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Ab initio and DFT investigations of lithium/hydrogen bonded complexes of trimethylamine, dimethyl ether and dimethyl sulfide

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Ab initio and DFT computations have been carried out on LiF and HF complexes of a set of n-donors *viz.* trimethylamine, dimethyl ether and dimethyl sulfide with a 6-31 + + G(d,p) basis set. The effect of correlation has been included with MP2, MP4 and DFT calculations. NBO analyses of the wavefunctions have been performed to examine the intermolecular interaction at the orbital level. Calculations reveal that these donors form strong $n \rightarrow \sigma^*$ complexes and computed binding energies of the $(\text{CH}_3)_2\text{O} \cdots \text{HF}$ complex agree very well with the experimental binding energies from IR spectroscopy. LiF forms stronger complexes than HF, and the effect of correlation on the hydrogen bond energy is considerable compared to the lithium bond energy. Though charge transfer interaction contributes to the stability of both LiF and HF complexes, it plays a less dominant role in lithium bonded complexes. While amine and ether donate their n_{σ} lone pair, sulfide donates an n_{π} lone pair and this results in perpendicular intermolecular bonds in sulfide complexes.

Introduction

The existence of mutual attraction and repulsion between closed-shell atoms and molecules is responsible for many phenomena at the molecular level. The hydrogen bond interaction is one among them and has a central place because of its relevance in chemistry and biology.¹⁻⁷ A great deal of information has accumulated over the years concerning hydrogen bonding from both experimental and theoretical perspectives. As a result of the investigation of a large number of hydrogen bonded dimers by rotational spectroscopy, Legon and Millen^{8,9} proposed some simple, essentially electrostatic rules for predicting the angular geometries of dimers. In particular, when a base molecule with a lone pair of electrons interacts with a proton donor (HX), at equilibrium the HX molecule lies along the axis of a nonbonding electron pair of the base with the proton pointing towards the lone pair. In more general terms, the most electrophilic site of HX *i.e.* the H-atom, seeks the most nucleophilic site of the base, but of course the nucleophilic end of HX will avoid this site on the base. This electrostatic approach to hydrogen bonding has received a quantitative interpretation by Buckingham and Fowler¹⁰ who have used a distributed multipole analysis to predict angular geometries. A donor-acceptor model for the hydrogen bond was first proposed by Mulliken¹¹ and later successively applied by many authors.

As the structures of these hydrogen bonded systems have become apparent, the nature of the binding forces has been widely discussed, with questions concerning the balance between 'electrostatic' *vs.* 'charge transfer' descriptions of the cluster binding. Recently Weinhold and co-workers^{12,13} have shown the importance of donor-acceptor interaction in hydrogen bonding using natural bond orbital (NBO) analysis.

The lithium bond, which appears to be similar to the hydrogen bond has not received much attention in this regard. Though the lithium bond resembles the hydrogen bond in many respects a number of dissimilarities between the two have been noted.^{14,15} We have investigated¹⁶ a series of lithium as well as hydrogen bonded complexes of various bases using donor-acceptor models based on NBO analysis

and discussed the participation of various orbitals in these bonding interactions. In this paper we have chosen a set of three n-donors namely trimethylamine, dimethyl ether and dimethyl sulfide and investigated their interaction with HF and LiF using higher level *ab initio* and DFT methods. While the case is much simpler with trimethylamine that has only one lone pair, it is rather difficult to decide in ether and sulfide complexes which of the two lone pairs is involved in donation. Specifically, we are trying to resolve this question using NBO analysis.

While there are scant reports on lithium bonded complexes of the n-donors, hydrogen bonded complexes of them have been well studied using theory and experiment. Legon and co-workers undertook a series of investigations¹⁷⁻²² on the structure of the complexes of hydrogen halides with trimethylamine using microwave spectroscopy. Latajka and co-workers^{23,24} have reported *ab initio* studies of the complexes of amines with HCl, HBr and HI. A combined photoelectron spectroscopy and *ab initio* investigation of the complexes of HF with dimethyl ether and dimethyl sulfide have been carried out by Carnovale *et al.*²⁵ LiF complexes of ammonia and water have been investigated theoretically by few authors²⁶⁻³¹ and Ault and Pimental³² have provided structures of $\text{H}_3\text{N} \cdots \text{LiCl}$ and $\text{H}_3\text{N} \cdots \text{LiBr}$ by studying the vibrations of these complexes isolated in inert matrices. Li^+ affinity of dimethyl ether has been reported by Abboud *et al.*,³³ Blint,³⁴ and also by Smith *et al.*³⁵ Woodin and Beauchamp³⁶ have studied the Li^+ affinity of trimethylamine and dimethyl ether. We present here an *ab initio* and DFT computational study of LiF/HF complexes with the above lone pair donors, and compare our results with the available experimental values.

