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Lithium bonding interaction in $\text{H}_2\text{CY}\cdots\text{LiF}$ ($\text{Y}=\text{O},\text{S}$) complexes: A theoretical probe

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Ab initio calculations at 6-31++G(d,p) level have been done on $\text{H}_2\text{CY}\cdots\text{LiF}$ ($\text{Y}=\text{O},\text{S}$) complexes choosing ten possible orientations in each complex. The effect of correlation on complex binding energies has been studied via single point MP2 (full) calculations done on 6-31++G(d,p) geometry. Binding energies have been corrected for basis set superposition error. Frequency calculations confirm that $\text{H}_2\text{CO}\cdots\text{LiF}$ and $\text{H}_2\text{CS}\cdots\text{LiF}$ complexes have three and two stable forms, respectively. The most stable form in each complex has been found to have a strong lithium bonding interaction and a secondary hydrogen bonding interaction. NBO analysis has revealed that in this form oxygen donates n_σ lone pair while sulfur donates its n_π lone pair. In yet another stable form of these complexes, mixed donation of π and n_σ electrons have been observed. © 1997 American Institute of Physics. [S0021-9606(97)01035-0]

INTRODUCTION

The weak interaction between closed-shell molecules plays a vital role in an enormous variety of chemical, physical, and biological phenomena.¹⁻⁴ The basic understanding of such weak but central interactions is necessary to enable design and manipulation of molecular systems that depend on noncovalent binding. There are many experimental techniques available to study the intermolecular complexes in condensed phases, which can provide information about the structure and energetics of the complexes.⁵ But the information obtained is, of course, affected by cooperative phenomena operating in condensed phases. The detailed knowledge about the specific bimolecular interaction can be obtained only if the study is carried out in gas phase or in inert solvent. Experimental methods may be powerful for gas phase study of the complexes, but none of them provides quantitatively accurate results on structural information as well as interaction energies. This makes the quantum chemical methods an important tool to study intermolecular interactions.⁶

Intermolecular interactions can be categorized mainly into three classes depending on their nature and strength. They are H-bonding, charge-transfer, and van der Waals interactions. Among them, hydrogen bonded systems have been well studied because of their significant role in chemical and biological interactions.⁷ Correspondingly, *ab initio* calculations on them are becoming increasingly common in the literature.⁸ Analogous to hydrogen, lithium can also participate in a three center interaction known as lithium bonding. While hydrogen bonding has been so widely and thoroughly investigated, reports on lithium bonding are very rare.⁹⁻¹² As the experimental studies on the lithium bond is very meagre, most of our current knowledge relating to lithium bonding has been derived from theoretical work.^{13,14} Lithium bonding was speculated as early as in 1959 by Shigorin,⁹ and later by West and Glaze¹⁰ and Brown and

co-workers.¹¹ While Ault and Pimental¹² were the first to provide experimental proof for the existence of a lithium bond in $\text{H}_3\text{N}\cdots\text{LiX}$ ($\text{X}=\text{Cl},\text{Br}$) complexes, Kollman and co-workers¹³ were the first to theoretically investigate the properties of lithium bonds using *ab initio* self-consistent-field (SCF) calculations. Subsequently there were few theoretical reports published on lithium bonded dimers.¹⁴ Though lithium bonding closely resembles hydrogen bonding in several ways, there are many differences between these two types of bonding.¹⁵ Notable among the differences is that lithium bonding is stronger than hydrogen bonding. Another important difference between hydrogen and lithium bonds is that the electrostatic interaction dominates over charge-transfer interaction in the lithium bonding, whereas charge-transfer interaction also contributes significantly in the case of hydrogen bonding.¹⁶ It is this feature that makes the comparative study of hydrogen and lithium bonding interactions interesting. The present study focuses on intermolecular interactions of lithium fluoride, a powerful lithium donor, with the prototype bases formaldehyde and thioformaldehyde, through theoretical calculations.

Formaldehyde, which is known as the most common base to form a hydrogen bond with a proton donor in many organic and biological systems, has different donor sites. It can act as a lone pair (n_σ) donor and a π ($>\text{C}=\text{O}$) donor. Further, the hydrogens of formaldehyde can form weak hydrogen bonds through CH protons with proton acceptors such as halogen—especially fluorine—oxygen, sulfur, etc. Hydrogen bonded complexes of formaldehyde have been the subject of several theoretical¹⁷ and experimental¹⁸ investigations. Lithium halides and lithium hydrides can also form complexes with formaldehyde in a similar way and yet studies of lithium bonded complexes, even with molecules having first row atoms, are rare. Lithium fluoride is chosen because the complex can simultaneously have both lithium and hydrogen bonding interactions and hence can have remark-

