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Insight into the lithium/hydrogen bonding in $(CH_2)_2X...LiY/HY$ (X: C=CH$_2$, O, S; Y=F, Cl, Br) complexes

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Abstract The nature of the lithium/hydrogen bonding between $(CH_2)_2X$(X: C=CH$_2$, O, S) and LiY/HY(Y=F, Cl, Br) have been theoretically investigated at MP2/6-311++G (d, p) level, using Bader's "atoms in molecules (AIM)" theory and Weinhold's "natural bond orbital (NBO)" methodology. The molecule formation density differences (MFDD) of the titled complexes are analyzed. Two kinds of geometries of the lithium/hydrogen bonded complexes are compared. As a whole, the nature of lithium bond and hydrogen bond are different. For the same electron donor and the same acceptor, lithium bond is stronger than hydrogen bond. For the same electron acceptor and different kind of donors, the interaction energies follows the n-type> π-type > pseudo-π-type order. For the same $(CH_2)_2X$, the interaction energy increases in the sequence of Y=F, Cl and Br for lithium bond systems while it decreases for hydrogen bond systems. Electron transfer plays an important role in the formation of lithium bond systems while it is less important in the hydrogen bond systems.

Keywords Hydrogen bond · Lithium bond · Topological analysis of electron density · Molecule formation density differences

Introduction

Intermolecular interactions play a significant role in chemical, physical, and biological science [1–3]. Among various types of intermolecular interactions, the hydrogen bonds have been well studied because of their significant roles in chemical and biological interactions [4]. Lithium, congener to hydrogen, can also participate in a three center interaction known as lithium bonding, while hydrogen bonding has been so widely and thoroughly investigated [5–8], reports on lithium bonding are relative rare [9–12]. Experimental proof of the existence of a stable 1:1 lithium-bonded complex was first provided by a matrix isolation infrared study by Ault and Pimentel [13]. It has been shown that the frequency shifts of LiCl and LiBr stretching bonds in complexes with amines are qualitatively similar to those observed for analogous proton donors such as HCl and HBr. More recently, the experimental works have provided experimental proof that lithium, similar to hydrogen, can form lithium bond with both the n-type and the π-type proton acceptor [14]. Kollman and Sannigrahi et al. [15, 16] were the first using *ab initio* self-consistent-field (SCF) calculations to study the lithium bonded systems. The systems between LiX (X=F, Cl, Br) and NH$_3$, H$_2$O and HF have been studied and contrasted with hydrogen bonded systems. Bonding, structures and energetic in organolithium compounds have been studied by Streiwiezer et al. [17]. These studies [9, 12, 15] are mainly theoretical in nature and have been extensively reviewed [16]. Subsequently there were few theoretical reports [18–21] published on lithium bonded dimmers. Although both, hydrogen and lithium bonds, appear to be the similar type of interaction that stabilize the former has been found to be different from that of the latter [11]. This has been observed to have led to different geometric preferences and strength of interactions in lithium/hydrogen bonded complexes. It is also this feature that makes the comparative study of hydrogen and lithium bonding interactions interesting.

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$(CH_2)_2X$ (X: C=CH_2, O, S) (Fig. 1) are likely to be of chemical interest because they have more than one electron donor sites. The double bond of $(CH_2)_2C=CH_2$ (MECP) can act as π-type electron donor, O/S atom of $(CH_2)_2O/(CH_2)_2S$ can act as n-type donor. Moreover, the CH_2-CH_2 bond of $(CH_2)_2X$ (X: C=CH_2, O, S) can act as the pseudo-π-type electron donor. The rotational spectra of $(CH_2)_2C=CH_2 \cdots HY$(Y=F, Cl) [22, 23], $(CH_2)_2O \cdots HY$ (Y=F, Cl) [24, 25], $(CH_2)_2S \cdots HCl$ [26] have been observed and their geometries are determined. No experimental work has reported on $(CH_2)_2X \cdots LiY$ complexes.

The observed complexes [22–26], formed between $(CH_2)_2X$ (X: C=CH_2, O, S) and HY(Y=F, Cl), have the similar structures, the similar distances of r(X...Y), the same Cs symmetry, the similar angular geometries, etc. Therefore, the present study focuses on the intermolecular interaction of the typical electron acceptor, LiY/HY(Y=F, Cl, Br), with prototype bases $(CH_2)_2X$ (X: C=CH_2, O, S) through theoretical calculations. The main objectives of this study are: (1) to compare the interaction between lithium/ hydrogen atom and the n-type, π-type and pseudo-π-type electron donor; (2) to compare the similarity and difference between lithium bond and hydrogen bond; (3) to trace the origins of lithium/hydrogen bond.

Computational details

The geometries of the complexes of $(CH_2)_2X \cdots LiY/HY$ (X: C=CH_2, O, S; Y=F, Cl, Br) and the related free monomers were fully optimized at the MP2 /6-311++G (d, p) levels of theories. The basis set superposition error (BSSE) [27] correction was considered in the geometry optimizations. The equilibrium structures were examined by the harmonic vibration frequency calculations. All calculations have been performed with the use of the Gaussian 03 set of codes [28].

The bonding characteristics of the complexes were analyzed by using two alternative procedures, namely the atoms in molecules (AIM) theory of Bader [29] and the natural bond orbital (NBO) method proposed by Weinhold et al. [30], which are based on the wave functions obtained from computation. The first method is based on a topological analysis of electron density and it's Laplacian. The NBO analysis will allow us to evaluate quantitatively the intramolecular attractive orbital interactions, which is important in the formation of hydrogen bonds and other charge-transfer complexes. Topological analyses of electron density were carried out with AIM2000 [31] and GTA2000 [32] programs, the latter was developed by the authors and registered at QCPE (register number QCPE-661). The