Computational details

Different possible structures for the title complexes have been proposed based on the direction of the lone pairs of the basic atoms. For the trimethylamine complex, only one structure with C_{3v} symmetry (**I**) with HF/LiF lying on the C_3 axis with the proton/lithium pointing towards the lone pair is possible. Three different structures (**II**, **III** and **IV**) have been considered for the complexes of dimethyl ether and dimethyl sulfide; structure **II** has C_{2v} symmetry in which the HF/LiF molecular axis is collinear with the C_2 axis of the donor. Structures **III** and **IV** have lower symmetry (C_s) where the molecular axis of

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HF/LiF makes an angle with the C_2 axis and lies in the molecular plane (III) or in the bisecting plane (IV). In total we have 14 trial geometries, 7 for LiF complexes and 7 for HF complexes.

All the above structures have been fully optimized at the Hartree–Fock level with a 6-31++G(d,p) basis set within their symmetry constraints; frequency calculations have been carried out on the optimized geometries to characterize the stationary points obtained. Geometry optimizations with the above basis set at Møller–Plesset perturbation at the second term level (MP2) and at the density functional theory (DFT) level have been carried out only for the HF stable structures. DFT calculations have been carried out with the exchange potential of Becke³⁷ and correlation functional of Lee, Yang and Parr³⁸ (B3LYP). Single-point energy calculations at the MP4 (SDTQ) level have also been performed on the MP2 geometries for dimethyl ether and dimethyl sulfide complexes. The interaction energies of the complexes calculated at the HF level are corrected for both basis set superposition error (BSSE) and zero-point vibrational energy (ZPE) and those calculated at DFT, MP2 and MP4 levels are corrected only for BSSE. BSSE has been calculated using the Boys–Bernardi counterpoise method³⁹ and by applying a modification⁴⁰ that takes into consideration the relaxation of the monomers upon complexation. The nature of the interactions at the orbital level has been studied using NBO analysis⁴¹ on the stable structures at all the levels employed with a 6-31++G(d,p) basis set. All the above calculations have been performed using the GAUSSIAN 94W program⁴² implemented on a Pentium computer.

Results and discussion

The results are discussed under the following four sub-headings: potential energy surfaces (PES), energetics; structure and bonding; and analysis of interactions. Each section starts with the discussion on LiF complexes, followed by HF complexes and ends with the comparison between these two complexes.

Potential energy surfaces

$(\text{CH}_3)_3\text{N}$, $(\text{CH}_3)_2\text{O}$ and $(\text{CH}_3)_2\text{S}$ form hydrogen and lithium bonds through the basic atoms and the geometry of the complexes is almost determined by the type and direction of the lone pairs involved in bonding. Therefore the PES of these complexes have been searched for stable structures from the various proposed geometries shown in Fig. 1.

(i) **LiF complexes.** Optimization and frequency calculations show that the $(\text{CH}_3)_3\text{N}\cdots\text{LiF}$ complex has a stable structure with C_{3v} symmetry (I). Among the three structures considered for $(\text{CH}_3)_2\text{O}$ and $(\text{CH}_3)_2\text{S}$ complexes (II, III, and IV) structure III of $(\text{CH}_3)_2\text{O}\cdots\text{LiF}$ and structure IV of $(\text{CH}_3)_2\text{S}\cdots\text{LiF}$ are found to be the stable structures from frequency analyses. Thus each complex has only one stable structure and the structural diversity indicates the subtle differences in the nature of the interactions that stabilize them.

(ii) **HF complexes.** The structure of $(\text{CH}_3)_3\text{N}\cdots\text{HF}$ is found to be similar to that of the LiF complex. Structure I with C_{3v} symmetry for the $(\text{CH}_3)_3\text{N}\cdots\text{HF}$ complex is confirmed to be the stable structure from frequency calculations. The potential energy surface of the $(\text{CH}_3)_2\text{O}\cdots\text{HF}$ complex is different from that of LiF complex. Here, frequency analysis reveals that structure II with C_{2v} symmetry is the stable structure. The $(\text{CH}_3)_2\text{S}\cdots\text{HF}$ complex is similar to that of $(\text{CH}_3)_2\text{S}\cdots\text{LiF}$ complex. Here again, IV is a minimum. As with the LiF complexes, only one stable structure is observed for each HF complex: I for $(\text{CH}_3)_3\text{N}\cdots\text{HF}$, II for $(\text{CH}_3)_2\text{O}\cdots\text{HF}$ and IV for $(\text{CH}_3)_2\text{S}\cdots\text{HF}$.

