Origin and Nature of Lithium and Hydrogen Bonds to Oxygen, Sulfur, and Selenium

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Lithium and hydrogen bonded complexes of LiF and HF with H_2CO, H_2CS, and H_2CSe have been investigated using higher level ab initio calculations. Extensive searches of the potential energy surfaces for equilibrium structures have been done at the Hartree−Fock level, and post Hartree−Fock calculations at *MP2*, *MP4* levels and *DFT* calculations with B3LYP functional have been performed on the stable forms. 6-311++G(d,p) and 6-31++G(d,p) basis sets on H, C, O, and S and 6-311++G(d,p) basis set on Se have been employed throughout. NBO analysis of the wave functions have been done to trace the origin of various interactions that stabilize the complexes. Harmonic frequencies computed at Hartree−Fock level show that, of the 10 proposed structures, LiF and HF complexes have three and one stable forms, respectively. Potential energy surface features, structure, and stability of LiF complexes are completely different from those of HF complexes. Though it is commonly observed that lithium and hydrogen bonding interactions stabilize the complexes, the origin and nature of them is found to be different in each form and in each complex. This is well reflected in complex geometries and energetics.

Introduction

Hydrogen bonded complexes are the most widely investigated among weakly bound systems as hydrogen bonds are recognized as important in the structural organization of chemical and biological systems and in molecular recognition.[1] But, most of the reports are confined to hydrogen bonds with first-row atoms, and hydrogen bonded systems involving second-row and down-group atoms received much less attention.[2−8] A closer look at the hydrogen bond energies and geometries of complexes involving oxygen and sulfur showed that the nature of hydrogen bonds involving these atoms are fundamentally different. This has been explained on the basis of electrostatics by Buckingham and Fowler,[6] using Laplacian of charge density by Carroll and co-workers,[7a] and as due to different hybridization of valence orbitals by Sennikov.[4] Recently we have observed[8] a similar phenomenon in the lithium bonding interaction with oxygen and sulfur bases, and through natural bond orbital (NBO) analysis we have found out that the difference in the “lithium bonding behavior” is due to the involvement of different lone pairs on donor atoms in the charge-transfer process. We have shown that once the origins of such bonds are traced, strength and directionality of them could be easily understood. We have also suggested the possibility of *antilithium* bonds in LiF complexes with oxirane and thiirane.[8c] NBO analysis[9] is very helpful in understanding such bonding interactions at orbital level, a key factor that provides deeper insight than any other approach. NBO analysis gives realistic and reliable orbital occupancies, orbital interaction energies, and atom charges that are vital in deciding the extent of electrostatic and charge transfer stabilization in lithium and hydrogen bonds. This method should therefore be useful, especially when lithium/hydrogen bonds with bases involving different donor atoms are considered. Lithium, analogous to hydrogen, can form weak bonds with bases and studies on them are rare.[10,11] Comparison of lithium and hydrogen bonds have been discussed by several workers.[10] Lithium ion association energies and structures of Li^+ complexes with various first-row bases have been thoroughly investigated at *HF* and *MP2* levels by Del Bene and co-workers.[12] Proton, lithium, and sodium ion affinities of 20 first- and second-row bases have been examined by using ab initio calculations at *HF* level and compared with experimental results by Smith and co-workers.[13] Molecular complex of lithium atom and formaldehyde was investigated at both Moller−Plesset perturbation and multireference configuration interaction (MRCI) levels by Yang and his group.[14] But studies on complexes involving LiF as the lithium donor are very limited. Structure and energetics of LiF complexes should be different from Li^+ complexes and Li atom complexes. First, lithium in LiF is neither fully ionized nor neutral and hence can exert a different influence on the approaching bases. Second, in LiF, the fluorine atom can have interactions with the protons of the bases. Besides this, the bond that connects these reactive Li and F atoms in LiF also controls the position of these atoms with respect to the base during complexation. Thus LiF provides a situation that is completely different from both Li^+ and Li atom for complexation. We report here the lithium bonding interactions in complexes of LiF with a set of Lewis bases—formaldehyde, thioformaldehyde, and selenoformaldehyde and for comparison, complexes of HF with the same bases are studied. Specifically the following questions are addressed in this paper; (i) How do lithium bonds differ from hydrogen bonds? (ii) How different are the lithium bonds/hydrogen bonds with bases involving atoms descending down a group? As for the second question we restrict ourselves to group VI atoms; extension of lithium and hydrogen bonds to selenium is new.

Computational Details

The calculations have been carried out using Gaussian 94W program[15] implemented on a Pentium Computer. Ten possible orientations of the monomers in each complex have been

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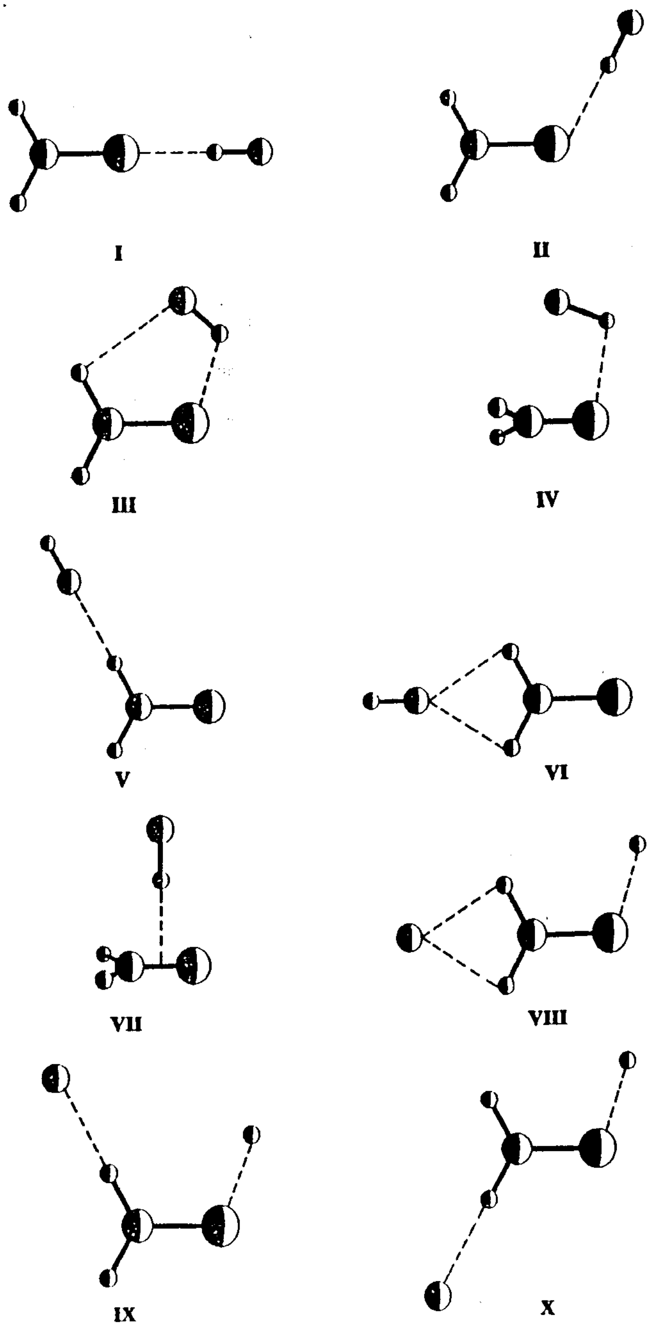

