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Recommended Citation
Ab initio comparison of H bonds and Li bonds. Complexes of LiF, LiCl, HF, and HCl with NH[sub 3] Z. Latajka and Steve Scheiner, J. Chem. Phys. 81, 4014 (1984), DOI:10.1063/1.448143

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Ab initio comparison of H bonds and Li bonds. Complexes of LiF, LiCl, HF, and HCl with NH_3

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(Received 21 May 1984; accepted 28 June 1984)

Ab initio calculations are carried out on the complexes H_3N–LiF, H_3N–LiCl and their analogs H_3N–HF and H_3N–HCl as well as the isolated subunits. Double-zeta basis sets, augmented by two sets of polarization functions, are used in conjunction with second-order Moller–Plesset perturbation theory (MP2) for evaluation of electron correlation effects. The Li bonds are found to be substantially stronger than their H-bonding counterparts, due in large measure to the greater dipole moments of the LiX subunits. Correlation has a large effect on the geometry and energetics of both H-bonded complexes, reducing the intermolecular separation and contributing between 20% and 40% to the total complexation energy. In contrast, the SCF and MP2 results for the Li bonds are nearly identical. The small net effect of correlation in these complexes is ascribed to cancellation between incorporation of dispersion and reduction of the electrostatic component. Another distinction between the two types of bonds arises from consideration of the stretch of the LiX and HX bonds resulting from complex formation. Whereas correlation increases the magnitude of this bond elongation in the H bonds, an opposite trend is noted in the Li bonds.

Although it is frequently assumed that hydrogen is unique in its ability to participate in a three-center interaction known as a hydrogen bond, there have been suggestions[1–3] over the years that lithium might also be involved in similar attractive bonds. Whereas the H bond has been investigated in great detail by experimental and theoretical approaches,[4–6] the analogous Li bond has remained relatively unexplored. Experimental proof of the existence of a stable 1:1 Li-bonded complex was first provided by a matrix isolation infrared study by Ault and Pimentel.[7] These workers found the frequency shifts of the LiCl and LiBr stretching bands in complexes with amines to be qualitatively similar to those noted for analogous proton donors. However, these frequency shifts were substantially smaller than in the H bonds and the infrared intensity changes characteristic of H bonds were absent.

More recently, Li-bonded complexes have been investigated at the *ab initio* SCF level by various investigators.[8–15] The results have furnished evidence that the Li bond is considerably stronger than analogous H bonds. However, the previous calculations were limited with respect to both the choice of Li-bonding molecules (LiF or LiH) and the size of basis set. Moreover, the previous work completely ignored the possible effects of electron correlation upon the results. Our aim in the present paper is a systematic study of Li bonding and comparison with the analogous H bonds. Extended basis sets are used along with incorporation of electron correlation to ensure reliable results.

The systems chosen for study are the complexes formed between LiF and LiCl on one hand and NH_3 on the other. Comparison between LiF and LiCl is expected to yield insights into the differences between first- and second-row atoms with respect to Li bonding. The analogous H-bonded systems studied here are the complexes of HF and HCl with NH_3. An advantage of working with the latter systems is the availability of experimental information[16–19] for purposes of comparison. Molecular-beam electric resonance and IR low-temperature matrix isolation measurements indicate these complexes belong to the C_{3v} point group. In addition, the intermolecular distance and dipole moments of the H_3N–HF complex in the gas phase have been determined. Despite previous *ab initio* SCF calculations of these H-bonded complexes,[14,20–24] reliable values of the complexation energy have still not been obtained. An additional objective of the present work is therefore accurate determination of the H-bond energies in H_3N–HF and H_3N–HCl.

