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The Lithium Bond Reexamined

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Contents

1. Introduction

Is there a "lithium bond" counterpart to the hydrogen bonds that are so important in chemistry and biology? Hydrogen bonds are characterized by attractive interactions between molecules called "proton donors" and "proton acceptors" even though no formal transfer of hydrogen takes place. Proton donors contain hydrogens bound to more electronegative elements or groups, e.g., F, O, Cl, N, P, Se, Br, I, and, in some cases, even C (if electron-withdrawing substituents are present). Proton acceptors have lone pairs, π-bonds, or polarizable electrons and include a rather large number of elements and functional groups. The small size (covalent radius) of hydrogen permits it to interact with two electron-rich atoms or groups simultaneously. The great importance of hydrogen bonding is widely appreciated;[1,2] further documentation is not needed here.

However, hydrogen is not the only monovalent electropositive element that might participate in similar interactions. Lithium, the closest congener of hydrogen, has been considered;[3–6] it was first suggested as a possibility by Shigorin in 1959.[3] This suggestion did not gain immediate acceptance. For example, West[4] and Brown[5] preferred to emphasize the multicenter electron-deficient bonding character (e.g., as in $Al_2(CH_3)_6$ and $[Be(CH_3)_2]_x$). In 1961, West[4] saw "no reason for regarding the bonds in alkyllithium polymers as essentially different from other electron-deficient bonds or in designating them by a special name". Clusters with polycoordinated lithium atoms characterize lithium chemistry. Dicoordinated lithium arrangements are much rarer in practice. Theoreticians first considered such possibilities computationally. The 1970 paper by Kollman, Liebman, and Allen entitled "The Lithium Bond"[23] was influencial in delineating the analogy with hydrogen bonding. The designation "lithium bond" refers specifically to situations in which lithium is dicoordinated.

Li^+ is the smallest singly charged metal atom. Because lithium is more electropositive than hydrogen, LiY bonds are more ionic than the corresponding HY bonds. As a consequence, X···LiY interactions (where X represents a species with a region of high electron density) are expected to be stronger than the X···HY interactions. Nevertheless, lithium bonds with properties somewhat similar to those of H bonds are found in X···LiY donor–acceptor complexes, where Y is, e.g., a halogen atom. Ault and Pimentel[24a] were the first to provide experimental proof for the existence of Li bonds in X···Li–Y (X = NH_3, Me_3N, H_2O, Me_2O; Y = Cl, Br) complexes from a matrix isolation IR study. The frequency shifts of the Li–Y stretching bands in these complexes are qualitatively similar to those observed for the 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 Ault[24b] carried out matrix isolation IR spectroscopic studies of the 1:1 complexes of NH_3 and H_2O with a number of alkali-metal halides.

The pronounced tendency of Li compounds to form oligomers has long been known from colligative measurements, NMR investigations, and mass spectrometric observations.[7–12] The existence of appreciable concentrations of dimers of alkali-metal halides in the vapor phase has been demonstrated.[13–22] In such dimers, lithium interacts with two atoms. Hence, a "lithium bond"[23] is present.

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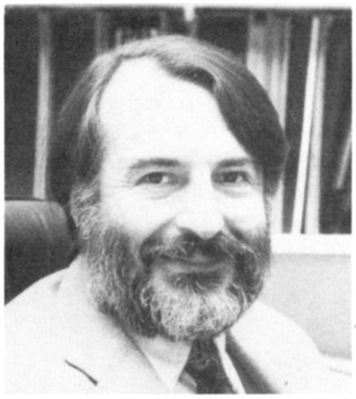

Paul von Ragué Schleyer was born on February 27, 1930, in Cleveland, OH. After education at Princeton University (A.B. 1951, magna cum laude) and at Harvard University (M.A. 1956, Ph.D. 1957), he joined the Chemistry Department of Princeton University in 1954 becoming Full Professor in 1965 and Eugene Higgins Professor of Chemistry in 1969. In 1976 Schleyer accepted his present position in Erlangen, West Germany, as Co-Director of the Organic Institute. His research contributions include the discovery of simple ways of synthesizing adamantane and other cage molecules by rearrangement, elucidation of solvolysis mechanisms, reactive intermediates, and a broad range of physical organic, organometallic, inorganic, and theoretical topics. The discovery of basically new molecular structures by computer, particularly those involving lithium, is one of his major achievements.

Despite the recognition of Li bonding as an important type of three-center interaction, relatively few experimental studies have been carried out to date on the Li-bonded complexes most closely related to the corresponding H-bonded complexes. One of the reasons is that the coordination sphere of lithium tends to be more complex. As shown most directly by many X-ray studies, lithium tends to engage in multicenter interactions with the substrate and donor solvent or ligands.[25] Thus, most of our current knowledge concerning the basic aspects of the Li bond is derived from theoretical work. Indeed, the systems examined here are not those most commonly encountered in chemical practice. Some investigators use the specific terms Li-bond or Li-bonded complexes, but most do not mention it. The structures, energies, and bonding of many organolithium compounds containing *dicoordinated* lithium atoms (on which we focus attention) are included in more general surveys.[26] We review here the results of ab initio studies on binary and higher complexes[23,27-69] containing at least one dicoordinated Li atom.

During writing of this review, a number of species was recalculated in Erlangen specifically in order to asses the basis set superposition error (BSSE) contribution. It has been demonstrated[1e,70b,92b,c] that BSSE can be corrected rigorously by using the Boys–Bernardi counterpoise method.[70a] The dimer BSSE we are discussing originates in the poor description of the subsystems. Streitwieser[70d,e] called attention to intramolecular BSSE within an isolated organolithium molecule. The electron-rich regions (e.g., the carbanion lone pair) try to improve their description by means of the atomic functions located at the electron-deficient lithium. The effect, which is particularly evident in minimal basis set calculations, also is manifested by unrealistic Mulliken populations.

On the basis of their structural features, the dicoordinate lithium complexes are classified into two categories, $(Li–Y)_2$ and X···Li–Y. In the latter, X may be a σ-bonded system containing atom A with lone-pair electrons or a π-bonded system. For convenience these two classes, as well as higher complexes, will be discussed separately. Finally, the nature of the Li bond, and the similarities and differences between Li bonds and H bonds, will be examined.

2. Structure and Energetics of Binary Complexes of the Type $(LiY)_2$

We consider here LiY dimers, where Y = H, Li, BeH, BH_2, CH_3, CN, NH_2, NF_2, OH, and F. Three additional complexes, $(Li_2NH)_2$, $(Li_3N)_2$, and $(CH_2LiF)_2$, also are included. Ab initio calculations on LiY dimers, where Y is a second-row substituent, are available in ref 69d. Only a few of the dimers with first-row substituents have been characterized experimentally.[13,71-83] In some cases, the parent dimers are not known but the structures of derivatives have been established by X-ray studies.[17,84-88] However, these X-ray structures mostly involve more complex coordination at lithium and afford only approximate comparisons. In the following subsection we shall discuss the structural features and energies of LiY dimers.

A. Results of SCF Calculations

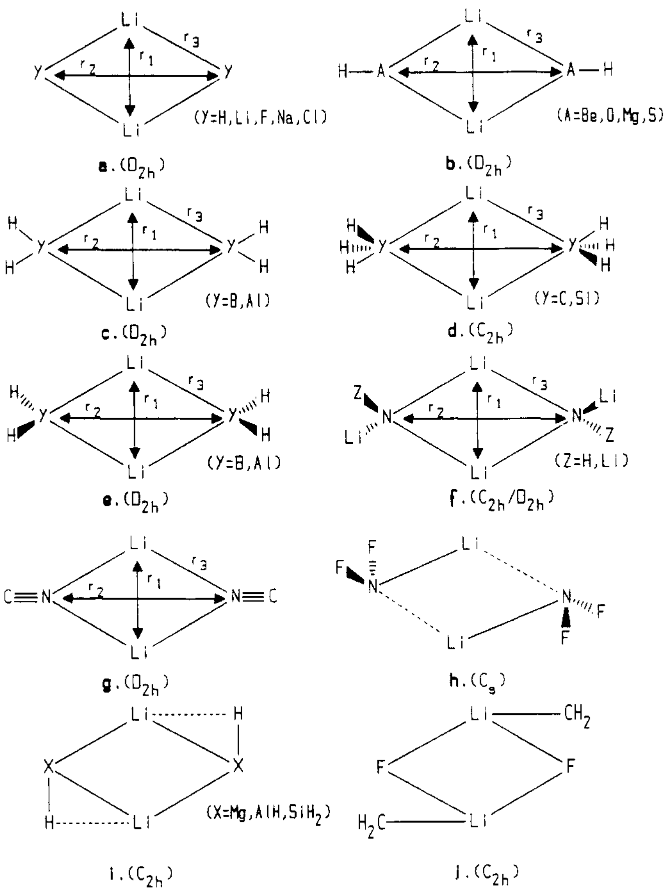

Figure 1. Most stable structures of the LiY dimers.

In order to deduce the most stable structure of LiY dimers with first-row substituents, various geometrical arrangements were explored. In $(LiH)_2$,[27,28,30,33] $(LiF)_2$,[23,28,46] $(LiCH_3)_2$,[67] $(LiCN)_2$,[54] and $(LiOH)_2$,[47] both cyclic and linear forms with bridging lithium atoms were considered. For the Li_2 dimer, besides the cyclic and T-form structures, various approaches of the two Li_2 molecules were investigated.[37] For the remaining dimers, only the most stable cyclic structures with bridging lithiums were examined, but for $(LiBH_2)_2$,[52] $(LiCH_3)_2$,[36,67] $(LiNH_2)_2$,[51,52] $(Li_2NH)_2$,[58] $(LiCN)_2$,[54] and $(LiNF_2)_2$[56] other geometries were included. Alternative cyclic structures with bridging hydrogen also were considered for $(LiNH_2)_2$ and $(Li_2NH)_2$.[58] The most stable structures of $(LiY)_2$ are displayed in Figure 1. D_{2h} symmetry is favored for all but the dimers of $LiCH_3$, Li_2NH, and $LiNF_2$ which belong to the C_{2h}, C_{2h}, and C_s point groups, respectively. In all the dimers, the two bridging lithiums and the two first-row atoms A (A = H, Li, Be, B, C, N, O, F) are coplanar, the intra- and intermolecular LiA distances are equal (the $LiNF_2$ dimer is an exception), and the LiLi distances are considerably shorter than the AA distances. Table I summarizes the SCF dimerization energies (DE = $E(LiY)_2 - 2E(LiY)$) and the geometries (the lengths of the extraring bonds are not given) for the structures displayed in Figure 1. The energies of some the less stable structures (not included in Table I) are discussed briefly in the text. The dimerization energy as defined above is a negative quantity. We have, however, used the absolute values while comparing DE of the molecules and discussing changes in DE caused by the variation of basis sets, geometries, etc.

