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# $\pi$ -systems as lithium/hydrogen bond acceptors: Some theoretical observations

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*Ab initio* calculations at the Hartree–Fock and correlated levels and density functional theory calculations have been performed with 6-31++G(*d,p*) and 6-311++G(*d,p*) basis sets on LiF and HF complexes of benzene, ethylene, and acetylene. Complex binding energies have been corrected for basis set superposition error, and zero point energy corrections have been done on Hartree–Fock binding energies. Computed results indicate that the complexes exist in different conformations and among them those with  $\pi$ -lithium and  $\pi$ -hydrogen bonds are the most stable.  $\pi$ -lithium bonds are stronger than  $\pi$ -hydrogen bonds. The computed binding energies and geometry of HF complexes correlate well with the available experimental results. LiF complexes with these  $\pi$  systems are found to be weaker than Li<sup>+</sup> complexes but they are stronger than Li atom complexes. Natural bond orbital analysis traces the origin of the weak interactions that stabilize the complex. Li, as found in earlier cases, prefers the most symmetric site for interaction whereas proton prefers a nonsymmetric site in benzene complexes. Surprisingly, such a change of interaction geometry in LiF and HF complexes is found to change the donating  $\pi$ -orbitals in the benzene complexes.

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## I. INTRODUCTION

Intermolecular interactions play a significant role in several biological<sup>1</sup> and chemical phenomena<sup>2</sup> and in view of this, much attention has been focused in recent years to understand the physics and chemistry of such interactions through experiment<sup>3</sup> and theory.<sup>4</sup> Mainly, the geometry and strength of interaction have been the topic of interest and very rarely,<sup>5,6</sup> the origin of such interactions have been traced. Even hydrogen bonded systems that are abundant and well studied are no exception to this. This is due to the reason that, only recently, advanced theoretical procedures are available and these enable one to analyze the interaction at a more deeper level and derive novel insights from them.

Hydrogen bonded systems have been especially studied due to their wide occurrence and relevance in biology and chemistry. Lithium, congener to hydrogen, can form similar bonds but comparatively lithium bonds are much less investigated.<sup>6–8</sup> Although both, hydrogen and lithium bonds, appear to be similar the type of interaction that stabilize the former has been found to be different from that of the latter. This has been observed<sup>9</sup> to have led to differential geometric preferences and strength of interactions in hydrogen/lithium bonded complexes. There are only very few reports on lithium bonded complexes. Lithium has been grouped with metal cations such as Na<sup>+</sup>, K<sup>+</sup>, Ca<sup>2+</sup>, etc. in certain occasions and in some other, it is considered as an isoelectronic replacement of the proton. Thus lithium occupies a unique position in that it forms weak bonds like hydrogen and at the same time behave as metal ions like Na<sup>+</sup>, K<sup>+</sup>, etc. Because

of such a position of lithium we became interested in probing lithium bonds with different lithium bond acceptors, and as a first part we have investigated lithium bonded complexes with (*n* +  $\pi$ ) donors and *n* donors, and presented our results elsewhere.<sup>6</sup> We have chosen here  $\pi$  systems—benzene, ethylene, and acetylene as lithium bond acceptors. LiF is chosen as the lithium donor. For comparison, we have performed calculations on the complexes of HF with the same set of donors; HF complexes of the above  $\pi$  bases have, already been studied experimentally and at lower levels of theory.

X–H $\cdots\pi$  interactions have been the subject of many experimental<sup>10–15</sup> and theoretical investigations<sup>16–24</sup> and in many occasions benzene, ethylene, and acetylene have been employed as hydrogen bond acceptors. Flygare and co-workers<sup>10,11</sup> have used microwave molecular beam techniques to examine the structure of HF complexes with acetylene and ethylene and they have concluded that the complex has T-shaped geometry with HF molecular axis pointing towards the midpoint of the carbon–carbon bond. The above results are fully consistent with *ab initio* predictions reported by Pople and co-workers.<sup>17</sup> Though HF complexes of acetylene and ethylene have been investigated at various levels of theory only few structural studies on the hydrogen bonded complex with benzene as the H-acceptor have been carried out due to complications of size.

