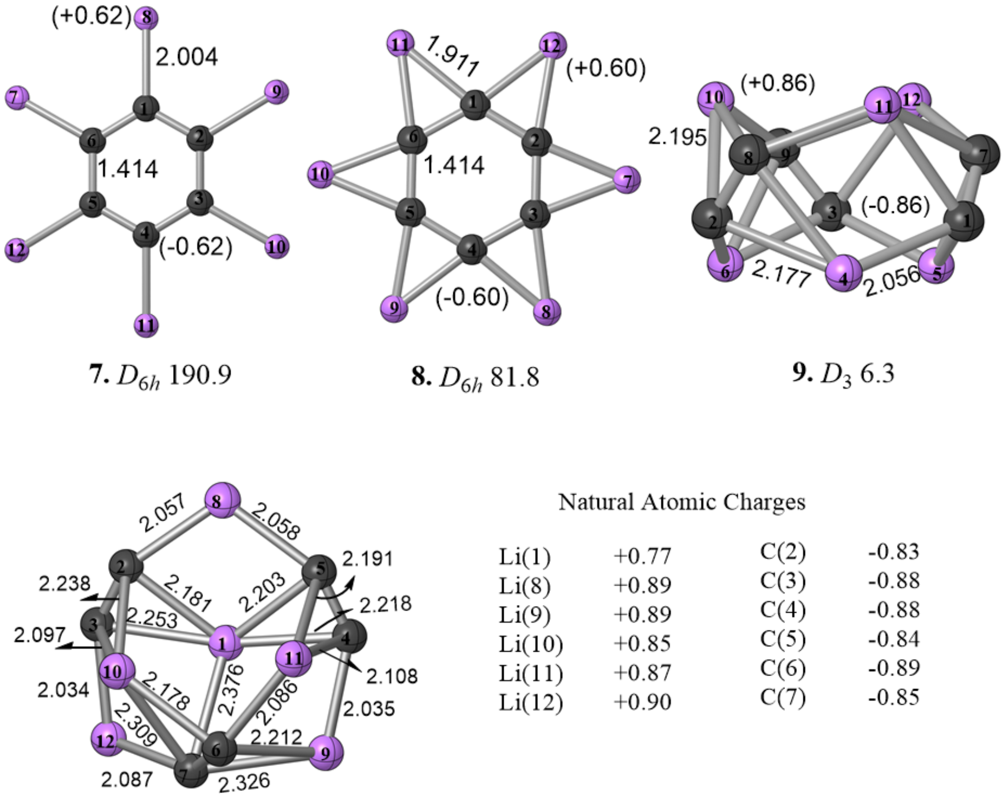
3.3 C_6Li_6

3.3.1 Structures for C_6Li_6

The study of C_6Li_6 started from the 1970s,[52] and its synthesis was first reported in the 1990s by Baran and Lagow.[53,54] However, no experimental structure of hexalithiobenzene has been reported. Our previous study[25] in 1991 at the MP2/TZP//SCF/TZP level of theory found that the benzene-like D_{6h} structure of C_6Li_6 (**7**, Figure 5) has eleven imaginary vibrational frequencies, while a Star-of-David-like structure **8** (D_{6h}, Figure 5) was predicted to be a local minimum lying lower in energy than **7** by over 100 kcal/mol. In structure **8** each lithium atom occupies a bridging position to the connect two carbon atoms.[25] Three years later, using early DFT methods, a trimer of C_2Li_2 units (structure **9**, D_3 symmetry, Figure 5) was discovered by Smith,[26] in which each Li atom interacts with three C atoms, and this structure **9** lies with even lower energy (by ~75 kcal/mol) than structure **8**. As a comparison, for the energetically high-lying benzene-like structure **7**, each Li atom interacts with only one C atom. As mentioned by Smith, the viability of the C_2Li_2 trimer can be correlated with the number of C-Li bonds.