Figure 1. Proposed geometries of H2CY⋯ZF (Y = O,S,Se; Z = H,Li) complexes.

considered (Figure 1). Structure I is linear and optimized with C_{2v} symmetry. Structures II and III are planar with C_s symmetry, but structure III is cyclic while II has open structure. Therefore III has both Y⋯Z and F⋯H bonds and II has only Y⋯Z bond. Structures IV and VII are not planar such that the ZF molecule approaches H_2CY from above, vertically downward toward either the base atom Y (IV) or the π-bond (VII). These structures have C_s symmetry; the plane of symmetry is the bisecting vertical plane of H_2CY and, during optimization, ZF is allowed to move within the above plane. Structures V and VI represent respectively, linear and bifurcated hydrogen bonds between the molecules ZF and H_2CY. VIII, IX, and X represent structures in which the molecule ZF completely ionizes and the separated ions bind at different sites of H_2CY. While Z^+ binds with Y on H_2CY, F^- forms bifurcated (VIII), linear-cis (IX), and linear-trans (X) hydrogen bonds with the hydrogen atoms of H_2CY. The above three structures have been optimized with C_s constraint.

All proposed geometries of the complexes have been fully optimized at Hartree–Fock level within symmetry constraints, and frequency calculations have been carried out on the optimized geometries to characterize the stationary points obtained. The standard Pople's split-valence triple-ζ 6-311G basis set[16] augmented by polarization[17] and diffuse functions[18] [6-311++G(d,p)] has been used for all the complexes. For comparison, the smaller split-valence double-ζ 6-31++G(d,p)[17–19] basis set has also been used for the complexes of H_2CO and H_2CS. Moller–Plesset perturbation at second term level (*MP2*) and density functional theory (*DFT*) calculations have been performed only on the stable structures of the complexes. *DFT* calculations have been done with the exchange potential of Becke and correlation functional of Lee, Yang, and Parr (B3LYP).[20] Single-point calculations including higher-order electron correlation contributions up to *MP4*(SDTQ) have also been performed at the *MP2* geometries. The interaction energies of the complexes have been corrected for basis set superposition error (BSSE) and for zero-point energy (ZPE). BSSE has been calculated using counterpoise method[21] and applying a modification[22] that takes into consideration the energy effect due to change of the monomer geometries upon complexation. NBO analysis[9,23,24] has been carried out for the stable conformations at the MP2 level.

Results and Discussion

We discuss the results in the following four subheadings: potential energy surface, energetics, structure and bonding, and analysis of interactions. In each section, LiF and HF complexes are grouped and discussed separately in view of the significant differences in the nature of LiF and HF complexes. However, a combined discussion is done at the end of each section.

I. Potential Energy Surface. The bases chosen here have a common molecular skeleton and differ only in the base atom; the base atoms (O, S, and Se) are the first three members of the VI group. The base molecule $H_2C{=}Y$ has a π-bond pair and two lone pairs on Y for donation. Besides this, they can form weak hydrogen bonds through their CH protons. Further, these bases can form ion molecular and ion-pair molecular complexes with LiF and HF. Such possibilities lead to 10 different geometries for the title complexes and are shown in Figure 1. Potential energy surface scans for locating the stable structures of these complexes H_2CY⋯ZF (Y = O,S,Se; Z = H,Li) have been done starting from these 10 proposed structures for each complex at Hartree–Fock level as described in the last section.

LiF Complexes. Potential energy surfaces of these complexes have very similar surface features, and the differences observed in them are characteristic of the base atoms. Both formaldehyde and thioformaldehyde complexes have five stationary points (I, III–VI), and in both of them structures II, VIII, and IX converge on III and X converges to a geometry with a markedly low value of the F^-⋯H distance, indicating a proton transfer. The only difference observed on the above complexes is that VII of the former converges on I while that of the latter converges on IV. As structures VII–X are not found to be stationary points both in H_2CO and H_2CS complexes, PES scan of H_2CSe complex has been restricted to only the first six geometries. Again, in H_2CSe complex, II converges on III as found in the other two. Therefore, in the above three complexes, there are altogether only five stationary points (I, III–VI). Frequency analysis has revealed that III, IV, and V are stable structures

TABLE 1: Interaction Energies Δ*E*, BSSE, Counterpoise Corrected Interaction Energies ΔE^{cp}, Zero-Point Vibrational Energy Correction (ZPEC), and Corrected Binding Energies Δ$E_{ZPEC}{}^{cp}$ (kcal/mol) for the Stable Structures of the Complexes of LiF with H_2CY (Y = O,S,Se) Calculated at Hartree−Fock Level

		6-311++G(d,p)					6-31++G(d,p)				
complex	structure	Δ*E*	BSSE	ΔE^{cp}	ZPEC	Δ$E_{ZPEC}{}^{cp}$	Δ*E*	BSSE	ΔE^{cp}	ZPEC	Δ$E_{ZPEC}{}^{cp}$
H_2CO···LiF	III	20.14	0.62	19.52	2.00	17.52	20.88	0.99	19.89	2.02	17.87
	IV	16.55	0.63	15.92	1.58	14.34	17.18	0.79	16.39	1.69	14.70
	V	5.01	0.18	4.83	0.69	4.14	5.07	0.31	4.76	0.68	4.08
H_2CS···LiF	III	16.33	0.55	15.58	1.72	13.86	16.14	0.52	15.62	1.72	13.90
	IV	9.60	0.95	8.65	1.27	7.38	9.41	0.82	8.59	1.32	7.27
	V	5.65	0.28	5.37	0.79	4.58	5.52	0.29	5.23	0.76	4.47
H_2CSe···LiF	III	16.01	0.40	15.61	1.64	13.97					
	IV	9.25	0.60	8.65	1.33	7.32					
	V	5.80	0.26	5.54	0.82	4.72					