The structure of the C<sub>6</sub>H<sub>6</sub> $\cdots$ HF complex has been an interesting subject for a long time but still the structure is a matter of controversy. Baiocchi *et al.*<sup>12</sup> and Andrews *et al.*<sup>14</sup> have investigated the structure of the C<sub>6</sub>H<sub>6</sub> $\cdots$ HF complex using molecular beam electric resonance and infrared spectroscopy, respectively, and concluded that the complex has

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the  $C_{6v}$  equilibrium structure. An electrostatic potential map of benzene shows that the  $\pi$ -electron cloud creates zones of negative potential above and below the benzene plane and so a favorable interaction occurs when the interacting dipole lies along the  $C_6$  ring axis with its positive terminus directed toward the face of the ring. But the simple HOMO-LUMO model for this interaction provides a conflicting structural prediction since the symmetries of benzene HOMO and HF LUMO do not favor  $C_{6v}$  geometry. Semiempirical CNDO calculations<sup>25</sup> predict an asymmetric structure in which the HF molecule mainly interacts with one of the C=C double bonds. The reported *ab initio* calculations<sup>18–20</sup> with smaller basis sets on the  $C_6H_6 \cdots HF$  complex point to the symmetric  $C_{6v}$  geometry. Single point MP2 calculations with larger basis set on this complex have been reported by Bredas and Street<sup>19</sup> and Cheney and co-workers<sup>18,20</sup> and they have predicted the  $C_{6v}$  structure for the complex. These conflicting predictions for the structure of the  $C_6H_6 \cdots HF$  complex stimulates further interest in this subject. Recently Rozas and co-workers<sup>24</sup> have studied  $H \cdots \pi$  interactions using the Bader's AIM approach.

Lithium can form lithium bonds with unsaturated hydrocarbons. The amount of experimental work done to date on such  $\pi$ -lithium bonded complexes have been rather meager and only theoretical reports are available.<sup>6–8</sup> Szczesniak and Ratajczak<sup>26</sup> have reported *ab initio* calculations for the complexes  $C_2H_4 \cdots LiF$  and  $C_2H_2 \cdots LiH$ . The complexes of Li, Na, and K atoms with  $C_2H_4$  have been studied with coupled-cluster and density functional theory (DFT) methods by Alikhani and co-workers.<sup>27</sup> The lithium ion affinity and lithium atom affinity for benzene have been reported by Fujii *et al.*<sup>28</sup> and Manceron and Andrews,<sup>29</sup> respectively. *Ab initio* molecular orbital study at the HF and MP2 levels with the 6-31G\* basis set on  $Li^+$  complexes of first row bases, that include ethylene and acetylene, have been done by Del Bene and co-workers.<sup>30</sup>

In continuation of our work on lithium bonded complexes with  $(n + \pi)$  donors and  $n$  donors, we report here our high level *ab initio* results on LiF/HF complexes of  $\pi$  donors. The main objective of this paper is to (1) observe how the  $\pi$  systems respond to lithium donors (2) look at the geometry around  $F-H \cdots \pi$  and  $F-Li \cdots \pi$  interactions (3) trace the origin of  $\pi$ -hydrogen and  $\pi$ -lithium bond interactions at the orbital level.

## II. COMPUTATIONAL DETAILS

All calculations have been carried out using the GAUSSIAN 94W program<sup>31</sup> implemented on a Pentium computer. The complex potential energy surface has been scanned at the Hartree-Fock level with 6-31++G(d,p) (Refs. 32–34) basis set by selecting five possible geometries (I–V) for the benzene complexes, three geometries (VI–VIII) for the ethylene complexes, and two geometries (IX–X) for the acetylene complexes (Fig. 1). In benzene complexes, in the first three structures (I–III) the  $\pi$ -hydrogen/lithium bond interaction is the main force and in the next two structures (IV–V) hydrogen bonding interaction involving benzene protons and the fluorine atom of HF/LiF is the stabilizing force. Structure I has been optimized with