able stability. Further, LiF can exist almost as Li^+F^- and there is a possibility that the ionic species Li^+ and F^- can interact at different sites of formaldehyde and form ionic molecular complexes. Singh and co-workers¹⁹ have studied the complex of NH_3 with LiCN , and proved that in the ground state, minimum energy geometry of the complex Li^+ binds with nitrogen and CN^- binds with the hydrogen of NH_3 . Besides formaldehyde, its thioanalogue thioformaldehyde is chosen to compare the directionality of lithium bonds to sulfur and oxygen. It is known²⁰ that sulfur forms slightly weaker hydrogen bonds with more “perpendicular” angles than oxygen, and this is believed to result from different hybridizations of valence orbitals in oxygen and sulfur. Recent calculations²¹ show that the reason for the different geometrical preferences is not as simple as has been explained above. The above report further reveals that the charge–charge interaction dominates in the $\text{O}\cdots\text{H}$ bond that prefers the linear orientation, while the charge–quadrupole interaction plays a significant role in the $\text{S}\cdots\text{H}$ interaction that prefers a perpendicular orientation. Therefore the hydrogen bond formed between sulfur and hydrogen is fundamentally different from the $\text{O}\cdots\text{H}$ bond. It is therefore interesting to look at the geometry and the factors responsible for the geometric preferences of the lithium bonded complexes with donors formaldehyde and thioformaldehyde. The results of the above complexes will be compared with those of $\text{H}_2\text{CY}\cdots\text{HF}$ complexes available in the literature^{21,22} with a view to observing the effect of the Li bond in complexation.

COMPUTATIONAL DETAILS

Different possible geometries considered for the complexes $\text{H}_2\text{CY}\cdots\text{LiF}$ where $\text{Y}=\text{O},\text{S}$ are shown in Fig. 1. Following are the details of fixation of various geometric parameters in optimizing the selected structures of the above complexes. Structure I has been optimized with C_{2v} symmetry constraint such that the LiF molecule is placed on the C_2 axis. C_{2v} symmetry has been relaxed to C_s symmetry in structure II by allowing all the bond lengths and bond angles to vary and fixing the torsion angles 5-1-2-3 and 6-5-1-2 at 0° . Structure III is planar and therefore has C_s symmetry. In this structure LiF is positioned on H_2CY such that both $\text{Y}\cdots\text{Li}$ and $\text{F}\cdots\text{H}$ bonds are present. In structure IV, LiF has been constrained to move within the bisecting vertical plane of H_2CY with Li anchored on the Y atom. In such an orientation the torsion angle of $\text{H}-\text{C}-\text{Y}-\text{Li}$ is always 90° . Structures V and VI have been optimized with C_s and C_{2v} symmetry, respectively, and in that V and VI have linear and bifurcated hydrogen bonds as shown in Fig. 1. In structure VII, electron donation from $>\text{C}=\text{O}$ π -bond is considered. The $\text{Li}-\text{F}$ molecule is placed vertically at the midpoint of the π -bond with the Li atom pointing downward towards the π -bond and the structure has been fully optimized. LiF can also exist in ionic form as Li^+F^- , and in that the ionic species Li^+ and F^- can bind with H_2CY at different sites. Various possibilities of this kind have been tried out with structures VIII, IX, and X presented in Fig. 1. In all these structures Li^+ binds with oxygen/sulfur atom and F^- forms

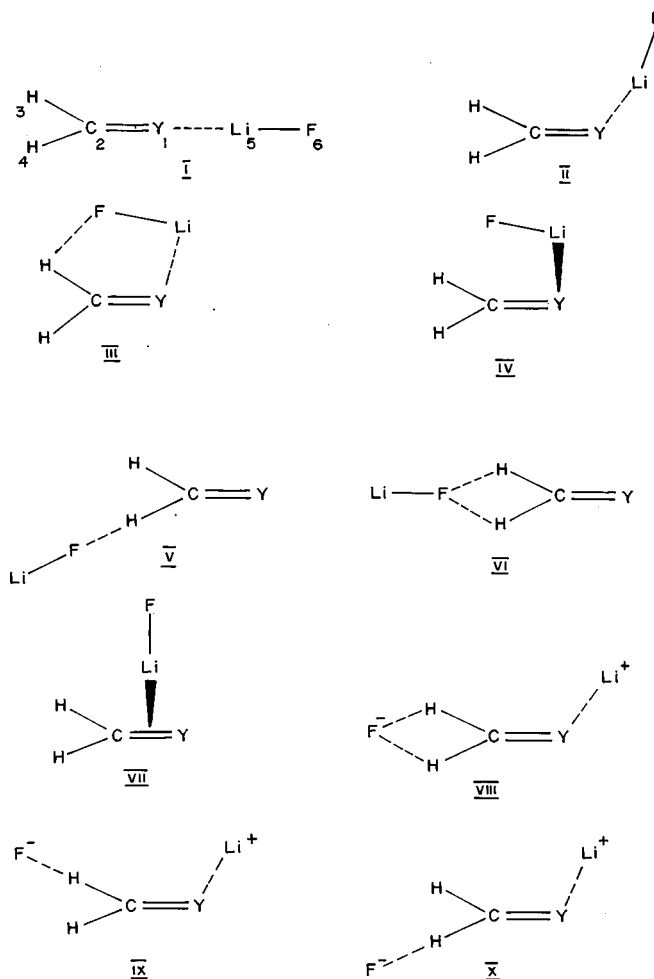


FIG. 1. Different possible geometries of $\text{H}_2\text{CY}\cdots\text{LiF}$ ($\text{Y}=\text{O},\text{S}$) complexes.

