

***Ab initio* calculations on lithium-bonded dimers: a brief review**

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Abstract. *Ab initio* calculations on a number of lithium-bonded dimers are reviewed and the properties of lithium bonds vis-a-vis that of hydrogen bonds are discussed.

Keywords. *Ab initio* calculations; lithium-bonded dimers; three-centre interaction.

1. Introduction

Association between molecules containing polar HX bonds and nonbonding electron pairs is characterised by relatively high energies of interaction and unique geometries. This type of molecular interaction is generally attributed to hydrogen bonding. Hydrogen is, however, not unique in its ability to participate in a three-centre interaction. There have been speculations (Shigorin 1959; West and Glaze 1961; Brown *et al* 1962) over the years that lithium being a congener of hydrogen might also be involved in a similar type of interaction giving rise to lithium-bonding.

Ault and Pimental (1975) were the first to provide experimental proof for the existence of a Li-bond in $\text{H}_3\text{N} \dots \text{LiX}$ ($X = \text{Cl}, \text{Br}$) complexes. They found the frequency shifts of the Li-X stretching bands in these complexes qualitatively similar to those observed for analogous proton donors. However, these frequency shifts were considerably smaller than in the corresponding H-bonded complexes and the IR intensity changes characteristic of H-bonds were absent. Later on, Ault (1978) carried out matrix isolation IR spectroscopic studies on the 1:1 complexes of ammonia and water with a number of alkali halides.

Despite the recognition of Li-bonding as an important type of three-centre interaction, the amount of experimental work done to date on Li-bonded complexes has been rather meagre. Thus most of our current knowledge concerning Li-bonding has been derived from theoretical work done in this field. Kollman *et al* (1970) were the first to theoretically investigate the properties of the Li-bond by means of *ab initio* SCF calculations. Since then a number of *ab initio* (Kollman *et al* 1972; Baskin *et al* 1973; Rychlewski and Sabin 1976; Szczesniak *et al* 1976; Szczesniak and Ratajczak 1977, 1980; Umeyama and Morokuma 1977; Kulkarni and Rao 1983; Latajka and Scheiner 1984) and semiempirical (Szczesniak *et al* 1976; Latajka *et al* 1977) calculations have been reported on a variety of Li-bonded dimers. Barring a few (Kollman *et al* 1972; Latajka and Scheiner 1984), these calculations have mostly been carried out at the SCF level. We have in the present article reviewed the results of *ab initio* calculations on a number of Li-bonded dimers in an attempt to elucidate the essential features of Li-

Dedicated to Professor Sadhan Basu on the occasion of his 65th birth anniversary.

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bonding. We have confined our attention only to dimers since to the best of our knowledge no *ab initio* calculation has yet appeared on larger systems.

The results of the *ab initio* calculations are presented and analysed in the next section which is followed by a discussion of the properties of Li-bonds vis-a-vis that of H-bonds. Some remarks concerning Na-bonds have been made in the concluding section of the article.

2. Results of *ab initio* calculations on some Li-bonded dimers

The predicted geometry and dimerisation energy* of the Li-bonded dimers, namely, $(\text{LiH})_2$ (linear and cyclic), $(\text{LiF})_2$ (linear and cyclic), HLiF_2 (linear and cyclic), $\text{H}_3\text{N} \dots \text{LiX}$ ($X = \text{H, F, Cl}$), $\text{H}_2\text{O} \dots \text{LiX}$ ($X = \text{F, Cl}$), $\text{CH}_3\text{OH} \dots \text{LiX}$ ($X = \text{F, Cl}$), $\text{C}_2\text{H}_4 \dots \text{LiX}$ ($X = \text{H, F}$) and $\text{C}_2\text{H}_2 \dots \text{LiH}$ are summarised in table 1. All these results refer to *ab initio* SCF calculations. We shall first discuss the results of calculations on individual or closely related systems and then attempt to generalise them as far as possible.

