against the copolymer composition which was determined by infrared spectroscopy. Calculations corresponding to such copolymer systems have been given in Figure 5. For comparison purposes, curves 2 and 3 in Figure 5c are reproduced in Figure 8. Here $\alpha = 72°$ is adopted in keeping with the previous treatment. Although not much is known for the copolymer structure, one may expect *a priori* a random or at most a moderately blocked arrangement, in consideration of the similarity in the molecular structure between the two components. When $\omega'' = 0.03$ is chosen for such a copolymer sequence, the agreement between theory and experiments may be satisfactory. A value of 0.03 for ω'', however, seems to be slightly high in comparison with that previously estimated from the study on poly-(*R*)(*S*)-4-methylhex-1-ene.

Concluding Remarks

Conformational rigidity of the vinyl polymer chain is largely determined by the bulkiness of the pendant groups. All the monomers treated in this paper have a methyl branch either at the β or at the γ position with respect to the vinyl group. Difference between these two series of monomers, when polymerized, may be found in the (t,t) element of the U' matrices. With the former structure, $U'(t,t) \cong \omega''$, suggesting that the transition between the two anticlined skeletal conformations through (tt) is as hard as those through (g^+g^-) or (g^-g^+). Stereochemistry of the side chain derived from the latter monomer permits such transition with the statistical weight of $U'(t,t) \cong \tau$. The optical rotatory properties of the binary copolymers chosen from these monomers apparently reflect characteristics of the structural feature for a given combination, and may provide some important information concerning the polymerization mechanism.

Within the reasonable range of conformational energies, optical rotatory behaviors of the copolymer derived from (*R*)- and (*S*)-4-methylhex-1-ene, or from (*R*)- and (*S*)-5-methylhept-1-ene were shown to be consistent with those expected from a moderately blocked structure, which may be the most probable one in consideration of the asymmetric nature of polymerization.[16] Experimental observations on the copolymers of (*S*)-4-methylhex-1-ene with 4-methylpent-1-ene may be interpretable based on a chain model with a moderately blocked or a random arrangement of the two monomer units.

According to Nozakura, *et al.*,[17] who polymerized a monomer mixture comprising (*S*)-4-methylhex-1-ene and its isomer 5-methylhex-1-ene (optical purity *ca.* 19%), the observed optical rotation of this copolymer was found to be *ca.* 20% of that for the polymer bearing the maximum optical purity. Calculations for such a copolymer system have been presented in Figure 6. If the copolymer is composed of a binary random array of the two components, some deviation from linearity is expected. The relation may be linear only when the polymerizate is a mixture of two homopolymers or a highly blocked copolymer. This is not likely to be the case, as Nozakura, *et al.*,[17] pointed out. Determination of the copolymer composition should clarify this point.

Acknowledgment. The author wishes especially to thank Professor P. J. Flory of Stanford University for his unflagging encouragement and critical reading of the manuscript.

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[16] P. Pino, F. Ciardelli, G. P. Lorenzi, and G. Natta, *J. Amer. Chem. Soc.*, **84**, 1487 (1962); P. Pino, F. Ciardelli, and G. P. Lorenzi, *ibid.*, **85**, 3890 (1963).

[17] S. Nozakura, S. Takeuchi, H. Yuki, and S. Murahashi, *Bull. Chem. Soc. Jap.*, **34**, 1673 (1961).

The Lithium Bond[1a]

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Abstract: Examples of lithium bonding analogous to hydrogen bonding are investigated. Systems studied and compared with available experimental data comprise H–F···Li–F, H—F···H–F, Li–F···H–F, LiF···Li–Li, Li–F···H–H, and Li–F···Li–F. In addition, calculations for ir frequency shifts and intensity enhancements reveal interesting characteristics of hydrogen and lithium bonding. A large difference in energy of complex formation and charge redistribution is shown to exist between the two dimers Li–F····Li–Li and Li–F····H–H. Cyclic *vs.* linear configurations were considered for the systems (LiF_2), $(HF)_2$, and LiFHF. The known cyclic structure of $(LiF)_2$ is correctly predicted with an energy of formation close to the experimental value. Molecular orbital energy changes as the characterizing feature of donor–acceptor complex formation are discussed.

There has been considerable theoretical and experimental interest in hydrogen bonding.[2] Hydrogen has been implicitly assumed to be unique with regard to intermolecular interactions, but since lithium is a congener of hydrogen, it is a logical isomorphic replacement to substitute the hydrogen with lithium in normal hy-

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[2] See P. A. Kollman and L. C. Allen, *J. Chem. Phys.*, **51**, 3286 (1969), for general references.

drogen bonded systems. Nevertheless there are few articles citing A_2Li^- or $ALi\cdots B$ complexes.[3] In the gas phase, HF appears to be predominantly the cyclic hexamer,[4a] whereas LiF vapor appears to be mainly composed of the cyclic dimer and trimer.[4b] It is therefore of interest to study the geometry of $(HF)_2$,[5] $(LiF)_2$, and HF–LiF. It has also been noted that the formation of a hydrogen bond in a system $A-H\cdots B$ should not require an ionic A–H bond,[6] and thus the interaction of the highly ionic LiF with the nonpolar diatomics Li_2 and H_2 has been examined.

This paper first discusses the interaction of LiF with HF in $H-F\cdots Li-F$ and compares it with the hydrogen bond in $Li-F\cdots H-F$. Second, $LiF-Li_2$ both perpendicular and colinear (see Figure 1 for geometries considered) has been investigated and compared with the same conformers in $LiF-H_2$. The orientation of complexes $LiF-Li_2$ and $LiF-H_2$ poses interesting questions on dipole–induced dipole interactions and multicenter bonding.

Third, the LiF dimer has been studied and a potential surface constructed. In the geometry search for HF-LiF, LiF-HF, and $(LiF)_2$, p orbitals on Li were found to be unnecessary to explain conformation energy differences. One finds in $(HF)_2$ and the mixed LiF–HF that the linear structure is more favored than the cyclic. For the LiF dimer, the opposite is true.

In all cases the energy shifts for the MO's of the donors and of the acceptors on complexation were analyzed and this quantity is found to be the principal organizing feature for lithium as well as hydrogen bonding. Finally, the interaction of LiH with small ions[7] and He[8] has been theoretically investigated by others and is not further considered here.