Fig. 1 The geometries and electrostatic potential of the monomers (red is negative and blue is positive)
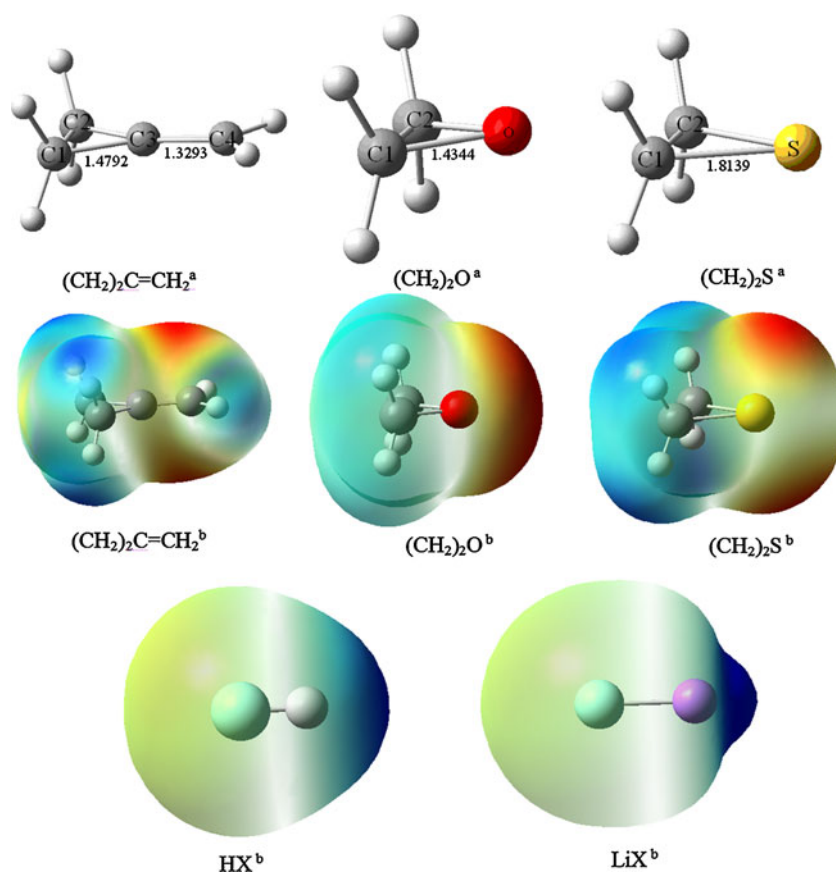
integration properties were calculated using AIM2000 [31], by integration over the basin of every atom in the AIM framework. The NBO analysis was carried out using the NBO package included in the Gaussian 03 suite of program.

Results and discussion

Geometrical parameters and interaction energies

As shown in Fig. 1, the positive electrostatic potential $(CH_2)_2X$ (X: $C=CH_2$, O, S) are concentrated around the X site and CH_2-CH_2 bond, therefore, $(CH_2)_2X$ could interact with LiY/HY (Y=F, Cl, Br) at X site and CH_2-CH_2 bond. Two kinds of geometries are located: (a) is the lithium/ hydrogen atom interact with $(CH_2)_2X$ via the pseudo-π bonding electron pair associated with a C-C bond of the ring, with C_{2v} symmetry (Fig. 2a); (b) is the lithium/ hydrogen atom interact with $(CH_2)_2X$ via the π-bonding electron pair of the C=C bond (Fig. 2(b-1)), lone pair of O or S atom (Fig. 2(b-2)), in $(CH_2)_2C=CH_2$, $(CH_2)_2O$ and $(CH_2)_2S$, respectively. All the geometries of the complexes are fully optimized within their symmetry constraints and the harmonic frequencies for each structure have been calculated at this level to characterize the stationary point and to correct the zero-point energy.

Table 1 presents the calculated geometrical parameters of the Li-Y bond existing within complexes analyzed.

From Fig. 2 and Tables 1 and 2, it can be seen that, for geometry (a), the Li-Y bond is vertical to the C1-C2 bond; the bond angle forms by Y atom, Li atom and the middle point of C1-C2 bond are all 180°. This kind of geometry is similar to that of the hydrogen bonded system [22, 27]. For geometry (b), the bond angle A1, which forms by Y atom, Li atom and X atom (in MECP, X atom refers to the middle point of C3-C4; in $(CH_2)_2O$ and $(CH_2)_2S$, X refers to O and

S atom) is about 120°, within the range of 110.6°–128.6°, the angel difference between lithium bonded system and hydrogen bonded system is visual, in hydrogen complexes, this bond angle is about 160° [22–27]. The bond angle A2, which forms by Li atom, X atom and the middle point of C1–C2 bond, varies from 89.9° to 121.7°, which are bigger than those in hydrogen bond system [22–27]. These geometries mean that lithium bonds with a more "perpendicular" angle than hydrogen bonds.

Furthermore, one can observe the well known tendencies. In geometry (a), there are the elongations of Li-Y bond and C1–C2 bond due to the complexation, such elongations of the X-Y and C1–C2 bonds denote that the weak interaction does exist between LiY and $(CH_2)_2X$(X: $C=CH_2$, O, S). For all of $(CH_2)_2X$ (X: $C=CH_2$, O, S), the bond length of lithium bond R_{Li*} (the distance between Li and the middle point of C1–C2 bond/O/S) decreases in the sequence of Y=F, Cl and Br. Δd (C1-C2), the bond length difference between the complexes and the monomers, increases in sequence of Y=F, Cl and Br. In geometry (b), R_{Li*} has the same tendency. These mean that for both geometry (a) and geometry (b), $(CH_2)_2X \cdots LiF$ bond is weaker than $(CH_2)_2X \cdots LiCl$ bond, $(CH_2)_2X \cdots LiBr$ bond is the strongest. Comparing geometry (a) with (b), for the same proton donor and the same proton acceptor, Δd(Li-Y) in geometry (a) is smaller than that in geometry (b), it means that the weaken extent of Li-Y bond in geometry (a) is smaller than that in geometry (b), it also implies that geometry (b) is more stable than geometry (a). For the same electron acceptor LiY and different kind of donor, the interaction strength follows the n-type>π-type> pseudo-π-type order.