The dimerization energy of LiH (cf. Table I) seems to be rather insensitive to the basis set. However, the correction for the basis set superposition error[70a] should be taken into account. For the 6-31G** geometry of the dimer the BSSE (with the subsystem geometry taken from the dimer) amounts to 11 kcal/mol for STO-3G but only about 1.0 kcal/mol for 3-21G, 4-31G, 6-31G*, and 6-31G** basis sets. Extension of the basis set (addition of polarization and of diffuse sp functions) affects DE only slightly. The most reliable DE's are 47.3 and 47.8 kcal/mol.[29] The contribution of zero-point energy (ZPE) to DE was estimated by Schleyer and Pople[63] at the 6-31G* level to be about 3.4 kcal/mol.

TABLE I. Ab Inito SCF Geometries (Å) and Dimerization Energies (DE, kcal/mol) of Different Complexes of the Type $(LiY)_2$

geometry[a]							
r_1	r_2	r_3	$r(m)$	Δr_3	$-DE$	basis set[b]	ref
Cyclic $(LiH)_2$ (Figure 1a)							
2.222	2.576	1.01	1.510	0.19	44.0	STO-3G	33
					46.8	6-31G*	
2.364	2.755	1.815	1.640	0.18	46.2	3-21G	52
2.386	2.745	1.819	1.638	0.18	45.1	4-31G	51
2.342	2.764	1.811	1.635	0.17	46.3	6-31G	63
2.335	2.760	1.807	1.630	0.18	46.2	6-31G**	
2.275	2.713	1.770	1.607	0.16	47.3	6-311G**	
					47.2	6-311++G**	
2.334	2.765	1.809			47.1	6-311G**//6-31++G**	
2.290	2.72	1.78	1.62	0.16	47.5	Li(7s1p/3s1p); H(5s1p/3s1p)	32
2.36	2.73	1.80	1.63	0.17	47.2	Li(9s3p/4s2p); H(5s2p/2s1p)	27
					44.6	4-31G	34
					47.4	Li(9s3p/4s3p); H(5s2p/4s2p)	27
2.277	2.706	1.768	1.605	0.16	46.9	Li,H(9s5p)	62
2.265	2.678	1.752	1.61	0.14	47.3	Li(9s2p1d/5s2p1d); H(6s2p1d/4s2p1d)	29
					+4.0	ZPE (6-31G*)	63
					52.6 ± 10	exptl	79
Rhombic $(Li_2)_2$ (Figure 1a)							
2.683	5.704	3.152	2.789	0.36	13.3	Li(4s1p)	37
2.699	5.440	3.036	2.732	0.30	9.3	Li(5s1p/4s1p), CEPA geometry	
					10.5	Li(8s2p/6s2p)	
2.686	5.728	3.164	2.816	0.35	12.4	3-21G	52
					11.7	6-21G	
2.694	5.750	3.175	2.812	0.36	12.0	6-31G*	
2.655	5.693	3.141	2.783	0.36	11.7	Li(9s5p)	62
					26.8	exptl	81
$(LiBeH)_2$ (Figure 1b)							
2.402	5.001	2.774	2.496	0.28	20.6	3-21G	52
					19.4	6-21G	
					19.7	6-31G*	
2.39	4.97	2.76			18.9	4-31G	
							51
Planar $(LiBH_2)_2$ (Figure 1c)							
2.325	4.255	2.424	2.261	0.16	36.9	3-21G	52
					35.3	6-21G	
					34.8	6-31G*	
2.292	4.182	2.385			34.5	4-31G	51
$(LiCH_3)_2$[c] (Figure 1d)							
2.088		2.110	2.009	0.10	40.0	STO-3G	36
		(2.143)		(0.13)			
2.174	3.710	2.143	2.001	0.14	46.3	3-21G	52
		(2.157)		(0.16)			
					45.1	6-21G	
					42.5	6-31G*	
					42.5	6-31G+6d(C)	67
					41.8	6-31G//6-31G	
2.164	3.683	2.136	1.990	0.15	42.6	4-31G	51
					+1.1	ZPE (3-21G)	67
Perpendicular $(LiNH_2)_2$ (Figure 1e)							
2.236	3.093	1.908	1.714	0.19	83.4	3-21G	52
					82.5	6-21G	
					72.3	6-31G*	
					67.2	3-21+G (diffuse functions on N only)	53
2.139	3.115	1.889	1.736	0.15	73.4	4-31G	51
2.28	3.14	1.94	1.74	0.20	72.5	6-31G	58
2.314	3.122	1.943	1.75	0.19	72.5	6-31G*	53
					65.1	6-31+G* (diffuse functions on N)	
2.255	3.135	1.931	1.759	0.17	66.5	3-21+G	
					+2.0	ZPE (3-21G)	53
$(Li_2NH)_2$ (Figure 1f)							
2.136	3.170	1.910	1.740	0.17	78.4	3-21G	56
					69.4	3-21+G (diffuse functions on N)	
2.157	3.191	1.924	1.750	0.17	72.2	6-31G	58
2.158	3.200	1.930	1.750	0.18	70.2	6-31G*	56
$(Li_3N)_2$ (Figure 1f)							
2.106	3.261	1.941	1.748	0.19	62.2	6-31G	58

TABLE I (Continued)

geometry[a]							
r_1	r_2	r_3	r(m)	Δr_3	−DE	basis set[b]	ref
					$(LiOH)_2$ (Figure 1b)		
2.184	2.685	1.730	1.537	0.19	82.5	3-21G	52
					81.9	6-21G	
					73.0	6-31G*	
2.21	2.75	1.76	1.577	0.18	74.1	4-31G	51
2.266	2.744	1.779	1.592	0.19	72.7	6-31G*	47
					65.5	6-31G*+sp on O	47
					+2.1	ZPE	47
					62.4 ± 12	exptl	75
					$(LiF)_2$ (Figure 1a)		
2.19	2.33	1.60	1.41	0.19	43.6	STO-3G	33
2.235	2.520	1.684	0.52	0.16	87.3	3-21G	52
					86.7	6-21G	
					71.4	6-31G*	
2.278	2.564	1.715	1.564	0.15	76.1	4-31G	51
2.23	2.56	1.70	1.54	0.16	86.4	DZ (7s3p/4s2p)	39
2.33	2.60	1.75	1.60	0.15	70.0	DZ (9s5p/4s2p)	
2.26	2.55	1.70	1.58	0.12	65.7	F(8s4p/4s2p)	
						Li(7s/3s) and diffuse p functions on both Li and F	32
2.22	2.65	1.73	1.56	0.17	66.7	F(9s5p2d/4s2p1d); Li(9s3p/4s2p)	28
					75.4	4-31G	
					66.7	DZ + polarized 3d	39
					67.1	TZ (10s6p/5s2p)	
					79.6	F(8s4p/4s2p)	
						Li(7s/3s) + diffuse p	32
					73.8	F(9s5p/5s3p)	
					69.3	F(8s4p/4s2p) + diffuse p	
					68.9	F(9s5p/5s3p) + diffuse p	
					68.0	F(8s4p/4s2p) + diffuse p + d	
2.157	3.191	1.924	1.750	0.17	72.2	6-31G	58
2.158	3.200	1.930	1.750	0.18	70.2	6-31G*	56
					$(Li_3N)_2$ (Figure 1f)		
2.106	3.261	1.941	1.748	0.19	62.2	6-31G	58
					67.6	F(9s5p/5s3p) + diffuse p + d	
					+3.2	ZPE	52
	2.765	1.764	1.564		61.4 + 8	exptl	76
	+0.02	+0.15					
					$(LiCN)_2$ (Figure 1g)		
2.40	3.022	1.93	1.765	0.17	49.0	6-31G + diffuse d functions on C and N (4-31G geometry)	54
					$(LiNF_2)_2$ (Figure 1h)		
$r(NLi_1) = 2.40 = r(LiLi)$					49.3	3-21G	56
$r(NLi_2) = 2.01$, $r(NF) = 1.52$							
$r(NF)(m) = 1.57$, $r(NLi)(m) = 2.32$							
					30.9	3-21G+G (diffuse functions on N and F)	56
					38.0	6-31G*	

[a] The geometrical parameters referred to in this table are defined in Figure 1. r(m) stands for the monomer LiA distance. [b] When the geometrical parameters are not tabulated against a given basis set, the calculations were carried out at the geometries optimized with the preceding basis set. A notation like A//B means that geometry was optimized with basis set B and other properties were calculated with basis set A. [c] The figures in parentheses denote the lengths of the two alternative CLi bonds in the ring.

Adding DE, BSSE, and ZPE and correcting to 298 K[63b] give 44.9 kcal/mol, a value within the experimental dimerization energy range (53 ± 10 kcal/mol[19]).

The HH and HLi bond lengths are less sensitive to the basis set than the LiLi distances. Inclusion of polarization functions in the hydrogen basis set (6-31G** vs 6-31G*) decreases all the bond lengths. Similar effects are observed when d orbitals are included on both Li and H or when the basis set is made more flexible (for instance, compare the 6-31G** and 6-311G** results). Although the individual bond lengths are basis set dependent, the elongation of the LiH bond upon dimerization is predicted to be about 0.17 Å by all basis sets.