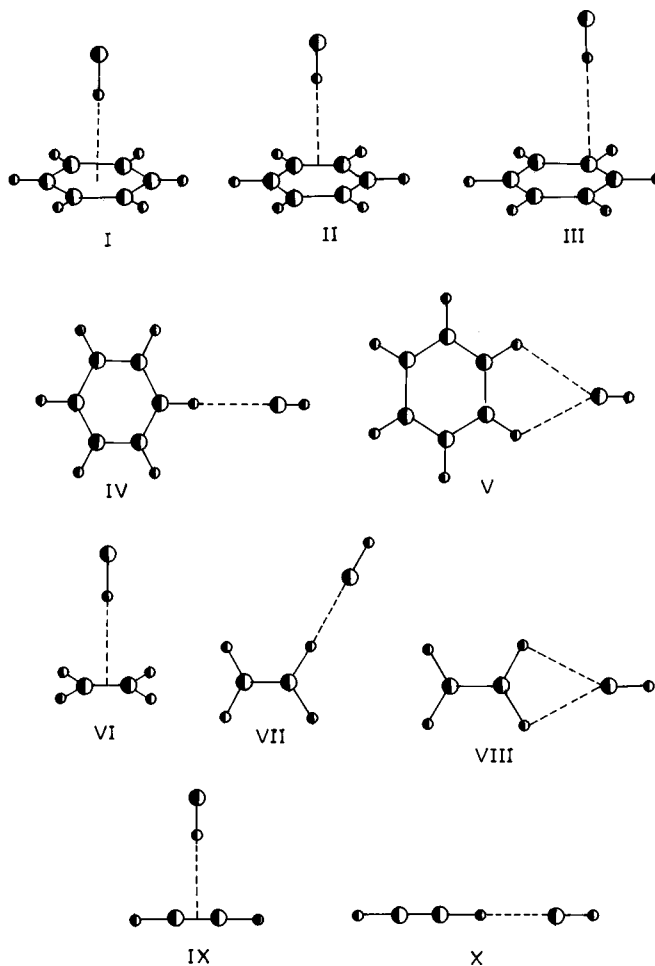


FIG. 1. Proposed geometries of the LiF/HF complexes of benzene, ethylene, and acetylene.

$C_{6v}$  symmetry in which the HF/LiF molecule aligns with the  $C_6$  axis of benzene. Structures II and III have  $C_s$  symmetry, where in II the interaction of the HF/LiF molecule is mainly with one of the C=C bonds and in III it is with one of the carbon atoms of benzene. Structures IV and V consider, respectively, the linear and bifurcated hydrogen bonding between the protons of benzene and the fluorine atom of HF/LiF.

Among the three structures considered for the ethylene complexes, structure VI has a T-shape geometry with  $C_{2v}$  symmetry in which the HF/LiF molecule interacts vertically at the midpoint of the C=C bond. The secondary hydrogen bonding interaction between the protons of ethylene and the fluorine atom of HF/LiF are considered in structures VII (linear,  $C_s$ ) and VIII (bifurcated,  $C_{2v}$ ). There are only two possible orientations for the interactions of HF/LiF with acetylene; one with a T-shape geometry ( $C_{2v}$ ) and another with the linear hydrogen bonding interaction between the proton of acetylene and fluorine atom of HF/LiF.

All the above mentioned structures of the complexes are fully optimized within their symmetry constraints and the harmonic frequencies for each structure have been calculated at this level to characterize the stationary point. Geometry optimizations have been carried out with larger triple-zeta 6-311G basis set<sup>35</sup> augmented by polarization<sup>33</sup> and diffuse functions<sup>34</sup> [6-311++G(d,p)] only for the stable struc-

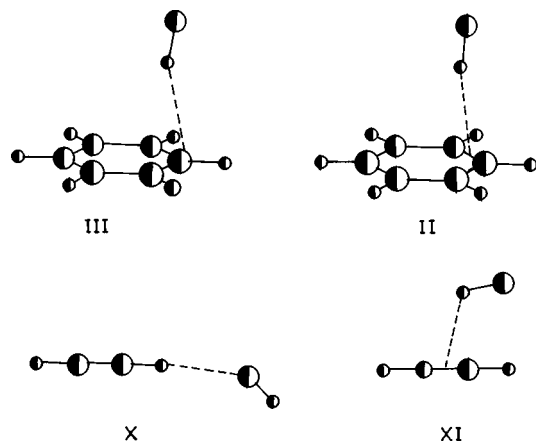


FIG. 2. Optimized structures of  $C_6H_6 \cdots HF$  (II, III),  $C_2H_2 \cdots HF$  (X), and  $C_2H_2 \cdots LiF$  (XI) complexes.

tures. The stable structures obtained from Hartree–Fock level have also been optimized at the MP2 and DFT level. DFT calculations have been done with the exchange potential of Becke and correlation functional of Lee, Yang, and Parr (B3LYP).<sup>36</sup> Inclusion of electron correlation at the higher level have been carried out for the ethylene and acetylene complexes by calculating single point MP4 (SDTQ) energies on the MP2 geometries. The complexation energies calculated at the Hartree–Fock level are corrected for both basis set superposition error (BSSE) and zero point vibrational energy (ZPE) and those calculated at the DFT, MP2, and MP4 levels are corrected only for the BSSE as frequency calculations at these levels have not been done. BSSE has been calculated using the Boys–Bernardi counterpoise method<sup>37</sup> and also considering the relaxation of the monomer geometries upon complexation.<sup>38</sup> Natural bond orbital (NBO) analysis<sup>39</sup> on the stable forms of the complexes have been carried out at the Hartree–Fock level.

