



# An *ab initio* study of the properties of some lithium-bonded complexes – Comparison with their hydrogen-bonded analogues.

## 2. Natural bond orbital and quantum theory of atoms in molecules analysis



Thomas A. Ford

School of Chemistry and Physics, University of KwaZulu-Natal, Westville Campus, Private Bag X54001, Durban 4000, South Africa

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### ABSTRACT

A series of lithium-bonded complexes containing lithium fluoride, chloride and bromide and the common bases ammonia, water, phosphine and hydrogen sulphide have been studied by means of *ab initio* molecular orbital theory. A similar set of complexes, in which the lithium halides were replaced by the hydrogen halides, was also investigated in order to establish the similarities and differences between the corresponding families of complexes. The molecular orbital properties were examined using natural bond orbital (NBO) theory with the object of determining which specific electron donor and acceptor orbitals were involved in each pair of interacting molecules. The electron density topologies were also studied, within the framework of the quantum theory of atoms in molecules (QTAIM), in an effort to ascertain in what ways the electron densities of the isolated monomers responded to the formation of the individual complexes. The parallels between the properties of the two sets of complexes have been described, and the differences traced back to the natures of the constituent monomers.

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## 1. Introduction

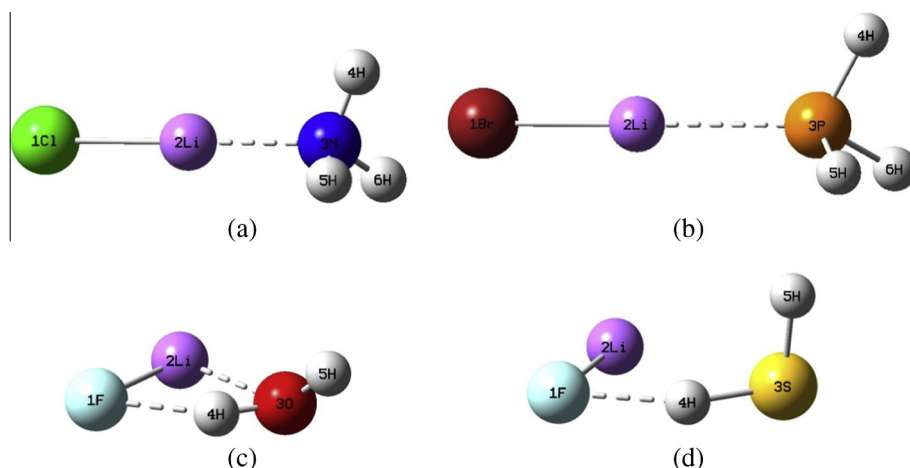
The lithium bond has been the subject of a great deal of research, both experimental and theoretical [1], ever since its first observation by Shigorin in 1959 [2]. In the first paper of this series [3], we briefly reviewed some of the literature on the properties of the lithium bond, and reported the results of our *ab initio* calculations on the twelve lithium-bonded complexes formed between lithium fluoride, chloride and bromide, as electron acceptors, and ammonia, water, phosphine and hydrogen sulphide, as electron donors. We determined the structures of these adducts, and found that the complexes with  $\text{NH}_3$  and  $\text{PH}_3$  possessed  $C_{3v}$  symmetry, with a linear  $\text{XLi} \dots \text{N(P)}$  fragment ( $\text{X} = \text{F, Cl, Br}$ ), while in the case of the  $\text{H}_2\text{O}$  and  $\text{H}_2\text{S}$  complexes, the structures featured a four-membered ring containing the Li, X, O(S) and one of the H atoms in a virtually planar arrangement, and with the second OH or SH bond projecting approximately normally to this pseudo-plane. The optimized structures of a sample of these complexes are shown in Fig. 1. The identities of the specific base and lithium halide orbitals which contribute to the stabilities of these complexes, determined by using natural bond orbital (NBO) theory