In fact, a nonstandard structure with no symmetry (**10**, Figure 5) was predicted in 2013 by Merino and coworkers. to lie even lower in energy than structure **9,** by 6.3 kcal/mol at the

CCSD(T)/def2-TZVP//PBE0/def2-TZVP level of theory.[27] Both structures **9** and **10** contain three C≡C triple bonds, and all the C≡C bond distances are nearly identical, namely 1.244~1.245 Å. This suggests that the energy difference between structures **9** and **10** is caused by the rearrangement of lithium atoms between the three C_2 units, especially the number of C-Li bonds. In fact, there is one more C-Li bond in structure **10** than in **9**.



7. D_{6h} 190.9

8. D_{6h} 81.8

9. D_3 6.3

10. C_1 0.0

Natural Atomic Charges

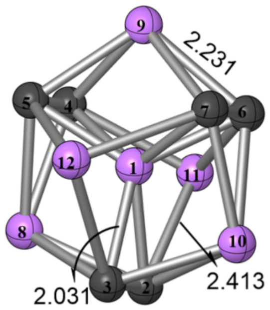
Li(1)	+0.77	C(2)	-0.83
Li(8)	+0.89	C(3)	-0.88
Li(9)	+0.89	C(4)	-0.88
Li(10)	+0.85	C(5)	-0.84
Li(11)	+0.87	C(6)	-0.89
Li(12)	+0.90	C(7)	-0.85

Figure 5. The geometries for C_6Li_6 structures (**7**, **8**, **9**, and **10**) optimized with the ωB97X-D/cc-pVQZ method (bond length in Å). Carbon and lithium atoms are denoted by black and purple spheres, respectively. The relative energies (kcal/mol) are from the CCSD(T)/cc-pVQZ single-point energies appended by the ZPVE corrections predicted with the ωB97X-D method.

In order to search for other possible low-lying C_6Li_6 structures, we attempted to design those with as many C-Li bonds as possible. Structure **11** was designed by us with twenty-four C-Li bonds (Figure **6**). In structure **11**, the six C atoms form a trigonal prism skeleton, five lithium atoms cap each face, and the remaining lithium atom resides in the center. Thus structure **11** is a penta-capped trigonal prism with D_{3h} symmetry. The C-Li distances for the Li atoms capped on the top faces are 2.413 Å, and those on the side faces are 2.231 Å. The lithium atom Li(1) in the center is adjacent to all six carbon atoms with the C-Li(1) distances of 2.031 Å. Although there are more C-Li bonds, structure **11** lies 24.6 kcal/mol higher than **10**.[27] This is because the central lithium atom is so close to other lithium atoms (2.302 Å or less), much shorter than those (> 2.5 Å) in other structures, and the repulsion between positively charged lithium atoms may increase the energy of structure **11**. There exists a degenerate imaginary vibrational frequency for **11**, namely 53*i* cm^{-1}, indicating a saddle point on the potential surface. Following the normal modes of these two frequencies, we obtained two lower-energy minima (Structure **14** and **15**, Figure 6).

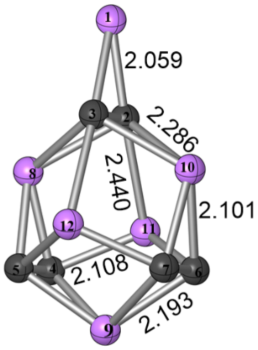
The C_s structure **14** (Figure 6) lies 13.6 kcal/mol lower in energy than structure **11**, and hence 11.0 kcal/mol higher than the Merino[27] structure **10**. In structure **14** there are 21 C-Li bonds, whose distances range from 2.04 Å to 2.46 Å. The repulsion effects among the Li atoms are smaller, because the distances between Li atoms are in the range 2.46 ~ 2.88 Å, which are much longer than those (2.06 Å ~2.31 Å) in structure **11**,