TABLE 2: Interaction Energies Δ*E*, BSSE, Counterpoise Corrected Interaction Energies ΔE^{cp} (kcal/mol) for the Complexes of LiF with H_2CY (Y = O,S,Se) Calculated at *DFT*, *MP2*, and *MP4* Levels

			6-311++G(d,p)			6-31++G(d,p)		
complex	level	structure	Δ*E*	BSSE	ΔE^{cp}	Δ*E*	BSSE	ΔE^{cp}
H_2CO···LiF	DFT	III	18.90	0.67	18.23	19.89	1.13	18.76
		IV	17.13	0.82	16.31	18.17	0.98	17.19
		V	4.95	0.34	4.61	4.99	0.36	4.63
	MP2	III	19.09	2.53	16.56	19.94	2.36	17.58
		IV	15.24	2.96	12.28	15.94	2.35	13.59
		V	4.90	0.69	4.21	5.22	0.80	4.42
	MP4//MP2	III	19.22	2.69	16.53	20.19	2.64	17.55
		IV	15.67	3.19	12.48	16.54	2.71	13.83
		V	4.95	0.77	4.18	5.30	0.94	4.36
H_2CS···LiF	DFT	III	16.10	0.71	15.39	16.57	0.90	15.67
		IV	13.95	1.41	12.54	15.03	1.45	13.58
		V	5.33	0.48	4.85	5.31	0.53	4.78
	MP2	III	17.09	3.89	13.20	17.32	3.70	13.62
		IV	9.23	4.24	4.99	9.41	3.92	5.49
		V	5.14	1.05	4.09	5.21	1.00	4.21
	MP4//MP2	III	17.54	4.12	13.42	17.65	3.92	13.73
		IV	9.92	4.46	5.46	9.99	4.13	5.86
		V	5.25	1.14	4.11	5.32	1.12	4.20
H_2CSe···LiF	DFT	III	15.81	0.58	15.23			
		IV	10.14	0.68	9.46			
		V	5.32	0.45	4.87			
	MP2	III	15.32	2.11	13.21			
		IV	7.29	2.27	5.02			
		V	5.13	0.90	4.23			
	MP4//MP2	III	15.95	2.35	13.60			
		IV	8.07	2.49	5.58			
		V	5.32	1.00	4.32			

and I and VI are saddles. Only the three stable structures III, IV, and V have been considered for *MP2* and *DFT* calculations and for further analysis. Earlier studies report that lithium ion associates with formaldehyde with Li^+ occurring at the C_2 axis[12,13] and lithium atom complexes with H_2CO to give two ion pair and one complex pair forms.[14] It should be noted here that the structure of the complex pair of the H_2CO···Li complex resembles form III of H_2CY···LiF.

HF Complexes. Similar to LiF complexes, HF complexes of H_2CY (Y = O,S,Se) have certain common surface features; III and IX converge on II, VIII and X lead to ionic structures resulting in proton transfer from H_2CY to F^-. But IV and VII of formaldehyde complex converge on I, while those of thioformaldehyde complex decompose into monomers. Similar to H_2CSe···LiF complex, only the first six structures of H_2CSe···HF complex have been studied for the reasons stated thereof; III converges on II; IV decomposes into monomers. Altogether, there are four stationary points I, II, V, and VI in the PES of HF complexes. In this, II alone is observed to be the stable structure and all other stationary points are either first-order or second-order saddles. VI of thio and selenoformaldehyde complexes turns out to be a minimum with very low frequency. As II is found to be the only stable structure in the H_2CY···HF complexes, it is selected for *MP2* and *DFT* calculations and for further analysis. Earlier experimental[2,3] and theoretical studies[4−6] have also confirmed this geometry for the H_2CY···HF complex.

While LiF complexes have three stable structures, HF complexes have only one stable form. LiF complexes prefer the cyclic form and HF complexes stabilize only in the open form. LiF complexes, in addition to the cyclic form, also stabilize in perpendicular conformation and in linear hydrogen bonded form.

II. Energetics. Interaction energies, BSSE, ZPE, counterpoise, and ZPE corrected interaction energies for the complexes of LiF with H_2CY (Y = O,S,Se) calculated at Hartree−Fock level are presented in Table 1. The above energies computed at *MP2*, *DFT* levels and single-point *MP4* energies computed on *MP2* geometries for the LiF complexes are given in Table 2. Interacting energies computed at *HF*, *DFT*, *MP2*, and *MP4* levels for the HF complex are presented in Table 3. ZPE corrections to the *MP2*, *MP4*, and *DFT* interaction energies

TABLE 3: Interaction Energies ΔE, BSSE, Counterpoise Corrected Interaction Energies ΔE^{cp} (kcal/mol) for the Structure II of the Complexes of HF with H_2CY (Y = O,S,Se) Calculated at *HF*, *DFT*, *MP2*, and *MP4* Levels[a]

		6-311++G(d,p)			6-31++G(d,p)		
complex	level	ΔE	BSSE	ΔE^{cp}	ΔE	BSSE	ΔE^{cp}
$H_2CO\cdots HF$	HF	7.16	0.45	6.71	7.48	0.45	7.03
	DFT	8.34	0.47	7.87	8.65	0.39	8.26
	MP2	7.86	1.47	6.39	8.48	1.25	7.23
	MP4//MP2	7.80	1.55	6.25	8.45	1.39	7.06
$H_2CS\cdots HF$	HF	0.76	0.15	0.61	0.69	0.06	0.63
	DFT	6.63	0.39	6.24	6.65	0.18	6.47
	MP2	6.46	2.02	4.44	6.35	1.67	4.68
	MP4//MP2	6.49	2.15	4.34	6.32	1.78	4.54
$H_2CSe\cdots HF$	HF	0.29	0.08	0.21			
	DFT	6.49	0.38	6.11			
	MP2	5.55	0.98	4.57			
	MP4//MP2	5.59	1.08	4.51			

[a] The BSSE and ZPE corrected interaction energies ΔE_{ZPEC}^{cp} for the H_2CY (Y = O,S,Se) complexes at HF level with basis set 6-311++G(d,p) are respectively 4.54, 2.30, and 2.32 kcal mol^{-1}; the same for the H_2CY (Y = O,S) complexes with basis set 6-31++G(d,p) are, respectively, 4.75 and 2.46 kcal mol^{-1}.

could not be done as frequency calculations at these levels are computationally demanding. The complexes are observed to derive stabilization mainly from two interactions: lithium and hydrogen bonding interactions. Again we classify the interaction as primary when the base atom is involved in the interaction and secondary when the base interacts through its protons. Primary interaction is stronger than secondary interaction. It should be noted that the primary interaction in LiF complexes is lithium bonding interaction and in HF complexes it is hydrogen bonding interaction, but the secondary interaction occurs only in LiF complexes and in this case it is a hydrogen bonding interaction.