[4], and their influence on the variations in the properties of the complexes are part of the subject of the present work. The second thrust is an analysis, using the quantum theory of atoms in molecules (QTAIM) [5,6], of the electron densities and their topologies, and their relationship with the structures and other properties of the complexes. We have already calculated the binding energies, corrected for basis set superposition error and zero-point energy differences, and the vibrational spectra of the lithium-bonded complexes [3], and the binding energies are reproduced in Table 1. We were interested in establishing the relationships between the orbital properties, the electron density characteristics and the strengths of interaction on complexation. At each stage we compared the properties of the lithium-bonded species with those of their hydrogen-bonded counterparts.

## 2. Computational details

Our original calculations [3] were carried out using the Gaussian-09 program [7]. Møller–Plesset perturbation theory at the second order level (MP2) [8] and Dunning's augmented correlation-consistent polarized valence triple-zeta basis set (aug-cc-pVTZ) [9–13] were employed. Natural bond orbital analyses [4] were carried out with the NBO program of Glendening et al. [14], which forms

E-mail address: [ford@ukzn.ac.za](mailto:ford@ukzn.ac.za)



**Fig. 1.** Optimized structures of (a) LiCl-NH<sub>3</sub>, (b) LiBr-PH<sub>3</sub>, (c) LiF-H<sub>2</sub>O and (d) LiF-H<sub>2</sub>S (from Ref. [3]). Structures of the corresponding remaining complexes are qualitatively similar.

**Table 1**

Binding energies, corrected for basis set superposition error and vibrational zero-point energy differences, of the lithium-bonded complexes with NH<sub>3</sub>, H<sub>2</sub>O, PH<sub>3</sub> and H<sub>2</sub>S, and their hydrogen-bonded analogues (reproduced from Ref. [3]).

Base	Binding energy/kJ mol <sup>-1</sup>					
	LiF	LiCl	LiBr	HF	HCl	HBr
NH <sub>3</sub>	72.02	82.28	84.55	43.32	31.41	29.77
H <sub>2</sub> O	77.31	74.79	75.33	25.51	15.97	13.20
PH <sub>3</sub>	34.41	41.75	43.52	14.44	9.90	8.82
H <sub>2</sub> S	43.74	43.18	44.08	13.45	9.29	8.18

part of the Gaussian-09 package [7]. The quantum theory of atoms in molecules (QTAIM), due to Bader [5,6], was applied to analyse the electron densities and their properties, through the use of Keith's AIMAll program [15].

### 3. Results and discussion

#### 3.1. Natural bond orbital analysis

The NBO analysis for the various complexes yielded the results shown in Table 2. They reveal, in the case of the lithium-bonded

**Table 2**

Major molecular orbital interactions of the lithium-bonded complexes with NH<sub>3</sub>, H<sub>2</sub>O, PH<sub>3</sub> and H<sub>2</sub>S, and their hydrogen-bonded analogues.