DETAILS OF CALCULATIONS

All calculations were carried out using the GAUSSIAN-80 package of computer codes.[25] Electron correlation was considered via Møller–Plesset perturbation theory[26,27] to the second (MP2) order and keeping the inner shells of first- and second-row atoms frozen. Quadrupole moments were evaluated with the molecular properties package of the MONSTERGAUSS program.[28]

Our choice of basis set was a modified form of the standard[29] 6-31G**. For N, F, and Cl, an additional set of five *d* functions was added with exponent $\zeta = 0.25$.[30] All hydrogen atoms in NH_3 were supplied with a diffuse set of *p* orbitals with $\zeta = 0.15$.[30] In the case of the H-bonding proton of HF and HCl, a second set of more contracted *p* functions was also included with exponent 1.1. The lithium atom of LiF and LiCl was described by the standard 6-31G* basis set. We may therefore use the notation 6-31G** (2*p*, 2*d*) to describe the basis set of HX, 6-31G** (1*p*, 2*d*) for NH_3, and 6-31G** (2*d*) for LiX.

Geometry optimizations were carried out at the SCF and MP2 levels for the isolated HF, HCl, LiF, and LiCl subunits. The structure of NH_3 was adopted from previous optimizations with the FOGO method[31] ($r_{NH} = 1.011$ Å and

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TABLE I. Properties of isolated molecules.

	SCF	MP2	Exp.[a]
	HF		
r(Å)	0.900	0.922	0.917
μ(D)	1.81	1.85[b]	1.83
θ_{zz}(B)	2.24		2.36
	HCl		
r(Å)	1.270	1.277	1.274
μ(D)	1.17	1.17[b]	1.11
θ_{zz}(B)	3.88		3.25
	LiF		
r(Å)	1.564	1.578	1.564
μ(D)	6.23	6.29[b]	6.32
θ_{zz}(B)	6.05		
	LiCl		
r(Å)	2.067	2.068	2.021
μ(D)	7.41	7.42[b]	7.13
θ_{zz}(B)	14.08		
	NH_3		
r(Å)	1.012[c]		1.012
θ(HNH)(deg)	107.6[c]		106.7
μ(D)	1.51		1.48
θ_{zz}(B)	2.70		3.25

[a] From Ref. 32.
[b] SCF value at MP2 geometry.
[c] From FOGO optimization, Ref. 31.

θ (HNH) = 107.6°). In line with the experimental information,[16–19] C_{3v} geometries were assumed for all complexes. For the lithium-bonded systems, the linearity of the N–Li–X bond was checked and verified using the 6-31G** basis set. The internal geometry of NH_3 was held fixed while the intermolecular separation R (N···X) and r(XY) bond lengths (where X = F or Cl and Y = H or Li) were optimized. Interaction energies were computed as the difference in total energy between each complex and the reference subunits at infinite separation.

RESULTS

Subunits

Before presenting our results for the complexes, we begin with an examination of the properties of the isolated subunits. The results of geometry optimizations of the diatomics at both the SCF and MP2 levels are contained in Table I along with experimental data for purposes of comparison. It is clear that inclusion of second-order correlation has a lengthening effect on each bond. This stretch ranges from a maximum of 0.022 Å for HF to a minimum of 0.001 Å for LiCl. In any pair of diatomics, the bond stretch is greater in the molecule containing F than Cl; similarly, HX is more susceptible to correlation than is LiX.

It is well known that electrostatic effects play a major role in H bonding. Previous investigations by Umeyama and Morokuma[13] indicate similar behavior in Li bonds. It is therefore extremely important that the theoretical method faithfully reproduce the electrical properties of each subunit. For this reason, the generally close agreement found between calculated dipole and quadrupole moments and the corresponding experimental estimates is gratifying. As may be seen in Table I, the calculated dipole moments all fall within 5% of the experimental values; quadrupole moments are also reproduced rather well. We therefore expect our basis set to provide a good measure of the quantitative contribution of electrostatic forces to each interaction.

A second important requirement of the basis set is that it provide an adequate framework for evaluation of correlation effects. Previous work has demonstrated that basis sets of the type being applied here which contain diffuse sets of polarization functions yield quantitatively correct descriptions of correlation effects in intermolecular interactions.[33–35] Moreover, the exponents used here are quite similar to those recommended by Kochanski[36,37] as being especially suitable for study of dispersion in molecular complexes.