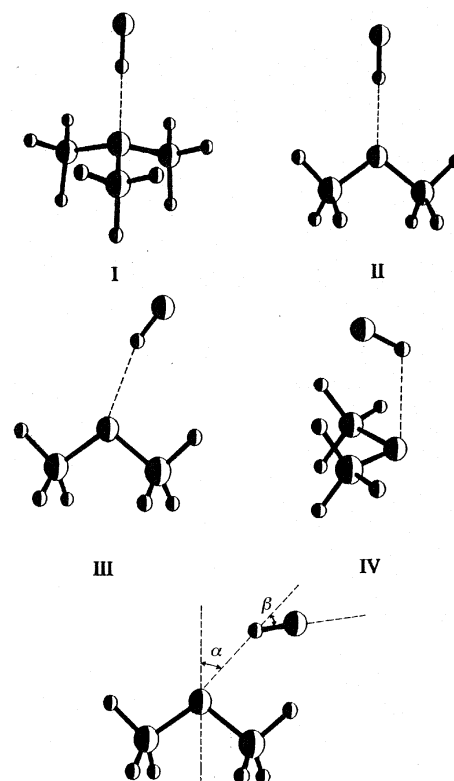


Fig. 1 Different possible geometries for the complexes of LiF–HF with amine (I), ether and sulfide (II–IV) and the model defining the angles α and β .

It appears from the above that LiF and HF complexes of amine and sulfide have quite similar geometries, while the geometries of HF and LiF complexes differ in ether. DFT and MP2 calculations have been undertaken only for the HF stable structures. The relative stability of the complexes, and the reason for the preferences of different forms for different complexes, are discussed in the following sections.

Latajka and co-workers^{23,24} have studied the complexes of amines with hydrogen halides and they proposed two geometries, neutral pair type and ion pair type for each complex based on their calculations. They showed that the $(\text{CH}_3)_3\text{N}$ complex always exists in ion pair type. Normally when a hydrogen halide (HX) approaches the amine in the direction of the lone pair, at long ranges it forms a weak complex (neutral pair) and on moving further in the same direction the HX molecule forms the TS with the amine and then reacts to give the ion-pair. In the ion-pair the bond between the base atom and the proton is of covalent type. It is also possible with LiF. As we are interested only in complex formation we have not scanned the PES for any TS or reaction product.

Energetics

The stable structures identified from the PES searches have been considered for further analysis. The relative stabilities of the complexes will be discussed from the energetics of the complexes. Complexation energies, calculated at HF, DFT, MP2 and MP4 levels are presented in Table 1. ZPE corrections to the DFT, MP2, and MP4 interaction energies could not be done as calculations of frequencies at these levels are computationally too demanding. For the same reason, MP4 single point energies are not reported for $(\text{CH}_3)_3\text{N}$ complexes.

(i) **LiF complexes.** In all the three complexes, the Li atom interacts only with the basic atom of the donor. The Li-bond is found to be linear in the $(\text{CH}_3)_3\text{N}$ complex and is angular in the other two complexes. The bent geometry of the Li-bond in $(\text{CH}_3)_2\text{O}$ and $(\text{CH}_3)_2\text{S}$ complexes is due to the following

Table 1 Complexation energies ΔE , BSSE, counterpoise corrected complexation energies ΔE^{cp} , zero point energy correction (ZPEC), corrected complexation energies $\Delta E_{\text{ZPEC}}^{\text{cp}}$ (kcal mol⁻¹) computed at various levels for the Hartree–Fock stable structures of the complexes with 6-31++G(d,p) basis set