Description of Calculation

The calculations were carried out with the aid of a set of computer programs written at Princeton. Essentially double ζ quality Gaussian lobe atomic orbitals were used a basis set[9]: (10s, 5p) Gaussian basis functions on fluorine, 10s gaussians on lithium, and 5s gaussians on hydrogen. The s gaussians on the fluorine were contracted into three groups, the lithium s's into three groups, and fluorine p's and the hydrogen s's into one group. Some of the points on the potential surface were calculated with one-component p functions on the lithium.[10] The hydrogen orbitals scale factor used for HF was obtained from calculations on the HF monomer.[11] For H_2, a scale factor was determined to closely approximate the experimental bond distance. Self-consistent field molecular orbital calculations were carried out following Roothaan's procedure. The energies, Mulliken population analysis,[12] charge density contours, and the dipole moments were determined. For each geometry, the individual orbital energies and the various energy components (V_{ne}, V_{ee}, V_{nn}, and T) were obtained. Table I summarizes the monomer geometry searches, the equilibrium distances found, and the experimental values. In Figure 2 the monomer population analyses are shown. It is interesting to note the effect of including p orbitals on the lithium. In LiF, the overlap charged increases and the net ionic character decreases quite drastically. In Li_2, the overlap also increases.

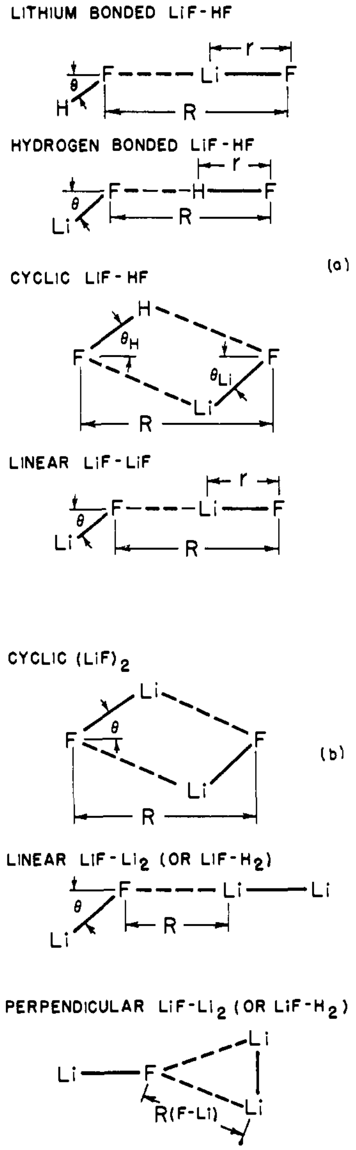

Figure 1. (a) The geometry of the lithium bonded LiF–HF, the hydrogen bonded LiF–HF, cyclic LiF–HF, and linear LiF–LiF. (b) The geometry of cyclic $(LiF)_2$, linear $LiF-Li_2$ (or $LiF-H_2$), and perpendicular $LiF-Li_2$ (or $LiF-H_2$).

Lithium Bonding Contrasted with Hydrogen Bonding

A prototype lithium bond was studied in the system $H-F\cdots Li-F$ and Table II summarizes the geometry

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(3) H. Schmidbaur and S. Waldman, *Angew. Chem.*, **76**, 753 (1964); P. Thate and P. Mayer, *Angew. Chem. Int. Ed.*, **5**, 972 (1966); J. E. Muhaney, *et al.*, *J. Amer. Chem. Soc.*, **91**, 388 (1969).

(4) (a) J. Janzen and L. S. Bartell, *J. Chem. Phys.*, **50**, 3611 (1969); (b) P. Kusch, *et al.*, *ibid.*, **29**, 797 (1958); $E\ (LiF)_2 = 58.94 \pm 2.1$ kcal/mol.

(5) Further details on the HF dimer and mixed dimers of HF and H_2O will be published.

(6) F. B. Van Duijenveldt, *J. Chem. Phys.*, **49**, 1424 (1968).

(7) (a) H. Preuss and G. Diercksen, *Int. J. Quantum Chem.*, **1**, 631, 635, 641 (1967); (c) A. A. Wu and F. O. Ellison, *J. Chem. Phys.*, **47**, 1458 (1967).

(8) L. M. Sachs and J. Kaufman, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., No. PHYS 092.

(9) J. L. Whitten, *J. Chem. Phys.*, **44**, 359 (1966).

(10) R. J. Buenker and S. D. Peyerimhoff, *ibid.*, **45**, 3682 (1966).

(11) W. H. Fink and L. C. Allen, unpublished results.

(12) The formulas for interatomic overlap populations and gross atomic populations are found in Mulliken's paper: R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955). The nonorthogonality of the orbitals on the same center (*e.g.*, 1s, 2s, 3s, on fluorine) does not affect the above result, as the overlap between all the orbitals is explicitly included.

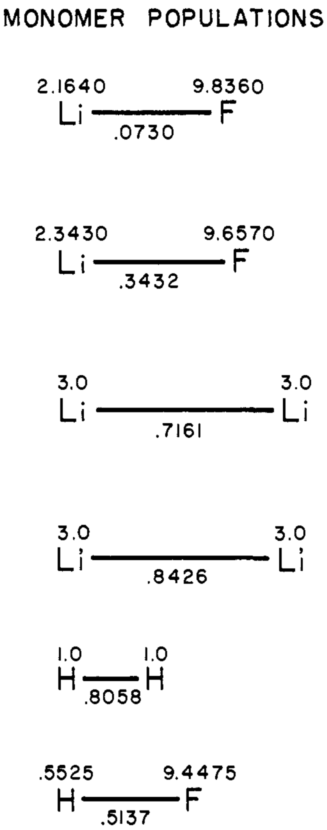

Figure 2. Monomer populations for LiF, R (Li–F) = 1.667 Å, without p's on Li; LiF, R (Li–F) = 1.588 Å, with p's on Li; Li_2, R (Li–Li) = 2.646 Å, without p's on Li; and Li_2, R (Li–Li) = 2.646 Å, with p's on Li; H_2, R (H–H) = 0.741 Å; and HF, R (H–F) = 0.916 Å.

Table I

Lithium fluoride without p's			With p's		
R, Å	E, au	μ, D	R, Å	E, au	μ, D
1.500	−106.8208	6.622	1.508	−106.8839	5.91
1.610	−106.8274	6.730	1.588	−106.8856	6.14
1.667	−106.8282	6.770	1.667	−106.8834	6.38
1.750	−106.8272	6.850			

Lithium molecule without p's		With p's	
R, Å	E, au	R, Å	E, au
2.117	−14.8368	2.117	−14.8435
1.646	−14.8571	2.646	−14.8643
3.175	−14.8569	3.175	−14.8631

Hydrogen molecule	E, au, using scale factor		
R, Å	1.2	1.5	1.8
0.529	−1.0692	−1.0408	−0.8414
0.741	−1.1277	−1.0313	−0.7538
0.953	−1.0960	−0.9427	−0.5891

Hydrogen fluoride molecule (scale factor = 1.414)		
R, Å	E, au	μ, D
0.915	−99.9946	2.13
0.947	−99.9958	2.18
0.979	−99.9943	2.23

Experimental values and very accurate calculations[a]