The calculated interaction energies (ΔE) of the titled systems are also listed in Tables 1 and 2, which were corrected by zero-point energy and BSSE. As it can be seen from Tables 1 and 2, these energetic results are nicely in line with the geometrical parameters. For the same proton donor and the same acceptor, ΔE of geometry (a) is smaller than that of geometry (b), which means that geometry (b) is

Fig. 2 The geometries of LiY interacted with (**a**) pseudo-π-type (**b-1**) π-type and (**b-2**) n-type acceptors
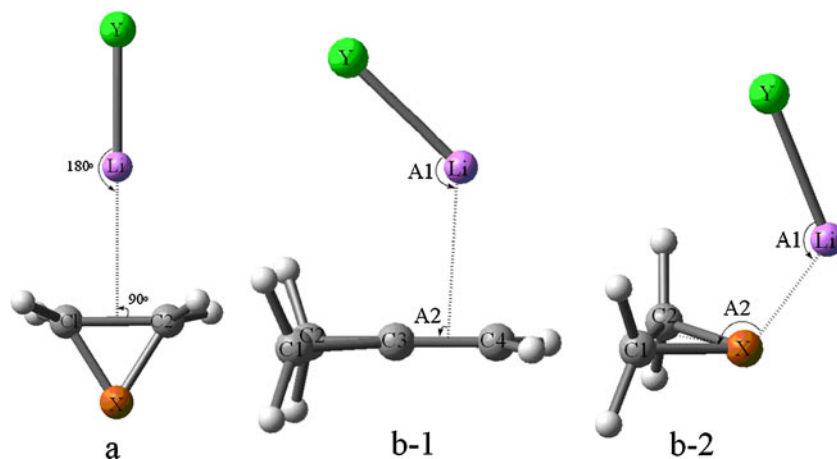
Table 1 The calculated interaction energies, bond length of lithium bond and the variations geometrical parameters of $(CH_2)_2X$ (X: C=CH2, O, S)… LiY(Y=F, Cl and Br)

		Geometry (a)[a,b]				Geometry (b)[a,b]				
		ΔE	R_{Li*}	Δd(Li-Y)	Δd(C1–C2)	ΔE	R_{Li*}	A_{YLiX}	A_{LiX*}	Δd(Li-Y)
MECP	LiF	−26.8	2.2664	0.0139	0.0282	−41.2	2.4614	116.7	89.9	0.0240
	LiCl	−32.5	2.2207	0.0152	0.0309	−45.9	2.4150	127.5	89.7	0.0257
	LiBr	−34.6	2.2070	0.0161	0.0322	−48.0	2.4034	128.6	93.3	0.0282
$(CH_2)_2O$	LiF	−6.6	2.3917	0.0054	0.0253	−69.2	1.9796	113.2	112.7	0.0360
	LiCl	−9.7	2.3376	0.0045	0.0281	−76.1	1.9562	120.7	120.0	0.0410
	LiBr	−10.8	2.3238	0.0041	0.0290	−79.0	1.9488	121.1	121.7	0.0458
$(CH_2)_2S$	LiF	−7.8	2.3737	0.0066	0.0228	−58.7	2.4849	110.6	90.2	0.0335
	LiCl	−11.5	2.3130	0.0062	0.0255	−63.2	1.4696	120.2	94.7	0.0367
	LiBr	−12.8	2.2965	0.0059	0.0269	−65.6	2.4642	121.1	95.7	0.0409

[a] All distances are in Å, energies are in kJ·mol^{-1}

[b] ΔE and Δd represent the difference of the properties between the complexes and the monomer molecules

more stable than geometry (a). For the same X, ΔE increases in sequence of Y=F, Cl and Br, which also means that the interaction strength is in the sequence of $(CH_2)_2X\cdots LiF<(CH_2)_2X\cdots LiCl< (CH_2)_2X\cdots LiBr$. All in all, for the same electron acceptor and different kind of acceptor, the interaction strength follows the n-type> π-type> pseudo-π-type order. O atom and S atom are both n-type acceptor, the interaction in $(CH_2)_2O\cdots LiY$ is larger than that in $(CH_2)_2S\cdots LiY$.

Compared with lithium bond, hydrogen bond is different in the bond strength and its order: the hydrogen bond is weaker than the lithium bond; the bond energies of hydrogen bond systems are within the range of 0.8~−6.3 and−8.7~−24.6 kJ mol^{-1} for geometry (a) and (b), respectively. That is, geometry (b) is more stable than geometry (a). It is notable for the studied 18 complexes, three of them have positive ΔE, these show that the interaction of hydrogen bond is weak, as well as the BSSE

corrections is excessive, which was also mentioned in reference 33. For the same X atom, the bond energy of hydrogen bond system decreases in sequence of Y=F, Cl and Br, the interaction energy (see Table 2) order and the change tendency of geometries parameters are all converse to those of lithium bonded systems.

Electrostatic potential

The origin of hydrogen bond could be explained as the electrostatic attraction between the positive potential of the hydrogen atom and the negative site on another molecule. The electrostatic potential, $V_S(r)$, has been shown to be an effective mean of analyzing and predicting noncovalent interactions [33–37]. The most positive and most negative values, $V_{S, max}$ and $V_{S, min}$, have been found to correlate quantitatively with hydrogen bond donating and accepting tendencies, respectively [38].

Table 2 The calculated interaction energies, bond length of hyhium bond and the variations geometrical parameters of $(CH_2)_2X$ (X: C=CH2, O, S)… HY(Y=F, Cl and Br)

		Geometry (a)[a,b]				Geometry (b)[a,b]				
		ΔE	R_{H*}	Δd(H-Y)	Δd(C1–C2)	ΔE	R_{H*}	A_{YHX}	A_{HX*}	Δd(H-Y)
MECP	HF	−6.3	2.1934	0.0055	0.0165	−11.3	2.2868	167.6	919	0.0187
	HCl	−4.7	2.4186	0.0043	0.0097	−8.4	2.5177	165.8	88.4	0.0080
	HBr	−4.9	2.4636	0.0042	0.0085	−8.7	2.5600	164.3	89.0	0.0086
$(CH_2)_2O$	HF	0.8	2.3730	0.0022	0.0118	−24.6	1.7613	169.4	118.7	0.0166
	HCl	0.2	2.6311	0.0015	0.0064	−16.3	1.9236	168.1	118.1	0.0164
	HBr	−0.8	2.6766	0.0014	0.0054	−14.7	1.9438	166.4	115.7	0.0181
$(CH_2)_2S$	HF	0.2	2.4188	0.0020	0.0099	−17.0	2.2553	163.2	91.5	0.0147
	HCl	−1.0	2.6183	0.0016	0.0058	−11.0	2.4071	162.0	67.5	0.0162
	HBr	−1.6	2.6486	0.0016	0.0050	−10.9	1.8471	161.9	88.2	0.0200

The $V_S(r)$ of $(CH_2)_2O$, $(CH_2)_2S$ and $(CH_2)_2C=CH_2$ are also shown in Fig. 1, the negative potential shown in blue. The $V_{S, min}$, at the outer portion of X, are−33.5,−22.3, and −14.8 kcal mol^{-1}, respectively. For the same LiY, the interaction energies between $(CH_2)_2X$ (X: C=CH$_2$, O and S) and LiY follows the $(CH_2)_2C=CH_2\cdots LiY< (CH_2)_2S\cdot\cdot LiY < (CH_2)_2O\cdots LiY$ order. It can be seen that the order of $V_{S, min}$ is conversed to that of interaction energies. That is, the smaller $V_{S, min}$, the stronger the interaction is.