Complexes

The calculated properties of the complexes are compiled in Table II along with data from previous calculations and the experimental information available for H_3N–HF. We begin with an examination of the effects of correlation upon the geometries of each complex. It is clear that inclusion of second-order effects significantly alters the structure of the H-bonded systems whereas only a very small change is noted in H_3N–LiF. The reductions in H-bond length R (N–X) are equal to 0.035 Å for H_3N–HF and 0.153 Å in H_3N–

TABLE II. Calculated properties of complexes.

	H_3N–HF				H_3N–HCl				H_3N–LiF			H_3N–LiCl
	SCF	MP2	a	Exp.[d]	SCF	MP2	a	b	SCF	MP2	c	SCF
R (N...X)(Å)	2.728	2.693	2.763	2.66	3.297	3.144	3.314	3.228	3.652	3.665	3.653	4.118
r(XY)(Å)	0.922	0.950	0.918		1.293	1.317	1.291	1.323	1.582	1.592	1.623	2.082
Δr(XY)[e] (Å)	0.022	0.028	0.019		0.023	0.040	0.021		0.018	0.014	0.02	0.020
ΔE^{SCF} (kcal/mol)	−11.84	−11.80	−11.81		−9.29	−6.59			−22.89	−22.81	−25.31	−25.46
ΔE^{MP2} (kcal/mol)	−14.86	−15.09			−10.42	−11.03		−9.0	−23.48	−23.52		−26.65
μ^{SCF} (D)	4.39	4.56	4.74	4.45	3.90	4.30	4.45		8.74	8.79		10.16
$\Delta\mu^{SCF}$ (D)	0.97	1.12	0.72	1.20	1.13	1.52	1.03		0.91	0.90		1.14

[a] From Ref. 24, $DZ + P$ basis set.
[b] From Ref. 23, [431/321/21] basis set, CI results.
[c] From Ref. 11, DZ basis set.
[d] From Ref. 19.
[e] Δr (XY) = r (XY)$_{complex}$ − r (XY)$_{subunit}$.

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HCl; the reverse trend of a small *increase* (0.013 Å) is observed in H_3N–LiF. It is noted that the MP2 value of R in H_3N–HF concurs rather well with the experimental bond length.

In all cases, formation of the complex leads to a stretch of the internal XY bond. This bond lengthening, compared to the value in the isolated subunit, is listed as Δr in the third row of Table II. A clear distinction between H bonds and Li bonds arises from consideration of the effect of correlation upon this bond stretch. Whereas an increase in the bond lengthening results from correlation effects in the H bonds (e.g., from 0.023 to 0.040 Å in H_3N–HCl), the MP2 value of Δr is smaller than the SCF quantity for H_3N–LiF. This point is particularly important in comparing H bonds and Li bonds with respect to Δr. At the SCF level, Δr for H_3N–HF and H_3N–LiF are nearly equal, which might lead to an erroneous conclusion of close similarity between the two types of bonds. However, when correlation is included, Δr in the H bond is twice the magnitude of Δr in H_3N–LiF, reflecting an important distinction between the two bonds.

The fourth row of Table II contains the interaction energy of each complex computed at the SCF level and using the geometry listed at the top of each column. Thus, the SCF interaction energy of H_3N–HF is -11.84 kcal/mol using the SCF geometry and the slightly smaller value of -11.80 with the MP2 geometry. Analogous complexation energies calculated at the MP2 level are contained in the next row. Comparison of these two rows illustrates the effect of correlation upon the interaction energy. Using geometries appropriate to each level of theory, MP2 increases the H-bond energy of H_3N–HF from -11.84 to -15.09 kcal/mol; the analogous increase in H_3N–HCl is from -9.29 to -11.03. If one is interested in the contribution of correlation to the total interaction energy at the equilibrium geometry, a more appropriate measure would be the difference between ΔE^{MP2} and ΔE^{SCF}, both evaluated at the MP2 geometry. Thus, correlation contributes -4.44 kcal/mol, or 40%, to the stability of H_3N–HCl (11.03–6.59) and the smaller amount of -3.29 (22%) to H_3N–HF.