Molecule	Bond distance, Å (exptl)	Dipole moment, D (exptl)	Bond distance, Å (calcd)	Total energy, au	Dipole moment, D (calcd)
HF	0.9171[b]	1.819[b]	0.916[e]	−100.070[e]	1.82[e]
LiF	1.564[c]	6.28[d]	1.528[e]	−106.992[e]	6.295[e]
Li_2	2.6725[c]		2.6829[f]	−14.902[f]	
H_2	0.7417[c]		0.7509[g]	−1.1745[g]	

[a] The HF and LiF calculations cited were of the single determinant LCAO-MO-SCF variety; the Li_2 and H_2 calculations employed a multideterminant wave function. [b] W. Klemperer, *J. Chem. Phys.*, **38,** 1203 (1963). [c] G. Herzberg, "Molecular Spectra and Molecular Structure, I: Spectra of Diatomic Molecules," 2nd ed, D. Van Nostrand Co., Inc., New York, N. Y., 1950. [d] R. Weiss, *Phys. Rev.*, **131,** 659 (1963). [e] W. D. McLean and M. Yoshimine, *IBM J. Res. Develop., Suppl.*, 11 (1967). [f] G. Das, *J. Chem. Phys.*, **46,** 1568 (1967). [g] W. Kolos and L. Wolniewicz, *ibid.*, **49,** 404 (1968); note this is the value for R_0, not R_e.

searches. A minimum energy is found at an F–F distance of 3.57 Å with a stabilization energy compared to isolated H–F and Li–F of 13.5 kcal/mol. When the same geometry search was carried out with p orbitals on the lithium, the stabilization energy relative to the separated monomers was 16.2 kcal/mol.

The hydrogen bonded system Li–F···H–F was investigated to compare the lithium bond with the hydrogen bond. The minimum energy occurs at an F–F distance of 2.38 Å with a stabilization energy of 24.7 kcal/mol. Unlike the case of the linear hydrogen fluoride dimer,[13] the hydrogen is considerably loosened in the H–F bond, indicating a tendency to form $Li^+HF_2^-$ with the hydrogen symmetrically placed between the fluorines. It is the presence of the highly positive lithium which makes the bond asymmetric.

In Figure 3 lithium and hydrogen bonding is compared in LiF–HF and HF–LiF *via* the population difference analysis. When only s orbitals are included on the lithium, lithium bonding is analogous to hydrogen bonding in that the central atoms in the bonds lose electron density when the hydrogen (lithium) bond is formed. However, when p orbitals are included on the lithium, the electron density on the lithium actually increases on bond formation.[14] This Li p function, of course, redistributes charge on the fluoride center to some extent. In contrast to the importance of a p polarization function on lithium in this calculation, work on $(HF)_2$[5] indicates that a p function on hydrogen causes little change in the electron density of the complex.

In Figure 4, charge difference density maps are plotted for the two complexes (wave functions with only s orbitals on lithium).

The charge difference plots are much more complex and subtle than the population analysis. A view of LiF–HF as Li^+ HF_2^- is supported, and the hydrogen in

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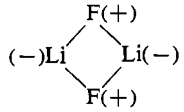
(13) In $(HF)_2$, the middle hydrogen is only shifted 0.003 Å upon complex formation.

(14) The following is a partial catalog of the roles of p orbitals on Li regarding chemical effects: (1) p orbitals on Li help reduce its positive charge by back bonding from F: (−)Li=F(+). (2) Such back-bonding can still occur in the dimer, although with only one p orbital, not two. (3) The p orbital along the Li–F bond (monomer or dimer) introduces a greater directionality, and thus the covalent contribution is greater, as Li^+ and F^- are still spherical. (4) p orbitals allow greater flexibility in the Li wave function and thus stabilize Li·F·. (5) As is probably the case with BeF_2, LiF_2^- is best represented as sp-hybridized. (6) One can invoke the resonance structure



for the cyclic dimer, and p orbitals facilitate having more than one bond.

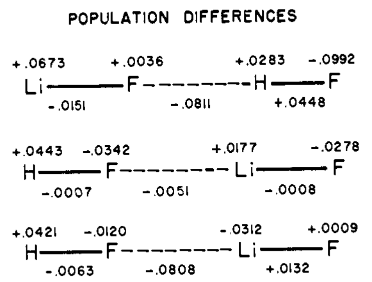


Figure 3. Population differences for the dimer and the two monomers. A negative number means gain of electron density upon dimerization, a positive number means loss of electron density. This is for LiF–HF, R (F–F) = 2.38 Å; HFLiF, R (F–F) = 3.567 Å without p's on Li; and HFLiF, R (F–F) = 3.567 Å with p's on Li.

the hydrogen bond is much more positive than in $(HF)_2$. In $(HF)_2$ the electron density loss at the hydrogen is 0.021 e/a_0^3, in LiFHF, it is 0.070 e/a_0^3. HFLiF can be interpreted as $HFLi^+$ F^-, with the hydrogen and lithium becoming even more positive on dimer formation.

Table II

		H–F···Li–F (without p's in LiF)		
R, Å	r, Å	θ, deg	E, au	μ, D
4.167	1.667	0	−206.8372	
3.867	1.667	0	−206.8412	
3.567[a]	1.667	0	−206.8443	9.49
3.367	1.667	0	−206.8404	
2.967	1.667	0	−206.7696	
3.567	1.667	40	−206.8429	
3.567	1.667	80	−206.8334	
3.567	1.725	0	−206.8439	9.60
3.567	1.7835	0	−206.8414	9.71
		H–F···Li–F (with p's on Li)		
R, Å	r, Å	θ, deg	E, au	μ, D
3.148	1.588	0	−206.8977	8.802
3.488	1.588	0	−206.9061	
3.888	1.588	0	−206.9010	
3.488	1.588	40	−206.9049	
3.488	1.641	0	−206.9053	8.98
3.488	1.694	0	−206.9028	9.16
		Li–F···H–F		
R, Å	r, Å	θ, deg	E, au	μ, D
2.9	0.915	0	−206.8485	
2.6	0.915	0	−206.8561	
2.351	0.915	0	−206.8623	
2.351	0.915	40	−206.8613	
2.12	0.915	0	−206.8517	
1.831	0.915	0	−206.7516	
2.381	0.947	0	−206.8613	10.62
2.381	0.979	0	−206.8669	10.86
2.381[b]	1.058	0	−206.8692	11.42
2.381	1.138	0	−206.8681	12.05
2.381	1.191	0	−206.8609	12.48
2.381	0.915	0	−206.8543	10.40

[a] At this geometry the hydrogen was moved to 0.79 and 1.00 Å from the fluorine. Both configurations were less stable than the H–F distance at the experimental value. [b] At this geometry, the lithium was moved to 1.4 and 1.92 Å. Both configurations were less stable than the one with R(Li–F) = 1.667.