The C_2 structure **15** has a lower energy compared to structures **11**-**14** and is only 5.7 kcal/mol higher than structure **10**. However, structure **15** still has one imaginary vibrational frequency (92*i* cm^{-1}), suggesting it is a transition state. Searching along this normal mode leads us back to the lowest-lying structure **10**. As shown in Figure 6, the geometry of structure **15** with twenty C-Li bonds is related to that of structure **10**. The C-Li distances in structure **15** are in the range of 2.02 Å ~2.66 Å, similar to those in structure **10** (2.03 Å ~2.55 Å). The Li-Li distances in **15** are in range of 2.42 Å ~2.59 Å, slightly shorter than those (2.52 Å~2.76 Å) in **10**. This may cause the energy of **15** to be slightly higher than **10**.



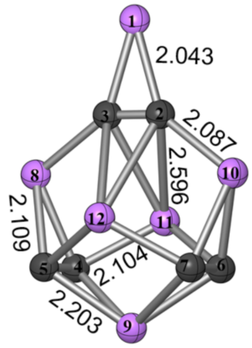
11. D_{3h} 24.6

Natural Atomic Charge	
Li(1)	+0.62
Li(8),Li(9),Li(10)	+0.87
Li(11),Li(12)	+0.91
C(2)~C(7)	-0.84



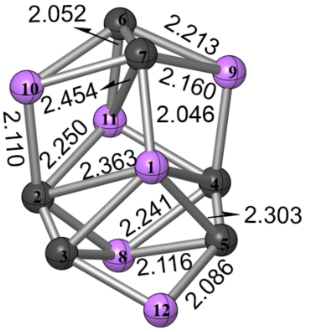
12. $\mathbf{C}_{2v}$ 17.7

Natural Atomic Charge	
Li(1)	+0.92
Li(8),Li(10)	+0.83
Li(11),Li(12)	+0.84
Li(9)	+0.85
C(2),C(3)	-0.86
C(4),C(5)	-0.85
C(6),C(7)	



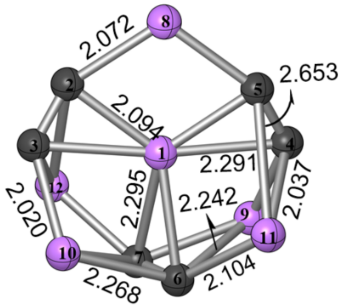
13. C_{2v} 12.9

Natural Atomic Charge	
Li(1)	+0.92
Li(8),Li(10)	+0.86
Li(11),Li(12)	+0.83
Li(9)	+0.86
C(2),C(3)	-0.88
C(4),C(5)	-0.85
C(6),C(7)	



14. C_s 11.0

Natural Atomic Charge	
Li(1)	+0.81
Li(8)	+0.85
Li(9),Li(10)	+0.88
Li(11)	+0.83
Li(12)	+0.90
C(2), C(4)	-0.91
C(3), C(5)	-0.82
C(6)	-0.79
C(7)	-0.91



15. C_2 5.7

Natural Atomic Charge	
Li(1)	+0.74
Li(8)	+0.89
Li(11), Li(12)	+0.90
Li(9), Li(10)	+0.89
C(2),C(5)	-0.74
C(3),C(4)	-0.98
C(6),C(7)	-0.87