The $V_{S, max}$ of lithium atom for LiY (Y=F, Cl and Br) are 294.9, 263.6, and 200.8 kcal mol^{-1}, respectively. The $V_{S, max}$ of hydrogen atom for HY (Y=F, Cl and Br) is 67.8, 42.3, and 35.6 kcal mol^{-1}, respectively. In the earlier discussion, it has been found that for the same X and Y atom, the interaction energy of lithium bonded system is larger than that of the hydrogen bonded system. That is, the larger $V_{S, max}$, the stronger the interaction is. Furthermore, although the positive potential is near Li/H atom in LiY/ HY, there is a striking difference between HY and LiY: the direction of $V_{S, max}$ in HY is on its outermost portion along the H-Y bond, while that of in LiY is around the Li atom, not the outermost. These are consistent with the geometry characters that lithium bonds with a more "perpendicular" angle than hydrogen bonds.

AIM analysis

In an attempt to characterize hydrogen bonds in a rigorous manner within the AIM theory, Popelier and coworkers studied systems with well-known intermolecular hydrogen bond and proposed eight AIM-based criteria indicative of hydrogen bonding [39–41]. Four of them are relevant to the topological properties of the electron density. The others are related to the integrated properties of H atom. They believed that the possible hydrogen bond which fails one or more these criteria can not be accounted as the real hydrogen bond. In this circumstance it is also assumed that they are equally applicable to the intermolecular and intramolecular hydrogen bonds [40].

Figure 3 presents the molecular graphs of geometry (a) and (b) based on the total electron density. Tables 3 and 4 lists the topological characteristics at BCPs of these weak interaction systems.

Topology and electron density (ρ_c) at the bond critical points (BCPs)

By analyzing the bond paths of geometry (a), a particular situation is found. There is an interaction line between the Li atom of LiY and the BCP at the midpoint of C1–C2 bond of the three member ring, that is, in geometry (a), the (3,−1) BCP of C1–C2 bond is the attractor for the bond path linking X and C1–C2 bond. All these configurations

found correspond to "conflict catastrophe structrue" [42]. The existence of the BCP proves the existence of the lithium bonding interaction. The electron densities ($\rho(r_c)$) at the BCPs are within the range of 0.0096–0.0154 a. u., the corresponding Laplacian ($\nabla^2\rho(r_c)$) are within the range of 0.0528–0.0856. The $\rho(r_c)$ and $\nabla^2\rho(r_c)$ are larger than those of hydrogen bond (listed in Table 4), which mean that the lithium bonding interaction is stronger than the hydrogen bonding interaction.

Again it has been shown that $\rho(r_c)$ is related to the bond strength. As a result, for complexes (a), the $\rho(r_c)$ at BCP of the weak bond is related to ΔE, Δd(Li-Y) and Δd(C1–C2). The smaller $\rho(r_c)$, the smaller ΔE and the larger R_{Li*} are, this relationship shows that the topological criteria [39–41] is very consistent with the geometric criteria [43].

The lithium bond path in geometry (b) is different from that in geometry (a). In geometry (b), the weak bond path links Li atom of LiY to X atom of $(CH_2)_2X$ (in $(CH_2)_2C=CH_2$, the bond path links to the C4 atom). The $\rho(r_c)$ at the BCPs are within the range of 0.0156–0.0317a. u., the $\rho(r_c)$ at the BCP of the lithium bond are larger than the proposed range of 0.002–0.040 a. u. for the hydrogen bond [39–41], which means that the lithium bond is stronger than the hydrogen bond. Expect for the lithium bond, the secondary interactions exist in geometry (b).

Comparing the $\rho(r_c)$ at the BCP of weak bond, it can be seen that for the same $(CH_2)_2X$ and the same LiY, the $\rho(r_c)$ in geometry (b) is larger than that in geometry (a). The larger of ρ_c, the stronger of the interaction, therefore, it can be concluded that geometry (b) is more stable than geometry (a). For the same $(CH_2)_2X$, the interaction between LiY and $(CH_2)_2X$ becomes stronger and stronger in the sequence of Y=F, Cl and Br. For the same LiY (the same electron acceptor) and different donor, the interaction order is: n-type>π-type>pseudo-π-type. The conclusions are well consistent with the energetic and geometric results discussed previous.

$\nabla^2\rho(r_c)$, G_c, V_c and H_c at the bond critical points(BCPs)

The parameters derived form the Bader theory, such as the Laplacian of the electron density $\nabla^2\rho(r_c)$, the electron energy density H_c (the sum of the kinetic electron energy density (G_c) and the potential electron energy density (V_c)) and-G_c/ V_c, indicate the type of interaction. The Laplacian of electron density at BCP is negative and -G_c/V_c is greater than 1 indicate that there is a shared interaction as is the covalent bond. If the Laplacian is positive but H_c is negative, and the -G_c/V_c is smaller than 1 means that the interaction is partly covalently in nature [44, 45]. The $\nabla^2\rho(r_c)$, G_c, V_c, H_c and-/ V_c at the BCPs are also listed in Tables 3 and 4. One can see that both for lithium bonded systems and hydrogen bonded systems, both in geometry (a) and (b), the $\nabla^2\rho(r_c)$ and H_c are