The complexes, $(\text{LiH})_2$, $(\text{LiF})_2$ and LiHF_2 have been investigated (Kollman *et al* 1970, 1972; Baskin *et al* 1973; Rychlewski and Sabin 1976) both in linear and cyclic forms. The linear form of $(\text{LiH})_2$ is found to be asymmetric ($C_{\infty v}$)—the LiH bond of one monomer is contracted and that of the other is elongated upon complex formation. Two sets of calculations (Kollman *et al* 1972; Baskin *et al* 1973; Rychlewski and Sabin 1976) which have been performed using different basis sets yield almost identical results. The cyclic (D_{2h}) form of $(\text{LiH})_2$ is found to be more stable than the linear one by about 21 kcal/mol. This extra stability is due to the formation of an additional Li-bond in the cyclic form. In this form the LiH distance is stretched by a much wider margin (0.16 Å) and the HH distance is substantially longer than the LiLi distance. The latter structural feature is attributed (Kollman *et al* 1972) to the fact that the HOMO (b_{2u}) of cyclic $(\text{LiH})_2$ has a node between the hydrogens and none between the lithiums. Configuration interaction (ci) calculations including all single and double excitations from the valence MO were carried out (Kollman *et al* 1972) for this system at its SCF—computed geometry. These results indicate that electron correlation has negligible effect on the dimerisation energy of $(\text{LiH})_2$.

Both the linear and the cyclic (D_{2h}) forms of $(\text{LiF})_2$ are far more stable than the corresponding form of $(\text{LiH})_2$. Moreover, like $(\text{LiH})_2$ the cyclic form of $(\text{LiF})_2$ has much higher dimerisation energy than the linear form. Inclusion of *p* orbitals on lithium decreases the LiF distance and the dimerisation energy, and increases the LiLi distance in the linear form of $(\text{LiF})_2$. When *d* orbitals on fluorine are included (Baskin *et al* 1973) the dimerisation energy is further reduced. It may be noted that the LiF distances of the monomers have been kept fixed while optimising the geometry of linear $(\text{LiF})_2$. Had these distances also been optimised, one could probably have found the asymmetric form to be more stable than the symmetric one as in the case of $(\text{LiH})_2$. The structural features of cyclic $(\text{LiF})_2$ are quite similar to those of cyclic $(\text{LiH})_2$ —the LiF distance is considerably elongated (by 0.16 Å) and the FF distance is longer than the

* For systems containing only one dicoordinated Li atom, the dimerisation energy is equal to the Li-bond energy while for systems containing two such Li atoms the dimerisation energy is twice the Li-bond energy.

Table 1. Equilibrium geometry and dimerisation energy (DE) of some lithium-bonded dimers.