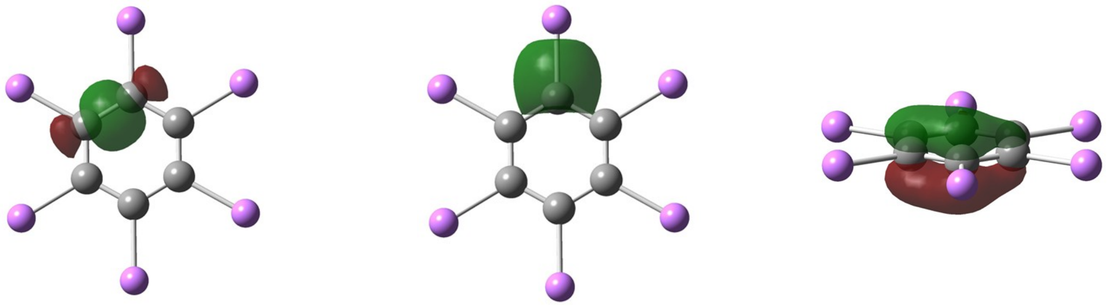
Figure 6. Optimized geometries (bond length in Å) and atomic natural charges for the C_6Li_6 structures (**11 - 15**) with the ωB97X-D/cc-pVQZ method. The relative energies (kcal/mol) are obtained from the CCSD(T)/cc-pVQZ single point energies appended by the ZPVE corrections predicted with the ωB97X-D method. Carbon and lithium atoms are denoted by black and purple spheres, respectively.

By moving the central Li(1) atom in structure **11** to an edge of the triangular prism, a C_{2v} structure **12** is obtained (Figure 6). It is 6.9 kcal/mol lower in energy than structure **11**. The C-C distances for the prism lateral edges increase by 0.06 ~ 0.18 Å due to the removal of the attractive Li ion. Five lithium atoms capping the faces of the triangular prism move closer to carbon atoms. This leads most C-Li bonds to be shorter than those in structure **11**. There are twenty C-Li bonds (2.10 Å ~ 2.44 Å) in structure **12**. Although there are fewer C-Li bonds in structure **12** compared to **11**, the energy decreases because of less repulsion between lithium atoms. Structure **13** (Figure **6**) is slightly different from structure **12** with a 90°-rotated C(2)-C(3) bond along the Li(1)-Li(9) axis. These two carbon atoms, C(2) and C(3), in structure **13** are placed in the plane of Li(8), Li(9), and Li(10). Structure **13** is 4.7 kcal/mol lower in energy than structure **12.**

3.3.2 Lithium Bonds in C_6Li_6

Among nine optimized C_6Li_6 structures, we selected four typical ones to study their LMOs. We first study the two structures (**7** and **8**) with high symmetry (D_{6h}), and then study the two low-lying structures (**9** and **10**).

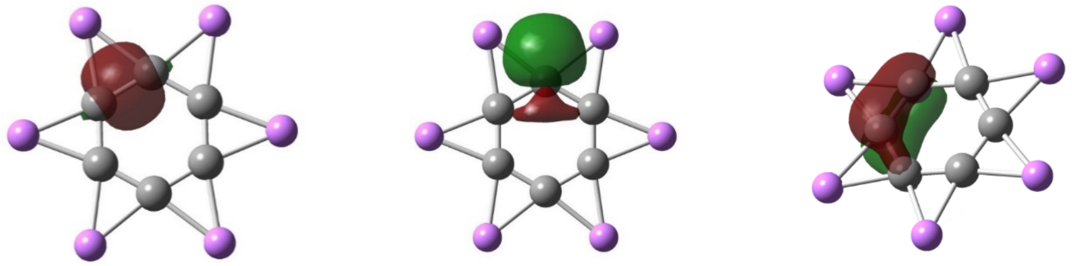
For the D_{6h} structures **7** and **8**, the LMOs for the skeleton are similar to those of benzene: six C-C σ bond orbitals, six C-Li bonds, and three π orbitals (Figure 7, only one of each type is shown). However, in contrast to the C-H bonds in benzene, the LMOs related to the C-Li bonds are basically on the C atoms, leaving the Li atoms with positive charges. Consistently, the natural atomic charges on the Li atoms are +0.62 for structure **7** and +0.60 for structure **8** (Figure 5). Accordingly, the charges are -0.62 and -0.60 for the C atoms in structures **7** and **8**, respectively. Thus, the C-Li bonds in these C_6Li_6 structures should be considered to be ionic bonds. Without covalent bonds connecting C and Li, the Li atoms in structure **7** are apt to move to the positions bridging two neighboring C atoms, leading to a more energetically favorable geometry (structure **8**). On the contrary, this is impossible for H atoms in the benzene molecule, because the C-H interactions in benzene are covalent bonds.