Fig. 3 The molecular graph of
the studied complexes

Integrated properties in atomic basin
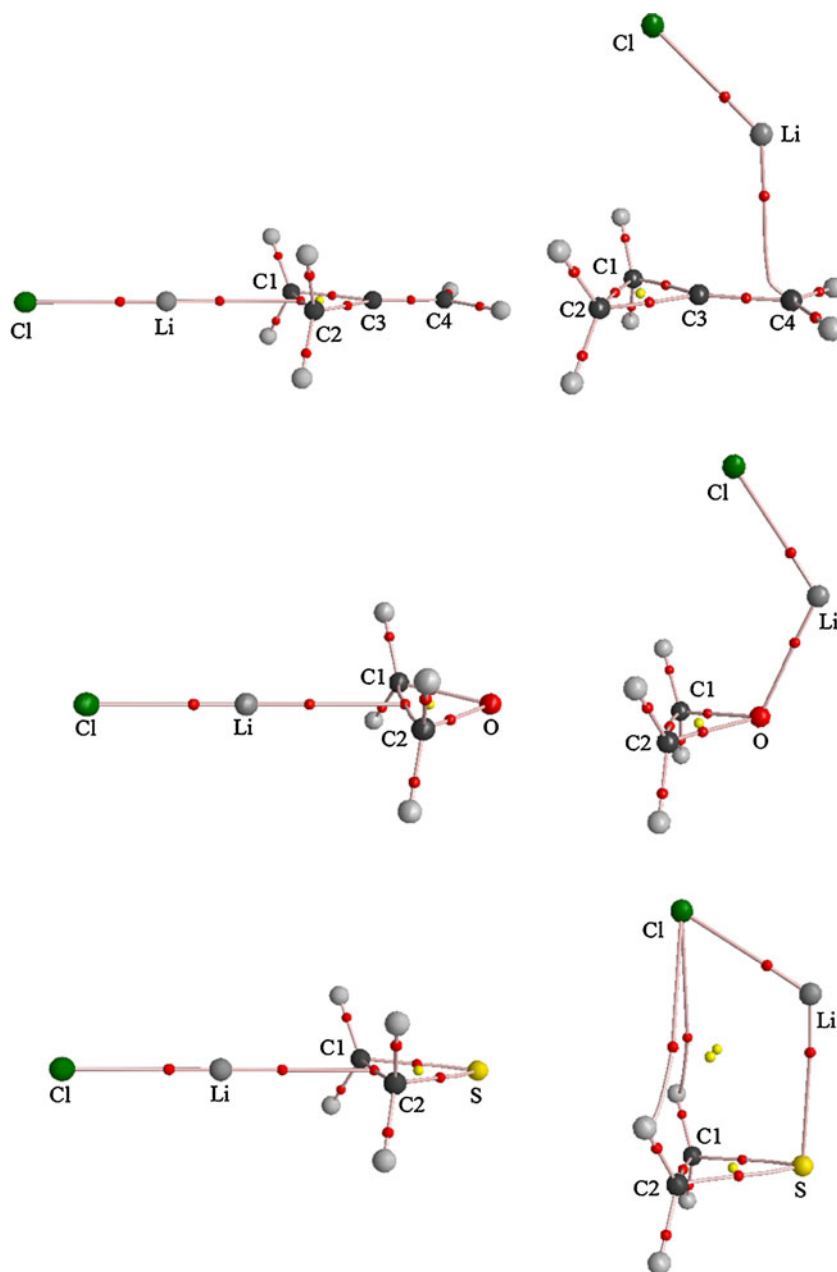
all positive,-G_c/V_c is greater than 1. According to Bader's [13] and Cramer's criteria [44], the quantities of $\nabla^2\rho(r_c)$, H_c and-G_c/V_c all indicate that the interactions between LiY/HY and (CH$_2$)$_2$X all belong to nonconvalent interactions. Comparing lithium bonded systems with hydrogen bonded systems, it can be seen that the $\nabla^2\rho(r_c)$ and H_c of lithium bond are greater than those of hydrogen bond, which mean that the lithium bonds have a more dominate ionic character than the hydrogen bonds do. For the same (CH$_2$)$_2$X (X: C=CH$_2$, O, S), the ionic character becomes more and more prominent in the sequence of F, Cl and Br in lithium bonded complexes, while it becomes weaker and weaker in the hydrogen bonded complexes.

Integrated properties in atomic basin

The integration of electron density over interatomic surface could provide useful bonding information for the interacting atoms. In order to compare the lithium bond and the hydrogen bond, the integrated properties of Li atom are calculated and listed in Table 5. The integrated properties in Li atomic basin are compared with Popelier's criteria [39–41].

Net charge According to Popelier's criteria, there is a loss of charge of the hydrogen atom in the hydrogen bonding formation process.

Table 3 Topological parameters at the BCP of the weak bond for lithium bond complexes

Geometry (a)		ρ_c	$\nabla^2\rho_c$	G_c	V_c	H_c	$-G_c/V_c$
MECP	LiF	0.0133	0.0736	0.0150	−0.0115	0.0035	1.3043
	LiCl	0.0149	0.0828	0.0170	−0.0132	0.0038	1.2879
	LiBr	0.0154	0.0856	0.0176	−0.0138	0.0038	1.2754
$(CH_2)_2O$	LiF	0.0101	0.0528	0.0106	−0.0081	0.0025	1.3086
	LiCl	0.0116	0.0608	0.0123	−0.0094	0.0029	1.3085
	LiBr	0.0120	0.0632	0.0128	−0.0098	0.003	1.3061
$(CH_2)_2S$	LiF	0.0096	0.0532	0.0106	−0.0079	0.0027	1.3418
	LiCl	0.0112	0.0620	0.0125	−0.0094	0.0031	1.3298
	LiBr	0.0116	0.0652	0.0131	−0.0099	0.0032	1.3232
Geometry (b)							
MECP	LiF	0.0142	0.0636	0.0134	−0.0108	0.0026	1.2407
	LiCl	0.0152	0.0672	0.0143	−0.0118	0.0025	1.2119
	LiBr	0.0155	0.0684	0.0146	−0.0121	0.0025	1.2066
$(CH_2)_2O$	LiF	0.0255	0.1916	0.0391	−0.0303	0.0088	1.2904
	LiCl	0.0269	0.2064	0.0420	−0.0324	0.0096	1.2963
	LiBr	0.0274	0.2112	0.0430	−0.0331	0.0099	1.2991
$(CH_2)_2S$	LiF	0.0177	0.0868	0.0191	−0.0166	0.0025	1.1506
	LiCl	0.0189	0.0908	0.0202	−0.0177	0.0025	1.1412
	LiBr	0.0192	0.0956	0.0205	−0.0181	0.0024	1.1326

The charges of the proton donor lithium atom all decrease upon complexation, as illustrated by Table 5. It means that there is a loss of charge of the lithium atom, just the same as hydrogen bond. While the smaller loss of charge of lithium atom does not correspond with the energetically weaker complex, i.e., for the same $(CH_2)_2X$ and LiY, there is no obvious difference between geometry (a) and geometry (b), and there is no other tendencies for different X or different Y atom.