Dimer	Structure ⁽ⁱ⁾	Geometry ⁽ⁱⁱ⁾	Δr (Å)	DE (kcal/mol)	Basis set	Reference
(LiH) ₂	1a	R = 3.44, r ₁ = 1.63 r ₂ = 1.68	$\Delta r_1 = -0.01$ $\Delta r_2 = 0.04$	25.11	Li(10s, 2p) H(8s, 1p)	Rychlewski and Sabin (1976)
(LiH) ₂	1a	R = 3.45, r ₁ = 1.62 r ₂ = 1.67	$\Delta r_1 = -0.01$ $\Delta r_2 = 0.04$	25.98	Li(9s, 5p/4s, 2p) H(5s, 2p/2s, 1p)	Kollman <i>et al</i> (1972)
(LiH) ₂	1b	r ₁ = 2.36 r ₂ = 2.73 r ₃ = 1.80	$\Delta r_3 = 0.16$	47.2	Li(9s, 5p/4s, 2p) H(5s, 2p/2s, 1p)	Kollman <i>et al</i> (1972)
(LiF) ₂	1a	R = 3.38/3.43 ⁽ⁱⁱⁱ⁾ r = 1.667/1.587	(iv)	56.3/ 46.0	F(10s, 5p/3s, 1p) Li(10s/3s) and (10s, 1p/3s, 1p)	Kollman <i>et al</i> (1970)
(LiF) ₂	1a	R = 3.36, r = 1.56	(iv)	36.4	Li(9s, 3p/4s, 2p)	Baskin <i>et al</i> (1973)
(LiF) ₂	1b	r ₁ = 2.22 r ₂ = 2.65 r ₃ = 1.72	$\Delta r_3 = 0.16$	66.7	F(9s, 5p, 2d/4s, 2p, 1d) Li(9s, 3p/4s, 2p) F(9s, 5p, 2d/4s, 2p, 1d)	Baskin <i>et al</i> (1973)
HFLiF	1c	R = 3.567/3.567 ⁽ⁱⁱⁱ⁾ r = 1.672/1.592 r' = 0.916	$\Delta r = 0.005/$ 0.004	13.5/ 16.2	F(10s, 5p/3s, 1p) Li(10s/3s) and (10s, 1p/3s, 1p) H(5s/1s)	Kollman <i>et al</i> (1970)
HFLiF	1d	R = 2.60 $\theta_H = 45,$ $\theta_{Li} = 60$ r = 1.667 r' = 0.916	(iv)	15.1	F(10s, 5p/3s, 1p) Li(10s/3s) and (10s, 1p/3s, 1p) H(5s/1s)	Kollman <i>et al</i> (1970)
H ₃ N-LiH	1e	R = 2.05/2.05 NH ₃ ^(v)	$\Delta r = 0.02/-$	23.01/-	Dz/dzp ^(vi)	Szczesniak and Ratajczak (1980)
H ₃ N-LiF	1e	R = 2.02, r = 1.634 NH ₃ ^(vii)	$\Delta r = 0.02$	28.65	N and F(10s, 5p) Li(10s) H(5s)	Szczesniak <i>et al</i> (1976)

Table 1. (Continued).

Dimer	Structure ⁶⁸	Geometry ⁶⁸	Δr (Å)	Δr (kcal/mol)	Basis set	Reference
H_3N-LiF	1c	$R = 2.05$ $r = 1.603$ $NH_3^{(11)}$	$\Delta r = 0.018$	25 31	N and F (6-31G) Li (6-31G) H_3N	Saxena and Rajashek (1977)
H_3N-LiF	1c	$R = 2.07$ $r = 1.582$ NH_3 geometry ⁽¹²⁾	$\Delta r = 0.014$	22 89(Si) ⁽¹²⁾ 22 81(M) Si 23 48(Si) M 23 52(M) M (for NH_3)	6-31G** ⁽¹²⁾ for LiF	Latajka and Schermer (1984)
H_3N-LiF	1c	$R = 1.951$ $r = 1.420$ $\angle HNLi = 112.6$ $\angle HNH = 106.1$ NH_3 geometry ⁽¹³⁾	$\Delta r = 0.013$	47 53	STO-3G	Kulkarni and Rao (1983)
$H_3N-LiCl$	1c	$R = 1.936$ $r = 1.955$ $\angle HNLi = 112.8$ $\angle HNH = 105.9$ NH_3 geometry ⁽¹⁴⁾	$\Delta r = 0.022$	54 3	STO-3G	Kulkarni and Rao (1983)
$H_3N-LiCl$	1c	$R = 2.036$ $r = 2.082$ NH_3 geometry ⁽¹⁵⁾	$\Delta r = 0.015$	25 46(Si) ⁽¹⁵⁾ 26 05(Si) M	6-31G** ⁽¹⁵⁾ for LiCl	Latajka and Schermer (1984)
H_3O-LiF	1f	$R = 1.774$ $r = 1.423$ $\angle HOLi = 126.8$ $\angle HOH = 104.6$ H_2O geometry ⁽¹⁶⁾	$\Delta r = 0.016$	48 34	STO-3G	Kulkarni and Rao (1983)
$H_3O-LiCl$	1f	$R = 1.744$ $r = 1.954$ $\angle HOLi = 126.5$ $\angle HOH = 105.5$ H_2O geometry ⁽¹⁶⁾	$\Delta r = 0.021$	55 23	STO-3G	Kulkarni and Rao (1983)