Schleyer and Pople studied the potential surface of Li_2H_2 resulting from the reaction of H_2 and Li_2[63a] and from the approach of two LiH molecules.[63b] In both cases the global minimum on the $(LiH)_2$ potential surface corresponds to the D_{2h} structure (Figure 1a). However, the dimerization, $2LiH \rightarrow (LiH)_2$, is more exothermic by about 18 kcal/mol than the reaction, $Li_2 + H_2 \rightarrow (LiH)_2$. Only the latter process involves an activation barrier. The linear form of $(LiH)_2$ with alternating Li and H was found[27,28,33,34] to be about 22 kcal/mol less stable than the cyclic form.

In contrast to $(LiH)_2$, the dimerization energy of $(LiF)_2$ is sensitive to the nature of the basis set. However, the variation in geometry is not as pronounced. The experimental DE of $(LiF)_2$, 61.4 ± 8 kcal/mol[76] (other literature values are 60.4,[77] 58.9 ± 2.1, and 67.0 ± −4.1 kcal/mol[14,17,82]), corresponds to the cyclic structure with R(FF) = 2.765 ± 0.02 Å and r(LiF) = 1.764 ± 0.015 Å.[80] As can be seen from Table I, almost all basis sets overestimate the dimerization energy. The STO-3G value is an exception; however, this basis set is not at all suitable for this purpose. The DE data presented in Table I were not corrected for BSSE. In contrast to $(LiH)_2$, where this correction was rather small and uniform (except for STO-3G), BSSE is considerably larger for $(LiF)_2$. This is due to the need to describe fluorine with more flexible basis sets. Taking the 3-21G geometry of the dimer (with the subsystem geometry taken from the dimer), the 3-21G, 6-21G, and 6-31G* BSSE's are 26.9, 9.5, and 8.0 kcal/mol, respectively. The best theoretical estimate[28] of DE including ZPE (~3 kcal/mol) is 63.5 kcal/mol. Adjusting for the BSSE of about 8 kcal/mol gives 55.5 kcal/mol. After correcting for vibration and rotation contributions, the calculated ΔH at 1127 K becomes 54.8 kcal/mol, i.e., within the error limits of the experimental values.[76] The correlation effect decreases slightly (see later text) the ΔH value. As with $(LiH)_2$, extension of the basis set should lead to closer agreement with the experimental data. Table I shows that almost all the basis sets underestimate the bond lengths, especially the FF distance. The best theoretical calculation[28] underestimates the FF distance by about 0.1 Å. Unlike the individual geometrical parameters, the elongation of the LiF bond is rather insensitive to the basis set; the average is 0.16 Å. Using a fixed geometry,[28] Rupp and Ahlrichs[32] studied the effect of basis set on the dimerization energy of $(LiF)_2$ and concluded that diffuse p orbitals on fluorine are more important than polarization functions. According to various calculations,[23,28,34,46] the linear dimer of LiF is about 30.0 kcal/mol less stable than the cyclic dimer.

The rhomboid (D_{2h}) structure of the Li_2 dimer was optimized with use of 4s1p, 3-21G, and 9s5p basis sets (the CEPA (5s1p/3s1p) results will be discussed below). The three geometries resulting are virtually the same. The monomer LiLi bond length is elongated by about 0.36 Å in the outer bonds of the dimer. This is the maximum elongation observed for LiA bonds in the present series. Note that one of the diagonal LiLi distances is almost twice as long as the other. Additional calculations on the 3-21G geometry, at 6-21G and 6-31G*,[52] showed the $(Li_2)_2$ dimerization energy to be rather insensitive to the basis set. The same is true of the BSSE, ca. 1.1 kcal/mol for the 3-21G and 0.8 kcal/mol for the 6-21G and 6-31G* basis sets (3-21G geometry). As discussed below, the correlation effect is more important for Li_4 than for other Li-containing complexes. The best estimate of DE(corr) from Table II is 4.2 kcal/mol (corrected for BSSE). The ZPE for Li_4 is only 1.8 kcal/mol. When the DE(corr) and ZPE are added to the best estimate of DE from Table I (about 11 kcal/mol after correction for BSSE), the estimated stabilization energy is about 14 kcal/mol. Very similar results are given by MRD-CI and CEPA calculations.[37] The MP4/6-311G*//6-31G* DE is 16 kcal/mol after BSSE and ZPE corrections. These values are far from the experimental estimate (26.8 kcal/mol[81]). This is the worst agreement between theory and experiment among all the $(LiY)_2$ dimers. While accuracy of the experimental data might be questioned, the discrepancy may result from the different nature of the stabilization in the Li_4 complex. Whereas for polar Li complexes the dominant stabilization comes from dipole–dipole interaction (included in the SCF interaction energy), for the $(Li_2)_2$ dimer stabilization originates from polarization (the MP4/6-311G* charges are +0.23 in the inner and −0.23 on the outer Li's) and the correlation effect. However, these contributions are not given fully even at this level. Diffuse d and f polarization functions may be needed for agreement with experiment. The only other bound state predicted[37] for the Li_2 dimer has a T-shape and lies about 6–7 kcal/mol above the global minimum.

TABLE II. Correlation Contribution to Dimerization Energies (DE(corr), kcal/mol) of Different Complexes of the Type $(LiY)_2$

basis set[a]	level of electron correln	DE(corr)	ref
	$(LiH)_2$		
6-31G**//6-31G**	MP2	−1.5	63
	MP3	−1.7	
	MP4	−1.8	
6-311G**//6-31+G**	MP2	−1.9	63
	MP3	−2.1	
	MP4	−2.0	
6-31++G**//6-311G**	MP2	−2.0	63
	MP3	−2.2	
	MP4	−2.1	
Li(9s3p/4s2p); H(5s2p/2s1p)	CI	+0.4	27
Li(9s2p1d/5s2p1d); H(6s2p1d/4s2p1d)	CEPA	−1.0	29
	$(Li_2)_2$		
Li(5s1p/4s1p)	CEPA	−6.9	37
Li(8s2p/6s2p)//Li(5s1p/4s1p)	CEPA	−4.9	
6-21G//3-21G	MP2	−3.6	52
6-31G*//3-21G	MP2	−4.8	
6-31G*//6-31G*	MP2	−5.2	this work
	MP3	−6.1	
	MP4	−5.1	
	$(LiBeH)_2$		
6-21G//3-21G	MP2	−1.9	52
6-31G*//3-21G	MP2	−2.5	
	Planar $(LiBH_2)_2$		
6-21//3-21G	MP2	+1.2	52
	$(LiCH_3)_2$		
6-21G//3-21G	MP2	0.0	52
6-31G//6-31G	MP2	+0.8	67
6-31G*//3-21G	MP2	−2.9	
	$(LiNH_2)_2$		
6-21G//3-21G	MP2	+0.6	52
	$(LiOH)_2$		
6-21G//3-21G	MP2	+4.1	52
6-31G** + sp//6-31G	MP2	+1.7	47
	MP3	+2.3	
	$(LiF)_2$		
6-21G//3-21G	MP2	+2.8	52
F(9s6p2d/5s4p2d); Li(7s1p/3s1p)	CEPA	+0.9	32

[a] For notation, see Table I.

The entire $(LiY)_2$ series, where Y is a first-row hydride, was studied by Schleyer and co-workers[26a,52] using 3-21G, 6-21G, and 6-31G* basis sets on the 3-21G geometries and by Hodoseck and Solmajer[51] using the standard 4-31G basis set (this implies the use of the 5-21G basis on Li and Be). There is no appreciable difference between the 3-21G and 4-31G optimized geometries (Table I). Both the basis sets predict a decrease in the AA (A = Be, B, C, N, O, F) and LiA distances and in the r_2/r_1 ratio (Figure 1) with increasing electronegativity of A. The LiLi distance decreases in going from Be to C but then increases from N to F. While the 3-21G LiC distances in $(LiCH_3)_2$ are calculated to be slightly different (by ~0.01 Å), they are assumed to be equal in Figure 1. In $(LiCH_3)_2$, the rotation of the methyl group with respect to the Li_2C_2 ring is nearly free.[36,37] The elongation of the LiBe bond (0.27 Å) is considerably larger than that of the corresponding LiA bonds in the other dimers (average value 0.17 Å). The dimerization energies of $(LiBeH)_2$, $(LiBH_2)_2$, and $(LiCH_3)_2$ vary within 2–3 kcal/mol with the basis sets and increase from Be to C. The BSSE for these complexes is rather small (~1 kcal/mol) and almost uniform for different basis sets. The $(LiNH_2)_2$, $(LiOH)_2$, and $(LiF)_2$ complexes are more sensitive to the quality of the basis set. The 3-21G BSSE is large (20–30 kcal/mol); its value decreases to 6–8 kcal/mol when polarization functions are included (6-31G* basis set). According to the 6-31G*//3-21G calculations, all three dimers $(LiNH_2)_2$, $(LiOH)_2$, and $(LiF)_2$ were predicted to have essentially the same DE value. Schleyer and co-workers[26a,52] and Hodoseck and Solmajer[51] considered both planar and perpendicular structures for $(LiBH_2)_2$ and $(LiNH_2)_2$. The stability of $(LiBH_2)_2$ is quite insensitive to basis sets in both the forms.[52b] The planar structure was found to be more stable than the perpendicular geometry by about 10 kcal/mol. However, the H-bridged form was found[52b] to be even more stable by about 5 kcal/mol (MP2/6-31G*//6-31G*, ZPE included). In contrast, the dimerization energy to give the perpendicular $(LiNH_2)_2$, unlike that to give the planar form, is highly basis set dependent. According to the calculations[53] with most extensive basis set, the perpendicular structure is predicted to be about 22 kcal/mol more stable than the planar arrangement.

Calculations on $(LiNH_2)_2$ (perpendicular) show the LiN and LiLi distances to increase with basis set extension (3-21G, 3-21+G, 6-31G, 6-31G*). The NN distance changes irregularly. As with the other dimers, the LiA (here A = N) distance is virtually independent of the basis set. X-ray studies[85–88] on complexed derivatives of $(LiNH_2)_2$ show the NLi distances to vary from 1.98 to 2.01 Å, and the LiNLi and NLiN angles lie within the 103–105° and the 75–77° ranges, respectively. The corresponding theoretical bond angles (not tabulated) vary from 107 to 108.5° and 71.5 to 73°, respectively, with the basis sets. The deviation of the theoretical bond length from experiment is only ~0.05 Å, and this can be attributed to the additional ligand coordination. According to the calculations[53] using the most extensive basis set, 6-31+G* (diffuse sp heavy atom functions), the dimerization energy of $(LiNH_2)_2$ is 65.1 - 2.0(ZPE) = 63.1 kcal/mol. Almost the same value of DE is obtained by 3-21+G (diffuse sp functions on first-row atoms) basis set. When the DE values are compared with those obtained from other basis sets, it appears that diffuse as well as polarization functions are needed for the adequate description of $(LiNH_2)_2$. Unfortunately, no experimental data are available to assess the accuracy of the theoretical DE values.