bifurcated (VIII), linear (cis) (IX), and linear (trans) (X) hydrogen bonds with hydrogen atoms of H_2CY . C_s symmetry has been maintained in all the three cases. The optimized structures of II and III have then been used to scan through the potential energy surface. Single point energies have been calculated with PES scan for change in the torsion angle 3-2-1-5 (structures II and III) from 0° to 90° and in steps of 10° .

The geometrical parameters of the complexes have been optimized using the supermolecule approach at SCF level. Pople's split-valence double-zeta 6-31 G basis set augmented by one set of d -polarization functions on heavy atoms and p -polarization function on hydrogens and also sp - (heavy atoms) and s - (hydrogens) diffuse functions $[6-31++G(d,p)]$ ²³ is used in the calculations. Additionally, single point energy calculations on the SCF optimized geometries have been carried out at the MP2 (full) level in order to include electron correlation correction to the interaction energy. The frequency calculations have been carried out to confirm the nature of the stationary points obtained. The interaction energies have been corrected for basis set superposition error (BSSE) using the Boys–Bernardi²⁴ counterpoise scheme and applying a modification²⁵ that takes into

consideration the geometrical relaxation of the monomers upon complexation. Natural bond orbital (NBO) analysis²⁶ on the stable forms III and IV of the complexes have been carried out to examine the nature of the interaction at the orbital level. All the calculations have been carried out using the HONDO7 program²⁷ implemented on a Digital Dec Alpha system.

RESULTS AND DISCUSSION

Lithium fluoride is both a lithium donor and a proton/lithium acceptor. Similar to LiCN, it can exist as an ion pair and therefore form ion pair molecular complexes and ionic molecular complexes. Formaldehyde and thioformaldehyde are proton/lithium acceptors and can donate their σ or π type lone pair or π bond pair to form (Lewis acid base) complexes. Further, the above bases have two protons and through them they can form either linear or bifurcated H-bonds. This is more so in the complex stage where formaldehyde/thioformaldehyde is sufficiently polarized to donate its protons. All these possibilities are considered here and are shown in Fig. 1. There are 20 total species—10 for formaldehyde and another 10 for thioformaldehyde—the geometries of which have been optimized. The binding energies have been calculated at Hartree–Fock level with basis functions of double-zeta quality augmented by diffuse and polarization functions on both heavy and hydrogen atoms. In H₂CO...LiF complex optimizations with starting geometries, VIII, IX, and X converged on structure III, and this shows that ionic complexes in these cases are absent. And the complex with initial geometry VII converged on IV. Thus structures I–VI alone represent stationary points on the PES, and in them I, V, and VI have turned out to be first order saddles. Therefore only structures II, III, and IV represent equilibrium geometries. Among them, structure III appears to be the most stable. In the H₂CS...LiF complex again, optimization with starting structure VIII and IX converged on III and that, with structure X, unlike the formaldehyde case, converged to a geometry with a markedly low value of the F[−]...H distance (0.93 Å), indicating a proton transfer. This shows that there are no ionic complexes present and, unlike the H₂CO...LiF complex, optimizations with initial geometries II and VII converged on III and IV, respectively. Therefore there are only five stationary points corresponding to structures I, III, IV, V, and VI. In them structures I and V have turned out to be first order saddles and VI a second order saddle. Fre-

TABLE I. Interaction energies ΔE_b , BSSE, counterpoise corrected interaction energies ΔE_b^{cp} (kcal/mol) and number of imaginary frequencies (n_i) for the complexes of LiF with H₂CO and H₂CS calculated at HF/6-31++G(*d,p*) level.

Structure	H ₂ CO...LiF				H ₂ CS...LiF			
	ΔE_b	BSSE	ΔE_b^{cp}	n_i	ΔE_b	BSSE	ΔE_b^{cp}	n_i
I	18.75	1.88	16.87	1	4.46	1.16	3.30	1
II	18.88	1.71	17.16	0
III	20.87	1.00	19.87	0	16.14	0.53	15.61	0
IV	17.17	0.78	16.39	0	9.40	0.81	8.59	0
V	5.59	0.30	5.29	1	6.06	0.28	5.78	1
VI	5.87	0.33	5.54	1	5.07	0.30	4.77	2
		H ₂ CO...HF				H ₂ CS...HF		
4-31G ^a	10.4	6.9

^aReference 22.

quency computations show that structures III and IV are stable equilibrium structures and between them III appears to be more stable. Beside these, PES scans have been made searching for possible minimum with LiF interacting with these bases from the molecular plane by changing H–C–Y–Li torsion from 0° to 90° in steps of 10°, and no stable geometry other than IV has been found in the process. Interaction energies, BSSE, etc., have therefore been calculated for the first six structures alone.