LiF Complexes. In the previous section LiF complexes have been shown to have three stable forms III, IV, and V; no ion-pair complexes are found to be stable. The order of stability among them in all the three complexes with both basis sets and at *HF*, *MP2*, and *DFT* levels is found to be III > IV > V. Increased stability of III over the other two is due to the fact that III is stabilized by primary lithium bonding as well as by secondary hydrogen bonding interactions; IV involves only lithium bonding and V only hydrogen bonding interaction. III is planar, and LiF forms a lithium bond by accepting a lone pair of the base atom and forms a hydrogen bond through the fluorine atom and one of the protons of H_2CY. V that is also planar has only the latter-type bond, and a comparison of interaction energies of III and V shows that lithium bond is much stronger than the hydrogen bond in these complexes. IV is nonplanar and forms a lithium bond involving the $>C{=}Y$ π-bond pair. As this bond is stabilized by lithium bond, the stability is closer to III than to V. Comparison of the stabilities of III, IV, and V shows the relative contribution of lithium and hydrogen bonds in the complexes to stability.

As noted earlier, LiF complexes are quite different from Li^+ and Li atom complexes and, therefore, any straightforward comparison of LiF complexes with those of Li^+ and Li are restrictive. However, comparison of the binding energies of the complexes of Li and Li^+ with H_2CO with that of $H_2CO\cdots LiF$ complex could reveal the strength of interaction of the related but various Lewis acids with a common base. Complexation energy of the $H_2CO\cdots Li$ complex calculated at MP2/6-311+G(2d,p)//MP2/6-31+G(2d,p) level has been reported as 7.73 kcal/mol[14] and that of $H_2CO\cdots Li^+$ complex calculated at MP2/6-31G*//HF/3-21G level as 35.5 kcal/mol[12] (experimental value: 36.0 kcal/mol[25]). This should be compared with the MP2/6-311++G(d,p) complexation energy of the most stable form III of the $H_2CO\cdots LiF$ complex reported here as 16.56 kcal/mol.

Relative stabilities of H_2CY (Y = O,S,Se) complexes can be observed by examining the counterpoise and ZPE corrected interaction energies of them structurewise. Complexation energies of III reveal that the strength of lithium bonding in formaldehyde complex is greater than in the other two and this is in accordance with our earlier observation[8a] that lithium bonding with first-row bases is stronger than that with second-row bases. A closely lying interaction energy of H_2CSe with that of H_2CS shows that the strength of lithium bonding in both situations is more or less same. The electronegativity of oxygen atom is higher than that of S and Se, and hence the dipole moment of H_2CO is greater than that of H_2CS and H_2CSe. As lithium bond is known to get stabilization from ion−dipolar interaction, $H_2CO\cdots LiF$ complex has stronger lithium bonding and greater stability over the other two. The same trend in stability is observed in IV of these complexes and is due to the reasons discussed above. But complexation energies of V show an interesting reverse trend: $H_2CSe > H_2CS > H_2CO$. The reason is that the stabilizing interaction here in V is the hydrogen bonding interaction and none other than that. The strength of this interaction depends on the quantum of charge transfer. The charge transfer in formaldehyde complex is relatively lower than in the other two and thus the stabilities of V of these complexes are in this order of amount of charge transferred. A detailed discussion on the quantum of charge transfer is done in section IV. Therefore, from the above, the reason why lithium bonding interaction decreases in the order $H_2CO > H_2CS > H_2CSe$ while secondary hydrogen bonding interaction increases in the order $H_2CO < H_2CS < H_2CSe$ is clear.

While *DFT* complexation energies show a trend similar to that of Hartree−Fock energies, *MP2* and *MP4* energies show minor variations. *HF* and *DFT* complexation energies are closer, but *MP2*, *MP4* energies are lower and this shows that the inclusion of electron correlation decreases the complexation energy. Similarly *HF* and *DFT* BSSE values are closer and lower and *MP2*, *MP4* BSSE are higher; as a consequence *MP2*, *MP4* corrected complexation energies are relatively lower than those computed at *HF* and *DFT* levels. No sizable basis set effects on complex binding energies have been noted in all the levels employed. If corrected complexation energies of the three complexes are compared, the following trends emerge: (i) in the most stable form III the order of stability is found to be $H_2CO > H_2CS > H_2CSe$; *HF*, *DFT*, and *MP2* calculations predict the same trend; (ii) in form IV the strength of the formaldehyde complex is distinctly higher and that of the other two are lying very close. While *DFT* calculations predict the H_2CS complex to be more stable than the H_2CSe complex, *MP2*, *MP4* calculations predict them to be very close in stability; (iii) in form V, *HF* and *DFT* levels predict the order to be $H_2CSe > H_2CS > H_2CO$. *MP2*, *MP4* binding energies of thioformaldehyde complexes appear to be slightly underestimated. As the difference in stability of these three complexes in form V is closer, any small difference in the computed value can upset the trend and therefore they should not be taken as a strong evidence for a different trend or deviation.

HF Complexes. It has been shown in the previous section that PES of HF complexes are markedly different from those of LiF complexes and HF complexes have only one stable form II. II is planar and is stabilized by the hydrogen bonding

TABLE 4: Selected MP2 Structural Parameters for the Monomers H_2CY (Y = O,S,Se) and their Complexes with ZF (Z = H,Li) Optimized with 6-311++G(d,p) Basis Set[d]