Energy At the hydrogen bond formation, there is an energetic destabilization of the hydrogen atom. While for

Table 4 Topological parameters at the BCP of the weak bond for hydrogen bond complexes

Geometry (a)		ρ_c	$\nabla^2\rho_c$	G_c	V_c	H_c	$-G_c/V_c$
MECP	HF	0.0122	0.0480	0.0089	−0.0058	0.0031	1.5345
	HCl	0.0094	0.0292	0.0058	−0.0044	0.0014	1.3182
	HBr	0.0091	0.0268	0.0055	−0.0043	0.0012	1.2791
$(CH_2)_2O$	HF	0.0061	0.0168	0.0035	−0.0029	0.0006	1.2069
	HCl	0.0063	0.0180	0.0037	−0.0029	0.0008	1.2759
	HBr	0.0061	0.0168	0.0035	−0.0029	0.0006	1.2069
$(CH_2)_2S$	HF	0.0070	0.0272	0.0048	−0.0028	0.0020	1.7143
	HCl	0.0062	0.0176	0.0038	−0.0030	0.0008	1.2667
	HBr	0.0062	0.0172	0.0037	−0.0030	0.0007	1.2333
Geometry (b)							
MECP	HF	0.0157	0.0472	0.0094	−0.0069	0.0025	1.3623
	HCl	0.0124	0.0304	0.0061	−0.0047	0.0014	1.2979
	HBr	0.0121	0.0284	0.0059	−0.0046	0.0013	1.2826
$(CH_2)_2O$	HF	0.0330	0.1380	0.033	−0.0316	0.0014	1.0443
	HCl	0.0255	0.0944	0.0213	−0.0189	0.0024	1.1270
	HBr	0.0253	0.0896	0.0201	−0.0180	0.0021	1.1167
$(CH_2)_2S$	HF	0.0234	0.0612	0.0154	−0.0154	0.0000	1.0000
	HCl	0.0193	0.0456	0.0106	−0.0098	0.0008	1.0816
	HBr	0.0203	0.0460	0.0108	−0.0102	0.0006	1.0588

Table 5 Integrated atomic properties (in a. u.)of lithium-bonded complexes

Geometry(a)	q(Li)	Δq((Li)	E(Li)	ΔE(Li)	M(Li)	ΔM(Li)	V(X)	ΔV(X)
MECP⋯LiF	0.9221	−0.0186	−7.3659	−0.0278	0.0177	0.0080	2.8205	0.2072
MECP ⋯LiCl	0.9100	−0.0213	−7.3605	−0.0263	0.0038	−0.0030	3.0306	0.2653
MECP ⋯LiBr	0.9087	−0.0217	−7.3532	−0.0244	0.0003	−0.0096	3.1377	0.2681
(CH$_2$)$_2$O⋯LiF	0.9253	−0.0154	−7.3589	−0.0208	0.0191	0.0094	2.8382	0.2249
(CH$_2$)$_2$O⋯LiCl	0.9129	−0.0184	−7.3557	−0.0215	0.0053	−0.0015	3.0741	0.3088
(CH$_2$)$_2$O⋯LiBr	0.9117	−0.0187	−7.3490	−0.0202	0.0012	−0.0087	3.1949	0.3253
(CH$_2$)$_2$S⋯LiF	0.9248	−0.0159	−7.3521	−0.0140	0.0186	0.0089	2.8567	0.2434
(CH$_2$)$_2$S⋯LiCl	0.9134	−0.0179	−7.3533	−0.0191	0.0044	−0.0024	3.1094	0.3441
(CH$_2$)$_2$S⋯LiBr	0.9118	−0.0186	−7.3480	−0.0192	0.0005	−0.0094	3.2134	0.3438
Geometry(b)								
MECP⋯LiF	0.9190	−0.0217	−7.3641	−0.0260	0.0213	0.0116	2.6832	0.0699
MECP ⋯LiCl	0.9083	−0.0230	−7.3594	−0.0252	0.0095	0.0027	2.8386	0.0733
MECP ⋯LiBr	0.9078	−0.0226	−7.3524	−0.0236	0.0006	−0.0093	2.9252	0.0556
(CH$_2$)$_2$O⋯LiF	0.9287	−0.0120	−7.3622	−0.0241	0.0102	0.0005	2.4460	−0.1673
(CH$_2$)$_2$O⋯LiCl	0.9187	−0.0126	−7.3562	−0.0220	0.0059	−0.0009	2.5884	−0.1769
(CH$_2$)$_2$O⋯LiBr	0.9191	−0.0113	−7.3488	−0.0200	0.0090	−0.0009	2.6582	−0.2114
(CH$_2$)$_2$S⋯LiF	0.9203	−0.0204	−7.3565	−0.0184	0.0197	0.0100	2.6468	0.0335
(CH$_2$)$_2$S⋯LiCl	0.9095	−0.0218	−7.3567	−0.0225	0.0071	0.0003	2.7945	0.0292
(CH$_2$)$_2$S⋯LiBr	0.9088	−0.0216	−7.3512	−0.0224	0.0050	−0.0049	2.8677	−0.0019

q: net charge; E: energy; M: dipole moment; V: volume. Δq, ΔE, ΔM, ΔV represent the difference of the properties between the complexes and the monomers

the studied lithium bond systems, both geometry (a) and (b), for all (CH$_2$)$_2$X⋯LiY(X: C=CH$_2$, O, S and Y=F, Cl, Br), the energy of lithium decreases upon dimerization, this tendency is converse to that of the hydrogen bond.

Dipolar polarization Popelier found there is a decrease of dipolar polarizations of the hydrogen atom. For the studied lithium bonded systems, the changes of dipolar polarization of lithium have no obvious tendency, ten decreased and the other eight increased.