Interaction energies, number of imaginary frequencies obtained for each structure, BSSE, and counterpoise corrected interaction energies are presented in Table I. Effect of correlation on complex binding energy has been studied only for the stable forms II, III, and IV in the case of H₂CO...LiF complex and III and IV of H₂CS...LiF complex using MP2 (full) calculation on 6-31++G(*d,p*) optimized geometry, and the results are presented in Table II. Selected geometric parameters of the monomers and complexes (III and IV) are presented in Table III. NBO analysis and orbital energy correlation have been done only for III and IV. Quantum of charge transfer q_{CT} , occupancies of the orbitals participating in the donor–acceptor interaction, and the second order energy lowering due to the interaction of the donor and acceptor orbitals $\Delta E^{(2)}$ obtained from NBO analysis, are collected in Table IV. Table V presents the orbital energies of monomers and complexes and, for obvious reasons, the energies of only a few top lying acceptor and donor orbitals have been presented.

TABLE II. MP2/6-31++G(*d,p*) interaction energies ΔE_b , BSSE, counterpoise corrected interaction energies ΔE_b^{cp} for the complexes of LiF with H₂CO and H₂CS (kcal/mol).

Structure	H ₂ CO...LiF			H ₂ CS...LiF		
	ΔE_b	BSSE	ΔE_b^{cp}	ΔE_b	BSSE	ΔE_b^{cp}
II	20.63	5.62	15.01
III	21.57	3.98	17.60	17.87	4.22	13.65
IV	17.44	3.61	13.83	9.85	4.45	5.40
		H ₂ CO...HF			H ₂ CS...HF	
MP2/6-311++G(<i>d,p</i>) ^a	7.72	1.12	6.60	6.33	1.74	4.59

^aReference 21.

TABLE III. Selected structural parameters for the monomers and the complexes III (IV) calculated at HF/6-31++G(d,p) level.

Parameters ^a	$\text{H}_2\text{CO}\cdots\text{LiF}$ $\text{Y}=\text{O}$	$\text{H}_2\text{CS}\cdots\text{LiF}$ $\text{Y}=\text{S}$	H_2CO $\text{Y}=\text{O}$	H_2CS $\text{Y}=\text{S}$	LiF
$R_{\text{Li-F}}$	1.614 (1.627)	1.611 (1.613)	1.576
$R_{\text{Y}\cdots\text{Li}}$	1.932 (1.961)	2.522 (2.623)
$R_{\text{C-Y}}$	1.202 (1.204)	1.613 (1.631)	1.186	1.598	...
$R_{\text{C-H}}$	1.087 1.088 (1.085)	1.078 1.082 (1.075)	1.092	1.079	...
$R_{\text{F}\cdots\text{H}}$	2.257 (2.729)	2.079 (2.523)
$\theta_{\text{Y}\cdots\text{Li-F}}$	111.5 (101.4)	108.9 (100.5)
$\theta_{\text{C-Y}\cdots\text{Li}}$	109.0 (99.1)	86.7 (72.9)
$\theta_{\text{H-C-Y}}$	120.5 119.9 (121.5)	120.8 120.4 (122.1)	121.8	122.1	...
$\theta_{\text{H-C-H}}$	119.6 (116.9)	118.9 (115.7)	116.3	115.8	...

^aBond lengths in Å and bond angles in degrees.

ENERGETICS AND STRUCTURE

Full geometry optimizations and PES scans reveal that the $\text{H}_2\text{CO}\cdots\text{LiF}$ complex has three stable structures, II, III, and IV, and the $\text{H}_2\text{CS}\cdots\text{LiF}$ complex has two stable structures, III and IV. Structures II and III are planar while IV is nonplanar. Structure III differs from II in that it has a secondary hydrogen bonding interaction with the proton of

H_2CY through fluorine atom. It is interesting to note that the form II exists in the H_2CO complex, but not in the H_2CS complex. This can be understood as follows. Sulfur due to its preference for “perpendicular” lithium bond allows the fluorine atom of LiF to come closer to the proton of H_2CS , and the form III stabilizes. But in H_2CO complex (II) the angle $\text{C-O}\cdots\text{Li}$ is so wide (148°) that it keeps the fluorine atom sufficiently away from the proton of H_2CO . With this angle, the form II stabilizes. Besides, this formaldehyde complex has another stable form (III) in which the angle $\text{C-O}\cdots\text{Li}$ is 109° . The interaction pattern in formaldehyde and its thioanalogue can be discussed as follows. As noted earlier, both have basic as well as acidic fragments. However, both are predominantly bases. As a base they can donate either of their lone pairs or the π -bond pair. It should be noted that in H_2CO and H_2CS , both lone pairs n_σ and n_π on oxygen/sulfur are lying in the molecular plane while π electrons are lying perpendicular to the molecular plane, and this should be contrasted with the direction of the lone pairs on O or S in ethers or thioethers. LiF, too, has both acidic and basic fragments and it is predominantly an acid. It is therefore clear from the above that the primary interaction in these complexes should be lithium bonding through an O or S base. There can be secondary hydrogen bonding interaction through fluorine atom to the protons of H_2CY if the fluorine and hydrogen atoms are disposed sufficiently closer in space. In such a case the stability of the complex will be enhanced, and this happens in structure III. The $\text{H}_2\text{CO}\cdots\text{LiF}$ complex has an equilibrium geometry corresponding to the structure II, and in that structure the secondary hydrogen bonding interaction is absent, as the fluorine atom is sufficiently away from the protons of H_2CO . This is again due to the 148°