	H_2CY^b			$H_2CY\cdots ZF^c$(II) Z = H			$H_2CY\cdots ZF$(III) Z = Li			$H_2CY\cdots ZF$(IV) Z = Li			$H_2CY\cdots ZF$(V) Z = Li		
parameters[a]	Y = O	Y = S	Y = Se	Y = O	Y = S	Y = Se	Y = O	Y = S	Y = Se	Y = O	Y = S	Y = Se	Y = O	Y = S	Y = Se
R_{Z-F}				0.932	0.930	0.929	1.635	1.634	1.635	1.653	1.632	1.626	1.606	1.605	1.606
$R_{Y\cdot\cdot Z}$				1.755 (1.793)	2.225	2.396	1.982	2.453	2.633	1.981	2.532	2.798			
R_{C-Y}	1.213 (1.206)	1.614 (1.611)	1.757 (1.743)	1.218	1.616	1.758	1.227	1.622	1.763	1.227	1.630	1.769	1.219	1.618	1.759
R_{C-H}	1.105 (1.108)	1.091 (1.092)	1.089 (1.090)	1.101	1.090	1.088	1.099 1.100	1.094 1.090	1.094 1.088	1.097 1.097	1.087 1.087	1.086 1.086	1.101 1.109	1.093 1.093	1.092 1.090
$R_{F\cdots H}$							2.235	2.079	2.043	2.634	2.549	2.578	2.086	2.029	2.016
$\theta_{Y\cdots Z-F}$				168.4	168.4	161.7	111.5	113.1	111.5	99.7	108.4	109.9			
$\theta_{C-Y\cdots Z}$				113.7 (115.0)	91.3	85.6	106.8	85.8	81.4	96.3	70.7	64.2			
θ_{H-C-Y}	121.9 (121.7)	121.9 (121.6)	121.5 (121.0)	121.6 121.0	121.9 121.3	121.4 120.9	120.2 119.8	120.3 120.0	119.8 119.6	121.6 121.6	122.1 122.1	121.8 121.8	123.0 120.2	122.6 120.3	122.1 119.7
θ_{H-C-H}	116.2 (116.6)	116.3 (116.8)	117.0 (117.9)	117.3	116.7	117.6	120.0	119.7	120.6	116.8	115.9	116.3	116.8	117.1	118.1

[a] Bond lengths in Å, and bond angles in degrees. [b] Ref 27. [c] Ref 2a; MP2/6-311++G(d,p) optimized (experimental, ref 28) values of HF and LiF are, respectively, 0.917 (0.917) and 1.579 (1.564). [d] Available experimental parameters are given in parentheses.

interaction between the HF proton and the base atom; either of the lone pair on the base atom could have been involved. A detailed discussion on this will be done in the last section. It is also found from the geometry of the HF complexes that in II the fluorine atom is sufficiently far away from the protons of H_2CY and therefore there is no secondary hydrogen bonding interaction between the two. Thus it is clear that HF complexes are stabilized only by the hydrogen bonding interaction involving the base atom. It is therefore natural to expect to have the order of stability as $H_2CO > H_2CS > H_2CSe$. *HF* and *DFT* complexation energies confirm this trend while *MP2*, *MP4* energies show the H_2CSe complex to be slightly more stable than the H_2CS complex. H_2CO, a first-row base, forms a stronger complex; H_2CS and H_2CSe, the second- and third-row bases, form slightly weaker complexes as revealed by Joesten and Schadd.[26] Between the two, the H_2CSe complex is found to be the weakest, though by a smaller extent.

Inclusion of correlation increased slightly the BSSE and the complexation energy, and as a result the corrected complexation energies are slightly lower than the *HF* energy. *DFT* complexation energies and BSSE are relatively higher. Change of basis set from double-ζ to triple-ζ quality increased BSSE marginally and correspondingly decreased the complexation energy. Platts and co-workers[5] have also reported the MP2/6-311++G(d,p) BSSE corrected binding energy to be 6.60 and 4.59 kcal/mol, respectively, for H_2CO and H_2CS complexes.

Energetics of LiF and HF complexes could not be compared straight-away for a possible correlation. This is in view of the fact that LiF and HF complexes stabilize in different forms—LiF in forms III, IV, and V and HF in form II. Form III is stabilized by primary lithium bonding interaction and secondary hydrogen bonding interaction. Because of these two stabilizing interactions the complex is found to be highly stable. From the geometry of IV one could infer that IV is stabilized by primary lithium bonding interaction involving the π-bond pair and therefore it is weaker than III but stronger than V. Form V is stabilized by the secondary hydrogen bonding interaction that is weaker than the lithium bonding interaction. Form II of HF complexes is stabilized by primary hydrogen bonding interaction alone. If one should correlate, at least roughly, the stabilities of LiF and HF complexes, the difference in the complexation energies of III and V of LiF complexes could be compared with the complexation energies of II of HF complexes. As a rough measure the differences in complexation energies of III and V of LiF complexes represent the primary lithium bonding energy and this difference is found to be higher than the complexation energy of II of HF complexes. This proves again that lithium bonds are stronger than hydrogen bonds.

III. Structure and Bonding. On complexation, geometric changes are observed and there are profound changes in those parameters that connect interacting atoms. Such parameters are taken for the discussion here. Table 4 lists selected *MP2* geometric parameters for the complexes as well as the monomers. Available experimental parameters for monomers and H_2CO...HF complex are also quoted in the Table 4 for comparison. As the trends observed in bonding changes on complexation at *HF*, *DFT,* and *MP2* levels are quite similar except a few cases noted below, only *MP2* parameters are given. *MP2* results are in excellent agreement with the available experimental bond parameters listed in the Table. We do not present Y⋯F distances here, as is usually done, because primary lithium bonds are angular and hydrogen bonds are not perfectly linear and in such circumstances the sum of van der Waals radii of Y and F are not meaningful; the same is the case with F⋯C distance in secondary hydrogen bonding situation.

LiF Complexes. Forms III and V are planar and IV is nonplanar. III is stabilized by primary lithium bonding interaction and secondary hydrogen bonding interaction, and V is stabilized by secondary hydrogen bonding interaction alone. IV is stabilized by again primary lithium bonding interaction. Geometries of these forms suggest that the lithium bonding in IV should involve the π-bond pair whereas it must be the lone pair on the base atom in III. This can be understood from the orientation of the donor orbitals. The presence of the secondary hydrogen bond interaction in III and V is evident from shorter F⋯H distances in all three complexes. The fact that the F⋯H distance is shorter in V than in III shows that the hydrogen bonding is stronger in V than in III. This also derives support from the fact that structure V has a linear hydrogen bond that is stronger while that in III is angular and therefore weaker. The F⋯H distance in IV is sufficiently larger to prevent secondary hydrogen bonding interaction. F⋯H distances in forms III and V of the complexes H_2CY (Y = O,S,Se) reveal that hydrogen bonding interaction increases from H_2CO to H_2CSe. This is due to the fact that electropositive nature of the protons increases from H_2CO to H_2CSe and this is in view of increased polarity of the C=Y bond down the series. Thus the greater the positive charge on the proton, the stronger will be the interaction. Next, LiF distance undergoes significant changes on complexation. Increase by a smaller extent in LiF bond in

V is understandable from the fact that it is the weakest among the three. LiF in III is constrained in a cyclic form and is not totally free to stretch, but it is totally free in IV. This is the reason that the LiF bond is perturbed strongly in IV than in III. An increase in the C═Y bond length is observed in all the three complexes and is found to be in the order IV > III > V. This again is due to the reasons outlined above. In IV, the additional factor that contributes to the greater increase of C═Y bond length is that the donation is from C═Y π-bond pair; this considerably weakens the π-bond. The Y···Li distances found in III and IV are characteristic of lithium bond, and this bond is stronger in III than in IV as expected. A stronger lithium bond in III is due to the donation of the lone pair; lithium bond in IV is relatively weaker as the π-bond pair is involved in donation.