CH ₃ OHLiF	1f	R = 1.795, r = 1.419 ∠ COLi = 127.9 ∠ HOC = 104.1 CH ₃ OH geometry ^(xiii) R = 1.776, r = 1.951 ∠ COLi = 115 ∠ HOC = 104.1 CH ₃ OH geometry ^(xiii)	Δr = 0.012	46.12	STO-3G	Kulkarni and Rao (1983)
CH ₃ OHLiCl	1f	R = 1.776, r = 1.951 ∠ COLi = 115 ∠ HOC = 104.1 CH ₃ OH geometry ^(xiii)	Δr = 0.018	52.12	STO-3G	Kulkarni and Rao (1983)
C ₂ H ₂ LiH	1g	R = 2.45/2.45 C ₂ H ₂ ^(xiv)	Δr = 0.0/-	8.14/8.93	DZDZP ^(iv)	Szczesniak and Ratajczak (1980)
C ₂ H ₄ LiH	1h	R = 2.50 C ₂ H ₄ ^(xiv)	Δr = 0.0	8.67	DZ	Szczesniak and Ratajczak (1980)
C ₂ H ₄ LiF	1h	R = 2.48 r = 1.603 C ₂ H ₄ ^(xiv)	Δr = 0.0	8.75	F(10s, 5p) Li(10s, 1p) C(9s, 5p) H(4s)	Szczesniak and Ratajczak (1977)

⁽ⁱ⁾For structure see figure 1; ⁽ⁱⁱ⁾bond length in Å and angles in degrees; ⁽ⁱⁱⁱ⁾without p/ with p; ^(iv)fixed monomer geometry; ^(v)geometry of NH₃ taken from Herzberg (1950); ^(vi)DZP = double-zeta + polarisation; ^(vii)geometry of NH₃ taken from Synder and Bash (1972); ^(viii)SCF geometry/MP2 geometry; ^(ix)S = SCF; M = MP 2; (S/M) = SCF geometry/MP 2 (calculation); ^(x)∠ (NH) = 1.011 Å, ∠ HNH = 107.6°; ^(xi)r (NH) = 1.03 Å; ∠ HNH not given in Kulkarni and Rao (1983); ^(xii)(OH) = 0.989 Å, ∠ HOH = 100.0°; ^(xiii)(OH) = 0.99 Å, r (CO) = 1.43 Å, r (CH) = 1.09 Å, ∠ COH = 103.0°; ^(xiv)geometry of NH₃ taken from Fisher-Hjalmar and Siegbahn (1973).

LiLi distance. The predicted dimerisation energy of $(\text{LiF})_2$ is in good agreement with experiment (Kusch 1958).

The mixed dimer of HF and LiF can exist either in the H-bonded form, $\text{Li-F} \dots \text{H-F}$ or in the Li-bonded $\text{H-F} \dots \text{Li-F}$ in the linear configuration. In table 1 we have included the results of calculations on the Li-bonded form only. It has been predicted (Kollman *et al* 1970) to be less stable than the H-bonded form. The cyclic dimer contains one Li-bond and one H-bond. Since the latter is considerably weakened due to the loss of linearity in the structure, the dimerisation energy of the cyclic form is only slightly higher than that of the linear Li-bonded form. In contrast to $\text{LiF} \dots \text{LiF}$, inclusion of Li p orbitals in the basis set has only a marginal effect on the Li-bond energy in $\text{HF} \dots \text{LiF}$. The stretching of the LiF distance in this complex is negligible.