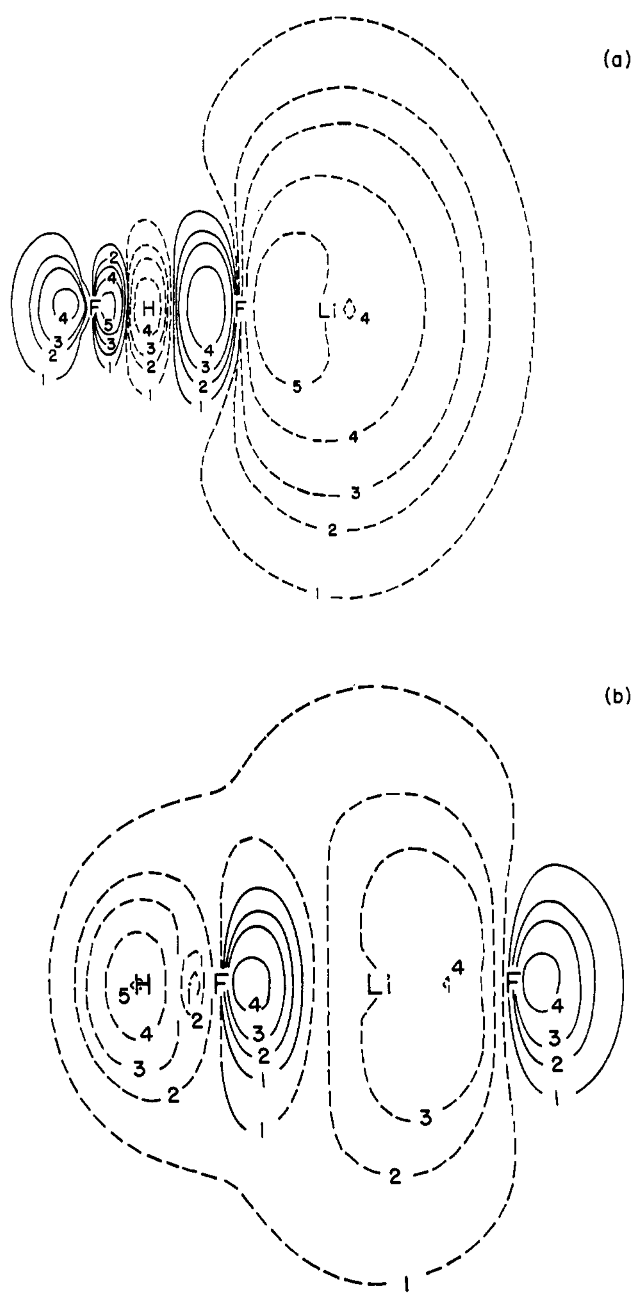


Figure 4. (a) Difference density plot for LiF–HF. A solid line, —1—, means an increase of electron density upon complex formation, and a dotted line, - - - 1 - - -, means a corresponding decrease of the same absolute magnitude. The contours are —1—, 0.0007, —2—, 0.0021; —3—, 0.0035; —4—, 0.0070; —5—, 0.0141 e/a_0^3, respectively. (b) Difference density plot for HF–LiF.

The LiF Dimer

The hydrogen fluoride dimer has a linear or near-linear structure more stable than the cyclic one (Figure 1). With this in mind, a potential surface search of cyclic HFLiF was undertaken; varying R, θ_H, and θ_{Li}, a minimum energy configuration was found at R = 2.6 Å, θ_H = 45°, and θ_{Li} = 60°. The stabilization energy, 15.1 kcal, is slightly more than the lithium bonded structure, but less stable than the hydrogen bonded one (Table III). Therefore, it was gratifying to find that for $(LiF)_2$, the cyclic structure was more stable than the linear.[4b] Two geometry searches were carried out, one with only s type functions on the lithium, the other with both s and p type functions on lithium. With only s type functions on lithium, the linear structure has a stabilization energy of 56.3 kcal and the cyclic structure was stable by 80.4 kcal. Including p functions on lith-

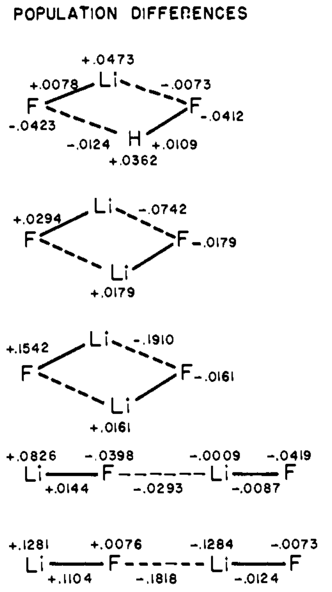


Figure 5. Population differences for: cyclic LiF–HF, R (F–F) = 2.6 Å, θ_{Li} = 60°, θ_H = 45°, without p's on Li; cyclic $(LiF)_2$, R (F–F) = 2.62 Å, without p's on Li; cyclic $(LiF)_2$, R (F–F) = 2.62 Å, with p's on Li; linear $(LiF)_2$, R (F–F) = 3.38 Å, without p's on Li; and linear $(LiF)_2$, R (F–F) = 3.434 Å, with p's on Li.

ium resulted in a stabilization energy of 46 (linear) and 66 kcal/mol (cyclic) (experimental, 58.9 kcal/mol (cyclic)[4b]).

Table III. Comparison of Ir properties

System[a]	K dimer stretch / K monomer stretch	$(\partial\mu/\partial r)^2$ dimer / $(\partial\mu/\partial r)^2$ monomer	Δr, Å
$(HF)_2$ R(F–F) = 2.88	1.00	2.0	0.004
$(LiF)_2$ R(F–F) = 3.567	1.255	6.0	0.076
HFLiF R(F–F) = 3.567	1.833	4.6	0.005
LiFHF R(F–F) = 2.381	0.45	21.2	0.120
HFLiF R(F–F) = 3.57[b]	0.99	1.3	0.004

[a] R is given in Å. θ = 0° for all systems. [b] p's on Li.

As seen in Figure 5, there is a large intermolecular overlap, and the intramolecular overlap decreases for the cyclic LiF dimer. Both of these trends are markedly accented by the presence of p orbitals on lithium, and it is quite clear that their presence is much more important in the study of systems involving LiF than p orbitals on hydrogen are in systems involving HF.

In the cyclic LiF–HF, the charges change in the same way that they do in the LiF dimer. Noting the increased ionic character of LiF over HF even in the complex, it is easy to rationalize the relative stability of the cyclic systems, $(LiF)_2$ > LiFHF > $(HF)_2$.

The role of p orbitals in the linear lithium fluoride dimer parallels its role in the cyclic case. Including p orbitals marks the outer lithium still more positive and the inner lithium still more negative. The small charge shifts on the fluorines are dwarfed by those on the lithiums. This implies reasonable contributions of $(Li\text{-}FLi)^+F^-$ and $Li^+(FLiF)^-$.