Atom volume At hydrogen bonding formation, there is a decrease in the volume of the hydrogen atom. While for lithium, expect the geometry (b) of (CH$_2$)$_2$O⋯LiY(Y=Cl, Br), the volumes of the lithium atom in other complexes all increased.

From the above discussion, it can be seen that except the net charge changes of the lithium atom is the same as those of the H atom, other criteria are different between lithium bond and hydrogen bond. These indicate the nature of the two types of intermolecular interactions are different.

Molecular formation of density difference

The idea of MFDD (molecule formation density difference) was put forward in 1996 by us [46], which is defined as

$$\rho_d(r) = \rho_{mol}(r) - \sum_A \rho_{atomA}(r).$$

This idea is also introduced to study of the weak interaction between molecule A and B, which is combined to a super molecule A-B model, the MFDD is modified as:

$$\rho_d(r) = \rho_{complex}(r) - \sum_A \rho_{molA}(r).$$

The explicit image of interaction between molecule A and B for chemists would be given by the distribution of function $\rho_d(r)$. Furthermore the integral of $\rho_d(r)$ inside of the given space area are significant for understanding the interaction. As representations, the MFDD graphs of the MECP/(CH$_2$)$_2$S⋯HCl/LiCl complexes are shown in Fig. 4. The MFDD graph shows clearly the formation processes of the lithium and hydrogen bond.

For geometry (a), the electron density of C1–C2 bond decreases in the formation of the lithium/hydrogen bond and it increases in the region between Li/H atom and C1–C2 bond, the increased volume between Li/H atom and C1–C2 bond has the order (CH$_2$)$_2$S⋯HCl < (CH$_2$)$_2$C=CH$_2$⋯HCl < (CH$_2$)$_2$S⋯LiCl< (CH$_2$)$_2$C=CH$_2$⋯LiCl. The integration of density difference in this region is 0.0009, 0.0034, 0.0079 and 0.0091, respectively. The positive value of the density difference means that the electron density increases in complexes compare to the monomer. For geometry (b), the electron density of X atom decreases and it increases in the region between Li/H atom and X bond, the increased volume of contour maps in the sequence of (CH$_2$)$_2$C=CH$_2$⋯HCl < (CH$_2$)$_2$S⋯HCl < (CH$_2$)$_2$C=CH$_2$⋯LiCl < (CH$_2$)$_2$S⋯LiCl, the integration of density difference in this region is 0.0201, 0.0412, 0.0749 and 0.1051, respectively. Comparing geom-

Fig. 4 The molecular formation density difference of the studied complexes (yellow is negative and purple is positive)

MECP-LiCla   MECP-LiClb   MECP -HCla   MECP -HClb

(CH₂)₂S-LiCla   (CH₂)₂S-LiClb   (CH₂)₂S-HCla   (CH₂)₂S-HClb
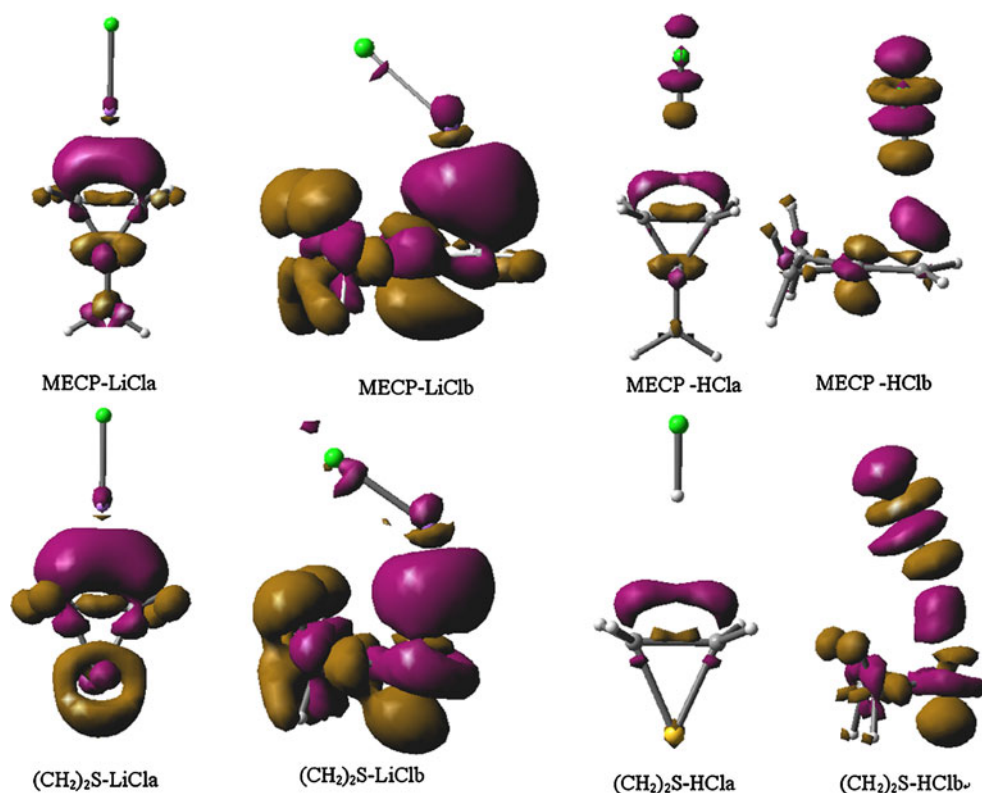
Table 6 A selection of NBO results (in kcal mol^{-1}) for the studied lithium bond complexes