Before comparing our theoretical H-bond energies with experiment, it is first necessary to subtract off zero-point vibrational contributions. Raffenetti and Phillips[23] have previously estimated this correction in H_3N–HCl to be 3.1 kcal/mol which is the value we adopt here. Combining this correction with our best (MP2) electronic interaction energy of -11.03, we arrive at a theoretical dissociation energy of 7.9 kcal/mol, in excellent agreement with the experimental value[38] of 8.0 ± 2.8.

The Li-bond energies in Table II are clearly much greater than the corresponding H bonds. For example, the SCF interaction energy of H_3N–LiF is approximately twice that of H_3N–HF. This fact is not surprising in view of the much higher dipole moments of the LiX molecules (see Table I). As was pointed out above, correlation has little influence on the geometry of H_3N–LiF. For this reason, geometry optimization was carried out only at the SCF level for H_3N–LiCl. It is clear from the data in Table II that correlation has little effect on the Li-bond energy of either complex. The total contribution of second-order perturbation effects to the complexation energy of H_3N–LiF is 0.7 kcal/mol, less than 3% of the total; the analogous quantity in H_3N–LiCl is 1.2 kcal/mol, amounting to 4%.

The penultimate row of Table II contains the SCF dipole moments of each complex computed for the SCF and MP2 geometries. Of particular interest are the enhancements of these moments which result from the molecular interaction; i.e., the difference between μ of the complex and the sum of the moments of the isolated subunits. This quantity is presented in the last row of Table II as $\Delta\mu$ and shows that the enhancement of dipole is considerable in all complexes, ranging between 0.9 and 1.5 D. The latter large value is associated with the MP2 geometry of the H_3N–HCl complex and has its roots in a number of effects. Most important is probably the lengthening of the HCl bond by 0.04 Å in the complex and the charge transfer to the NH_3 subunit. The dipole data in Table II may be checked against experimental information for H_3N–HF where molecular beam electric resonance techniques[19] have yielded a dipole moment of 4.45 D which concurs nicely with our calculated data. Also in good agreement are the theoretical and experimental values of the dipole moment enhancement $\Delta\mu$.

DISCUSSION

The data reported here have elucidated several fundamental differences between hydrogen and lithium bonds. Li bonds are generally quite a bit stronger, due in large part to the higher dipole of the LiX subunit than of the HX counterpart. Indeed, by far the largest component of the complexation energies in Li bonds is electrostatic. In contrast, although the contribution of electrostatic energy is rather large in H bonds, other components make major contributions as well. One of these components is dispersion which our results indicate has a substantial effect of the properties of the H bond. The intermolecular separation is shortened considerably when correlation is included and an increase is observed in the HX bond stretch resulting from complexation. The geometry changes resulting from correlation in the Li bonds are much smaller and of opposite sign; the N–X bond is slightly lengthened and the LiX stretch is reduced.

Another important distinction between the two bond types concerns the amount of stabilization contributed by correlation. MP2 increases the H-bond strengths over the SCF values by 20% to 40% whereas only very small increases of less than 5% occur in the Li bonds. These above trends may be explained rather well in terms of two competing effects. From the work of Amos[39] and Diercksen *et al.*[40] it is known that second-order perturbation theory leads to a reduction in the dipole moment of each subunit and hence to a drop in the electrostatic attraction in the complex. On the other hand, correlation introduces attractive dispersion forces into the calculations. The introduction of dispersion clearly outweighs the decrease of the electrostatic attraction in the H bonds, as evidenced by the increase in H-bond energy and reduction of intermolecular distance. As further verification of this point, it is noted that the greater polarizability of HCl than of HF is expected to lead to a greater dispersion energy, in accord with the more pronounced effects of correlation in H_3N–HCl than in H_3N–HF. The mag-