The Li-bond energy in the $A \dots \text{LiX}$ ($A = \text{NH}_3$; $X = \text{H, F, Cl}$) complexes increases with increasing dipole moment of the LiX molecule [the dipole moments (Kollman *et al* 1970; Latajka and Scheiner 1984) of LiH, LiF and LiCl are 5.88, 6.32 and 7.13 D respectively]. In the $\text{H}_3\text{N} \dots \text{LiH}$ system, inclusion of polarization functions in the basis set does not have any significant effect on its Li-bond energy. The situation is, however, different in the case of $\text{H}_3\text{N} \dots \text{LiF}$ complex where the Li-bond energy is reduced (Latajka and Scheiner 1984) when polarization functions are included. Some CI calculations (Latajka and Scheiner 1984) were carried out on this system using the Moller-Plesset perturbation theory to the second order (MP2) and keeping the mo

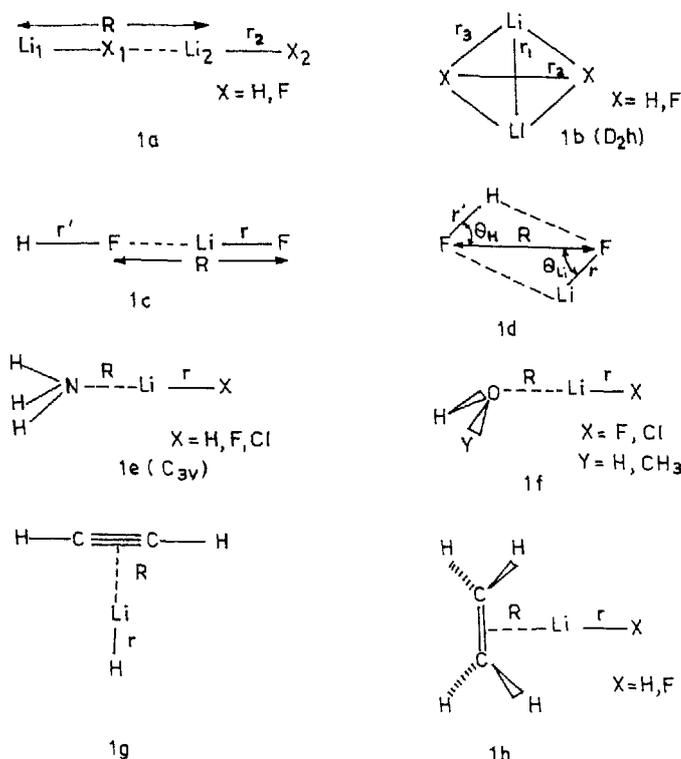


Figure 1. Structure of some Li-bonded dimers.

corresponding to the inner shells of first-row atoms frozen. The results of this calculation indicate that electron correlation does not have any significant effect on the Li-bond energy. This is in accord with the observation (Kollman *et al* 1972) made earlier in the case of cyclic (LiH)₂.

The geometry and Li-bond energy of the H₃N . . . LiF and H₃N . . . LiCl complexes were calculated (Kulkarni and Rao 1983) also by using STO-3G basis set. A comparison of these results with the ones (Latajka and Scheiner 1984) obtained by using larger basis set reveals that the STO-3G calculations underestimate the NLi and LiX bond lengths by about 0.1 Å and overestimate the Li-bond energy by about 100%. Errors of comparable magnitude might have occurred also in the calculations on H₂O . . . LiX (X = F, Cl) and CH₃OH . . . LiX (X = F, Cl) complexes. Thus the STO-3G basis set seems to be inadequate for a quantitative description of the Li-bonded systems. Nevertheless, the results are useful for making a qualitative comparison of the properties of a related series of complexes.

Turning our attention back to the STO-3G results of the A . . . LiX (A = NH₃, H₂O, CH₃OH; X = F, Cl) complexes we find that for a given halide the Li-bond energy increases in the order H₃COH < H₃N < H₂O. The dipole moments of these molecules also vary in the same order. It is further observed that for a given electron donor (A) LiCl forms stronger Li-bond than LiF (recall that the dipole moment of LiCl is higher than that of LiF). The stretching of the LiX bond varies roughly from 0.01 to 0.02 Å in the various A . . . LiX complexes.