complex	level	ΔE	BSSE	ΔE^{cp}	ZPEC	$\Delta E_{\text{ZPEC}}^{\text{cp}}$
I (CH ₃) ₃ N···LiF	HF	21.62	2.24	19.38	1.46	17.92
	DFT	22.13	2.65	19.48	—	—
	MP2	23.48	4.33	19.15	—	—
III (CH ₃) ₂ O···LiF	HF	20.82	1.93	18.89	1.41	17.48
	DFT	20.88	2.05	18.83	—	—
	MP2	21.74	3.33	18.41	—	—
	MP4/MP2	21.99	3.67	18.32	—	—
IV (CH ₃) ₂ S···LiF	HF	15.02	0.86	14.16	1.34	12.28
	DFT	16.57	1.30	15.27	—	—
	MP2	17.90	3.70	14.20	—	—
	MP4/MP2	18.22	4.06	14.16	—	—
I (CH ₃) ₃ N···HF	HF	11.95	1.00	10.95	2.71	8.24
	DFT	16.08	1.05	15.03	—	—
	MP2	16.84	3.06	13.78	—	—
II (CH ₃) ₂ O···HF	HF	9.39	0.82	8.57	2.22	6.35
	DFT	11.02	0.78	10.24	—	—
	MP2	11.62	2.21	9.41	—	—
	MP4/MP2	11.54	2.45	9.09	—	—
IV (CH ₃) ₂ S···HF	HF	5.62	0.28	5.34	1.74	3.60
	DFT	8.45	0.37	8.08	—	—
	MP2	7.90	1.54	6.36	—	—
	MP4/MP2	7.73	0.96	6.77	—	—

reasons: (i) lithium can make bent bonds in view of the increased ion–dipole interactions, and (ii) the presence of a weak secondary attraction between the F atom of LiF and a methyl proton of the base. The binding energies calculated at all the levels show that the stability of the complexes decreases in the order (CH₃)₃N > (CH₃)₂O >> (CH₃)₂S. BSSE and ZPE corrected binding energies of these complexes show that (CH₃)₃N and (CH₃)₂O complexes lie close in stability while the (CH₃)₂S complex is far less stable. (CH₃)₃N forms a stronger complex compared to (CH₃)₂O though the electronegativity increases in the row from the left to the right. Legon and Millen⁴³ have calculated the nucleophilicities and electrophilicities of various bases and acids and their calculations show that the nucleophilicities decrease in the order NH₃ (11.5) > H₂O (10.0) > H₂S (4.8). This trend clearly shows that the bases with an N atom can form stronger complexes than those with O and S atoms; comparing oxygen and sulfur bases the latter forms much weaker complexes than the former. As mentioned earlier, there are no experimental or computational studies available for the complexes of LiF with (CH₃)₃N, (CH₃)₂O and (CH₃)₂S for a straightforward comparison of our results. Abboud *et al.*³³ have calculated the Li atom affinity of (CH₃)₂O with a 4-31G basis as 50.9 kcal mol⁻¹ and Blint³⁴ has calculated the same with a D95V** basis set as 39.4 kcal mol⁻¹ and compared it with the experimental value 41.5 kcal mol⁻¹.³⁶ Smith *et al.*³⁵ reported the BSSE corrected binding energies for the (CH₃)₂O···Li⁺ complex calculated at the MP2 level with a (5s3p2d/D95+**) and (5s3p2d/cc-pVTZ + sp) basis set as 39.12 and 38.41 kcal mol⁻¹, respectively. These values confirm that LiF forms a weaker complex with a base than with Li⁺ as observed earlier.¹⁶

Comparison of the binding energies of the LiF complexes of n-donors with our earlier results¹⁶ on $\pi \rightarrow \sigma^*$ and $(n + \pi) \rightarrow \sigma^*$ complexes shows the following trend. $n \rightarrow \sigma^*$ complexes are stronger than $\pi \rightarrow \sigma^*$ complexes but they are weaker than $(n + \pi) \rightarrow \sigma^*$ complexes. It should be noted here that in the stable structure of $(n + \pi)$ donor H₂CO and H₂CS complexes, the secondary hydrogen bonding interactions are stronger than those found in (CH₃)₂O and (CH₃)₂S complexes.

(ii) HF complexes. HF forms a C_{3v} complex with (CH₃)₃N similar to LiF, whereas the structures of (CH₃)₂O···HF (C_{2v}) and (CH₃)₂S···HF (C_s) are slightly different from those of the LiF complexes. The stability order of the HF complexes decreases in the order (CH₃)₃N > (CH₃)₂O > (CH₃)₂S. The difference in the binding energies of the HF complexes of (CH₃)₃N and (CH₃)₂O is larger than that of LiF complexes. This trend is again in accordance with the relative nucleophilicities of N, O, and S bases.