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TABLE III. Equilibrium distance to N atom and complexation energy.

	r(N–H)(Å)	ΔE^{MP2}(kcal/mol)
H_3N–H^+	1.021[a]	−213.4[a]
H_3N–HF	1.743	−15.13
H_3N–HCl	1.827	−11.03
	r(N–Li)(Å)	
H_3N–Li^+	2.037[a]	−39.72[a]
H_3N–LiF	2.073	−23.52
H_3N–LiCl	2.036[b]	−26.65[b]

[a] From Ref. 35; 6-31G**(2p, 2d) basis set.
[b] SCF geometry.

nitudes of the two opposing effects are more equally balanced in the Li bonds with their greater electrostatic character; hence, the net result of including correlation is extremely small.

Comparison of distances of approach of the H and Li nuclei to nitrogen provides some enlightening information about these two bonds. These distances are listed in Table III for the complexes with geometries optimized at the MP2 level, along with computed energies of interaction. For purposes of comparison, we have provided also the analogous data for attack on NH_3 by a naked proton or lithium cation. It is obvious that the N–H distances are considerably shorter than N–Li, not surprising in light of the presence of a core of 1s electrons in Li^+. The naked proton can deeply penetrate the NH_3 charge cloud, leading to a very short N–H distance in H_3N–H^+ and high complexation energy. However, this situation is quite different when the proton is initially bound to a halogen atom: the distances are nearly twice as long and the interaction energies reduced by more than an order of magnitude. In contrast, there is much less difference between the attack on NH_3 by a naked Li^+ or by a LiX molecule. The Li-bond energies are more than half as large as the complexation energy of H_3N–Li^+. Moreover, the N–Li distances in the Li-bonded complexes are quite similar to the optimal distance of approach of the naked lithium cation. In fact, the lithium nucleus in H_3N–LiCl is approximately midway between the N and Cl atoms. We therefore conclude that whereas the proton in H bonds is definitely associated with the X atom, the Li nucleus is more fully shared between the N and X atoms.

ACKNOWLEDGMENTS

Allocations of computer time were made available by the SIU Computing Center. This work was supported by grants from NIH (GM29391 and AM01059) and from the Research Corporation.