TABLE IV. Natural bond orbital analysis for geometries optimized at HF/6-31++G(d,p) level.

Structure	$\text{H}_2\text{CO}\cdots\text{LiF}$	$\text{H}_2\text{CS}\cdots\text{LiF}$	H_2CO	H_2CS	LiF
III	q_{CT} (a.u.)	0.006	0.024
	Occupancy (a.u.)				
	$n_\sigma(\text{Y})$	1.982	1.991	1.987	1.994
	$n_\pi(\text{Y})$	1.929	1.930	1.911	1.941
	$\sigma^*(\text{Li-F})$	0.025	0.045
	$n_\pi(\text{F})$	1.991	1.987
	$\sigma(\text{Li-F})$	1.985	1.984
	$\sigma^*(\text{C-H})$	0.033	0.027	0.043	0.028
	$\Delta E^{(2)}$ (kcal/mol)				
	$n_\sigma(\text{Y}), \sigma^*(\text{Li-F})$	5.17	2.12
	$n_\pi(\text{Y}), \sigma^*(\text{Li-F})$	3.23	13.25
	$n_\pi(\text{F}), \sigma^*(\text{C-H})$	2.37	3.14
	$\sigma(\text{Li-F}), \sigma^*(\text{C-H})$	0.27	1.75
	q_{CT} (a.u.)	0.011	0.015
IV	Occupancy (a.u.)				
	$\pi_{\text{C=Y}}$	1.996	1.978	1.999	1.999
	$n_\sigma(\text{Y})$	1.981	1.989	1.987	1.994
	$n_\pi(\text{Y})$	1.925	1.947	1.911	1.941
	$\sigma^*(\text{Li-F})$	0.023	0.031
	$\Delta E^{(2)}$ (kcal/mol)				
	$\pi_{\text{CY}}, \sigma^*(\text{Li-F})$	1.96	5.53
	$n_\sigma(\text{Y}), \sigma^*(\text{Li-F})$	5.11	2.67

TABLE V. Calculated orbital energies for the monomers and complexes at HF/6-31++G(d,p) level (a.u.).

Molecule	Orbital energy		Assignment
LiF		-0.4728	$n_\pi(\text{F})$
		-0.4728	$n_\pi(\text{F})$
		-0.4972	$\sigma_{\text{Li-F}}$
		-1.3776	$n_\sigma(\text{F})$
		-0.4422	$n_\pi(\text{O})$
H_2CO		-0.5465	$\pi_{\text{C=O}}$
		-0.6587	$n_\sigma(\text{O})$
		-0.7034	σ_{CH}
$\text{H}_2\text{CO}\cdots\text{LiF}$	III	IV	
	-0.4648	-0.4733	$n_\pi(\text{F})$
	-0.4664	-0.4789	$n_\pi(\text{F})$
	-0.4858	-0.4616	$n_\pi(\text{O})$
	-0.4906	-0.4988	$\sigma_{\text{Li-F}}$
	-0.5848	-0.5887	$\pi_{\text{C=O}}$
	-0.6964	-0.6793	$n_\sigma(\text{O})$
	-0.7372	-0.7182	σ_{CH}
H_2CS		-0.3519	$n_\pi(\text{S})$
		-0.4210	$\pi_{\text{C=S}}$
		-0.5450	$n_\sigma(\text{S})$
		-0.6492	σ_{CH}
$\text{H}_2\text{CS}\cdots\text{LiF}$	III	IV	
	-0.3894	-0.3586	$n_\pi(\text{S})$
	-0.4394	-0.4171	$\pi_{\text{C=S}}$
	-0.4763	-0.4950	$n_\pi(\text{F})$
	-0.4780	-0.5070	$n_\pi(\text{F})$
	-0.4997	-0.5207	$\sigma_{\text{Li-F}}$
	-0.5662	-0.5521	$n_\sigma(\text{S})$
	-0.6692	-0.6601	σ_{CH}

angle of $\text{C}-\text{O}\cdots\text{Li}$. Therefore, in this complex there is only a primary lithium bonding interaction, and consequently this complex is relatively weaker than III. $\text{H}_2\text{CO}\cdots\text{LiF}$ has another equilibrium structure IV, and in that $>\text{C}=\text{O}$ π -bond pair seems to be involved in the donation of charge to lithium, and here also the $\text{F}\cdots\text{H}$ distance is 2.729 Å—sufficiently large to prevent the secondary hydrogen bond interaction. Therefore, this structure also has the lithium bonding interaction alone. This makes this structure IV relatively weaker than III. Between II and IV, II relatively appears to be marginally stronger and this difference in binding energy could be due to the donation of a lone pair in the former and π electrons in the latter. The $\text{H}_2\text{CS}\cdots\text{LiF}$ complex has only two stable structures, III and IV, and III is much stronger than IV, as observed in the H_2CO complex and due to the reasons outlined above.