In the H_2CO complex, a decrease in C−H bond length is noted in all the three forms and this is in consequence of the flow of charge from the σ^*(C−H) orbital toward oxygen on complexation as will be seen in the next section. But in III and V of H_2CS and H_2CSe complexes an increase in C−H bond length is observed. This can be explained as follows. Here, in III the σ^*(C−H) orbital loses its density by moving it toward S and Se on complexation and gains density through secondary hydrogen bonding. The net gain has led to the lengthening in C−H bond and thus established reduced flow of electrons toward sulfur and selenium rather than toward oxygen and that is quite natural. Back-donation of electrons from LiF to C−H antibond orbitals are more in both H_2CS and H_2CSe complexes than in H_2CO complex, and this lengthens the C−H bond. The net effect is an increase in the C−H bond length in H_2CS and H_2CSe. In V only hydrogen bonding is present and this involves a transfer of electron density to σ^*(C−H) orbital and therefore should result in lengthening of the C−H bond. But the C−H bond shortens in form IV of all the complexes and this is due to the absence of secondary hydrogen bonding interaction in this form. The above observation in C−H bond length changes in III, IV, and V clearly indicates that the primary interaction takes off electron density from the σ^*(C−H) orbital and the secondary interaction accumulates it there.

The bond angles Y···Li−F in III are characteristic of the five-membered cyclic structure of the complexes; in IV LiF is not constrained in a plane and the above angle is smaller by 10° than those found in III. Significant changes in the bond angles C−Y···Li are noted in the complexes. Both in III and IV the angles decrease in the order H_2CO > H_2CS > H_2CSe. The difference is more between the H_2CO and H_2CS complexes and relatively less in the latter pair. This shows that both sulfur and selenium prefer a perpendicular lithium bond than oxygen and smaller C−Se···Li angle than C−S···Li is due to an additional effect from a stronger secondary hydrogen bonding interaction in III in H_2CSe than in H_2CS. In IV the angle C−O···Li is 96.3° and as a consequence the lithium atom is away from the π-bond and is located almost on the oxygen atom. A considerably lower value of C−S···Li and C−Se···Li shows that lithium atom is positioned just above the π-bond. There are two H−C−Y bond angles in the complexes and the angles are altered differently in V, both decrease in III and no changes are observed in IV. In any form changes within the set of the complexes are not significant. In III, the secondary hydrogen bonding interaction attracts the proton toward the fluorine atom and this lead to the change in the H−C−Y angle whereas such an interaction is absent in IV and hence no such changes are observed. In V, one proton is involved in secondary hydrogen bonding interaction and the other is free and this leads to unequal changes in the H−C−Y bond angles in this form. A change in H−C−Y bond angles poses a change in H−C−H bond angle. A smaller increase in H−C−Y angles in III leads to slight widening of the H−C−H angle and no alterations of these angles in IV again results in no change in the H−C−H angle. In V, H−C−Y angles undergo slight change in the opposite direction and this results in no net change in the H−C−H angle.

The changes observed in the geometry of the monomers upon complexation at *HF* and *DFT* levels are almost similar to those found at the *MP2* level except for the *DFT* results on the H_2CS···LiF complex. *DFT* results for the above complex predict relatively longer C═S and Li−F bonds, shorter Y···Li and F···H distances, and a smaller Y···Li−F angle, and this seems to suggest a possibility of LiF undergoing a double-bond addition with H_2CS. A larger *DFT* binding energy of this complex is also indicative of this possibility.

HF Complexes. The only stable form of the HF complexes II has been seen to derive its stability from the primary hydrogen bonding interaction. On complexation, H−F and C═Y bonds are weakened and Y···H distances predict hydrogen bonding interaction between the monomers. The C−H bonds do not show any significant change. The Y···H−F bond angles are above 160° in all three complexes as reported by Platts and co-workers[5] and is in evidence of the preference of an almost linear hydrogen bond. Whatever deviation in the angle from 180° is on account of considerable electrostatic attraction between the fluorine and the base proton. It is interesting to note that such attraction in HF complexes is not enough to bend the C═Y···H bond angle to make the cyclic form III stable as observed in LiF complexes. Gradual decrease of the above angle from oxygen to selenium base is in line with the increase in the electrostatic attraction between the base proton and the fluorine atom. As the fluorine atom is sufficiently far away from the base protons in all the three complexes there is no secondary hydrogen bond in the complex. Considerable changes in C−Y···H angle are noted and it is in the order $H_2CO \gg H_2CS > H_2CSe$. The value of the angle is around 90° in sulfur and selenium base complexes, and this reveals the preference of a perpendicular hydrogen bond.[4,5] The difference in preference between oxygen base and sulfur and selenium bases should originate from the involvement of different lone pairs on the base atoms in the donation process and this will be examined in detail in the next section. Such an angular preference was explained by Platts and co-workers[5] as the domination of charge−multipole interaction in sulfur-based complexes and by an electrostatic model by Buckingham and Fowler.[6] H−C−Y and H−C−H bond angles do not show any change as there is no secondary hydrogen bonding interaction involving the base protons. The trends observed at *HF* and *DFT* levels are similar to those observed at *MP2* level.

The preceding discussion shows that there is a wide variation in structure and bonding in LiF and HF complexes. Notable among them are the following. (1) LiF complexes prefer the cyclic form while HF complexes stabilize in the open form. (2) Lithium bonds are formed in LiF complexes through either the donation of lone pair or π-bond pair whereas only lone pair donated HF complexes are stable. (3) Lithium bonds are stronger and angular, and hydrogen bonds are weaker and linear. (4) In both cases, sulfur and selenium prefer perpendicular H/Li bonds compared to oxygen. (5) Secondary hydrogen bonds involving the base protons and fluorine atoms are stronger with sulfur and selenium bases than in the oxygen base.