Analogous to π -hydrogen bonds (Del Bene 1974) π -lithium bonds are formed by the interaction of the LiX dipole with the π -charge cloud of the multiple bonds in molecules like C₂H₂, C₂H₄ etc. The Li-bond energies in these complexes are relatively small (\approx 8–9 kcal/mol) and the LiX bond remains virtually unaltered upon complex formation.

On the basis of the strength of the Li-bonds we can classify the Li-bonded dimers considered above roughly into three classes (A, B and C). In class A dimers like (LiH)₂ and (LiF)₂, the Li-bond energy is greater than 25 kcal/mol. These are systems with very strong Li-bonding. In class B dimers like HF . . . LiF and A . . . LiX (A = NH₃, H₂O, CH₃OH; X = H, F, Cl) the Li-bond energy lies in the range of 10 to 25 kcal/mol. These are systems with fairly strong Li-bonding. Class C dimers are the π lithium-bonded complexes with Li-bond energy less than 10 kcal/mol. These are systems with weak Li-bonding. The stretching of the LiX bond increases in the order, class C < class B < class A.

The size of the basis set is a very important factor in *ab initio* calculations on Li-bonded complexes. In general, the DZP basis set seems to be good enough. However, a more straightforward criterion in this regard is that those basis sets should be used which are capable of reproducing the dipole moments of the monomers with quantitative accuracy. The effect of electron correlation seems to be negligible for systems composed of highly polar monomer units. But in the π -complexes where one of the monomers is a neutral species, dispersion interaction and, hence, electron correlation is expected to play a more important role.

In table 2 the population differences which result from the formation of Li-bonds are given for some Li-bonded dimers. This quantity often provides a criterion for the characterisation of Li-bonds. For example, in complexes like LiH . . . LiH, LiF . . . LiF, HF . . . LiF, H₃N . . . LiF, C₂H₄ . . . LiF the electron density on the bridging lithium increases upon complex formation. Use of different basis sets in the

Table 2. Population differences in some Li-bonded dimers⁽ⁱ⁾, ⁽ⁱⁱ⁾.

Dimer	Structure ⁽ⁱⁱⁱ⁾	M ₁	X ₁	M ₂	X ₂	Reference
(LiH) ₂	1a	-0.158	+0.032	+0.060	+0.066	Rychlewski and Sabin (1976)
(LiH) ₂	1a	-0.236	+0.366	-0.194	+0.064	Kollman <i>et al</i> (1972)
(LiH) ₂	1b	-0.067	+0.067			Kollman <i>et al</i> (1972)
(LiF) ₂ ^(iv)	1a	-0.083/	+0.04/	+0.001/	+0.042	Kollman <i>et al</i> (1970)
		-0.128	-0.008	+0.128	+0.007	
(LiF) ₂	1b	+0.007	-0.007			Baskin <i>et al</i> (1973)
(LiF) ₂ ^(iv)	1b	-0.018/	+0.018/			Kollman <i>et al</i> (1970)
		-0.016	+0.016			
HFLiF ^(iv)	1c	-0.044/	+0.034/	-0.018/	+0.028/	Kollman <i>et al</i> (1970)
		-0.042	+0.012	+0.031	-0.001	
HFLiF ^(v)	1d	-0.036	+0.041	-0.047	+0.042	Kollman <i>et al</i> (1970)
H ₃ NLiF	1e	-0.070	+0.207	+0.0163	-0.013	Szczesniak <i>et al</i> (1976)
C ₂ H ₄ LiF ^(vi)	1h	-0.047	+0.066	+0.049	+0.007	Szczesniak and Ratajczak (1977)