LiF–X_2

It is of interest to study nonionic hydrogen and lithium bonds. Keeping the monomer distances fixed, a linear LiF—Li–Li was studied. A minimum energy was found for a nearly symmetric $(Li\text{-}F\text{-}Li)^+Li^-$. With only s orbitals on the lithium, the stabilization was 36 kcal/mol; inclusion of p functions on all lithiums made the dimer 37.7 kcal/mol more stable than isolated monomers. After finding a minimum F–Li distance, the Li–Li distance was varied. In the isolated Li_2 molecule, the theoretically calculated minimum was 2.906 Å; in the dimer, the bond length expanded to 3.051 Å. In the case of Li–F—H–H, a minimum energy was found at an F–H distance of 2.0 Å corresponding to a stabilization energy of 2 kcal/mol. (See Table IV.)

Table IV

R, Å	θ Li, deg	θ H, deg	E, au
2.35	45	45	−206.8423
2.10	45	45	−206.8162
2.60	45	45	−206.8457
2.85	45	45	−206.8423
2.60	45	60	−206.8455
2.60	45	30	−206.8429
2.60	60	45	−206.8469
2.60	30	45	−206.8438
2.60	75	45	−206.8438
$(LiF)_2$ without p's (r monomer = 1.667 Å)			
Linear		Cyclic	
R (F–F), Å	E, au	R (F–F), Å	E, au
3.334	−213.7321	2.357	−213.7824
3.175	−213.7036	2.622	−213.7849
3.863	−213.7165	3.151	−213.7481
$(LiF)_2$ with p's (r monomer = 1.587 A)			
Linear		Cyclic	
R, Å	E, au	R, Å	E, au
3.174	−213.8408	2.45	−213.8597
3.439	−213.8456	2.510	−213.8772
3.703	−213.8372	2.774	−213.8699

Li_2 with only s orbitals, and H_2 were allowed to approach the lithium fluoride in a perpendicular fashion, and the H_2 approach was purely repulsive; however, a stabilization energy of 27.6 kcal was found for the LiF–Li_2 dimer at R (F—Li) = 1.957 Å.

It is possible to construct a pictorial description of the LiF–H_2 interaction. This complex is weakly bound and, not surprisingly, there is little perturbation on the LiF. However, the H_2 electronic distribution is markedly distorted by the presence of a nearby dipole when one examines the population analysis in Figure 3 and the charge density contour in Figure 7b. One sees in the population analysis that along the internuclear axis, the H_2 is hardly disturbed, while the changes in the LiF mimic those in LiFHF, although the changes are smaller. In analogy to LiF–H_2, one may also consider the parallel and then the perpendicular approach of Li_2 to LiF. As with all donor-acceptor complexes, the population analysis shows an increase in electron density between the monomers (Figure 6). The charge difference plot (Figure 7a) clearly suggests the structure Li_2F^+ Li^- just as the polarization of LiF–H_2 indicates $LiFH^+$ H^- (the total charge shifts in the two dimers mimic the relative strengths of the interaction). Despite the fact that the Li–Li interatomic distance is greater than the corresponding F–Li distance (Li–F—Li–Li), there is a greater charge between the lithiums

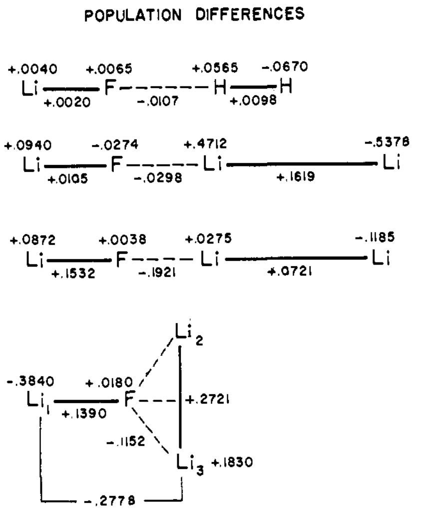


Figure 6. Population differences for colinear LiF–H_2, R (F–H) = 2.117 Å; colinear LiF–Li_2, R (F–Li) = 1.667 Å, without p's on Li; colinear LiF–Li_2, R (F–Li) = 1.588 Å, with p's on Li, and perpendicular LiF–Li_2, R (F–Li_2) = 1.693 Å.

(−0.2778) than between the lithium and the fluorine (−0.1152) in the perpendicular approach. Furthermore, there is almost no change in the fluoride charge, but a marked change in the lithiums. These results strongly suggest the visualization of this species as $Li_3^+F^-$ with the fluoride ion in the middle of the triangle of lithiums.

Ir Properties

To compare ir shifts of the lithium bonded dimers and the hydrogen bonded dimers $(HF)_2$, HFLiF, and $(LiF)_2$ are considered (Table III). For the studies with only s orbitals on lithium, the expected decrease in stretching frequency is not found; both HFLiF and $(LiF)_2$ actually show an increase in the intramolecular Li–F frequency upon complex formation. However, when p orbitals are included in the lithium bonded case HFLiF, the ir frequency shift and intensity enhancement closely parallel that of the hydrogen bonded dimer. In all the dimer stretches an intensity enhancement is predicted and all equilibrium F–H(F–Li) distances are increased on dimer formation. The system LiFHF can be reasonably represented as $Li^+(FHF)^-$, since there is a great decrease in stretching frequency and a large increase in F–H distance. The FHF^- part is not symmetric, but quite close to this (R(F–F) = 2.38, R(F–H) = 1.06 Å).[15]

At this point it is worthwhile to evaluate the role of p polarization functions on lithium. If lithium bonding were completely analogous to hydrogen bonding, there would be no fundamental change in any of its features upon addition of a p orbital.[5] It is clear, however, from the population analysis results that p orbitals are necessary to adequately represent the charge redistribution upon dimer formation. Comparing the Li–F stretching force constant with the experimental value (2.79×10^5 dyn/cm)[12,16] reveals why the s-orbital-only calculations show an increase in LiF frequency upon dimer formation. While the LiF force constant with p orbitals included is close to the experimental (2.69×10^5 dyn/cm), the s-orbital-only calculation predicts a force constant of 1.62×10^5 dyn/cm—far too low to adequately represent the potential surface on stretching. As has been noted before, p orbitals on lithium are not needed to represent the relative stability of different possible dimer structures involving lithium, although they are significant for quantitative estimate of the energy of formation.