Geometry (a)	Donor NBOs	δ	Acceptor NBOs	δ	q_{CT}[a]	Δ^2E
MECP···LiF	C1–C2 bond pair	1.9490	Li anti-lone pair	0.0228	−0.0057	1.45
MECP···LiCl	C1–C2 bond pair	1.9450	Li anti-lone pair	0.0736	−0.0112	3.07
MECP···LiBr	C1–C2 bond pair	1.9446	Li anti-lone pair	0.0945	−0.0130	3.90
(CH₂)₂O···LiF	C1–C2 bond pair	1.9753	Li anti-lone pair	0.0193	−0.0096	1.22
(CH₂)₂O···LiCl	C1–C2 bond pair	1.9715	Li anti-lone pair	0.0685	−0.0151	2.65
(CH₂)₂O···LiBr	C1–C2 bond pair	1.9704	Li anti-lone pair	0.0895	−0.0170	3.38
(CH₂)₂S···LiF	C1–C2 bond pair	1.9874	Li anti-lone pair	0.0201	−0.0064	0.53
(CH₂)₂S···LiCl	C1–C2 bond pair	1.9854	Li anti-lone pair	0.0687	−0.0109	1.66
(CH₂)₂S···LiBr	C1–C2 bond pair	1.9847	Li anti-lone pair	0.0897	−0.0126	2.24
Geometry (b)						
MECP···LiF	C3–C4 bond pair	1.9663	Li anti-lone pair	0.0281	−0.0114	5.88
MECP···LiCl	C3–C4 bond pair	1.9587	Li anti-lone pair	0.0725	−0.0200	6.77
MECP···LiBr	C3–C4 bond pair	1.9569	Li anti-lone pair	0.0900	−0.0208	7.42
(CH₂)₂O···LiF	O lone pair	1.9860	Li anti-lone pair	0.0231	−0.0101	4.22
		1.9579				4.02
(CH₂)₂O···LiCl	O lone pair	1.9822	Li anti-lone pair	0.0591	−0.0152	5.37
		1.9563				5.39
(CH₂)₂O···LiBr	O lone pair	1.9813	Li anti-lone pair	0.0773	−0.0156	5.99
		1.9563				6.09
(CH₂)₂S···LiF	S lone pair	1.9935	Li anti-lone pair	0.0505	−0.0381	2.5
		1.9314				20.5
(CH₂)₂S···LiCl	S lone pair	1.9921	Li anti-lone pair	0.0931	−0.0518	3.31
		1.9185				25.1
(CH₂)₂S···LiBr	S lone pair	1.9917	Li anti-lone pair	0.1094	−0.0537	3.64
		1.9158				26.1

a q_{CT} refers to the charge transferred from (CH₂)₂X to LiY

Table 7 A selection of NBO results (in kcal mol^{-1}) for the studied hydrogen bond complexes

Geometry (a)	q_{CT}	Δ^2E	Geometry (b)	q_{CT}	Δ^2E
MECP···HF	−0.0011	0.29	MECP···HF	−0.0109	0.34
MECP···HCl	−0.0014	0.15	MECP···HCl	−0.0107	0.39
MECP···HBr	−0.0022	0.15	MECP···HBr	−0.0133	0.37
$(CH_2)_2O$···HF	−0.0013	0.28	$(CH_2)_2O$···HF	−0.0238	16.7
$(CH_2)_2O$···HCl	−0.0012	0.28	$(CH_2)_2O$···HCl	−0.0216	13.0
$(CH_2)_2O$···HBr	−0.0017	0.30	$(CH_2)_2O$···HBr	−0.0250	14.4
$(CH_2)_2S$···HF	0.0003	0.16	$(CH_2)_2S$···HF	0.0383	17.0
$(CH_2)_2S$···HCl	−0.0001	0.47	$(CH_2)_2S$···HCl	−0.0401	15.6
$(CH_2)_2S$···HBr	−0.0005	0.24	$(CH_2)_2S$···HBr	−0.0503	18.9

etry (a) with (b), the integration of density difference of geometry (a) is smaller than that of geometry (b). The order of the integration of density difference is very consistent with that of intermolecular interaction energy. This means that in the formation of the lithium/hydrogen bond, the electron transfers from the pseudo-π bond in geometry (a) and from X atom in geometry (b) to Li/H atom. The direct proportion relationship between the interaction energy and the integration of density difference means that the electron transfer plays an important role in the formation of the lithium bond complexes.

NBO analysis

The NBO analysis of several typical hydrogen-bonded systems has demonstrated that the formation of a hydrogen bonded complex involves charge transfer from proton acceptor to the proton donor and it plays a major role in it. Δ^2E can be taken as an index to judge the strength of hydrogen bonds [37].

The frontier molecular orbital and their occupancy (δ) involving the charge transfer between subsystems, the quantum of charge transferred from donor to the acceptor q_{CT}, the second-order perturbation energy lowering (Δ^2E) due to the interaction of donor and acceptor orbital, provided by NBO analysis, are collected in Tables 6 and 7. For the studied lithium bonded system, the case is similar. In geometry (a), the charge transfers from the C=CH$_2$ double bond to the anti-lone pair orbital of electron acceptor LiY(Y=F, Cl, Br). In geometry (b), it transfers from lone pair orbital of O, S to the anti-lone pair orbital of LiY. The q_{CT} and Δ^2E value of geometry (b) are larger than those of geometry (a), and the q_{CT} and Δ^2E increase in the order of LiF, LiCl and LiBr, these orders exactly match the order of the bond energy ΔE. These confirm that the charge transfer interaction is more prominent and it determines the stability order. A notable difference exists between the hydrogen bond and lithium bond: in hydrogen bonded complexes, the q_{CT} and Δ^2E increase in the order HF, HCl, HBr, while the bond energy is converse to this order. This

means that the charge transfer plays an important role in lithium bonded complexes while it is less important in hydrogen bonded complexes.

Conclusions

The nature of the lithium and hydrogen bond between $(CH_2)_2X$ (X: C=CH$_2$, O, S) and XY(X, Y=H, F, Cl, Br) have been theoretically investigated. Two geometries of lithium/hydrogen bonded complex were compared. The analyses carried out in this work lead to the following main features:

(1) The geometry, bond energy, integrated properties of lithium/hydrogen atom and topological analyses all show that the lithium bond and the hydrogen bond are different.
(2) For the same electron donor and the same electron acceptor, lithium bond is stronger than hydrogen bond.
(3) For the same electron acceptor and different kinds of electron donors, the interaction energies follows the n-type> π-type > pseudo-π-type order.
(4) For the same electron donor and acceptor, geometry (b) is stable than geometry (a).
(5) For the same X atom, the interaction energy increases in the sequence of Y=F, Cl and Br for lithium bonded systems while it decreases for hydrogen bonded systems.
(6) The electrostatic potential influences the interaction energy and the geometry of the complexes.
(7) Electron transfer plays an important role in the formation of lithium bonded systems while it is less important in the hydrogen bonded systems.

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