Complex	Lithium-bonded complexes		Complex	Hydrogen-bonded complexes	
	Orbital interaction	Orbital interaction energy/kJ mol <sup>-1</sup>		Orbital interaction	Orbital interaction energy/kJ mol <sup>-1</sup>
LiF-NH <sub>3</sub>	n(N)(2sp <sup>3</sup> ) → Li(2sp)	75.3	HF.NH <sub>3</sub>	n(N)(2sp <sup>3</sup> ) → σ*(HF)	172.7
LiF-H <sub>2</sub> O	n(O)(2sp <sup>3</sup> ) → Li(2p)	68.8	HF.H <sub>2</sub> O	n(O)(2sp <sup>3</sup> ) → σ*(HF)	86.2
	n(F)(2p) → σ*(OH)	69.3			
LiF-PH <sub>3</sub>	n(P)(3sp <sup>3</sup> ) → Li(2sp)	139.7	HF.PH <sub>3</sub>	n(P)(3sp <sup>3</sup> ) → σ*(HF)	58.9
LiF-H <sub>2</sub> S	n(S)(3p) → Li(2p)	109.3	HF.H <sub>2</sub> S	n(S)(3p) → σ*(HF)	59.6
	n(F)(2p) → σ*(SH)	82.6			
LiCl-NH <sub>3</sub>	n(N)(2sp <sup>3</sup> ) → Li(2sp)	139.7	HCl.NH <sub>3</sub>	n(N)(2sp <sup>3</sup> ) → σ*(HCl)	181.4
LiCl-H <sub>2</sub> O	n(O)(2sp <sup>3</sup> ) → Li(2p)	93.8	HCl.H <sub>2</sub> O	n(O)(2sp <sup>3</sup> ) → σ*(HCl)	63.6
	n(Cl)(3p) → σ*(OH)	16.8			
LiCl-PH <sub>3</sub>	n(P)(3sp <sup>3</sup> ) → Li(2sp)	240.7	HCl.PH <sub>3</sub>	n(P)(3sp <sup>3</sup> ) → σ*(HCl)	48.5
LiCl-H <sub>2</sub> S	n(S)(3p) → Li(2p)	145.0	HCl.H <sub>2</sub> S	n(S)(3p) → σ*(HCl)	55.0
	n(Cl)(3p) → σ*(SH)	12.0			
LiBr-NH <sub>3</sub>	n(N)(2sp <sup>3</sup> ) → Li(2sp)	146.3	HBr.NH <sub>3</sub>	n(N)(2sp <sup>3</sup> ) → σ*(HBr)	231.9
LiBr-H <sub>2</sub> O	n(O)(2sp <sup>3</sup> ) → Li(2p)	98.2	HBr.H <sub>2</sub> O	n(O)(2sp <sup>3</sup> ) → σ*(HBr)	64.4
	n(Br)(4p) → σ*(OH)	14.9			
LiBr-PH <sub>3</sub>	<sup>a</sup>		HBr.PH <sub>3</sub>	n(P)(3sp <sup>3</sup> ) → σ*(HBr)	53.2
LiBr-H <sub>2</sub> S	n(S)(3p) → Li(2p)	194.1	HBr.H <sub>2</sub> S	n(S)(3p) → σ*(HBr)	59.7
	n(Br)(4p) → σ*(SH)	14.3			

<sup>a</sup> NBO analysis indicates that BrLiPH<sub>3</sub> is a single molecule, with a LiP σ bond.

complexes with NH<sub>3</sub> and PH<sub>3</sub>, a single donor–acceptor interaction involving donation from a N or P sp<sup>3</sup> hybrid lone pair orbital into a vacant axial 2sp hybrid orbital on lithium. This finding is consistent with the linear XLi...N(P) arrangement determined by the geometry optimizations [3]. For the hydrogen-bonded aggregates the donor orbitals are again N and P lone pairs, and the acceptor orbitals are σ\*(HF,HCl,HBr) antibonding orbitals. In the case of the H<sub>2</sub>O and H<sub>2</sub>S complexes the principal source of electron donation is from an O or S lone pair to either an empty Li 2p or a σ\*(HF,HCl,HBr) antibonding orbital. The Li 2p orbital axes lie approximately perpendicular to the LiX bond, resulting in XLi...Y bond angles close to 90° (Y = O,S). For this series there is also back donation from a F(Cl,Br) p orbital of the halogen atom to an empty σ\*(OH) or σ\*(SH) orbital, resulting in an almost perpendicular OH...X or SH...X hydrogen bond, explaining the cyclic nature of this set of complexes (see Fig. 1). Only for the LiF-H<sub>2</sub>O and LiF-H<sub>2</sub>S complexes does this back donation compare energetically with the major source of interaction.

The orbital interaction energies might be expected to correlate, at least partly, with the binding energies of the complexes, especially if the orbital interaction were a major source of the attraction, and this is indeed the case for the NH<sub>3</sub> and PH<sub>3</sub> complexes of the

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