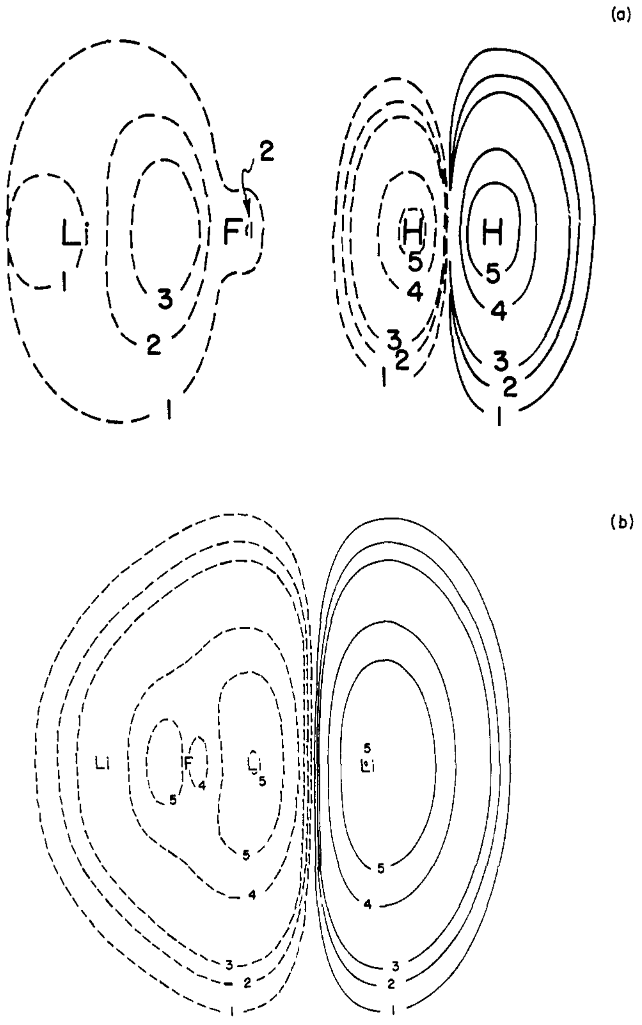


Figure 7. (a) Difference density plot for colinear LiF–Li_2. The contours have the absolute values: —1—, 0.025; —2—, 0.045; —3—, 0.064; —4—, 0.191; and —5—, 0.318 e/a_0^3, respectively. (b) Difference density plot for colinear LiF–H_2. The contours have the absolute values: —1—, 0.004; —2—, 0.007; —3—, 0.010—; —4—, 0.030; and —5—, 0.049 e/a_0^3, respectively.

MO Energies

In a previous paper,[2] it was proposed that the decrease in all MO energies of the electron pair donor and the increase in all the MO energies of the electron pair acceptor be a quantitative organizing principle for donor acceptor complex formation. Table V summarizes the MO changes in the dimers LiFHF, HFLiF, $LiFLi_2$, $(HF)_2$, $(H_2O)_2$, HFH_2O, and H_2OHF,[5] each case involving a hydrogen or a lithium bond. There is good correlation between the average molecular orbital energy change and the total energy change. One should also note that the MO energy changes are not dominated by one particular orbital, but that all orbital energies

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(15) Data on HF_2^- ion is presented by R. Erdahl, Ph.D. Thesis, Princeton University, 1965.

(16) For force constant information see: T. L. Cottrell, "The Strength of Chemical Bonds," Butterworth & Co. Ltd., London, 1958.

Table V

R, Å	r, Å	E, au	R, Å	r, Å	E, au
Linear[a] $LiF–Li_2$ (no p's)			Linear $LiF–Li_2$ (with p's only on Li_2)		
1.058	2.646	−121.4481	1.323	2.646	−121.7414
1.588	2.646	−121.7301	2.117	2.646	−121.7742
2.117	2.646	−121.7311	2.910	2.646	−121.7392
2.646	2.646	−121.7123	Linear $LiF–Li_2$ (with p's on all lithiums)		
5.292	2.646	−121.6869			
1.588	2.117	−121.7174			
1.588[b]	3.175	−121.7385	1.687	2.646	−121.8101
1.588	3.704	−121.7301	2.116	2.646	−121.8068
			2.646	2.646	−121.7876
Linear $LiF–H_2$			Perpendicular $LiF_2–H_2$		
1.058		−101.8766	1.121		−107.6663
1.588		−107.9524	1.630		−107.8939
2.117		−107.9587	2.149		−107.9455
2.646		−107.9576	2.672		−107.9542
3.175		−107.9567			
			Perpendicular[b] $LiF–Li_2$		
			1.349		−121.6079
			1.693		−121.7064
			2.275		−121.6963

[a] One calculation was done on pyramidal $F^-–Li_3^+$. All the Li–Li distances were 2.646 and the Li–F distances 1.667 Å. The energy for this configuration was −121.6976 au. [b] A movement of each of the lithiums off linearity resulted in an increase in energy.

move in a concerted fashion. The molecular orbital energy decreases on the electron pair donor sometimes, but not always, exceed the increases on the acceptor.

Donor acceptor complex formation is fundamentally different from ordinary covalent molecule formation in a molecular orbital model. In the formation of covalent bonds in Li_2 and LiF from the constituent atoms, all the molecular orbitals increase in energy. In our hydrogen (lithium) bonded systems and in the donor–acceptor system $BH_3 \cdot NH_3$,[17] it is seen that the molecular orbital levels follow the above noted donor–acceptor trend. There is no reason why BH_3NH_3 is unique; if one looks at an analogous system such as $BeH_2 \cdot H_2O$, one will observe the same trends.

Further Considerations

An attempt to derive the molecular orbital energy changes by means of perturbation theory is now in progress.

One expects that allowing more SCF flexibility in the basis set used for fluorine (*e.g.*, (4s, 2p) rather than the (3s, 1p) used here) will lower the total energy and bring the calculated properties in closer agreement with experiment. Also, polarization functions (d functions on fluorine and p functions on hydrogen) will have a similar (albeit much smaller) effect.[18] However, this basis set with p polarization functions on lithium predicts the bond length and dipole moment of the monomer and the heat of dimerization in quite good agreement with experiment; thus, this basis set appears to be adequate within the single determinant approximation.

The role of other valence bond structures in the hydrogen bond has been of great interest[19] and a nonorthogonal valence bond calculation on the hydrogen fluoride dimer is now underway at this laboratory.

One would expect a greater change in the $(LiF)_2$ wave function than the $(HF)_2$ upon including more valence bond structures, since in the lithium fluoride dimer, unlike the hydrogen fluoride dimer, the intermolecular distances are not much greater than the intramolecular, thus increasing the contribution of "charge transfer type" structures. However, a valence bond calculation on $(LiF)_2$ would not be meaningful until a better SCF wave function is available for the dimer.

Conclusions

In the lithium bonded systems studied, the molecular orbitals on the donor fall in energy while the molecular orbitals on the acceptor rise. This appears to be a general feature of not only lithium and hydrogen bonded systems, but all donor–acceptor interactions. In terms of MO energy changes, there is a fundamental difference between covalent bond formation (where electrons pair) and donor–acceptor bond formations.