⁽ⁱ⁾A negative value denotes loss of electron density and a positive value denotes gain of electron density upon dimerisation; ⁽ⁱⁱ⁾M = H, Li; X = H, F, N or C; ⁽ⁱⁱⁱ⁾for structure see figure 1; ^(iv)without p on Li/with p on Li; ^(v)without p on Li; ^(vi)population difference on the C atom is +0.066.

case of LiH . . . LiH (Kollman *et al* 1972) and HF . . . LiF (Kollman *et al* 1970) yields electron densities which do not obey this criterion. In the cyclic form of (LiH)₂ both the lithium atoms lose electron density, while in (LiF)₂ two opposing trends are predicted by calculations (Kollman *et al* 1970; Baskin *et al* 1973) performed using different basis sets. Since the population analysis is an artifact which is highly sensitive to the choice of basis sets it is not possible to characterise Li-bonds solely on the basis of local charge densities.

A more reliable criterion for the characterisation of Li-bonds is provided by the dipole moment, a quantity which depends not on local (a fictitious quantity) but on global charge distribution. It has been found (Kollman *et al* 1970; Kulkarni and Rao 1983; Latajka *et al* 1984) that the formation of a Li-bond is always accompanied by an increase in dipole moment. Another criterion for the identification of Li-bonds is the change in MO energies of the monomers upon complex formation. It has been observed that those MO of the complex which are mainly centred on the monomer acting as the electron donor are stabilised (more negative orbital energies), and those orbitals which are mainly centred on the monomer acting as the electron acceptor are destabilised. This is a characteristic feature (Kollman and Allen 1969) of donor-acceptor complexes, shared also by Li-bonded dimers.

3. Properties of Li-bonds vis-a-vis those of H-bonds

Umeyama and Morokuma (1977) used an energy decomposition scheme to study the origin of H-bonding. They suggested that at the Hartree-Fock level the stabilisation energy due to H-bonding has three attractive components [Electrostatic (ES), polarisation (PL), charge transfer (CT), and one repulsive (exchange repulsion, EX)] component. They applied this energy partitioning scheme to some Li-bonded dimers as well and made a comparative study of hydrogen-bonding and lithium-bonding. The

systems chosen for this purpose were $(\text{LiF})_2$, $(\text{LiH})_2$ and $(\text{HF})_2$. According to their classification the linear form of $(\text{LiF})_2$ is a strong ES complex while $(\text{HF})_2$ is an ES > CT complex. This implies that in the former system the stabilisation energy is derived mainly from the ES interaction while in the latter both ES and CT (to a lesser extent than ES) interactions contribute significantly. In this way they classified the linear form of $(\text{LiH})_2$ as a strong ES > PL, CT complex, the cyclic form of $(\text{LiH})_2$ as a strong ES, CT > PL complex, and the cyclic form of $(\text{LiF})_2$ as a very strong ES \gg PL, CT complex. In general the Li-bonded systems are predominantly ES complexes very much like the strong H-bonded systems like FHF^- , ClHCl^- etc.

Apart from the nature of interactions pointed out above there are a number of similarities and dissimilarities between Li-bonds and H-bonds (Schuster *et al* 1976; Ratajczak and Orville-Thomas 1981). Some of these are as follows.