One of the C-C σ bonds in structure **7**

One of the C-Li bonds in structure **7**

One of the C-C π bonds in structure **7**



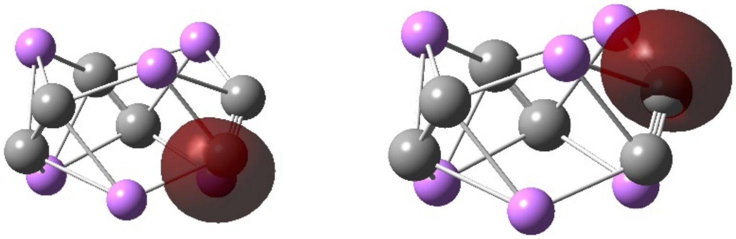
One of the C-C σ bonds in structure **8**

One of the C-Li bonds in structure **8**

One of the C-C π bonds in structure **8**

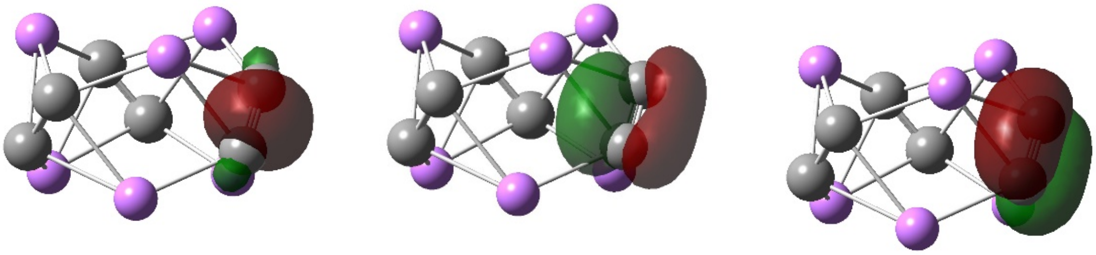
Figure 7. Selected localized molecular orbitals for the high-symmetric C_6Li_6 structures **7** and **8**. Carbon and lithium atoms are denoted by black and purple spheres, respectively.

For structure **9**, there are three equivalent C≡C triple bonds, each of which is bridged by two Li atoms. In this C_2Li_2 trimer the bridging Li atoms in one C_2Li_2 unit connect carbon atoms in another C_2Li_2 unit (Figure 5). Each C_2Li_2 unit (with 10 valence electrons) carries five doubly occupied valence orbitals, and in our LMO analysis it is clear to see three of those LMOs correspond to one C-C σ bond and two C-C π bonds (Figure 8). The remaining two LMOs are mainly on the two C atoms, without contribution from the Li atoms, indicating no valence electrons on the Li atoms and an extra electron on each of the carbon atoms. The natural atomic charges in the NBO analysis confirm this prediction with a positive charge of +0.86 on each Li atom, and a negative charge of -0.86 on each C atom. Thus, the C-Li bonds in structure **9** are verified to have ionic character.



A lone pair of a C_2 unit in structure **9**

Another lone pair of a C_2 unit in structure **9**



C-C σ bond in structure **9**

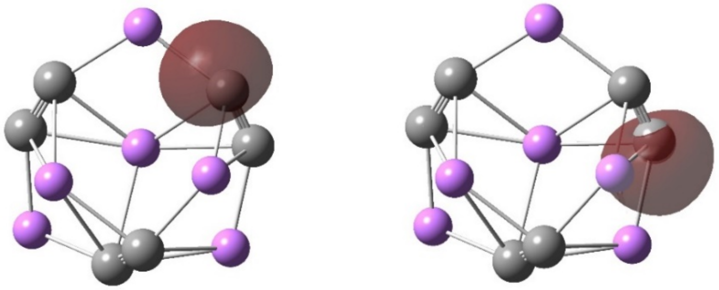
One C-C π bond in structure **9**

Another C-C π bond in structure **9**

Figure 8. Five LMOs on one of the C_2 units for structure **9**. Carbon and lithium atoms are denoted by black and purple spheres, respectively.