The lithium bond is a normal donor–acceptor system, even though it may occur rarely in chemical systems. Dicoordinated lithium is expected only in the gas phase, and perhaps in molten salts.[20]

As the calculated geometries for $(HF)_2$ and $(LiF)_2$ are consistent with known experimental data, the authors have confidence in the hybrid dimer HFLiF. Before these calculations on the lithium fluoride dimer were done, it was easy to reconcile its cyclic structure on the basis of donation of the p electrons on fluorine to the vacant p orbitals on lithium. However, placing p orbitals on Li made no qualitative difference in the relative stability of the cyclic and linear structures, and actually reduced the energy of formation from isolated monomers.

The interaction of LiF with H_2 and Li_2 has been studied in an attempt to study hydrogen and lithium bonding with nonpolar diatomics. $LiF–H_2$ was found to be weakly bound, with the linear conformation the most stable. Both linear and perpendicular approaches were considered for $LiF–Li_2$ and the linear found to be more stable. Here, considerable structural and electronic reorganization was found with a tendency to form the near symmetric Li_2F^+ and Li^- ion pair.

Acknowledgments. The authors are grateful to Dr. Steven Rothenberg and Mr. William Jorgensen for the computer programs used in these calculations. The services and computer time made available to us by the Princeton University Computer Center (supported in part by National Science Foundation Grant No. NSF-GP579) is very much appreciated. Two of us (P. A. K. and J. F. L.) thank the National Science Foundation for fellowship support.

Appendix

Qualitative extrapolation of the results contained in the main body of the program used here leads the authors to suggest the desirability of experimental work on the following systems.

(1) The differences between lithium fluoride and

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(17) M. C. Moreau and A. Veillard, *Theor. Chim. Acta*, **11**, 344 (1968).

(18) D. Neumann and J. Moskowitz, *J. Chem. Phys.*, **49**, 2056 (1968), and A. Rauk, L. C. Allen, and E. Clementi ("The Ammonia Inversion Barrier"), to be submitted for publication, are studies of the role of d functions in water and ammonia, respectively.

(19) C. Coulson and L. Danielson, *Ark. Fys.*, **8**, 245 (1954).

(20) M. V. Smirnov, V. A. Khokntov, and T. A. Ruzonova, *Chem. Abstr.*, **67**, 47759*c* (1966); evidence is cited for $LiCl_4^{-3}$ and $CsCl_4^{3-}$ in molton LiCl/CsCl solutions. Other less symmetric species should be observable.

Table VI. MO Energies in au

Isolated LiF	Isolated HF	Isolated H_2O	Isolated H_2	Isolated Li_2
−25.6275	−26.1873	−20.4577	−0.5922	−2.4760
−2.4705	−1.5690	−1.3220		−2.4760
−1.1808	−0.7185	−0.6828		−0.1884
−0.2927	−0.6188	−0.5374		
−0.2927	−0.6188	−0.4846		
−0.2817				

$(H_2O)_2$ linear, $R = 3.0$ A, $\theta = 0°$

Donor (H_2O)	Δ	Acceptor (H_2O)	Δ
−20.4802	−0.0225	−20.4102	+0.0475
−1.3469	−0.0249	−1.2833	+0.0387
−0.7072	−0.0248	−0.6517	−0.0311
−0.5678	−0.0304	−0.4970	+0.0404
−0.5111	−0.0265	−0.4477	+0.0369

Average absolute value of MO energy changes = 0.0324 au

$(HF)_2$, $R = 2.88$ Å, $\theta = 0°$

Donor	Δ	Acceptor	Δ
−26.2208	−0.0335	−26.1495	+0.0378
−1.6061	−0.0371	−1.5389	+0.0301
−0.7711	−0.0526	−0.6825	+0.0360
−0.6566	−0.0378	−0.5898	+0.0290
−0.6566	−0.0378	−0.5898	+0.0290

Average absolute value of MO energy changes = 0.0361 au

HF–HOH (hydrogen fluoride as electron pair donor)

Donor	Δ	Acceptor (H_2O)	Δ
−26.2073	−0.0200	−20.4313	−0.0264
−1.5914	−0.0224	−1.2993	+0.0227
−0.7489	−0.0304	−0.6574	+0.0254
−0.6418	−0.0230	−0.5157	+0.0217
−0.6417	−0.0231	−0.4628	+0.0218

Average absolute value of MO energy changes = 0.0237 au

H_2O–HF (water as electron pair donor)

Donor (H_2O)	Δ	Acceptor (HF)	Δ
−20.5036	−0.0459	−26.0989	+0.0884
−1.3692	−0.0472	−1.5065	+0.0625
−0.7294	−0.0466	−0.6874	+0.0311
−0.5751	−0.0377	−0.5581	+0.0607
−0.5338	−0.0492	−0.5581	+0.0607

Average absolute value of MO energy changes = 0.0530

LiF–HF, R(F–F) = 2.381 A

Donor (LiF)	Δ	Acceptor (HF)	Δ
−25.7050	−0.0775	−25.9909	+0.1964
−2.5053	−0.0348	−1.4301	+0.1389
−1.2567	−0.0859	−0.6050	+0.1135
−0.3635	−0.0608	−0.4814	+0.1374
−0.3635	−0.0608	−0.4814	+0.1374
−0.3553	−0.0736		

Average absolute value of MO energy changes = 0.1015

HF–LiF, R(F–F) = 3.567 Å

Donor (HF)	Δ	Acceptor (LiF)	Δ
−26.2816	−0.0943	−25.5812	+0.0463
−1.6700	−0.1010	−2.4263	+0.0442
−0.8410	−0.1225	−1.1472	+0.0336
−0.7228	−0.1040	−0.2594	+0.0433
−0.7228	−0.1040	−0.2594	+0.0433
		−0.2546	+0.0271

Average absolute value of MO energy changes = 0.0694

LiF–Li_2, R(F–Li) = 1.588 Å

Donor (LiF)	Δ	Acceptor	Δ
−25.7438	−0.1164	−2.3981	+0.0779
−2.5296	−0.0591	−2.3694	+0.1066
−1.3144	−0.1336	−0.1275	+0.0609
−0.4433	−0.1616		
−0.4217	−0.1290		
−0.4217	−0.1290		

Average absolute value of MO energy changes = 0.1082

LiF_2-H_2, R(F–H) = 2.117 A

Donor (LiF)	Δ	Acceptor (H_2)	Δ
−25.6420	−0.0145	−0.5202	+0.0720
−2.4749	−0.0044		
−1.1926	−0.0118		
−0.3039	−0.0112		
−0.3039	−0.0112		
−0.2898	−0.0081		

Average absolute value of MO energy changes = 0.019

lithium hydride should be of interest. Although both are highly ionic, there is no orbital directionality in the hydride ion, while the fluoride ion has three p lobes.[21] Another contrast in the hydride and fluoride is the greater resonance contribution of Li^-H^+ to the lithium hydride wave function than the contribution of Li^-–F^+ to the lithium fluoride wave function. This difference could be best illustrated by reacting the two molecules with a nucleophilic reagent X:. Thus, X: + LiF will certainly form $(XLi)^+F^-$ ($(XF)^+Li^-$ is very unfavorable); X: + LiH should yield both $(XLi)^+H^-$ and $(XH)^+Li^-$ as bound states. A third distinguishing feature of LiF and LiH is illustrated by their cyclic structures. In the LiF cyclic dimer, the Li–F–Li linkage could be considered as a three-center, four-electron bond. On the other hand, in the LiH cyclic dimer, the H participates in a three-center, two-electron bond. Other chemical examples of the behavior are: $Pt_2F_{11}^-$ (three-center, four-electron bond) and B_2H_6 (three-center, two-electron bond).