The results on $(LiOH)_2$ (Table I) show the bond lengths to increase while going from the 3-21G through the 4-31G to the 6-31G* basis set (the 4-31G and 6-31G* OO distances are virtually identical). As usual, the LiO distance is practically basis set independent. The BSSE for $(LiOH)_2$ is slightly smaller than for $(LiF)_2$. For 3-21G geometry of the dimer (with subsystem geometry taken from the dimer) the 3-21G, 6-21G, and 6-31G* BSSE's are 19.8, 18.6, and 6.3 kcal/mol, respectively. After correcting for BSSE, very similar DE's result. Taking the best estimate (65.5 kcal/mol) for $(LiOH)_2$ and correcting it for the BSSE (~6.0 kcal/mol) and ZPE (~2.0 kcal/mol) gives 57.5 kcal/mol, which agrees well with the experimental values (62.4 ± 12 kcal/mol,[76] 60 kcal/mol[70]). It is necessary to add that correlation effects are not important for the present complex (similarly as for other polar Li complexes). Raghavachari[47] studied the potential energy surface for H_2O with Li_2O at 3-21G and found that the reaction proceeds without any activation energy to give the cyclic dimer (D_{2h}) of LiOH (Figure 1b). At the Hartree–Fock level (6-31G** + sp on oxygen) the exoergicities of the reactions $H_2O + Li_2O \rightarrow (LiOH)_2$ and $2LiOH \rightarrow (LiOH)_2$ were found to be 88.1 and 65.5 kcal/mol, respectively.

The effect of successive replacement of H by Li in $LiNH_2$ on the structures and energies of the corresponding dimers was studied by Armstrong et al.[58] at 6-31G. The dimerization energy gradually decreases on going from $(LiNH_2)_2$ to $(Li_3N)_2$. The LiLi distance in the dimers decreases from 2.28 to 2.11 Å, and the NN distance increases from 3.14 Å to 3.26 Å. The effect of successive replacement of H by Li has virtually no effect on the NLi distances in the dimer ring. These bonds are all elongated by about 0.2 Å, relative to the monomer values. The extraring N–Li bonds increase negligibly upon dimerization.

$(LiCN)_2$ isomers were examined by Marsden,[54] who optimized the geometry of several Li-bridged cyclic (both 4- and 6-membered) and linear structures using the 4-31G basis set. For two 6-membered and one 4-membered (Figure 1g) cyclic structures, modified 6-31+G* (i.e., no d functions on Li, diffuse p functions on C and N) single-point calculations were made. Other structures were found to be much less stable compared to the three cyclic structures. With respect to two LiNC molecules, the D_{2h} (Figure 1g) and C_{2h} (two NC bonds joined by angular C···Li···N and N···Li···C fragments) dimers were bound by 49.0 and 44.7 kcal/mol, respectively. The C_{2v} (two NC bonds joined by angular N···Li···N and C···Li···C fragments) structure was 44.4 and 50.9 kcal/mol more stable than two LiNC monomers or LiCN and LiNC, respectively. At this level the LiNC monomer was about 6.5 kcal/mol more stable than LiCN. However, MP4/6-311+G* calculations[89] indicate LiNC and the bridged form to have nearly the same energy and LiCN to be about 2 kcal/mol less stable. The potential energy surface was reinvestigated[89a] with (DZ+P) basis set and MP2 optimization and frequency analysis. LiNC, LiCN, and the bridged form are all energy minima; these minima are separated by two saddle points. The bridged form is more stable than LiCN and LiNC by about 1.3 and 1.4 kcal/mol. The intramolecular basis set superposition error as well as higher correlation energy contribution are important.

Marsden's[54] conclusions were based on SCF calculations (i.e., without correlation, BSSE, and ZPE corrections); hence, it is not definite which of the three structures corresponds to the most stable dimer of LiCN.

The 3-21G-optimized geometry of $(LiNF_2)_2$[56] was employed for single-point 3-21+G and 6-31G* calculations. The most stable structure (Figure 1h) is predicted to have nonequivalent LiN bonds. Compared to the bond length in the monomer, one LiN distance in the dimer is shortened by ~0.3 Å and the other is elongated by ~0.1 Å. The dimerization energy decreases by about 11 kcal/mol when polarization functions on N and F are present (6-31G*). Inclusion of diffuse sp functions (3-21+G) on these atoms has a still more drastic effect, and the DE decreases by about 18 kcal/mol. Calculations at 6-31+G* would be desirable, but these have not yet been carried out.

A preliminary study of the $(LiY)_2$ dimers with second-row elements (Y = Na, MgH, AlH_2, SiH_3, PH_2, SH, Cl) has been carried out at the 3-21G level;[69d] the structures investigated were similar to those of corresponding dimers with the first-row elements (cf. Figure 1). The DE's, as expected, are smaller for complexes containing the second-row elements due to their lower electronegativity and larger size. For the dimers in D_{2h} symmetry, the DE's (kcal/mol) are as follows: $(LiNa)_2$, 11.1; $(LiMgH)_2$, 3.1; $(LiAlH_2)_2$, 18.3; $(LiSiH_3)_2$, 28.6 (C_{2h}); $(LiPH_2)_2$, 58.8; $(LiSH)_2$, 55.6; $(LiCl)_2$, 54.8. However, these structures may not be the most stable ones. For the $(LiY)_2$ dimers (Y = MgH, AlH_2, SiH_3), H-bridged forms (Figure 1i) appear to be lower in energy, apparently because of interactions between lithium and negatively charged hydrogens. For $(LiSH)_2$, DE = 58.2 kcal/mol for a perpendicular, C_{2h} dimer. Additional studies with larger basis sets are needed.

The CH_2LiF dimer was optimized[69a] at the 3-21G with a C_{2h} symmetry constraint (Figure 1j). The dimerization energy (56.2 kcal/mol) is between the values calculated for LiF and for CH_3Li at the same level. The geometry of the CH_2LiF unit in the dimer differs only slightly from that in the monomer.[69b] Dimerization facilitates the fragmentation of singlet methylene considerably. This models the "methylene transfer" process[69c] observed experimentally for carbenoids.

B. Results of Calculations Using Correlated Wave Functions

The effect of electron correlation on the dimerization energy of a number of LiY dimers was ascertained using Møller–Plesset (MP) perturbation,[90a] direct configuration interaction (CI),[91] and coupled electron pair approximation (CEPA)[92a] theory. With the exception of the Li_2 dimer, all these calculations were performed at the SCF geometries (given in Table I). Using a 5s1p/4s1p basis set, Beckmann et al.[37] obtained the following geometrical parameters for Li_4 at the SCF/CEPA levels (cf. Figure 1): r_1 = 2.707/2.699 Å, r_2 = 5.732/5.44 Å, r_3 = 3.170/3.036 Å. These values indicate that electron correlation reduces r_2 and r_3 by about 0.3 and 0.1 Å, respectively.

The data in Table II show that the contributions of correlation energy to DE for the LiY dimers (Y = H, Li, BeH, BH_2, CH_3, NH_2, OH, F) are small or negligible with the exception of $(Li_2)_2$. The correlation contributions to DE are even positive for some complexes. These values are not corrected for BSSE. After correction is made for BSSE, even more positive values will result.[70c,92b–d] The MP2/6-31G*//3-21G BSSE's for $(Li_2)_2$, $(LiBeH)_2$, $(LiOH)_2$, and $(LiF)_2$ are 0.6, 1.3, 6.3, and 4.8 kcal/mol, respectively. The MP2, MP3, and MP4 BSSE's of $(LiH)_2$ at 6-31G**//6-31G** are 3.2, 3.8, and 4.0 kcal/mol, respectively.

The correlation correction, DE(corr), to the dimerization energies, corrected for the BSSE values, are destabilizing for all the complexes (except $(Li_2)_2$). The explanation is simple. There are two major correlation contributions to the interaction energy: the intersystem correlation energy and the change in the intrasystem correlation energy during dimerization. The first contribution is always negative (stabilizing) and corresponds to the dispersion energy. But the second contribution may be positive or negative, as the leading component is the change of the electrostatic energy due to correlation. If the dipole–dipole interaction is attractive (as it is with all the complexes investigated), and if the subsystem dipole moment is reduced in passing from HF to post-HF, then effect of correlation on the electrostatic energy will be repulsive.[92d] The decrease of dipole moments of Li systems due to correlation is rather uniform; hence, we can expect destabilizing intrasystem correlation energy contributions for $(LiY)_2$ complexes. As a consequence, a small negative or even positive total correlation interaction energy contribution results. The only exception is $(Li_2)_2$, where correlation contribution to DE is determined almost exclusively by the negative intersystem correlation energy.

3. Binary X···LiY Complexes

The binary X···LiY complexes have not been studied as thoroughly as the LiY dimers. The binary complexes with the general formula X···Li–Y (X = NH_3, H_2O and Y = H, Li, BeH, BH_2, CH_3, NH_2, OH, F, Cl; X = CH_3OH and Y = F, Cl; X = $MeNH_2$, Me_2NH, and Y = Cl, X = HF and Y = LiH and LiF) are considered in this section. A few more systems, namely, C_2H_2···LiH and C_2H_4···LiY (Y = H, F), also are included. The LiY dipoles can interact with lone-pair electrons of the first-row atoms (N, O, F) or with the π-electron clouds of C_2H_2 and C_2H_4. Similar types of interaction are well-known for H-bonded complexes.[1,2] One may refer to the complexes with lone-pair donors like NH_3, H_2O, etc., as σ Li-bonded and those with π-bond donors like C_2H_2 and C_2H_4 as π Li-bonded systems. Although a number of σ Li-bonded complexes have been characterized experimentally (mostly by X-ray[83]), their stabilization energies are not known. The geometries and the complexation energies of σ and of π Li-bonded complexes predicted by SCF calculations are summarized in Table III and in Figure 2. The geometrical parameters, other than those involved in the three-center interaction, B···Li–A (B = N, O, F; A = H, Li, Be, B, C, N, O, F, Cl), are excluded from the table. For some of the complexes, more than one structural arrangement was considered. In such cases, only those results are tabulated that correspond to the most stable structure obtained when the most extensive basis set is used.

