# Blue-shifted lithium bonds

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**A number of lithium bonding systems (X–Li⋯Y) have been found in which the X–Li bond is shortened due to the lithium bond formation.**

A characteristic feature of H⋯Y hydrogen bonding in an X–H⋯Y system is X–H bond elongation with a concomitant red shift of the X–H stretching frequency.[1] The latter, readily detected in the IR spectra, is widely regarded as the "signature of hydrogen bonding". However, some recent studies have reported the existence of blue-shifted hydrogen bonds in which hydrogen bond formation leads to X–H bond shortening and to a blue shift of the X–H stretching frequency.[2,3]

Initially blue-shifted hydrogen bonds were reported for C–H bonds only.[2] Recent studies showed that N–H, O–H, Si–H and P–H bonds could also form blue-shifted hydrogen bonds.[4] A comprehensive theory for the blue shift has been proposed.[5] According to it, there is a balance between the X–H elongation effect due to orbital interactions and the X–H contraction effect due to Pauli and nuclei repulsions. If the former effect wins, a red shift will occur. Otherwise, a blue shift will take place.

An interesting interaction analogous to hydrogen bonding is lithium bonding.[6] Its existence was theoretically predicted by Kollman *et al.* in 1970.[7] Experimental evidence for lithium bonding, *i.e.* a large red shift of the X–Li stretching frequency in some X–Li⋯Y systems, was provided by Pimentel *et al.* in 1975.[8] To date lithium bonding has been identified in a variety of systems and the concept of lithium bonding has become important in many fields. However, it remains unknown whether there is any blue-shifted lithium bond.

Herein we wish to report our study on blue-shifted lithium bonds. We will focus on two lithium bond donors, $F_3C$–Li and $F_3Si$–Li, because $F_3C$–H and $F_3Si$–H have been found to be good hydrogen bond donors for the blue shift. For the lithium bond acceptors, we choose $NH_3$, $H_2O$, HF, $N_2$, He, Ne, Ar, $F_2$, $Cl_2$, $CF_4$, and $C_6H_6$. For each lithium bonding system, we also compare it with the corresponding hydrogen bond.

Our calculations are performed at the MP2/6-311++G(d,p) level for the complexes of $NH_3$, $H_2O$, HF, $N_2$, He, Ne, Ar, $F_2$, $Cl_2$.[9] For the complexes of $CF_4$ and $C_6H_6$ we use the MP2/6-31+G(d) method. Both the zero point energy (ZPE) and basis set super-position error (BSSE)[10] corrections are considered in the calculations. The results are listed in Table 1.

It is found that for most of the $F_3C$–H⋯Y and $F_3Si$–H⋯Y systems the C–H or Si–H bond is shortened due to the formation of the hydrogen bond. This bond contraction leads to a blue shift of the C–H or Si–H stretching frequency.[2–5] However, it is also found that for the lithium bonds an increase in X–Li bond length may cause a blue shift of the X–Li stretching frequency. For example, in $F_3C$–Li⋯$NH_3$ the C–Li bond length increases substantially by 0.0216 Å but the C–Li stretching frequency also increases significantly by 99.7 cm$^{-1}$.

The reason for the inconsistency between X–Li bond length and stretching frequency in the lithium bonds is probably that the X–Li

stretching frequency is not much higher than that of other bonds (*e.g.* C–F). Hence, the coupling between X–Li vibration and the vibration of other bonds can be very strong. The "observed" X–Li frequency does not completely belong to the X–Li vibration and the "observed" blue shift of the X–Li frequency is not fully caused by the change of bonding between X and Li.[11]

Since we are more interested in the effects of lithium bonding on the properties of the X–Li bond itself, a blue shift of the "observed" X–Li frequency caused by the vibrations of other bonds is not an interesting phenomenon to the present study. Compared to the "observed" X–Li frequency, the X–Li bond length is a property completely belonging to the X–Li bond itself. Therefore, in the following we decide to focus on the blue-shifted lithium bonds where the X–Li bond is shortened due to the lithium bond formation.