(2) As experimental evidence for LiH_2^-,[22] CsF_2^-,[23]

Table VII. Summary of Molecular Orbital Energy Results[a]

System	ΔE (formation)	Average absolute value of MO energy change	Average change on donor	Average change on acceptor
$(H_2O)_2$	0.00804	0.0324	−0.026	0.039
$(HF)_2$	0.00732	0.0361	−0.040	0.032
HFHOH	0.00421	0.0237	−0.02378	0.02360
H_2OHF	0.01470	0.0530	−0.045	0.061
LiFHF	0.03950	0.1015	−0.066	0.145
HFLiF	0.02150	0.0694	−0.105	0.040
$LiFLi_2$	0.05760	0.1082	+0.121	0.082
$LiFH_2$	0.00286	0.0190	−0.010	0.072

[a] All energies in au.

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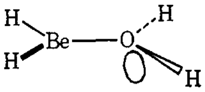
(21) By Unsöld's theorem, both H^- and F^- are spherically symmetric. One should note that we used no polarization functions (p's on H, d's on F) in our calculations. As s orbitals are individually spherically symmetric, the H^- here, even in a molecular environment, still has an isotropic environment regarding its contribution to the total wave function. Contrariwise, the p_x, p_y, and p_z orbitals are directional and independent, and thus an arbitrary linear combination, $c_1p_x + c_2p_y + c_3p_z$, is not sphericaliy symmetrical. Anisotropy is thus possible with F^- but not H^-.

and CsF_2^+[24] has been published, LiF_2^- and LiF_2^+ are of interest.

(3) In line with studying the donor–acceptor and internal rotation aspects of H_3NBH_3, a complete study of H_2OBeH_2 is logically the next step. While this system is isoelectronic to ethylene, there exists another reasonable geometry with its rotamers



(4) There is still considerable disagreement on the structure of the Grignard reagent (RMgX·etherate). The following isomorphic replacement should not alter the characteristics of the Grignard reagent as a donor–acceptor complex: H for R, Be for Mg, F for X (Cl, Br, I), H_2O for an ether.

(5) The simple triatomic system involving H, Be, and F is of interest. HBeF is isoelectronic to HCN. The isomer BeHF is reasonable as this is a normal donor–acceptor complex. HFBe should be considered by analogy to the Ar–HCl gas interaction,[25] where the observed structure is ArClH.

(6) Li_2F^+ appears to be a highly bound cation, which by analogy to Li_2O[10] is probably linear. It therefore seems reasonable that at least one crystalline phase of mixed crystal LiF·LiX should have the structure $Li_2F^+X^-$. This would be facilitated by a large and noncomplexing anion X such as SbF_6^-, as crystal packing favors equally sized ions.

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(22) H. Baumann, K. Tetige, and E. Heinicke, *Nucl. Instrum. Methods*, **46**, 43 (1967). Using a Penney discharge through a Ne/H_2/Li gas mixture, of the negative charged species, one with *m/e* 9 was observed. This appears to be due to LiH_2^-.

(23) E. W. Lawless and I. C. Smith, "Inorganic High Energy Oxidizers," Marcel Dekker, New York, N. Y., 1968, p 117. A mixture of CsF and ClF_3 at 0° was found to yield a conducting solution. Other evidence showed this was not $Cs^+ClF_4^-$. It was thus attributed to $CsF_2^+ClF_2^-$ and/or $ClF_2^+CsF_2^-$.

(24) As pointed out in ref 23, CsF_2^+ is isolectronic to XeF_2. Therefore LiF_2^+ offers an interesting contrast with the previously studied HeF_2 (L. C. Allen, R. M. Erdahl, and J. L. Whitten, *J. Amer. Chem. Soc.*, **87**, 3769 (1965)) and HF_2^- (R. M. Erdahl, see ref 15).

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π Complexation in Ion Pair Bonding. The Structure of Benzyllithium Triethylenediamine[1]

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Abstract: The crystal structure of benzyllithium triethylenediamine, $C_6H_5CH_2^-Li^+N(C_2H_4)_3N$, has been determined from three-dimensional X-ray data collected by counter methods. A full-matrix least-squares refinement on 714 reflections resulted in a final unweighted discrepancy factor of 7.9%. The material crystallizes in the orthorhombic space group $P2_12_12_1$ in a cell of dimensions $a = 16.231(8)$, $b = 6.255(3)$, $c = 11.800(6)$ Å. The measured and calculated densities are 1.17 and 1.16 g/cm^3, respectively. The structure consists of infinite polymeric chains of solvated ion pairs linked by triethylenediamine cages which propagate along the *c* direction. Each ion pair molecule consists of a benzyl carbanion and two half triethylenediamine cages coordinated to a lithium cation. The average C–C distance in the carbanion is 1.40 (1) Å and the average Li–N distance is 2.10 (1) Å. Each lithium atom is formally sp^2 hybridized if the point on the carbanion which is closest (2.17 Å) to the lithium atom is considered as a coordination site. Evidence is presented for complexation of the lithium cation with the π cloud of the benzyl carbanion. A discussion of the bonding is presented.

The lack of structural knowledge of organolithium compounds is in sharp contrast to their widespread use.[2] The only detailed crystallographic structural investigations have been of unsolvated CH_3Li,[3a] C_2H_5Li,[3b] and $LiAl(C_2H_5)_4$.[4] In these and other alkyllithium compounds,[5] polynuclear species are formed which have structural properties which suggest electron deficient bonding similar to that found in organoaluminum, -beryllium, and -magnesium compounds.

Addition of Lewis bases greatly enhances the reactivity of organolithium reagents in metalation, substitution, and polymerization reactions. Examples are the telomerization process,[6] where stable aryl-lithium–amine adduct intermediates give rise to high molecular weight "telomers," and rapid metalations of previously unreactive hydrocarbons by *n*-butyllithium activated by 1,4-diazabicyclo[2.2.2]octane (triethylenediamine) or N,N,-N′,N′-tetramethylethylenediamine.[7,8] Eberhardt and Butte[6] have postulated that the amine decreases the polarizing power of the lithium moiety, thus weakening the covalent nature of the carbon–lithium bond. This

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(1) This work was supported by the Advanced Research Projects Agency under Contract SD-131 and the National Science Foundation.

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