Most of the σ Li-bonded complexes have open structures with linear Li–X bonds (Figure 2). Structures with bent Li bonds were investigated for H_3N···$LiNH_2$/LiOH/LiF,[65] MeH_2N/Me_2HN···LiCl,[57] H_2O···Li_2/LiH/$LiNH_2$/LiOH/LiF,[33,65] and HF···LiH/LiF[33,23] complexes.

Of these complexes, only H_2O···LiOH and H_2O···LiF are predicted[65a] to have cyclic structures. With H_2O···LiOH, HF theory favors the cyclic structure: however,

TABLE III. Ab Initio SCF Geometries (Å) and Complexation Energies (CE, kcal/mol) of Different Complexes of the Type X···Li–Y

system (Figure 2)	geometry[a]					
	R	*r*	Δ*r*	CE	basis set[b]	ref
$H_3N\cdots LiH$ (a)	1.944	1.514	0.004	49.7	STO-3G	33
				25.4	6-31G*	
	1.999	1.672	0.03	35.6	3-21G	65
	2.059	1.664	0.02	25.8	6-31G*	
				23.5	6-31+G*	
				+2.9	ZPE (3-21G)	
	2.05			23.0	DZ	38
				23.3	DZ+P	
$H_3N\cdots Li_2$ (a)	1.983	2.886	0.07	31.9	3-21G	65
	2.056	2.875		20.3	6-31G*	
				18.6	6-31+G*	
				+2.6	ZPE (3-21G)	
$H_3N\cdots LiBeH$ (b)	1.995	2.541	0.045	33.8	3-21G	65
	2.067	2.509		23.5	6-31G*	
				21.2	6-31+G*	
				+2.5	ZPE (3-21G)	
$H_3N\cdots LiBH_2$ (c)	2.003	2.295	0.034	33.9	3-21G	65
	2.077	2.261		23.9	6-31G*	
				21.8	6-31+G*	
				+2.4	ZPE (3-21G)	
$H_3N\cdots LiCH_3$ (d)	2.012	2.031	0.03	33.4	3-21G	65
	2.090	2.026		24.1	6-31G*	
	2.076	2.026		22.1	6-31+G*	
				+2.3	ZPE (3-21G)	
$H_3N\cdots LiNH_2$ (e)	2.010	1.742	0.028	32.2	3-21G	65
	2.085	1.776		23.6	6-31G*	
	2.083	1.777		21.6	6-31+G*	
				+2.3	ZPE (3-21G)	
$H_3N\cdots LiOH$ (b)	2.003	1.559	0.023	31.8	3-21G	65
	2.087	1.615		23.4	6-31G*	
				21.7	6-31+G*	
				+2.0	ZPE (3-21G)	
$H_3N\cdots LiF$ (a)	1.951	1.420	0.013	47.5	STO-3G	49
	1.955	1.540	0.02	34.5	3-21G	65
	2.089	1.576	0.02	24.8	6-31G*	
				23.3	6-31+G*	
	2.085	1.576	0.02	24.4	6-31G**	64
	2.101	1.587	0.02	24.4	6-31G**//MP2/4-31G**	66
	2.070	1.582	0.018	22.9	LiF, 6-31G*(2d); NH_3, 6-31G** (1p; 2d)–DZ + 2P	55
	2.073	1.592	0.014	23.5	DZ+2P//MP2/DZ+2P	
	2.02	1.603	0.02	28.7	N and F (10s5p) Li(10s) and H(5s) (DZ quality)	31
				+2.2	ZPE (3-21G)	65
$H_3N\cdots LiCl$	1.936	1.955	0.022	54.3	STO-3G	49
	2.008	2.104	0.03	35.8	4-31G	57
				+3.0	BSSE	
	2.036	2.802	0.015	25.5	LiCl, 6-31G*(2d); NH_3, 6-31G** (1p2d)-DZ+2P	55
$MeNH_2\cdots LiCl$ (f)	2.018	2.101	0.03	32.7	4-31G	57
				+3.3	BSSE	
$Me_2NH\cdots LiCl$ (g)	2.004	2.102	0.03	32.7	4-31G	57
				+3.8	BSSE	
$H_2O\cdots LiH$ (h)	1.765	1.513	0.003	53.3	STO-3G[c]	33
				21.8	6-31G*	
	1.823	1.671	0.03	36.8	6-21G	65
	1.916	1.657		22.6	6-31G*	
	1.923	1.654		20.2	6-31+G*	
				+2.4	ZPE (3-21G)	
$H_2O\cdots Li_2$ (h)	1.808	2.869	0.05	33.5	3-21G	65
	1.919	2.859		17.4	6-31G*	
				15.4	6-31+G*	
				+2.0	ZPE (3-21G)	
$H_2O\cdots LiBeH$ (i)	1.818	2.531	0.04	35.7	3-21G	65
	1.926	2.501		20.5	6-31G*	
				+2.0	ZPE (3-21G)	
$H_2O\cdots LiBH_2$ (j)	1.825	2.288	0.03	35.8	3-21G	65
	1.932	2.254		21.0	6-31G*	
				18.7	6-31+G*	
				+1.9	ZPE (3-21G)	
$H_2O\cdots LiCH_3$ (k)	1.836	2.027	0.03	35.0	3-21G	65
	1.945	2.021		21.0	6-31G*	
	1.949	2.020		19.0	6-31+G*	
				+1.8	ZPE (3-21G)	

TABLE III (Continued)

system (Figure 2)	geometry[a] *R*	*r*	Δ*r*	CE	basis set[b]	ref
$H_2O\cdots LiNH_2$ (l)	1.838	1.740	0.03	33.7	3-21G	65
	1.941	1.771		20.7	6-31G*	
				18.7	6-31+G*	
				+1.9	ZPE (3-21G)	
$H_2O\cdots LiOH$ (m)	1.826	1.672	0.14	36.1	3-21G	65
	1.951	1.679		23.2	6-31G*	
				19.9	6-31+G*	
	1.947	1.675		20.2	6-31+G*	
				+2.1	ZPE (3-21G)	
$H_2O\cdots LiF$ (h)	1.825	1.540	0.02	38.1	3-21G	65
	1.954	1.574		22.6	6-31G*	
				19.6	6-31+G*	
	1.954	1.594		20.0	6-31+G*	
				+2.5	ZPE (3-21G)	
	1.774	1.423	0.02	48.3	STO-3G[c]	49
$H_2O\cdots LiCl$ (h)	1.774	1.954	0.02	55.2	STO-3G	49
	1.859	2.909	0.02	31.3	4-31G	57
				+3.4	BSSE	
$CH_3OH\cdots LiF$ (n)	1.795	1.419	0.01	46.1	STO-3G	49
$CH_3OH\cdots LiCl$ (n)	1.776	1.951	0.01	52.1	STO-3G	49
$HF\cdots LiH$ (o)	1.627	1.512	0.002	49.8	STO-3G	33
				13.4	6-31G*	
$HF\cdots LiF$ (p)	1.895	1.672	0.005	13.5	F(10s5p/3s1p); Li(10s/3s); H(5s/1s)	23
	1.985	1.592	0.004	16.2	F(10s5p/3s1p); Li(10s1p/3s1p); H(5s/1s)	
$C_2H_2\cdots LiH$ (q)	2.45			8.14	DZ	38
				8.93	DZ+P	
	2.421	1.646	0.006	11.7	3-21G	60
	2.471	1.647	0.004	11.0	6-31G*	
$C_2H_4\cdots LiH$ (r)	2.436	1.648	0.008	12.9	3-21G	60
	2.50			8.7	DZ	38
$C_2H_4\cdots LiF$ (r)	2.48	1.605		8.8	F(10s5p); Li(10s1p); C(9s5p); H(4s)	35a

[a] The geometrical parameters referred to in this table are defined in Figure 2. [b] For notation, see Table I. [c] The geometrical parameters correspond to a bent structure, not given in Figure 2.

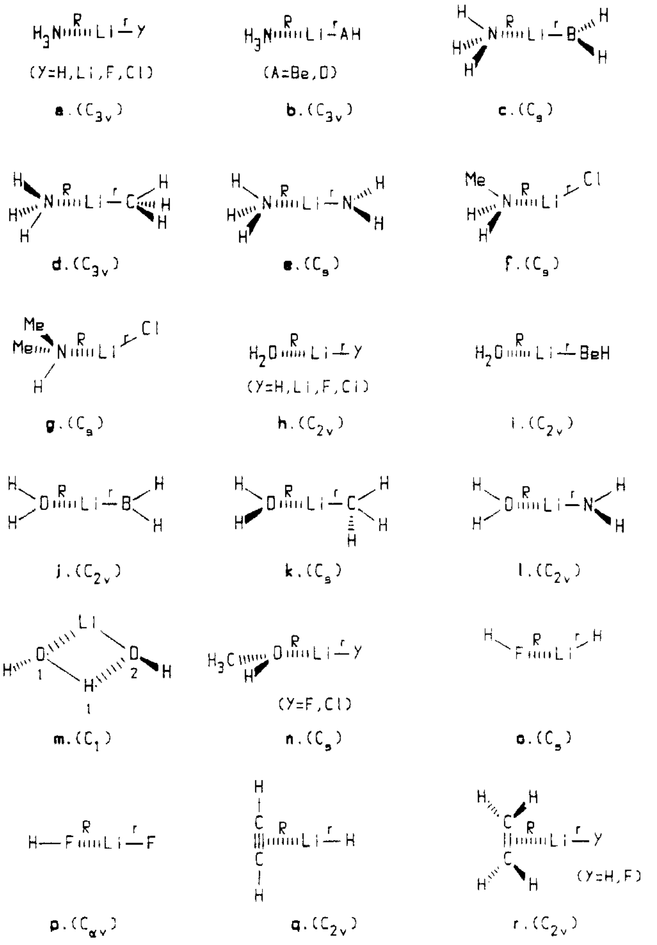

Figure 2. Most stable structures of teh X···Li–Y complexes.