It is found that the X–Li stretching frequency is blue shifted in all the $F_3C$–Li⋯Y complexes. Nevertheless, $NH_3$, $H_2O$, and $N_2$ lead to elongation of the C–Li bond, whereas Ne, Ar, $F_2$, $Cl_2$, $CF_4$, and $C_6H_6$ lead to contraction of the C–Li bond. Therefore, the blue-shifted and shortened lithium bonds do exist. It is worthy of note that the variation of the C–Li bond length in lithium bonding is much more dramatic than that of the C–H bond length in hydrogen bonding. In $F_3C$–Li⋯$NH_3$ the C–Li bond is elongated by 0.0216 Å, whereas in $F_3C$–Li⋯$C_6H_6$ the C–Li bond is shortened by 0.0167 Å (See Fig. 1).

For $F_3Si$–Li, $NH_3$, $H_2O$, and $N_2$ lead to elongation of the Si–Li bond whereas He, Ne, Ar, $F_2$, $Cl_2$, $CF_4$, $C_6H_6$ lead to contraction of the Si–Li bond. The largest contraction is seen for $F_3Si$–Li⋯$C_6H_6$ (−0.0187 Å). Thus the blue shifted and shortened lithium bonds also exist in some $F_3Si$–Li complexes.

In order to understand the mechanism of the shortened lithium bonds, we studied $F_3C$–Li⋯Ne (shortened) and $F_3C$–Li⋯$OH_2$ (elongated) in detail. By fixing the C⋯Y distances in $F_3C$–Li⋯Y and by optimizing the remaining coordinates of the complexes, we obtained curves of the interaction energy ($\Delta E$, not corrected with BSSE) and the variation of the C–Li bond length ($\Delta d$) as functions of the C⋯Y distance (Fig. 2).

The potential energy curves of the two complexes are very similar in shape. At long distance, $\Delta E$ becomes more negative as the C⋯Y distance decreases. This behavior is clearly caused by the electrostatic interaction between $F_3C$–Li and Y. On the other hand, at short distance $\Delta E$ becomes less negative as the C⋯Y distance decreases. This behavior is undoubtedly due to the Pauli and nuclei-nuclei repulsions between $F_3C$–Li and Y.

The curves for the variation of C–Li bond length are also very similar in shape for the two complexes. At long distance, the C–Li bond is elongated for both $F_3C$–Li⋯Ne and $F_3C$–Li⋯$OH_2$. This elongation can only be explained by either the electrostatic attractions or the orbital interactions (*e.g.* charge transfer). On the other hand, the C–Li bond is shortened for both $F_3C$–Li⋯Ne and $F_3C$–Li⋯$OH_2$ at short C⋯Y distance. This contraction can only be explained as a result of Pauli and nuclei–nuclei repulsions.

The equilibrium position for $F_3C$–Li⋯Ne is in the contraction region of the curve so that $F_3C$–H⋯Ne has a shortened C–Li bond. In comparison, the equilibrium position for $F_3C$–Li⋯$OH_2$ is in the elongation region so that $F_3C$–Li⋯$OH_2$ has an elongated C–Li bond. Thus the difference between shortened and elongated lithium

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bonds is very simple. For the shortened ones, the bond shortening is greater than bond lengthening when the energy reaches the