Relative stabilities of $\text{H}_2\text{CO}\cdots\text{LiF}$ and $\text{H}_2\text{CS}\cdots\text{LiF}$ complexes can be compared justifiably by choosing complexes with similar geometries, and is done as follows. For both of the complexes, structure III is found to be the most stable, and the H_2CO complex is found to be stabler by approximately 4 kcal/mol than the corresponding H_2CS complex. Geometry of the complexes indicates that lithium bonding is stronger in the formaldehyde complex than in the thioformaldehyde complex, and at the same time the secondary hydrogen bonding is stronger in the latter than in the former. The net effect appears to stabilize the formaldehyde complex more than the thioformaldehyde complex, and the over-

whelming change is brought out by a much stronger lithium bonding in the formaldehyde complex. This trend falls completely in line with the similar observation²⁰ that hydrogen bonding interaction decreases, descending down a given group. $\text{H}_2\text{CO}\cdots\text{LiF}$ shows a substantial difference in stability over the $\text{H}_2\text{CS}\cdots\text{LiF}$ complex in form IV as well. In fact, the difference in stability between the former and latter is more in IV than in III. Now the interaction energies of formaldehyde and thioformaldehyde with hydrogen fluoride are compared with our results using the data reported by Platts and co-workers,²¹ as well as Flakus and Boyd.²² Both of them have missed structure III and have reported the binding energies for structure II. It is therefore reasonable to compare the interaction energies of HF complexes with those of structure II type LiF complexes. Counterpoise uncorrected binding energy for $\text{H}_2\text{CO}\cdots\text{LiF}$ complex (Table I) is found to be higher than for the corresponding HF complex. A straight comparison of LiF and HF complexes of thioformaldehyde complex could not be made, as there is no stable structure II in the LiF complex. The comparison made between HF and LiF complexes with formaldehyde shows clearly that lithium bonding is definitely stronger than hydrogen bonding. BSSE correction in all these cases is found to be small.

Single point MP2 (full) interaction energies of the LiF complexes with formaldehyde and thioformaldehyde have been compared in Table II. Expectedly, uncorrected MP2 interaction energies are higher than the corresponding uncorrected SCF interaction energies. BSSE correction at the correlated level is found to be more, and due to this, corrected binding energies at the MP2 level are found to be lower than the corresponding uncorrelated values. Otherwise, the trends in interaction energies of complexes with various types of geometry, namely II, III, and IV of formaldehyde and thioformaldehyde with LiF and HF are the same as discussed above.

Changes in the geometries of H_2CY and LiF on complexation can be discussed based on the vital geometric data compiled in the Table III. Formaldehyde complex in the forms II and IV have strong lithium bonding interaction, but as already mentioned, form II is planar and the other is non-planar. The geometries of these forms suggest that II and IV may have a donation from lone pair and π -bond orbitals, respectively. III has strong lithium bonding and secondary hydrogen bonding interaction, and because of the presence of both attractive interaction, this form is relatively more stabilized. The presence of secondary hydrogen bonding interaction in III and the lack of it in IV is clear from the shorter $\text{F}\cdots\text{H}$ distance and the wider HCH angle and slightly closer HCY angle in III. Considerable differences in $\text{C}-\text{Y}\cdots\text{Li}$ in structures III and IV are due to the fact that the former involves a lone pair donation and the other possibly a π -bond pair.

A decrease in C-H bond length is noted both in III and IV, and is due to the flow of the CH bond pair towards oxygen on complexation. The $>\text{C}=\text{O}$ π -bond lengths in both cases $\text{O}\cdots\text{Li}$ in III is constrained to form a closed ring, whereas it is free in IV. The Li-F bond lengthens on complexation, but is shorter in III than in IV. This can be again,

as described earlier, due to the fact that LiF in III is constrained in a ring.