IV. Analysis of Interactions. Through orbital occupancies and second-order perturbation energy lowering (ΔE^2) due to the interaction of the donor and acceptor orbitals, one can

TABLE 5: Natural Bond Orbital Analysis for the Complexes of ZF (Z = Li,H) with H_2CY (Y = O,S,Se) Calculated at the MP2 Level with 6-311++G(d,p) Basis Set[a]

		$H_2CY \cdots ZF$					$H_2CY \cdots ZF$		
structure	parametersl	Y = O	Y = S	Y = Se	structure	parameters	Y = O	Y = S	Y=Se
III	$q_{CT}{}^{a}$(a.u)	0.004	0.030	0.031	IV	$q_{CT}{}^{a}$(a.u)	0.019	0.005	0.003
Z = Li	occupancy (a.u.)				Z = Li	occupancy (a.u.)			
	n_σ(Y)	1.985	1.990	1.993		$\pi_{C=Y}$	1.996	1.976	1.977
	n_π(Y)	1.930	1.921	1.926		n_σ(Y)	1.983	1.987	1.991
	σ^*(Li−F)	0.020	0.048	0.050		n_π(Y)	1.922	1.938	1.949
	n_π(F)	1.992	1.988	1.987		σ^*(Li−F)	0.021	0.038	0.035
	σ(Li−F)	1.986	1.983	1.983					
	σ(Li−F)	0.033	0.027	0.024					
	ΔE^2 (kcal/mol)					ΔE^2 (kcal/mol)			
	n_σ(Y), σ^*(Li−F)	4.01	3.01	2.44		$\pi_{C=Y}$, σ^*(Li−F)	1.26	8.90	8.50
	n_π(Y), σ^*(Li−F)	1.29	17.58	18.01		n_σ(Y), σ^*(Li−F)	4.31	3.91	2.55
	n_π(F), σ^*(C−H)	1.63	3.25	3.22					
	σ(Li−F), σ^*(C−H)	0.07	0.61	1.05					
V	$q_{CT}{}^{a}$ (a.u)	0.006	0.006	0.006	II	q_{CT} (a.u)	0.024	0.040	0.031
Z=Li					Z=H				
	occupancy (a.u.)					occupancy (a.u.)			
	n_σ(F)	1.996	1.996	1.995		n_σ(Y)	1.983	1.991	1.994
	σ(Li−F)	1.988	1.987	1.987		n_π(Y)	1.907	1.907	1.924
	σ^*(C−H)	0.039	0.029	0.025		σ^*(H−F)	0.024	0.036	0.028
	ΔE^2 (kcal/mol)					ΔE^2 (kcal/mol)			
	n_σ(F), σ^*(C−H)	1.45	1.32	1.19		n_σ(Y), σ^*(H−F)	3.96	1.12	0.64
	σ(Li−F), σ^*(C−H)	3.13	4.01	4.24		n_π(Y), σ^*(H−F)	12.84	16.90	12.78

		H_2CY					ZF	
	parameters	Y = O	Y = S	Y = Se		parameters	Z = Li	Z = H
monomers	n_σ(Y)	1.989	1.994	1.995	monomers	n_σ(F)	1.998	
	n_π(Y)	1.909	1.934	1.947		n_π(F)	1.994	
	$\Pi_{C=Y}$	1.999	1.999	1.999		σLi−F	1.991	
	$\sigma^*{}_{C-H}$	0.045	0.032	0.026		σ^*Li−F	0.010	
						σ^*H−F		0.000

[a] q_{CT} refers to the quantum of charge transferred from H_2CY to LiF in structures III and IV and from LiF to H_2CY in V and from H_2CY to HF in II.

unambiguously fix the exact orbitals that are involved in the charge-transfer process; in effect the origin of the various kinds of interactions that stabilize the complex can be traced. The occupancies of the orbitals of the monomers which involve in the charge-transfer interactions are summarized in Table 5. The quantum of charge-transfer q_{CT}, occupancies of the orbitals participating in the donor acceptor interaction, and the ΔE^2 values for the three stable structures III, IV, and V of the complexes of LiF with H_2CO, H_2CS, and H_2CSe and structure II of the complexes of HF with these bases calculated at *MP2* level with the basis set 6-311++G(d,p) are also collected in Table 5.

LiF Complexes. The preceding discussion on LiF complexes has revealed that the nature of the interactions that stabilize III, IV, and V are different and therefore the analysis of interactions in the above forms are done separately. Form III is stabilized mainly by primary lithium bonding interaction, and to a smaller extent by secondary hydrogen bonding interaction. q_{CT} value increases in the order $H_2CO < H_2CS < H_2CSe$ but the stability order shows a reverse trend. Such opposing trends imply that the primary lithium bonding interaction is mainly electrostatic and derives less strength from charge transfer interaction. This is very evident if the charges on the base atoms are examined. The analysis of atomic charges in monomers shows that oxygen is negatively charged while sulfur and selenium are positively charged. The interaction of the negatively charged oxygen and the positively charged lithium atom of LiF is therefore electrostatically attractive. In the case of sulfur and selenium the interaction becomes repulsive. From H_2CO to H_2CSe the electrostatic interaction becomes increasingly less stabilizing but the charge transfer interaction increasingly more stabilizing. The net effect is observed to be the decreasing stability in the $H_2CO > H_2CS > H_2CSe$ order. This clearly establishes the dominance of the electrostatic interaction in the lithium bonding interaction. On complexation the occupancy of the n_σ orbital of the oxygen atom decreases and n_π increases but the occupancies of n_σ and n_π of both sulfur and selenium show a decrease. In the latter case the decrease in n_π is more than in n_σ. The above trend in orbital occupancies confirms that oxygen donates its n_σ electrons while sulfur and selenium their n_π electrons. Comparison of ΔE^2 values for n_σ(Y), σ^*(LiF) and n_π(Y), σ^*(LiF) interactions further establishes the above fact. Because of the involvement of n_π orbitals in the donation process in sulfur and selenium bases they show a preference for a more perpendicular lithium bond than oxygen. A similar observation was made by Platts and co-workers[5] in HF complexes of H_2CO and H_2CS and by us[8] in LiF complexes of the above bases. Occupancies of LiF antibond orbitals increase in the order $H_2CO < H_2CS < H_2CSe$ a trend parallel to charge transfer in the complexes. Second-order perturbation energy lowering due to donor−acceptor interaction decreases in the order $H_2CSe > H_2CS > H_2CO$, and this again shows the order in which the charge-transfer interaction contributes to lithium bonding interaction in III of the LiF complexes. NBO analysis of the secondary hydrogen bonding interaction in III reveals the following. The occupancies of fluorine lone pair n_π and LiF bond pair and ΔE^2 values show that electrons are donated from n_π(F) and LiF bond orbital to C−H antibond orbital. The interesting observation here is that the acceptor orbital σ^*(C−H) occupancies decrease instead of an expected increase. This is due to the fact that complexation induces electronic flow from σ^*(C−H) orbital toward the base atom. That is, the base atom donates its pair to the LiF antibond orbital and this in turn induces an electronic flow from the σ^*(C−H) orbital toward the base atom. This results in a net decrease in the occupancy of the antibond orbitals. The decrease in σ^*(C−H) orbital occupancy on complexation is more in the H_2CO complex, less in the H_2CS complex, and least in the H_2CSe complex. This can be understood as follows. Charge transfer from H_2CY to LiF increases from oxygen to selenium due to primary lithium bonding interaction, and this in turn increases the back-donation of charge from LiF to H_2CY in the same order. Migration of electrons from σ^*(C−H) orbital toward the base atom stabilizes the base and increases the stability of the complex.