**Table 1** Bond lengths, stretching frequencies, and interaction energies of X–H···Y and X–Li···Y from MP2/6-311++G(d,p) or MP2/6-31+G(d) calculations

| X–H or X–Li | Y | $d^a$ | $\Delta d^b$ | $v^c$ | $\Delta v^d$ | $\Delta E^e$ |
|---|---|---|---|---|---|---|
| F$_3$C–H | — | 1.0877 (1.0881$^f$) | — | 3223.3 (3250.0$^f$) | — | — |
| | NH$_3$ | 1.0875 | −0.0002 | 3221.2 | −2.1 | −12.2 |
| | H$_2$O | 1.0854 | −0.0023 | 3260.1 | +36.8 | −9.8 |
| | HF | 1.0851 | −0.0026 | 3267.3 | +44.0 | −5.6 |
| | N$_2$ | 1.0865 | −0.0012 | 3243.2 | +19.9 | −1.6 |
| | He | 1.0876 | −0.0001 | 3224.9 | +1.6 | 0.2 |
| | Ne | 1.0876 | −0.0001 | 3224.1 | +0.8 | 0.8 |
| | Ar | 1.0871 | −0.0006 | 3235.2 | +11.9 | 0.8 |
| | F$_2$ | 1.0862 | −0.0015 | 3247.7 | +24.4 | 0.6 |
| | Cl$_2$ | 1.0856 | −0.0021 | 3257.6 | +34.3 | 0.8 |
| | CF$_4$ | 1.0868$^f$ | −0.0013 | 3271.9$^f$ | +21.9 | −0.6 |
| | C$_6$H$_6$ | 1.0840$^f$ | −0.0041 | 3320.7$^f$ | +70.7 | −7.2 |
| F$_3$C–Li | — | 2.0218 (2.0378$^f$) | — | 501.4 (486.6$^f$) | — | — |
| | NH$_3$ | 2.0434 | +0.0216 | 601.1 | +99.7 | −85.9 |
| | H$_2$O | 2.0391 | +0.0173 | 607.0 | +105.6 | −73.3 |
| | HF$^g$ | — | — | — | — | — |
| | N$_2$ | 2.0278 | +0.0060 | 545.1 | +43.7 | −21.4 |
| | He | 2.0218 | +0.0000 | 510.7 | +9.3 | −0.7 |
| | Ne | 2.0208 | −0.0010 | 519.6 | +18.2 | −1.2 |
| | Ar | 2.0205 | −0.0013 | 538.7 | +37.3 | −4.3 |
| | F$_2$ | 2.0199 | −0.0019 | 539.1 | +37.7 | −5.9 |
| | Cl$_2$ | 2.0164 | −0.0054 | 567.5 | +66.1 | −8.6 |
| | CF$_4$ | 2.0306$^f$ | −0.0072 | 528.2$^f$ | +41.6 | −12.8 |
| | C$_6$H$_6$ | 2.0211$^f$ | −0.0167 | 568.2$^f$ | +81.6 | −52.6 |
| F$_3$Si–H | — | 1.4488 | — | 2456.8 | — | — |
| | NH$_3$ | 1.4479 | −0.0009 | 2456.7 | −0.1 | −3.6 |
| | H$_2$O$^g$ | — | — | — | — | — |
| | HF | 1.4467 | −0.0021 | 2476.9 | +20.1 | −2.5 |
| | N$_2$ | 1.4493 | +0.0005 | 2457.6 | +0.8 | −0.1 |
| | He | 1.4492 | +0.0004 | 2455.5 | −1.3 | 0.2 |
| | Ne | 1.4485 | −0.0003 | 2462.3 | −5.5 | 0.8 |
| | Ar | 1.4487 | −0.0001 | 2461.4 | −4.6 | 0.6 |
| | F$_2$ | 1.4481 | −0.0007 | 2468.9 | −12.1 | 0.3 |
| | Cl$_2$$^g$ | — | — | — | — | — |
| | CF$_4$$^g$ | — | — | — | — | — |
| | C$_6$H$_6$$^g$ | — | — | — | — | — |
| F$_3$Si–Li | — | 2.4822 (2.5080$^f$) | — | 487.2 (474.1$^f$) | — | — |
| | NH$_3$ | 2.5039 | +0.0217 | 594.3 | +107.1 | −90.0 |
| | H$_2$O | 2.4990 | +0.0168 | 603.2 | +116.0 | −76.9 |
| | HF$^g$ | — | — | — | — | — |
| | N$_2$ | 2.4845 | +0.0023 | 528.4 | +41.2 | −22.3 |
| | He | 2.4821 | −0.0001 | 494.4 | +7.2 | −0.5 |
| | Ne | 2.4795 | −0.0027 | 501.2 | +14.0 | −1.3 |
| | Ar | 2.4793 | −0.0029 | 516.8 | +29.6 | −4.8 |
| | F$_2$ | 2.4786 | −0.0036 | 518.3 | +31.1 | −6.6 |
| | Cl$_2$ | 2.4728 | −0.0094 | 551.7 | +64.5 | −9.7 |
| | CF$_4$ | 2.5041$^f$ | −0.0039 | 517.6$^f$ | +43.5 | −14.3 |
| | C$_6$H$_6$ | 2.4893$^f$ | −0.0187 | — | — | −68.7$^h$ |