Thioformaldehyde complex has only two stable forms, III and IV. In III, both lithium bonding and secondary hydrogen bonding are present. This results in elongation of LiF bond length and $>\text{C}=\text{S}$ bond. $\text{S}\cdots\text{Li}$ distance is characteristic of lithium bonding and is relatively stronger in III than in IV. Though $>\text{C}=\text{S}$ π -bond undergoes elongation on complexation it is relatively shorter in III than in IV, and this reflects that IV involves π electrons in donation, and therefore naturally the π -bond is weaker. C–H bonds are shortened on complexation in both III and IV, which has been observed by various workers and has been explained by assuming that the C–H bond pair acts as a reservoir of electrons in H_2CS complexes and charge flows from the C–H bond towards the base atoms as the C–S π -bond donates electrons. Two C–H bonds of H_2CS have slightly different bond lengths in III as one of them is involved in secondary hydrogen bonding. But, both are equal in IV and this is because in IV the fluorine atom is above the H_2CS plane and is equidistant from both protons. $\text{F}\cdots\text{H}$ distance in III is much shorter than in IV, and this is obviously due to the existence of secondary hydrogen bonding in III. The bond angle $\text{S}\cdots\text{Li}-\text{F}$ 108° in III is characteristic of the pentagon form of the complex. Complex III is planar and the angle C–S \cdots Li 86.7° shows that sulfur prefers perpendicular lithium bonding than oxygen, and this is similar to the one observed in hydrogen bonding with sulfur.²¹ Therefore it appears that lithium bonding involving the oxygen atom is stabilized by charge–charge interaction, whereas lithium bonding through sulfur is stabilized by charge–multipole interaction. There is little change in the bond angles H–C–S in III, while there is no change in IV, which is due to the secondary hydrogen bonding observed in III involving H_2CS protons. This change in H–C–S induces small changes in the H–C–H angle in III.

The complex stabilization can also be viewed as resulting from dipole–dipole interactions moderated by steric repulsions. But this classical way of looking at the complex is only qualitative and does not provide deeper insight. Therefore, the interaction between the monomers at the orbital level has been analyzed and is discussed in the next section.

ANALYSIS OF INTERACTIONS

Though the energetics and structure of the complexes provide a clear idea of the type of interaction *viz.* charge transfer, hydrogen bonding, lithium bonding, that stabilize the complex, a much more thorough and quantitative analysis can be made through NBO analysis. NBO analysis provides dependable orbital occupancies and the second order perturbation energy lowering due to the interaction of the donor and acceptor orbitals $\Delta E^{(2)}$ that can give a clue as to which orbitals participate in charge transfer.

$\text{H}_2\text{CO}\cdots\text{LiF}$ COMPLEX

Among the three stable structures II, III, and IV, III has lithium bonding interaction and a secondary hydrogen bond-

ing interaction. Orbital occupancies and the $\Delta E^{(2)}$ values (Table IV) for III indicate that n_σ electrons are donated to the LiF antibond orbitals and both $n_\pi(\text{F})$ and $\sigma_{\text{Li}-\text{F}}$ are back donated to C–H antibond orbitals. n_σ , σ^* participation in the $\text{O}\cdots\text{Li}$ bond is further confirmed by $\Delta E_{n,\sigma^*}^{(2)}$, but as far as the secondary hydrogen bonding interaction is concerned, orbital occupancies and $\Delta E^{(2)}$ values show an opposite trend. Structure IV has only a lithium bonding interaction, and in that complex orbital occupancies show that both $>\text{C}=\text{O}$ π -bond pair and n_σ lone pair on oxygen are donated to LiF antibond orbitals. One can see from the orbital occupancy values that the π contribution is relatively low compared to n_σ . It is surprising to have a mixed donation, and it is the first occasion such a phenomenon is observed. It is for this reason that the geometry of the $\text{H}_2\text{CO}\cdots\text{LiF}$ complex has a structure in which the Li atom is sufficiently away from the π -bond and is located on the oxygen atom. However, it could not be denied that there is also a π charge transfer to the acceptor orbitals. Overall, the quantum of charge transfer from H_2CO to LiF is small though the complex is stronger. The relative participation of π -bond pair and n_σ lone pair is also evident from the $\Delta E^{(2)}$ values.

$\text{H}_2\text{CS}\cdots\text{LiF}$ COMPLEX

Of the two stable forms III and IV, III has a strong lithium bond and a strong secondary hydrogen bonding. In fact, the secondary hydrogen bonding interaction in thioformaldehyde complex is observed to be stronger than in formaldehyde complex. In the lithium bonding, n_π of sulfur and σ^* of LiF are involved, and in the secondary hydrogen bonding, the lone pair of fluorine and the LiF bond pair are donated to the C–H antibond orbitals. In the thioformaldehyde complex, back donation of the lone pair electrons from the fluorine atom towards C–H antibond orbitals are relatively greater, implying a stronger secondary hydrogen bonding interaction. This is also clearly evident from the shorter $\text{C}\cdots\text{H}$ distance (Table III) in thioformaldehyde complex compared to that in formaldehyde complex. On complexation, n_π orbital occupancy decreases and σ^* orbital occupancy increases. $\Delta E^{(2)}$ value is also greater for n_π and σ^* interaction. Generally, in both complexes occupancy of the C–H antibond orbital increases instead of decreasing. Increase in the orbital occupancy is expected as lone pairs on fluorine are donated to the orbital. But as already noted, the C–H bond electrons act as a reservoir of electrons and a charge flow towards oxygen and sulfur is induced in formaldehyde and thioformaldehyde, respectively, on complexation. There should be a greater outflow of electrons from the C–H bond due to lithium bonding and smaller inflow of the same due to the secondary hydrogen bonding. This results in a net decrease in occupancy in CH bond and antibond orbitals. Structure IV has only lithium bonding interaction, and orbital occupancies indicate, as observed in the $\text{H}_2\text{CO}\cdots\text{LiF}$ complex, there is a mixed donation from $>\text{C}=\text{S}$ π -bond pair and n_σ lone pair on sulfur; but this time the contribution from the π -bond pair is greater than n_σ on sulfur. $\Delta E^{(2)}$ values are in clear support of this phenomenon.