Orbital occupancies listed in Table 5 for IV show that there is mixed donation from two orbitals; both π(C=Y) bond pair and n_σ(Y) lone pair are found to be donating. n_π(Y) and LiF σ^* orbitals show an increase in occupancy. ΔE^2 values also confirm the participation of n_σ(Y) and π(C=Y) bond pair in the charge-transfer process. Interestingly, H_2CO complex involves n_σ-dominated mixed donation while the latter complexes involve π-dominated mixed donation. It is for this reason, in H_2CO complex the LiF is slightly away from the π-bond and is located on the oxygen atom while in the other two, LiF is straight above the π-bond. What is more surprising is that even changes by small proportions at orbital level lead to considerable changes in geometry of the complex.

In V, the q_{CT} values for all the complexes are more or less equal as expected; it is the base proton that is involved in the secondary hydrogen bonding interaction that stabilizes the complex. Orbital occupancies and ΔE^2 values indicate that it is the n_σ of fluorine atom and LiF bond pair that donate electrons and C−H antibond orbitals that accept it. But a decrease in occupancy of σ^*(C−H) orbital is noted and this reveals that the charge accumulated in the σ^*(C−H) orbital is delocalized in the H_2CY unit to stabilize the complex. The increased secondary hydrogen bonding strength in the sulfur and selenium complexes could be understood from the most electropositive nature of the H_2CY protons in their monomers. There are two interesting observations here. (1) This is again a case of mixed donation involving a lone pair and a σ-bond pair with the latter slightly dominating the donation process. (2) Here it is the σ-type lone pair n_σ of fluorine atom is involved and not n_π as found in form III. The change of lone pair in the secondary hydrogen bonding interaction changes the geometry of the complex in III, the hydrogen bond is angular or more perpendicular and in V it is linear. It is similar to n_π-donation in sulfur and selenium atoms that makes more perpendicular lithium bonding favorable compared to n_σ-donation by oxygen atom. In III, the situation needs a more bent or perpendicular hydrogen bond and this perhaps switched the donating orbitals.

HF Complexes. The q_{CT} values in Table 5 indicate that the charge transfer increases from H_2CO to H_2CS and then declines further, from H_2CS to H_2CSe. Similar to LiF complexes, HF complexes show the following characteristics. In H_2CO complex there is mixed donation of n_σ and n_π lone pairs with greater participation of n_π lone pair. In the other two complexes, dominantly n_π donates and this in fact is a reason for a more perpendicular hydrogen bond as reported by us[8a] and Platts and co-workers[5] in the H_2CS and H_2CSe complexes compared to H_2CO complex.

NBO analysis clearly fixes the origin of the various interactions that stabilize the LiF and HF complexes of H_2CY (Y = O,S,Se). Evidently the lithium bonding stabilizes the cyclic form as the most stable form while the hydrogen bonding stabilizes the open form. In LiF complexes, the primary lithium bonding interaction is found to involve either lone pair donation from the base atom (III) or mixed donation involving the C=Y π-bond pair and lone pair (IV). But in HF complexes, the primary hydrogen bonding interaction involves the donation of the lone pair on the base atom alone and any participation of π-bond pair is clearly ruled out. The effect of the nature of base atoms on donations is similar in both LiF and HF complexes.

Conclusions

The high-level computational study of the structure and stability of LiF and HF complexes of H_2CY (Y = O,S,Se) and the consequent NBO analysis of the ab initio wave functions reveal the following important information. Out of the 10 proposed conformations, LiF complexes are found to have three stable forms—III, IV, and V, and HF complexes stabilize in only one form, II. The above complexes are mainly stabilized by lithium and hydrogen bonding interactions. Structure and stability of these complexes give a clue that these interactions should differ in their origin and in their nature and NBO analysis confirms it.

Lithium bonding interactions in LiF complexes involve the donation of either of the lone pair on the base atom, n_σ in H_2CO and n_π in H_2CS and H_2CSe in form III and a mixed donation of n_σ(Y) and π(C=Y) in form IV and LiF antibond orbitals. The weak hydrogen bonding interaction in LiF complexes involves the participation of both n_π of fluorine atom and σ(Li−F) orbitals in III and n_σ of fluorine atom and σ(Li−F) in V in the donation process; in both cases the electrons are accepted into σ^*(C−H) orbital. HF complexes are stabilized by the hydrogen bonding interaction alone that is mainly n_σ(O), n_π(O)−σ^*(H−F) in the H_2CO complex and n_π(S,Se)−σ^*(H−F) in the other two complexes.

Different origins of these lithium and hydrogen bonding interactions lead to different geometric preferences and stabilities and such differences in their origin are due to the nature of the atoms involved in the interaction and the molecular framework in which they are embedded.

No substantial changes in the properties of the complexes are noted when the basis set is changed from double-ζ to triple-ζ quality. Inclusion of correlation increased BSSE.

It is generally observed that (1) the complexes are stabilized by lithium bonding and/or hydrogen bonding interactions; (2) in both interactions, the electrostatic component plays a more dominant role than charge transfer component as evident from the energetics of the complexes; (3) while the lithium bonding interaction is stronger and angular, the hydrogen bonding interaction is relatively weaker and linear; this again proves the relative dominance of charge−multipole interaction in the former and charge−charge interaction in the latter; (4) in both situations, sulfur prefers a more perpendicular bond than oxygen and lithium and hydrogen bonds to sulfur are weaker than to oxygen; (5) selenium shows striking similarity in geometrical preference, donation, and strength of interaction with sulfur than to oxygen.

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