the linear and cyclic structures are predicted at MP2/6-31+G*//6-31+G* to be comparably stable. The cyclic structure is exceptional and has no precedent among binary H-bonded complexes (with exception of $(NH_3)_2$[65d]). However, the effect of counterpoise correction is especially important for comparison of two structures of a complex. The possibility of mutual "borrowing" of the AO is larger for cyclic structures. Thus, the 3-21G BSSE of the cyclic (C_s) form of $H_2O\cdots LiF$ is much larger than that of the linear (C_{2v}) structures. The uncorrected 3-21G stabilization energy prefers the cyclic structure of $H_2O\cdots LiF$ by 3 kcal/mol, but if BSSE is taken into account, the linear structure becomes more stable (by about 5 kcal/mol). Surprisingly, the opposite is true at higher levels. At the MP2/6-31+G*//6-31+G* + BSSE + ZPE level the cyclic structure becomes more stable by about 1 kcal/mol (−16.3 and −15.2 kcal/mol). Both structures were found at 6-31+G*//6-31+G* to be minima. Inclusion of higher level of correlation (MP4) with a larger basis set (6-31++G(2df,2pd)) favors the C_1 structure over the C_{2v} by about 1.5 kcal/mol. ΔG^{298}(association) values for the C_1 and C_{2v} structures of $H_2O\cdots LiF$ are −10 and −9.5 kcal/mol, respectively.[65c] The difference is small, and both forms should be found in the gas phase. The behavior of the $H_2O\cdots LiOH$ complex is similar, but the cyclic structure is preferred by a larger amount, about 3 kcal/mol (17.2 vs 13.9 kcal/mol), over the linear form. Therefore, the cyclic structure should be preferred in the gas phase. A cyclic form also has been described for the $H_2O\cdots LiNH_2$ complex at lower theoretical levels, but it should rearrange to the more stable $HOLi\cdots NH_3$ without a barrier.[65b]

The structures for $MeNH_2\cdots LiCl$ and $Me_2NH\cdots LiCl$ (Figure 2f,g)[57] as well as the $H_2O\cdots LiH$ and $HF\cdots LiH$[33] were optimized by the 4-31G and STO-3G basis sets, respectively (4-31G is not defined for lithium; instead, the 5-21G basis set is standard). However, a linear C_{2v} structure is predicted[65a] for $H_2O\cdots LiH$ and for $H_2O\cdots Li_2$ (Figure 2h) at higher levels (6-31G*). Thus, further calculations using extended basis sets and taking the BSSE into account are needed in order to verify whether or not the bent structures are artifacts of the smaller basis sets. The bent structures of $H_3N\cdots LiOH$ and $H_3N\cdots LiF$, predicted[65a] by 3-21G, also do not persist at 6-31G*. The $H_3N\cdots LiNH_2$ complex is bent more at 3-21G (∠NLiN = 156.3°) than at 6-31G* (168.8°) and is essentially linear at 6-31+G*.[65a] The C_s (bent Li bond) and planar C_{2v} forms were almost as stable as the perpendicular C_{2v} $H_2O\cdots LiNH_2$ arrangement (Figure 2).[65a] For $H_2O\cdots Li_2$, the bent C_s and the linear C_{2v} structures (Figure 2h) have virtually the same energy. In general, the differences in stability of various alternative structures of these complexes are so small (~1.0 kcal/mol) at 6-31+G*//6-31G* that it is not possible to predict with certainty which is the most stable.

All the LiA bonds of the electron acceptor are elongated slightly (with respect to the monomer bond length) upon complexation (Table III). However, the changes are smaller than those in the LiY dimers (Table I) and, in general, range from 0.002 to 0.07 Å. In most of the ammonia and water complexes, geometry optimizations were carried out[65a] with use of the 3-21G and the 6-31G* basis sets. Compared to 6-31G*, 3-21G overestimates the LiA bond lengths in the Li_2, LiBeH, $LiBH_2$, and $LiCH_3$ complexes and underestimates them in the $LiNH_2$, LiOH, and LiF complexes. The intermolecular distances are always too short at 3-21G by about 0.11 and 0.08 Å in the water and the ammonia complexes, respectively. However, with a given basis set the Li···N and Li···O distances are remarkably constant in the whole series of complexes with the same electron donor (NH_3, H_2O, CH_3OH). Due to BSSE, both the B···Li and the Li–A STO-3G bond lengths are much too short.[49] STO-3G[33,49] also predicts C_s structures for the $H_2O\cdots LiH$, $H_2O\cdots LiF$, and $H_2O\cdots LiCl$ complexes, in contradiction to the (C_{2v}) preferences[57] at 6-31G*[65a] for $H_2O\cdots LiH$ and $H_2O\cdots LiF$ and at 4-31G for $H_2O\cdots LiCl$.

The cyclic structure of the $H_2O\cdots LiOH$ complex (Figure 2m) is exceptional. The ring O_1H_1 and O_2H_1 bonds are elongated while the extraring bonds are virtually unaffected due to complex formation. When the basis set is extended from 3-21G through 6-31G* to 6-31+G*, the O_1H_1 bond length gradually decreases and tends to attain the monomer value. Concomitantly, the O_2H_1 bond length increases by about 0.5 Å. The ring structure tends to expand when the basis set is extended.

Due to the very large BSSE's, the complexation energies (CE) of all the complexes are overestimated with the STO-3G basis set. As mentioned above, STO-3G is not suitable for calculating molecular interactions. The CE's obtained with the 3-21G and 4-31G basis sets are larger than those obtained at 6-31G*; however, if the 3-21G or 4-31G energies are corrected for BSSE, reasonable CE values result. The $H_2O\cdots LiH/LiF$ and $NH_3\cdots LiH/LiF$ complexes serve as examples. 3-21G DE + BSSE for these complexes are 27.8, 28.3 and 29.4, 27.2 kcal/mol, respectively. These energies are within about 5 kcal/mol of 6-31G* values. The 6-31G* BSSE's (ca. 3 kcal/mol) are almost constant for all the complexes. For the $H_2O/H_3N/MeH_2N/Me_2HN\cdots LiCl$ complexes, the 4-31G BSSE has been estimated[57] to be 3–4 kcal/mol. The 3-21G basis set is known[1e] to give larger BSSE's than other split-valence basis sets: the values for the present complexes are between 6 and 10 kcal/mol. The CE's are reduced[65a] when the basis set is extended from 3-21G to 6-31G*. These energies are lowered further by 1–3 kcal/mol when diffuse functions (6-31+G*) are present. At STO-3G,[49] the Li bond energy increases in the order $NH_3 < CH_3OH < H_2O$ for a given lithium halide, and for a given electron donor the LiCl forms a stronger Li bond than LiF. According to more accurate calculations,[55,65] the Li bond energy is greater for NH_3 than H_2O but the order $NH_3 > H_2O$ and LiCl > LiF remains. For the X···LiH (X = NH_3, H_2O, HF) complexes, the STO-3G calculations predict[33] almost equal CE values. However, the results[33] of single-point 6-31G* calculations made at the STO-3G optimized geometry indicate that CE varies in the order $NH_3 > H_2O > HF$. Smaller basis sets, e.g., STO-3G, 3-21G, etc., have another deficiency: they tend to give bent B···LiA bonds. This may be attributed to the overemphasis of lithium p-orbital contributions of bonding (BSSE). A careful examination of the entries in Table III would indicate that the minimum requirement for the calculation of DE of σ Li-bonded systems would be a split-valence basis augmented at least with a single set of polarization functions.

Kaufmann et al.[65a] observed that interaction energies are almost constant within a given series of $H_2O\cdots LiX$ and $H_3N\cdots LiX$ complexes. Their final estimates for CE of the water and the ammonia sets are 18.0 ± 1.2 and 21.5 ± 1.3 kcal/mol, respectively. These values are obtained by including ZPE corrections (which vary from 2 to 3 kcal/mol) and taking electron correlation (MP2) into account. Both energies should be reduced further by about 6 kcal/mol for the BSSE (HF, ~3 kcal/mol; MP2, ~3 kcal/mol). The $H_3N\cdots LiOH$, $H_2O\cdots LiF$, $H_2O\cdots LiNH_2$, and $H_2O\cdots LiF$ complexes have been reinvestigated at higher levels and slightly higher bonding energies obtained.[65b,c] The near constancy of the CE values of the binary complexes of water and ammonia with Li compounds has been attributed to the higher ionic character of the Li compounds. This, in turn, indicates that the complexation energy stems mainly from the electrostatic interaction. A small degree of net charge transfer (estimated by natural population analysis) is indicated[65a] by a rather constant shift of negative charge from water (0.02) and ammonia (0.05) to the lithium compounds. However, these small changes arise in part from compensation. The charge back-transfer ($XLi \rightarrow OH_2$) is significant, especially in the X = Li, BeH, and BH_2 cases, which also benefit from strong XLi bond polarization. Thus, the constancy of the complexation energy with respect to X also is a result of compensating factors.