It is appropriate to compare our results with earlier reported values. Carnovale *et al.*²⁵ reported the binding energies calculated with STO-3G* and 4-31G basis sets for the (CH₃)₂O···HF complex as 14.34 and 13.62 kcal mol⁻¹, and for the (CH₃)₂S···HF complex as 8.60 and 7.65 kcal mol⁻¹, respectively. The hydrogen bond energy observed in IR spectroscopic study is available only for the (CH₃)₂O···HF complex, and is 10.28 kcal mol⁻¹.⁴⁴ This value agrees well with our calculated binding energy at the DFT level. These complexes ($n \rightarrow \sigma^*$) are found to be stronger than $\pi \rightarrow \sigma^*$ and $(n + \pi) \rightarrow \sigma^*$ complexes.¹⁶

The comparison of binding energies of LiF and HF complexes predict that LiF forms stronger complexes with lone-pair donors than HF. The stability order observed in the complexes of LiF and HF with different electron donors are found to be the same and this parallels the trend observed in the nucleophilicities of the bases. The effect of electron correlation on the binding energy is considerable in HF complexes and almost negligible in LiF complexes.

Structure and bonding

The formation of hydrogen and lithium bonds induces electronic flow from the electron donor to the acceptor; almost all the atoms of the interacting molecules are involved in this. This results in changes in the geometrical parameters of the interacting molecules besides forming an intermolecular bond. Therefore structural analyses of the complexes give useful clues as to the nature of interactions that stabilize the complex. The geometric data of the monomers and complexes that are vital for the structural analyses are compiled in Table

Table 2 Selected MP2 structural parameters for the monomers and complexes optimized with 6-31 + +G(d,p) basis set

parameter ^a	monomers ^b			LiF complexes			HF complexes		
	(CH ₃) ₃ N	(CH ₃) ₂ O	(CH ₃) ₂ S	I	III	IV	I	II	IV
<i>R</i> _{Z-F}	—	—	—	1.627	1.634	1.636	0.989	0.949	0.945
<i>R</i> _{Y-Z}	—	—	—	2.076	1.911	2.444	1.559	1.639	2.183
<i>R</i> _{C-Y}	1.455	1.419	1.805	1.471	1.429, 1.443	1.815	1.466	1.427	1.806
<i>R</i> _{C-H}	1.103, 1.089	1.086, 1.095	1.788, 1.089	1.098, 1.089	1.087, 1.091	1.088, 1.089	1.097, 1.089	1.086, 1.092	1.088, 1.089
<i>R</i> _{F-H}	—	—	—	4.361	2.529	2.479	3.353	3.362	3.516
<i>θ</i> _{Y-Z-F}	—	—	—	180.0	128.6	110.9	180.0	180.0	169.9
<i>θ</i> _{C-Y-Z}	—	—	—	109.3	141.3, 106.5	88.7	108.2	123.6	99.1
<i>θ</i> _{C-Y-C}	110.6	111.2	98.2	109.6	112.1	97.9	110.7	112.9	98.9
<i>θ</i> _{H-C-Y}	112.4, 109.5	106.9, 111.0	107.7, 112.2	111.3, 109.6	107.3, 110.1	107.9, 107.8	111.4, 109.2	106.8, 110.3	107.7, 110.9
<i>θ</i> _{H-C-H}	108.4, 108.6	109.5, 108.9	108.6, 109.6	108.8, 108.9	109.8, 109.6	110.2, 110.8	109.1, 108.7	109.9, 109.6	108.9, 109.9
<i>α</i>	—	—	—	0.0	17.5	91.9	0.0	0.0	75.9
<i>β</i>	—	—	—	0.0	51.4	69.1	0.0	0.0	10.1

I amine complex, **II** and **III** ether complexes and **IV** sulfide complex. ^a Bond lengths in Å and bond angles in degrees. For *α* and *β* see Fig. 1. Z = Li, H in LiF and HF respectively, Y = N, O, S in amine, ether, and sulfide, respectively. ^b MP2 LiF and HF bond lengths are 1.609 and 0.927 Å.

2. The overall geometry of these complexes can be best described using two parameters *α* and *β*, which are indicated in Fig. 1. While *α* shows the extent of the deviation of the position of the Z atom from the major axis (the C₃ axis in amine and the C₂ axis in ether and sulfide), *β* is a measure of the deviation from collinearity of the intermolecular bond axis and the Z–F molecular axis. The torsion angle CYCZ is 180° for the ether complex and 90° for the sulfide complex. *α* and *β* can be derived from the computed structural parameters shown in Table 2.