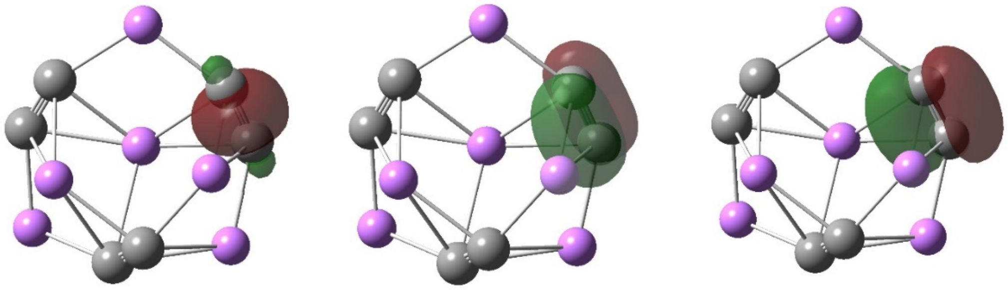
The global minimum structure **10** (C_1 symmetry) has its geometry similar to structure **9**. Both structures have three C≡C triple bonds. Although these C≡C bonds are not strictly equivalent to each other by symmetry, they have very similar C≡C distances. Thus we show a group of LMOs for only one of the C_2 units in Figure 9. Similar to structure **9**, each C_2 unit of **10** possesses five valence LMOs, i.e., one C-C σ bond, two C-C π bonds, and two lone pairs on the ends of the C_2

unit. There are no LMOs on any of the Li atoms. The natural atomic charges of the carbon atoms are in the range of -0.83 to -0.88, while those of the lithium atoms are in the range of +0.77 to +0.90. As expected, the nature of the bonding between C and Li atoms is ionic. Furthermore, based on the natural atomic charges for structures **7** and **10**, the ionic bonds in this lower-lying structure (**10**) are stronger than those in benzene-like C_6Li_6 structure (**7**).



A lone pair of a C_2 unit in structure **10**

Another lone pair of a C_2 unit in structure **10**



C-C σ bond in structure **10**

One C-C π bond in structure **10**

Another C-C π bond in structure **10**

Figure 9. Five LMOs on one of the C_2 units for the global minimum structure **10**. Carbon and lithium atoms are denoted by black and purple spheres, respectively.

4. Conclusions

Since a monovalent Li atom can connect to more than one atom, as is the case for a H atom involved in H-bonds, the concept "lithium bond" was proposed analogous to the hydrogen bond.[12,15] In 2011, a novel definition for the hydrogen bond is recommended by IUPAC: "*The* *hydrogen bond is an attractive interaction between a hydrogen atom from a molecule or a molecular fragment X–H in which X is more electronegative than H, and an atom or a group of atoms in the same or a different molecule, in which there is evidence of bond formation*".[16] This definition could be extended to define a lithium bond. In the present paper we have studied the structures and energetics of HF-LiF, LiF-LiF, $C_2H_2Li_2$, and C_6Li_6 molecules at up to the CCSD(T)/cc-pVQZ level of theory, and investigated the nature of bonds related to Li atoms using NBO and LMO analyses with the ωB97X-D functional. With the concept of the lithium bond, the "abnormal" structures for the Li-containing molecules can be satisfactorily explained.

To form a hydrogen-bond, elements that are more electronegative than hydrogen are required. Since the electronegativity of hydrogen is 2.2, only a few elements (e.g., F, O, and N) are eligible to form hydrogen bonds. Compared with H-bond, since the electronegativity of Li is as small as 1.0, so there would be more elements, such as F, O, N, C, Cl, S, Se, and H, eligible to form lithium bonds.[15,55,56] In fact, in the present study, most of the elements involved in the Li-bonding are carbon and hydrogen atoms.