[1] D. N. Shigorin, Spectrochim. Acta **14**, 198 (1959).
[2] F. West and W. Glaze, J. Am. Chem. Soc. **83**, 3581 (1961).
[3] T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, J. Am. Chem. Soc. **84**, 1371 (1962).
[4] *The Hydrogen Bond*, edited by P. Schuster, G. Zundel, and C. Sandorfy (North–Holland, Amsterdam, 1976).
[5] *Molecular Interactions*, edited by H. Ratajczak and W. J. Orville-Thomas (Wiley, New York, 1981), Vols. I and II.
[6] P. Hobza and R. Zahradnik, *Weak Intermolecular Interactions in Chemistry and Biology* (Elsevier, Amsterdam, 1980).
[7] B. S. Ault and G. C. Pimentel, J. Phys. Chem. **79**, 621 (1975).
[8] P. A. Kollman, J. F. Liebman, and L. C. Allen, J. Am. Chem. Soc. **92**, 1142 (1970).
[9] P. Kollman, C. F. Bender, and S. Rothenberg, J. Am. Chem. Soc. **94**, 8016 (1972).
[10] M. M. Szczęśniak, H. Ratajczak, U. P. Agarwal, and C. N. R. Rao, Chem. Phys. Lett. **44**, 465 (1976).
[11] H. Ratajczak and M. M. Szczęśniak, C. R. Acad. Sci. Paris **285C**, 341 (1977).
[12] M. M. Szczęśniak and H. Ratajczak, J. Chem. Phys. **67**, 5400 (1977).
[13] H. Umeyama and K. Morokuma, J. Am. Chem. Soc. **99**, 1316 (1977).
[14] M. M. Szczęśniak and H. Ratajczak, Chem. Phys. Lett. **74**, 243 (1980).
[15] M. M. Szczęśniak, Z. Latajka, P. Piecuch, H. Ratajczak, W. J. Orville-Thomas, and C. N. R. Rao, Chem. Phys. (in press).
[16] B. S. Ault and G. C. Pimentel, J. Phys. Chem. **77**, 1649 (1973).
[17] B. S. Ault, E. Steinback, and G. C. Pimentel, J. Phys. Chem. **79**, 615 (1975).
[18] G. L. Johnson and L. Andrews, J. Am. Chem. Soc. **104**, 3043 (1982).
[19] See Ref. 11 in Ref. 18.
[20] P. A. Kollman and S. Rothenberg, J. Am. Chem. Soc. **99**, 1333 (1977).
[21] J. D. Dill, L. C. Allen, W. C. Topp, and J. A. Pople, J. Am. Chem. Soc. **97**, 7220 (1975).
[22] J. A. Pople, Faraday Discuss. Chem. Soc. **73**, 7 (1982).
[23] R. C. Raffenetti and D. H. Phillips, J. Chem. Phys. **71**, 4534 (1979).
[24] A. Hinchliffe, J. Mol. Struct. **105**, 335 (1983).
[25] J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn, and J. A. Pople, GAUSSIAN-80, Program No. 406 (1981).
[26] C. Møller and M. S. Plesset, Phys. Rev. **46**, 618 (1934).
[27] J. S. Binkley and J. A. Pople, Int. J. Quantum Chem. **9**, 229 (1975).
[28] M. R. Peterson and R. A. Poirier, MONSTERGAUSS, Department of Chemistry, University of Toronto, Toronto, Ontario, M5S 1A1 Canada.
[29] P. C. Hariharan and J. A. Pople, Theor. Chim. Acta **28**, 213 (1973); P. C. Hariharan and J. A. Pople, Mol. Phys. **27**, 209 (1974); M. M. Franck, W. J. Pietro, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees, and J. A. Pople, J. Chem. Phys. **77**, 3654 (1982).
[30] J. G. C. M. van Duijneveldt-van de Rijdt and F. B. van Duijneveldt, J. Mol. Struct. **89**, 185 (1982).
[31] Z. Latajka, S. Scheiner, and P. Huber (manuscript in preparation).
[32] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure* (Van Nostrand Reinhold, New York, 1979), Vol. IV.
[33] P. Čarsky and M. Urban, *Ab Initio Calculations, Lecture Notes in Chemistry* (Springer, Berlin, 1980), Vol. 16, p. 186.
[34] S. Wilson, in *Methods in Computational Molecular Physics*, edited by G. H. F. Diercksen and S. Wilson, NATO ASI Series C, (Reidel, Dordrecht, 1983), Vol. 113, pp. 71–93.
[35] Z. Latajka and S. Scheiner, Chem. Phys. (submitted).
[36] E. Kochanski, in *Intermolecular Forces, The Jerusalem Symposium on Quantum Chemistry and Biochemistry*, edited by B. Pullman (Reidel, Dordrecht, 1981). Vol. 14, p. 15.
[37] E. Kochanski, J. Mol. Struct. **107**, 49 (1984).
[38] P. Goldfinger and G. Verhaegen, J. Chem. Phys. **50**, 1467 (1969).
[39] R. D. Amos, Chem. Phys. Lett. **73**, 602 (1980).
[40] G. H. F. Diercksen and A. J. Sadlej, J. Chem. Phys. **75**, 1253 (1981); G. H. F. Diercksen, V. Kellö, and A. J. Sadlej, *ibid.* **79**, 2918 (1983); G. H. F. Diercksen, B. O. Roos, and A. J. Sadlej, Int. J. Quantum Chem. Symp. **17**, 265 (1983).

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