(i) LiF complexes. The amine complex has a linear lithium bond *α* = 0°, *β* = 0°, while the ether and sulfide complexes have bent lithium bonds with *α* and *β* respectively 16.4°, 49.6° and 92.3°, 66.4°. The C–N···Li angle is characteristic of the tetrahedral geometry of the complex. Two different C–O···Li bond angles observed here show that the Li–F axis deviates from the C₂ axis of ether but it is confined within the C–O–C plane. Such a deviation may arise due to the electrostatic interaction between the fluorine atom and methyl protons. Sulfur prefers a perpendicular lithium bond with the C–S···Li angle nearly 90°. Here LiF is confined to the C–S–C angle bisecting plane. The Y···H–Li–F angles differ considerably in the complexes. F···H distances listed in Table 2 reveal that the ether and sulfide complexes have secondary hydrogen bonding interaction involving the fluorine atom and the methyl protons, while the amine complex doesn't. DFT and MP2 computations show a stronger hydrogen bond between these atoms as both methods include correlation energy that is a significant component of the hydrogen bond energy. The secondary hydrogen bond is a bifurcated hydrogen bond in sulfide and is the simple hydrogen bond in ether.

On complexation, the Li–F bond length increases as expected and the increase in this Li–F distance is in the order (CH₃)₃N < (CH₃)₂O < (CH₃)₂S. It should be noted here that the stability of the complexes is in the reverse order. This is due to the presence of the weak secondary hydrogen bonding interaction in (CH₃)₂O and (CH₃)₂S complexes; it is absent in the (CH₃)₃N complex. The Li–F bond stretches further to form the hydrogen bond in (CH₃)₂O and (CH₃)₂S complexes.

(ii) HF complexes. HF complexes are stabilized only by the hydrogen bonding interaction Y···H. The hydrogen bonds are perfectly linear in amine and ether complexes and slightly bent in the sulfide complex. The C–Y···H angle in (CH₃)₂S···HF (*ca.* 100°) shows that sulfur prefers a perpendicular hydrogen bond in line with earlier observations.⁴⁵ It is interesting to observe that the lithium bonds to sulfur are more perpendicular than hydrogen bonds. On complexation, H–F and C–Y bonds are weakened and the increase in bond lengths is in the order (CH₃)₃N > (CH₃)₂O > (CH₃)₂S.

This trend parallels the trend observed in the stability of the complexes which again proves that these complexes are stabilized only by the primary hydrogen bonding interaction and charge transfer interaction is the main force. The Y···H distances predict the formation of a hydrogen bond between the monomers and these bond lengths are found to be shorter than their corresponding Y···Li bonds though the hydrogen bonds are weaker than the lithium bonds. The greater intermolecular distance in the lithium bonds is attributed to the fact that Li almost exists as Li⁺ in lithium halides and this Li⁺ with an inner closed shell cannot penetrate deeply into the charge cloud of the electron donor molecule, whereas a hydrogen atom can do so because of the smaller size of its charge cloud.

Analysis of interactions

NBO analyses have been performed on the 6-31 + +G(d,p) wavefunction of the stable forms of the complexes at all levels. The occupancies of the monomer orbitals that are involved in the charge transfer interaction the charge transfer *q*_{CT} from the base to LiF/HF, occupancies of the frontier molecular orbitals and the second order perturbation energy lowering (*ΔE*²) due to the interaction of the donor and acceptor orbitals are summarized in Table 3.

(i) LiF complexes. The structures of the complexes have suggested that the (CH₃)₃N complex is stabilized only by lithium bonding, whereas (CH₃)₂O and (CH₃)₂S complexes derive stability mainly from lithium bonding and to a smaller degree from weak secondary hydrogen bonding interactions. The *q*_{CT} values listed in Table 3 show that the charge transfer increases in the order (CH₃)₂S > (CH₃)₂O > (CH₃)₃N; a larger *q*_{CT} means a larger charge transfer stabilization. This trend in *q*_{CT} does not concur with the stability order found in these complexes. For instance the sulfide complex that has the highest charge transfer is found to be the least stable among the three. Such differing trends in *q*_{CT} and binding energy only indicate the dominance of the electrostatic interaction to the overall stability. The charge transfer interaction contributes only slightly to stability.