We now consider the π Li-bonded systems, namely acetylene with LiH and ethylene with LiH, $LiCH_3$, and LiF.[38,60] As shown in Figure 2, the perpendicular attachment of LiY to the middle of the C=C and C≡C bonds characterizes these complexes. The interaction

TABLE IV. Correlation Contribution to Complexation Energies (CE(corr), kcal/mol) of Different Complexes of the Type X···Li–Y[a,b]

system	CE(corr)	system	CE(corr)
$H_3N\cdots LiH$	−2.5	$H_2O\cdots LiH$	−2.2
	−1.2		−0.6
$H_3N\cdots Li_2$	−3.2	$H_2O\cdots Li_2$	−2.8
	−1.8		−1.1
$H_2N\cdots LiBeH$	−2.7	$H_2O\cdots LiBeH$	−2.3
	−1.5		−0.8
$H_3N\cdots LiBH_2$	−2.7	$H_2O\cdots LiBH_2$	−2.3
	−1.5		−0.8
$H_3N\cdots LiCH_3$	−2.7	$H_2O\cdots LiCH_3$	−2.3
	−1.5		−0.8
	−1.5		−0.9
$H_2N\cdots LiNH_2$	−2.9	$H_2O\cdots LiNH_2$	−2.2
	−1.6		−0.9
	−1.5	$H_2O\cdots LiOH$	−3.8
$H_3N\cdots LiOH$	−2.8		−2.7
	−2.0		−2.3
$H_3N\cdots LiF$	−2.8	$H_2O\cdots LiF$	−2.0
	−1.7		−0.8
	−0.7[c]		−0.8
$H_3N\cdots LiCl$	−1.2[c]		

[a] All calculations refer to MP2 values. [b] The two sets of values refer to 6-31G*//6-31G* and 6-31+G*//6-31G* calculations, respectively, and the third set refers to 6-31+G*//6-31+G* data.[65] [c] Results from ref 55. Basis sets used: NH_3, 6-31G(2d,1p); LiX, 6-31G(2d).

energies (8–9 kcal/mol) of these systems are significantly smaller than that of the σ Li-bonded complexes. Due to the weak interaction, the LiY bonds remain practically unperturbed. The addition reactions of LiH to C_2H_2 and C_2H_4 and of $LiCH_3$ to C_2H_4 have been predicted[60] to proceed via intermediates that can be considered to have dicoordinated Li atoms. At 3-21G level these species are about 12 kcal/mol more stable than the reactants. At 6-31+G*//6-31G*, the CE of $C_2H_2\cdots LiH$ is ca. 9 kcal/mol[60b] and electron correlation (MP2) increases the DE by about 2 kcal/mol. Intermediates with dicoordinated Li atoms also are formed[61] during the reactions between H_2CO and LiH, $LiCH_3$, $(LiH)_2$, and $(LiCH_3)_2$. However, these complexes are of the σ- rather than the π-type; the 3-21G stabilization energies are all about 28 kcal/mol.

The effect of electron correlation on the energy of interaction between NH_3/H_2O and the whole first-row set, LiY (Y = H, Li, BeH, BH_2, CH_3, NH_2, OH, F), was studied by Kaufmann et al.[65a] at the MP2 level using 6-31G* and 6-31+G* basis sets. These values are summarized in Table IV, which also includes the results of $H_3N\cdots LiF/LiCl$ obtained by Latajka and Scheiner[55] at the MP2 level using (DZ + 2P) basis sets. Unlike the LiY dimers (Table II), CE(corr) is uniformly negative and slightly higher (in the absolute sense). With the extension of basis sets the correlation contribution decreases; this change is almost the same in all the complexes. The BSSE is also found to be uniform for the complexes studied (about 2.4 kcal/mol at 6-31G*). Addition of the BSSE will reduce CE(corr) nearly to zero or even to positive values. For a given LiY, CE(corr) values of the ammonia complexes are in general slightly higher than that of the water complexes. The dispersion energy contributions to CE of $LiH\cdots NH_3/C_2H_2/C_2H_4$ were calculated at SCF geometries by Szczesniak et al.[38] using a DZ basis set. For the NH_3 complex, the correlation contribution is negligible (−1.68 kcal/mol) in comparison to the SCF value (−23.0 kcal/mol). However, in the C_2H_2 and C_2H_4 complexes, this contribution is proportionately larger: −1.57 vs −8.14 for C_2H_2 (MP2 gives[60b] −2.1 vs −9.1) and −0.85 vs −8.67 kcal/mol for C_2H_4 complex. The dispersion interaction also has negligible effect on the stability of the LiCl complexes with H_3N, MeH_2N, Me_2HN, and H_2O.[57]

Geometry optimization using correlated wave functions was reported[55,66] only in the case of $H_3N\cdots LiF$. Two basis sets, DZ+2P and 4-31G**, were employed. The LiF MP2/DZ + 2P distance increases only marginally (~0.01 Å) over the HF value, while the intermolecular distance remains virtually constant.

These results and those of the previous section indicate that the electron correlation effect is small or negligible on the stability of the complexes of Li compounds with polar molecules. The intersystem and intrasystem correlation interaction energy contributions tend to compensate (see above).

4. Higher Complexes of the Type $(LiY)_n$ (n = 3–6)

The $(LiNH_2)_3$ trimer was studied at HF and MP2 levels with several basis sets up to 6-31G*.[53] In agreement with X-ray results on derivatives, the trimer prefers a symmetrical D_{3h} geometry with all hydrogen atoms perpendicular to the planar heavy-atom ring. The trimerization energy is about 120 kcal/mol. Electron correlation corrections are small. Trimers and tetramers of CH_3Li were investigated similarly.[67] Association energies for the 6-membered ring trimer and the tetrahedral tetramer are 79.0 and 122.9 kcal/mol, respectively. The binding is largely electrostatic. The most stable structures have C_{3h} and T_d symmetry (eclipsed methyl groups); alternative tetramer isomers (a T_d structure with staggered methyl groups and a C_{4h} structure) are higher in energy by 7 and 12 kcal/mol, respectively. Electron correlation effects are more pronounced for the T_d eclipsed tetramer (about 6 kcal/mol) but are still small. Tetramers of LiY (Y = F, OH, NH_2) were calculated[59] at MP2 and MP3 levels with different basis sets up to 6-31+G*. Tetrahedral structures are favored by the $(LiF)_4$ and $(LiOH)_4$ tetramers whereas a planar 8-membered ring structure is more stable for $(LiNH_2)_4$. Electron correlation effects are very small. The tetramerization energies are computed to be 185–190 kcal/mol for LiF and LiOH and about 165 kcal/mol for $LiNH_2$. Hexamers of LiY (Y = F, OH, NH_2) were investigated[92e] at the HF level with the 3-21G and 6-31+G* basis sets. Distorted octahedral forms (D_3) were found to be more stable than the planar (D_{6h}) forms for all three complexes. The energies of hexamerization were calculated to be about 310 kcal/mol for LiF and LiOH and about 270 kcal/mol for $LiNH_2$. The predicted geometry (two short Li–N bonds, ca. 1.99 Å; one long bond, 2.06 Å) is in reasonable agreement with X-ray results on derivatives,[92f] although three different Li–N bond lengths (1.98, 2.01, and 2.05 Å) are found.

5. Nature of Bonding in LiY Dimers and X···LiY Complexes

What is the nature of the bonding and the reason for the exceptional stability of LiY dimers? The only localized MO study[93] at the semiempirical level (using

TABLE V. Energy Decomposition of Dimerization Energy (DE) of $(LiY)_2$ Complexes into Electrostatic (ES), Exchange (EX), Polarization (PL), Charge-Transfer (CT), and Mixed (MIX) Terms (kcal/mol)

monomer unit	DE	ES	EX	PL	CT	MIX	DE[a]
LiH	−45.1	−77.7	49.3	−13.5	−55.3	48.2	
LiBeH	−18.9	−49.2	49.7	−39.7	−102.6	113.1	−8.1
$LiBH_2$ (planar)	−34.5	−82.5	61.1	−34.4	−68.2	76.6	−33.3
$LiBH_2$ (perpendicular)	−23.4	−65.0	59.9	−35.2	−63.8	69.0	−19.0
$LiCH_3$	−42.6	−102.4	64.9	−24.3	−34.8	37.1	−43.6
$LiNH_2$ (planar)	−43.2	−94.4	51.6	−20.0	−11.4	11.3	−53.2
$LiNH_2$ (perpendicular)	−73.4	−115.0	51.1	−15.7	−15.1	10.3	−52.7
LiOH	−74.1	−113.5	47.3	−12.9	−10.9	−0.2	−59.7
LiF	−76.1	−98.9	42.4	−8.7	−14.5	−4.5	−71.4

[a] Calculated by using Coulomb's law.[52]

PRDDO wavefunctions[94]) suggested that $(LiCH_3)_2$ contains two equivalent three-center LiCLi bonds. Three-center two-electron LiHLi bonds in $(LiH)_2$ and three-center four-electron LiFLi bonds in $(LiF)_2$ were suggested to be present[23,51] on the basis of the nature of their delocalized MO's. Schleyer and co-workers[52] calculated the electrostatic dimerization energies of $(LiY)_2$ (Y = Li, BeH, BH_2, CH_3, NH_2, OH, F) by replacing Li and Y by unit positive and negative charges at the 3-21G-optimized heavy-atom positions of both the monomers and the dimers. These electrostatic dimerization energies agree remarkably well with the values at MP2/6-31G*//3-21G. However, $(Li_2)_2$, $(LiBeH)_2$, $(LiBH_2)_2$ (perpendicular), $(LiNH_2)_2$ (perpendicular), and $(LiOH)_2$ are more stable than predicted by the electrostatic model. This extra stability was ascribed to the presence of some multicenter bonding. A linear relationship between the calculated (MP2/6-31G*//3-21G) DE values and the Pauling electronegativity[95a] of the first-row atoms also was noted.[52] Moreover, only the $(LiNH_2)_2$ and $(LiOH)_2$ dimers deviate from this correlation line. Multicenter bonding (or other special interactions) may explain these deviations. On the basis of these observations, the bonding in all LiY species appears to be higly ionic.

Schleyer and co-workers[52,53] advanced the following arguments in order to explain why planar $(LiBH_2)_2$ but perpendicular $(LiNH_2)_2$ are the most stable forms. The greater stability of planar $(LiBH_2)_2$ (Figure 1c) is due to favourable interaction between inplane π BH_2 orbitals and the unsymmetrical combination of the Li 2s orbitals. The electrostatic interactions between the positive lithium and the partially negatively charged hydrogens also favor the planar form. The point charge electrostatic model predicts[52] almost equal CE values (53 kcal/mol) for planar and perpendicular (Figure 1e) $(LiNH_2)_2$. However, the actual MP2/6-31G*//3-21G dimerization energies (44.5 and 76.7 kcal/mol, respectively) deviate appreciably from this value and from one another. The greater stability of the perpendicular over the planar arrangement was attributed to the more favorable orientation of the nitrogen localized lone-pair orbitals toward the two adjacent Li atoms. This enhances the possibility both of multicenter bonding and of electrostatic interactions in the perpendicular, but not in the planar form.