Overall, the quantum of charge transfer in the thioformaldehyde complex is greater than in the formaldehyde complex, but the formaldehyde complex is stronger than the thioformaldehyde complex. This shows that the electrostatic interaction stabilizes the former rather than the latter. Lithium bonding interaction in the former involves the n_σ orbital while it is n_π that donate electrons in the latter. This change in the type of lone pair shows up in the geometry of the complex with sulfur preferring a more “perpendicular” lithium bonding than oxygen. Formaldehyde complex in both forms is found to be stronger than the thioformaldehyde complex in spite of a greater charge transfer in the latter. Another notable difference in both the complexes occurs in structure IV. Although both of them, in this form, show a $(n_\sigma + \pi)$ mixed donation of electrons, there is an increased contribution from n_σ in the former while it is π that contributes more in the latter.

ORBITAL ENERGIES

When a donor and an acceptor form a complex, electrons are donated from the donor orbital to the acceptor orbital and the orbital occupancies therefore change, resulting in a net charge transfer. An accompanying change would be stabilization and destabilization of participating orbitals; donor orbitals stabilize and acceptor orbitals destabilize. Therefore, it would be worthwhile to examine the relative reordering of certain top lying orbitals on complexation and to make some remarks on the involved orbitals in the process. One can observe the following from the orbital energies listed for both complexes.

In the formaldehyde complex (III) all acceptor orbitals destabilize and donor orbitals stabilize as expected, whereas in the thioformaldehyde complex (III) both acceptor and donor orbitals stabilize. The above trend can be attributed to a weak secondary hydrogen bonding in the former and a relatively strong hydrogen bonding in the latter. This makes the LiF both acceptor and donor in the latter complex, and in such a case net stabilization of orbitals can be anticipated. This is more so if relative changes on lithium and a monomer have both donating and accepting fragments. It should be mentioned here that the stabilizing/destabilizing trends in the orbitals of both the complexes in form IV are not in order with NBO analysis data.

CONCLUSIONS

We have investigated the interactions in the complexes of LiF with H_2CO and H_2CS . Out of ten possible orientations considered in each case, H_2CO and H_2CS complexes are observed to have, respectively, three and two stable forms. The most stable form (III) of these complexes has strong lithium bonding interaction, and in addition to that there is a secondary hydrogen bonding interaction through the fluorine atom and proton of H_2CY . While the lithium bonding interaction is stronger in the H_2CO complex, the hydrogen bonding interaction is stronger in the H_2CS complex. Overall, the former is found to be stabler than the latter, though the quantum of charge transfer is more in the latter.

The $\text{H}_2\text{CO}\cdots\text{LiF}$ complex (II) is found to be stronger than its corresponding $\text{H}_2\text{CO}\cdots\text{HF}$ complex reported, and this implies that lithium bonding is stronger than hydrogen bonding. Sulfur prefers a more perpendicular lithium bond than oxygen, as found in $\text{H}_2\text{CY}\cdots\text{HF}$ complexes. NBO analysis clearly shows that this happens because sulfur donates its n_π lone pair while oxygen donates its n_σ lone pair in complexes. $\text{H}_2\text{CY}\cdots\text{LiF}$ complexes have another stable form IV that is nonplanar. Surprisingly, the complexes in this form have donations from both π as well as n_σ orbitals; the H_2CO complex has n_σ dominated mixed donation while the H_2CS complex has π dominated mixed donation. It is found from NBO analysis that the π contribution is responsible for the nonplanar geometry and n_σ contribution makes the lithium bond slightly away from the π -bond center, locating it around the base atom. This should be contrasted with another planar form II of the $\text{H}_2\text{CO}\cdots\text{LiF}$ complex, where pure n_σ lone pair is involved in donation. BSSE correction at the SCF level is found to be smaller than at the MP2 level. NBO analysis indicates that though the donating levels vary in H_2CO and H_2CS complexes, electrons are accepted in the LiF antibond orbital. In the secondary hydrogen bonding interaction observed in the most stable form, fluorine lone pairs are donated to the CH antibond orbital. As both the monomers H_2CY and LiF have both basic and acidic fragments in them, and thus are involved in donation and acceptance of electrons simultaneously, orbitals are subjected to stabilization and destabilization to varying extents. This results in a net shift in orbital energies that is difficult to resolve and interpret.

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