The *ΔE*² value for the (CH₃)₃N complex clearly shows that the nitrogen lone pair n(N) and the antibonding orbital of Li–F are involved in the charge transfer process. The occupancy of *σ*_{Li-F}^{*} increases and that of n(N) also increases slightly instead of an expected decrease. This is due to the increased charge flow from the methyl protons towards the nitrogen atom during complexation, indicated by the greater decrease in the occupancy of the *σ*_{C-H}^{*} orbital in the (CH₃)₃N complex compared to the other two complexes. In the (CH₃)₂O complex, the occupancy of the n_σ orbital of oxygen decreases and that of n_π increases whereas the occupancies of both n_σ

Table 3 Natural bond orbital analysis for the monomers and LiF and HF complexes calculated with 6-31 + +G(d,p) basis set

parameters ^a	DFT			MP2		
	monomer ^b					
	(CH ₃) ₃ N	(CH ₃) ₂ O	(CH ₃) ₂ S	(CH ₃) ₃ N	(CH ₃) ₂ O	(CH ₃) ₂ S
$n_{\sigma}(Y)$	1.878	1.969	1.989	1.915	1.978	1.991
$n_{\pi}(Y)$	—	1.923	1.944	—	1.947	1.952
$\sigma^*(C-H)$	0.029	0.009	0.015	0.020	0.007	0.013
LiF complexes						
	I	III	IV	I	III	IV
q_{CT}	0.032	0.014	0.036	0.030	0.015	0.038
occupancy						
$n_{\sigma}(Y)$	1.889	1.959	1.988	1.914	1.967	1.989
$n_{\pi}(Y)$	—	1.939	1.918	—	1.958	1.927
$\sigma^*(Li-F)$	0.055	0.036	0.060	0.048	0.033	0.056
$n_{\sigma}(F)$	1.993	1.988	1.986	1.996	1.994	1.992
$\sigma^*(C-H)$	0.020	0.010	0.014	0.015	0.007	0.012
ΔE^2 (kcal mol ⁻¹)						
$n_{\sigma}(Y), \sigma^*(Li-F)$	10.13	9.61	1.40	13.51	12.04	1.89
$n_{\pi}(Y), \sigma^*(Li-F)$	—	—	12.75	—	—	17.64
$n_{\pi}(F), \sigma^*(C-H)$	—	1.17	0.84	—	1.18	1.00
HF complexes						
	I	II	IV	I	II	IV
q_{CT}	0.105	0.049	0.081	0.089	0.037	0.058
occupancy						
$n_{\sigma}(Y)$	1.822	1.925	1.986	1.858	1.945	1.987
$n_{\pi}(Y)$	—	1.937	1.881	—	1.956	1.909
$\sigma^*(H-F)$	0.106	0.052	0.075	0.087	0.037	0.051
ΔE^2 (kcal mol ⁻¹)						
$n_{\sigma}(Y), \sigma^*(H-F)$	44.19	25.03	1.25	57.78	28.47	1.52
$n_{\pi}(Y), \sigma^*(H-F)$	—	—	23.77	—	—	26.13

I amine complex, II, III ether complexes and IV sulfide complex. ^a Y = N, O and S in amine, ether and sulfide, respectively. ^b DFT (MP2) occupancies $n_{\sigma}(F)$ and $\sigma^*(Li-F)$ in Li-F are 1.991 (1.994) and 0.009 (0.009) respectively. $\sigma^*(H-F)$ in HF is 0.000 (0.000). q_{CT} and occupancies in number of electrons.

and n_{π} of sulfur decrease in the (CH₃)₂S complex on complexation. The decrease in n_{π} of sulfur is more than in n_{σ} and these trends reveal that oxygen donates its n_{σ} electrons while sulfur donates its n_{π} electrons to the σ^*_{Li-F} orbital. The above fact is further confirmed by the ΔE^2 values for the $n_{\sigma}(Y)-\sigma^*_{Li-F}$ and $n_{\pi}(Y)-\sigma^*_{Li-F}$ interactions. The occupancies of the Li-F antibonding orbitals increase in the order (CH₃)₂O < (CH₃)₃N < (CH₃)₂S, a trend parallel to the amount of charge transfer in the complexes.

NBO analyses of the secondary hydrogen bonding interaction in (CH₃)₂O and (CH₃)₂S complexes reveal the following. The ΔE^2 values show that the n_{π} of the fluorine atom and the C-H antibond orbitals are involved in the charge transfer process. The occupancy of the $n_{\pi}(F)$ orbital in the (CH₃)₂O complex remains almost unchanged at the HF and MP2 levels and decreases at the DFT level. This is a consequence of the relatively strong hydrogen bonding predicted at the DFT level. In the (CH₃)₂S complex, a decrease in the occupancy of the $n_{\pi}(F)$ is observed at all levels, which confirms that the hydrogen bond is stronger in this complex than in the (CH₃)₂O complex. In both complexes, σ^*_{C-H} occupancies decrease instead of an expected increase. This decrease is found to be less compared to the (CH₃)₃N complex and is due to the flow of the C-H antibond electrons towards the base atom during complexation. The ΔE^2 values calculated at the HF level are greater for the (CH₃)₂S complex, whereas at the DFT and MP2 levels they are greater for the (CH₃)₂O complex. It is to be noted here that, in the (CH₃)₂O complex the interaction of $n_{\pi}(F)$ is with one C-H bond while it is with two C-H bonds in the (CH₃)₂S complex. This again confirms that the secondary hydrogen bonding interaction is stronger in the (CH₃)₂S complex than in the (CH₃)₂O complex. In both

cases, the hydrogen bond is perpendicular and therefore it selects the $n_{\pi}(F)$ orbital for interaction rather than the $n_{\sigma}(F)$ orbital.