1. Both H-bonding and Li-bonding involve donor-acceptor type of interaction. This is evident (Kollman and Allen 1969; Kollman *et al* 1970) from the MO energy changes and charge transfer accompanied by the formation of the pertinent complexes.
2. The H-bonds ($Y \dots \text{H}-X$) are linear or nearly so whereas the Li-bonds ($Y \dots \text{Li}-X$) may even be cyclic as in $(\text{LiH})_2$ and $(\text{LiF})_2$. The ease of formation of cyclic structure is due mainly to the low force constant of the LiX bonds.
3. The Li-bonds are quite a bit stronger than the H-bonds due in large part to the higher dipole moment of the LiX subunit.
4. Most hydrogen bonds are known (Schuster *et al* 1976; Ratajczak and Orville-Thomas 1981) to have double minimum potential whereas only single minimum potential is likely to exist for Li-bonds (Szczesniak *et al* 1976). This aspect of Li-bonding has not been properly explored in the *ab initio* calculations reviewed herein.
5. In both H-bonds and Li-bonds, the formation of the complex leads to an elongation of the HX or LiX bonds and consequently a decrease in the stretching frequencies.
6. The $Y \dots X$ distance in the H-bond is invariably shorter (Emsley 1980) than the sum of the van der Waals radii of X and Y . In strong H-bonded systems (Sannigrahi and Peyerimhoff 1984, 1985) like FHF^- this shortening is about 0.5 Å. In the Li-bond the $Y \dots X$ distance is substantially longer than the sum of the van der Waals radii of X and Y . For example, in $\text{H}_3\text{N} \dots \text{LiF}$ and $\text{H}_3\text{N} \dots \text{LiCl}$ complexes (Latajka and Scheiner 1984) the $\text{N} \dots \text{F}$ and $\text{N} \dots \text{Cl}$ distances are 3.66 and 4.12 Å respectively (the corresponding sums of van der Waals radii are 2.95 and 3.30 Å). This difference in the X - Y distance in H-bonded and Li-bonded systems is attributed to the fact that Li^+ (in lithium hydride and halide molecules the net positive charge on Li is close to unity) with a lone pair of electrons cannot penetrate deeply into the charge cloud of the electron donor molecule, while a partially positively charged hydrogen atom can do so because of the smaller size of its charge cloud.
7. The formation of both H-bonds and Li-bonds is accompanied by an increase in dipole moment.
8. The effect of electron correlation is significant in the case of H-bonds (Latajka and Scheiner 1984) and negligible in the case of Li-bonds.
9. The bridging Li-atom gains electron density during complex formation while the bridging H atom loses electron density. As pointed out previously, this is however, not a general characteristic of Li-bonds.
10. Alkyl lithiums can form (Latajka *et al* 1977) Li-bonded complexes with ammonia and aliphatic amines. Similar complexes of alkanes with amines which may involve H-bonding are not known.

4. Concluding remarks

After the above characterisation of H-bonds and Li-bonds the question that naturally arises is: Can sodium also form similar bonds? Obviously, the large size of the charge cloud of Na^+ will be a major hindrance in the formation of a Na-bond. However, if the electrostatic, polarization and charge transfer interactions can overcome the exchange repulsion, then there will be a net stabilisation in energy upon complex formation. *Ab initio* calculations (Baskin *et al* 1973; Kulkarni and Rao 1983) have been reported on a few Na-bonded dimers. Baskin *et al* (1973) have found that $(\text{NaH})_2$, like $(\text{LiH})_2$, can exist in two forms-linear ($C_{\infty v}$) and cyclic (D_{2h}). The cyclic form is more stable than the linear one by about 14 kcal/mol. Moreover the dimerisation energy of $(\text{NaH})_2$ is less than that of $(\text{LiH})_2$ by about 10 kcal/mol (cyclic form) and 3 kcal/mol (linear form). The STO-3G calculations of Kulkarni and Rao (1983) on the $A \dots MX$ ($A = \text{NH}_3, \text{H}_2\text{O}, \text{CH}_3\text{OH}$; $M = \text{H}, \text{Li}, \text{Na}$ and $X = \text{F}, \text{Cl}$) complexes indicate that the strengths of the Na-bonds lie between that of H- and Li-bonds. These calculations (Baskin *et al* 1973; Kulkarni and Rao 1983) also indicate that properties like the changes in *mo* energies, increase in dipole moment, elongation of the electron acceptor (*MX*) bond length, charge shift etc., which are associated with Li-bonds, are exhibited by Na-bonds also. Because of higher dipole moments of NaX than LiX molecules the electrostatic interaction in Na-bonded complexes is expected to be stronger than in their Li-bonded counterparts. However, the exchange repulsion in the former outweighs this extra stability gained and as a result Na-bonds are weaker than Li-bonds.

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