Table 2. Summary of natural atomic charge in structures **1** ~ **15**.

Structure	Li	X
1 $C_2H_2Li_2$	0.87	-0.65 (X = C), -0.84 (X = H)
2 $C_2H_2Li_2$	0.82, 0.87	-0.66, -1.22 (X = C)
3 HF-LiF	0.96	-0.74 (X = F)
4 HF-LiF	0.94	-0.58 (X = F)
5 LiF-LiF	0.95	-0.95 (X = F)
6 LiF-LiF	0.94, 0.98	-0.95, -0.96 (X = F)
7 C_6Li_6	0.62	-0.62 (X = C)
8 C_6Li_6	0.60	-0.60 (X = C)
9 C_6Li_6	0.86	-0.86 (X = C)
10 C_6Li_6	0.77, 0.85, 0.87, 0.90	-0.83, -0.84, -0.85, -0.88, -0.89 (X = C)
11 C_6Li_6	0.62, 0.87, 0.91	-0.84 (X = C)
12 C_6Li_6	0.83, 0.84, 0.85, 0.92	-0.85, -0.86 (X = C)
13 C_6Li_6	0.83, 0.86, 0.92	-0.85, -0.88 (X = C)
14 C_6Li_6	0.81, 0.83, 0.85, 0.88, 0.90	-0.79, -0.82, -0.91 (X = C)
15 C_6Li_6	0.74, 0.89, 0.90	-0.74, -0.87, -0.98 (X = C)

Compared with hydrogen bonds, a striking feature of lithium bonds is the ionic nature, because the Li atom has a small ionization energy to give up its *2s* electron. The LMOs reported in the present paper (Figures 2 and 4) exhibit that no valence electrons are located on the Li atoms, indicating that the single valence electron of Li atom has been transferred almost entirely to nearby atoms whose electronegativity is greater than that of Li. Consistently, the NBO analyses also show that the natural atomic charges for Li atoms are close to one (in the range of +0.74 ~ +0.98, excluding those in the high-lying structures **7** and **8**) (Table 2), further supporting the ionic nature for the lithium bonds.

It is known, albeit much debated, that there is covalent contribution to H-bonding,[57,58,59] and this covalent nature shapes its geometry to be dicoordinated (saturation) and quasi-linear (directionality), i.e., the well-known X···H-Y arrangement. On the contrary, based on its ionic nature, the lithium bond usually leads to molecular geometries quite different from those associated with hydrogen bonds. Without the constraints of saturation and directionality, the molecules with Li-bonds prefer multicoodinated and nonlinear arrangements. Thus, the molecular structures will be determined by the magnitude of the Coulomb interaction between the charged atoms or clusters, often leading to geometries far from those based on common chemical intuition. For example, in the global minimum for $C_2H_2Li_2$ (structure **1**), both the Li atoms are in the positions bridging carbon and hydrogen atoms to form an unusual four-membered ring.

For the C_6Li_6 system, the benzene-like structure (**7**) has very high energy with eleven imaginary vibrational frequencies. The star-of-David-like structure (**8**) is a local minimum, but still high-lying in energy. The minima with much lower energies are those with abnormal geometries (structures **9** and **10**), which have many more C-Li bonds. Based on the relationship between the energies and the number of the Li-C bonds, we have designed some novel C_6Li_6 structures (**11** – **15**) that possess energies comparable to the lowest-lying structures **9** and **10**.

The ongoing development of the lithium bond theory will undoubtedly bring deeper understanding to lithium chemistry. It has been applied for the exploration of novel Li-bonded materials, such as the recently reported study of the Li-S batteries.[18] We hope the present study will stimulate further research in many new applied directions.

Acknowledgment

This work was supported by the U. S. National Science Foundation (Grant CHE-1661604).

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