(ii) HF complexes. NBO analysis of the HF complexes again confirms that these complexes are stabilized only by the primary hydrogen bonding interaction. The q_{CT} values decrease in the order (CH₃)₃N > (CH₃)₂S > (CH₃)₂O. The (CH₃)₃N···HF complex is the strongest among the three and the charge transfer from the base to HF is also larger in this complex. This reveals that the charge transfer interaction has a significant role in hydrogen bonds. However, the charge transfer is more in (CH₃)₂S···HF compared to (CH₃)₂O···HF though the former is weaker than the latter. The hydrogen bonds with a sulfur base are perpendicular and are dominated by a charge-multipole interaction whereas with an oxygen base the bond is linear and is dominated by a charge-charge interaction.⁴⁵ Similar to LiF complexes, HF complexes show the following characteristics. In the (CH₃)₃N complex the lone pair of nitrogen $n(N)$ donates electrons to the σ^*_{C-H} orbital. In the (CH₃)₂O complex, $n_{\sigma}(O)$ is involved in donation whereas it is $n_{\pi}(S)$ in the (CH₃)₂S complex. The occupancies of the corresponding donor orbitals decrease and that of σ^*_{H-F} increases upon complexation. The ΔE^2 values decrease in the order (CH₃)₃N > (CH₃)₂O > (CH₃)₂S and this parallels the trend observed in the stability of the complexes. This again would indicate that the charge transfer interaction is far more important in hydrogen bonds than in lithium bonds. Usually when a charge transfer interaction makes a dominant contribution to stability, the change transfer energy ΔE_{CT} (dominated by ΔE^2) is greater than the complexation energy, ΔE .⁴⁶ Roughly a transfer of 0.01e charge would correspond to 6 kcal mol⁻¹ of

ΔE_{CT} . This high ΔE_{CT} is partially offset by the exchange repulsion at closer distance and results in a lower ΔE . When the electrostatic contribution is high, $\Delta E > \Delta E_{CT}$.⁴⁶ Trends observed in ΔE^{CP} and ΔE^2 in the LiF and HF complexes here (Table 3) made it clear further that charge transfer plays a more significant role in hydrogen bonds than in lithium bonds.

Conclusions

LiF and HF form $n \rightarrow \sigma^*$ complexes with trimethylamine, dimethyl ether and dimethyl sulfide and each complex is found to have only one stable conformer. While LiF and HF complexes of the amine and sulfide have quite similar geometries, those of the ether differ considerably. These complexes are stronger than the analogous $\pi \rightarrow \sigma^*$ complexes.¹⁶ The amine and ether form stronger complexes than the sulfide as predicted by the order of nucleophilicities of the bases. An experimental hydrogen bond energy of 10.28 kcal mol⁻¹ for the (CH₃)₂O...HF complex observed from IR studies agrees excellently with the DFT binding energy. LiF forms stronger complexes than HF. Electron correlation has a considerable effect on the binding energies of HF complexes compared to LiF complexes. The main stabilizing force in the LiF and HF complexes is the lithium or hydrogen bonding interaction, but the LiF complexes of the ether and sulfide also have stabilization from secondary hydrogen bonding interactions. Generally, the amine and ether prefer linear lithium/hydrogen bonds, while sulfur prefers perpendicular lithium/hydrogen bonds in line with the previous studies.^{4,5} Slight deviation from linearity in the LiF...O(CH₃)₂ complex arises from an electrostatic interaction of fluorine with methyl protons. NBO analysis reveals that the amine and ether donate their n_{σ} lone pair and sulfide donates its n_{π} lone pair. In the secondary hydrogen bonding interaction, found in (CH₃)₂O...LiF and (CH₃)₂S...LiF complexes, the $n_{\sigma}(F)$ and $\sigma^*(C-H)$ orbitals are involved. Charge transfer interactions contribute almost equally to Li and H-bonds but the electrostatic interaction is greater in the Li-bond.

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