$^a$ X–H or X–Li bond length (Å). $^b$ Change of X–H or X–Li bond length due to the complexation (Å). $^c$ X–H or X–Li stretching frequency (cm$^{-1}$). $^d$ Change of X–H or X–Li stretching frequency due to the complexation (cm$^{-1}$). $^e$ Binding energy between Y and X–H or X–Li (kJ mol$^{-1}$). This energy is corrected with ZPE and BSSE. $^f$ MP2/6-31+G(d) results. $^g$ Optimization on these complexes fails. $^h$ Frequency calculation on this particular complex fails due to the large size and therefore, the binding energy of this complex has not been corrected with ZPE.
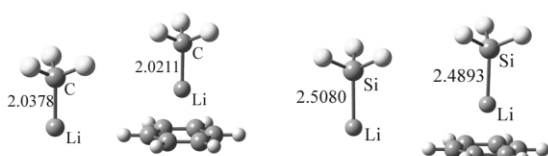


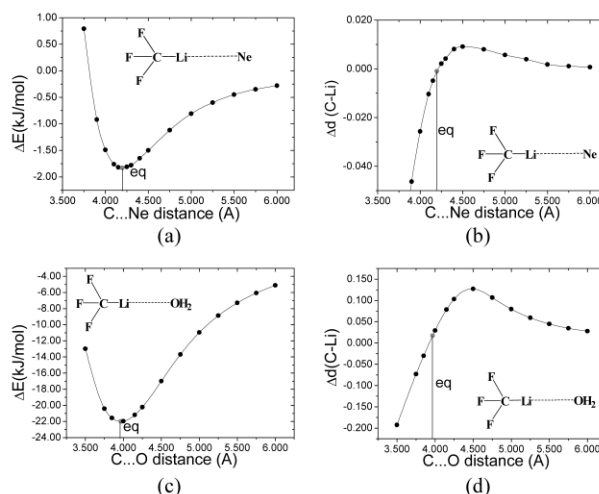**Fig. 1** F$_3$C–Li, F$_3$Si–Li, and their complexes with C$_6$H$_6$.



**Fig. 2** Interaction energy ($\Delta E$) and variation of C–Li bond length ($\Delta d$) as a function of the distance between F$_3$C–Li and Y: (a) Y = Ne, (b) Y = OH$_2$ (equilibrium C···Y distances indicated by the line labeled "eq").

minimum. On the other hand, for the elongated lithium bonds, there is an additional bond lengthening due to orbital interactions that is not overcome by the modest bond compression resulting from the repulsive interactions.

The above analyses suggest that the mechanism for the blue-shifted and shortened lithium bonds should be the same as that for the blue-shifted hydrogen bonds.[5] There is a balance between the X–Li elongation effect due to orbital interactions and the X–Li contraction effect due to Pauli and nuclei repulsions. If the former effect wins, the X–Li bond will elongate. Otherwise, the X–Li bond will contract.

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