In perpendicular $(LiBH_2)_2$, the empty $p\pi$ orbitals on boron can only accept electrons from the Li 2s orbitals but these have very low occupancies. Li 2s is a very poor donor but has a more pronounced tendency to accept electrons from the B–H bonding orbital in the planar dimer. Hence, any covalent (CT) character would favor the planar form of this dimer over the perpendicular form. In contrast, the lone-pair p orbitals on N in $LiNH_2$ are filled and can serve as donors (with the Li 2s orbitals as the acceptors). Overlap with the Li 2s orbitals is more effective when the NH_2 groups are rotated by 90°. This factor favors the perpendicular form over the planar arrangement of $(LiNH_2)_2$.

In order to clarify the nature of the Li bond, Umeyama and Morokuma[34] employed an energy decomposition scheme on $(LiH)_2$ and $(LiF)_2$ using the 4-31G basis set. Hodoseck and Solmajer[51] extended this work at the same level to the entire first-row $(LiY)_2$ series. The results of this energy decomposition study along with electrostatic dimerization energies evaluated with unit charges[52] are given in Table V. The electrostatic (ES) energy term increases (in the absolute sense) while the polarization (PL) and charge-transfer (CT) terms decrease with the increasing electronegativity of the first-row atoms. The exchange (EX) term remains almost constant along the series. In $(LiBeH)_2$, CT is the dominating attractive contribution while in all other dimers the electrostatic term prevails. The increasingly large positive value of the mixed (MIX) term when the electronegativity is lowered (i.e., going toward Be) indicates an increasing interaction between EX and CT, EX and PL, and CT and PL contributions. In other words multicenter covalent bonding is important especially in $(LiCH_3)_2$, $(LiBH)_2$, and $(LiH)_2$. In the dimers with the most electronegative atoms (N, O, F), the contribution from the ES term dominates strongly. These results emphasize the decreasing importance of three-center covalent bonding and increasing importance of electrostatic interaction in the $LiNH_2$, LiOH, and LiF dimers. However, conclusions based on the energy decomposition scheme should be taken with some reservations, when the MIX term is large. Interpretation based on Umeyama and Morokuma analysis should be taken with caution.[95b] According to this analysis the electrostatic energy plays the central role in the hydrogen bond.[95c] Instead, the charge-transfer contribution is believed to dominate.[95b] Morokuma analysis does emphasize the higher ionic character of the lithium bond (over the hydrogen bond) and also the greater electrostatic interaction.

Attempts[23,27,28,33,53,56,58,63,67] have also been made to understand the nature of the bonding in these dimers on the basis of Mulliken population analysis (MPA). In some cases natural population analysis (NPA)[63,67] also has been employed. Results obtained with MPA are questionable as MPA is known to fail for ionic systems.[96] The NPA is much better suited for these $(LiY)_2$ complexes. The charges on the constituent atoms change little during dimerization. The Li atoms become slightly more positive while the negative charge on the first-row atoms increases. Compared to the NPA values,[63,67] the magnitude of these changes is slightly overestimated by MPA. Kollman et al.[27] pointed out that the large difference between the HH and LiLi distances in $(LiH)_2$ (r(HH) > r(LiLi)) is due to the positive LiLi and negative HH overlap populations (OP). However, a negative OP (LiLi) was noted by Armstrong et al.[58] and by Schleyer and co-workers[53] in $(LiNH_2)_2$. The greater stability of perpendicular $(LiNH_2)_2$ over the planar form is also reflected in the OP (LiN) values, which are significantly higher in the former. In the planar form, the π-overlap populations between N and Li are positive but are nearly zero between nitrogens. That the LiLi distance in these dimers is considerably shorter than the AA distance can also be understood qualitatively by noting that cations typically have smaller radii than anions. Experimentalists sometimes assume erroneously that short LiLi distances found in some X-ray structures indicate the presence of metal–metal bonding. Table I shows that LiLi distances considerably shorter than that in metallic lithium (3.016 Å) or in Li_2 are always found in these highly ionic $(LiY)_2$ dimers.

Sannigrahi and Kar[68b] have recently reexamined the nature of the bonding in LiY dimers (Y = H, BeH, BH_2, CH_3, NH_2, OH, F) on the basis of localized MO's, bond orders, bond overlap populations, atomic charges, and valencies using 4-31G, mixed (4-31G(5-21G)/6-31G*/6-31G**), and 6-31G* basis sets. For LiH, LiBeH, and their dimers in mixed basis set contains 5-21G functions on Li and Be and 6-31G** functions on H, while for the rest it consists of 5-21G functions on Li, 4-31G on H, and 6-31G* functions on B, C, N, O, and F. The mixed basis contains d functions only on those atoms that are more electronegative than H. The calculations were performed on the 4-31G (5-21G) optimized geometries. The results indicate that the LiY dimers (Y = H, BeH, BH_2, CH_3) can be described by symmetric three-center two-electron LiALi (A = H, Be, B, C) bonds and the appropriate number of AH bonds. However, no clear-cut evidence was obtained for the existence of three-center bonds in the more ionic dimers, namely $(LiNH_2)_2$, $(LiOH)_2$, and $(LiF)_2$. Hence, the fully charge-separated electrostatic model is more accurate for the description of the bonding in these cases. These conclusions agree with the results of the energy decomposition study of Hodoseck and Solmajer.[51] The localized MO picture of bonding as deduced by Sannigrahi and Kar[68b] is supported by changes on bond orders, overlap population, and valencies occurring upon dimerization.

The nature of bonding in the X···Li–Y and the $(LiY)_2$ complexes differ. The Li–Y distance is lengthened due to complex formation, more than that occurring in H-bonded complexes. The largest changes were found for LiCl, where the distance increases by as much as 0.03 Å. Whereas the hydrogen in a H bond is clearly located near the more electronegative atom, the lithium in a Li bond in X···Li–Y adopts a position nearer the center between atoms X and Y. The XY distances in X···HY complexes (especially when these are strong) are considerably shorter than the sum of the van der Waals radii of X and Y. In contrast, these distances in X···LiY complexes are significantly greater than the same radii sum. This is due to the influence of the 1s electrons in Li^+, which prevents the close approach of two electronegative atoms.

Li bonds are much stronger than the corresponding H bonds. This is due to the higher dipole moments in LiY than in HY. The interaction energy is dominated by the electrostatic contribution; the other energy terms are smaller. The electrostatic term also is important with the H bond, but other energy contributions (charge transfer, correlation) are comparable in magnitude. This conclusion is supported by the following findings: (1) The intermolecular bending force constants are smaller for Li-bonded than for H-bonded complexes; i.e. the bonding is more directed in the H bond. Orbital overlap is important in H bonding. The relative energy differences between equilibrium and bent structures are much larger than the corresponding differences in Li-bonded complexes. A different blend of stabilizing contributions is important in Li-bonded than H-bonded complexes. (2) Charge transfer/delocalization plays a proportionately smaller role in the binding energy in Li bonds than in H bonds. The association energies due to the charge-transfer component in absolute magnitude are similar in H as in Li bonds, but the electrostatic contribution to Li bonds is much greater and dramatically higher complexation energies result.

Correlation plays a different role with Li bonds than with H bonds. Correlation influences the stabilization energy for Li-bonded complexes only to a minimal extent, and frequently it even lowers the complexation energy. On the other hand, correlation is much more important for the H-bonded complexes where it can increase the stabilization considerably (by 10–50%).[92b] Correlation also affects the geometries differently: the intermolecular separation is shortened in the H-bonded complexes, whereas it is lengthened slightly in the Li-bonded complexes.[55]

6. Concluding Remarks

We have considered four types of Li-bonded complexes: LiY dimers, X···LiY σ Li-bonded complexes, X···LiY π Li-bonded complexes, and LiY oligomers.

In general, LiY dimers have rhomboid structures and high dimerization energies (30–70 kcal/mol). Due to the low electronegativity of Li and Be, the complexation energies of $(Li_2)_2$ (~15 kcal/mol) and of $(LiBeH)_2$ (~20 kcal/mol) are rather small. The nature of bonding in the $(LiY)_2$ dimers is different from that of other types of lithium complexes because cyclic structures are favored. These are best considered as an quadrupolar ion aggregates, although some multicenter covalent bonding may be present in some of the cases. Thus, it appears that the "Li-bonding" concept may be less appropriate with reference to these complexes.

The σ-bonded X···LiY complexes generally have open structures and association energies ranging from 15 to 25 kcal/mol. In the π Li-bonded complexes the interaction energies are about 10 kcal/mol. The elongation of the monomer Li–A bond is most pronounced (~0.2 Å) on going to the $(LiY)_2$ dimers, but the changes are smaller in σ Li-bonded X···Li–Y (~0.01 Å) complexes and negligible for those in the π category. The stability of the X···Li–Y complexes stems mainly from the electrostatic interaction with some polarization of the X electrons.

The accurate calculation of stabilization energies requires larger basis sets (e.g., of at least DZ quality) augmented by polarization and preferably also by diffuse sp functions. BSSE should be taken into account, especially when different structures of a complex are compared. The effect of electron correlation both on the association energies and on the geometries is, in general, rather small. The geometries and energies of Li-bonded complexes, providing that an adequately high level is employed, agree reasonably well with the limited experimental results available.

Li bonds and H bonds differ considerably. The geometries are quite different. Li bonds are largely electrostatic, whereas H bonds result from charge-transfer, electrostatic, and electron correlation contributions.

The Li bonds and H bonds do have certain analogous features, such as charge transfer. However, the electrostatic contributions and the bonding energies are considerably greater for the Li bond. Moreover, lithium is a larger atom, so that lithium complexes are not restricted to dicoordination. Additional ligands can be attached by similar bonding modes to lithium, but not to hydrogen. Most lithium compounds are associated and solvated in solution and in the solid state and the Li bond–H bond analogy is less appropriate. Nevertheless, the concept is useful in helping to understand the nature of bonding involving lithium.

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