### III. RESULTS AND DISCUSSION

HF and LiF form weak hydrogen/lithium bonded complexes with acetylene, ethylene, and benzene through  $F \cdots H \cdots \pi$  and  $F-Li \cdots \pi$  interactions and secondary hydrogen bonds. The results are discussed as follows: Potential energy surface, energetics, structure and bonding, and finally the analysis of interactions. Totally eleven structures have been proposed for these complexes and are presented in Figs. 1 and 2. The complex binding energies, BSSE, ZPEC, corrected binding energies, and the number of imaginary frequencies obtained for each structure of the complexes at the Hartree–Fock level are given in Table I and those at the DFT, MP2, and MP4 level in Table II. It should be noted that MP2 calculations with triple zeta basis set and MP4 calculations with both double and triple zeta basis sets for benzene complexes could not be done as they are computationally more demanding. Selected MP2 structural parameters and Hartree–Fock frequencies of the monomers, complexes are listed in Table III. The results of NBO analysis for the monomers, and the complexes are summarized in Table IV.

#### A. Potential energy surface

The  $\pi$ -bases employed here are highly symmetric and this limits the number of distinct interaction sites in the bases; consequently there are fewer interaction geometries for the complexes and this greatly reduces the scan time of the PES. The above bases can interact with LiF/HF by two ways; (i) through their  $\pi$  electrons, that is the primary interaction and (ii) through their protons, that is the secondary interaction. Benzene has three primary interaction sites, viz., face center, bond center, and atom center, and two secondary interaction sites as shown in Fig. 1. Ethylene and acetylene have bond center and atom center as the primary interaction sites and ethylene has two secondary interaction sites and acetylene has one secondary interaction site. Atom center

TABLE I. Interaction energies  $\Delta E$ , BSSE, counterpoise corrected interaction energies  $\Delta E^{cp}$ , zero point vibration energy correction (ZPEC), corrected binding energies  $\Delta E_{ZPEC}^{cp}$  (kcal/mol), and number of imaginary frequencies ( $n_i$ ) for the complexes calculated at the Hartree–Fock level.

Complex	Structure	6-31++G(d,p)						6-311++G(d,p)					
		$\Delta E$	BSSE	$\Delta E^{cp}$	ZPEC	$\Delta E_{ZPEC}^{cp}$	$n_i$	$\Delta E$	BSSE	$\Delta E^{cp}$	ZPEC	$\Delta E_{ZPEC}^{cp}$	$n_i$
$C_6H_6 \cdots LiF$	I	13.44	1.67	11.77	1.04	10.73	0	12.61	1.08	11.53	1.04	10.49	0
	IV	2.91	0.34	2.91	0.38	2.19	0	2.98	0.30	2.68	0.22	2.46	0
	V	2.60	0.37	2.60	0.23	2.00	2	...	...	...	...	...	...
	VI	9.70	1.11	8.59	1.15	7.44	0	8.70	0.45	8.25	1.03	7.22	0
$C_2H_4 \cdots LiF$	VII	2.17	0.26	1.91	0.55	1.36	0	2.19	0.16	2.03	0.55	1.48	0
	VIII	1.36	0.24	1.12	0.24	0.88	1	1.31	0.18	1.13	0.19	0.94	2
	IX	9.61	1.00	8.61	0.82	7.79	0	8.67	0.41	8.26	0.67	7.59	0
	X	6.62	0.49	6.13	0.87	5.26	0	6.72	0.43	6.29	0.92	5.37	0
$C_2H_2 \cdots LiF$	XI	9.58	0.55	9.03	0.85	8.18	0	9.29	0.33	8.96	0.88	8.08	0
$C_6H_6 \cdots HF$	I	2.90	0.24	2.66	0.61	2.05	2	...	...	...	...	...	...
	II	2.98	0.26	2.72	0.85	1.87	0	3.11	0.47	2.64	0.85	1.79	0
	III	2.98	0.26	2.72	0.84	1.88	1	3.11	0.46	2.65	0.81	1.84	0
	IV	0.50	0.06	0.44	0.18	0.26	1	...	...	...	...	...	...
	V	0.51	0.07	0.44	0.27	0.17	1	...	...	...	...	...	...
$C_2H_4 \cdots HF$	VI	3.18	0.19	2.99	1.57	1.42	0	3.06	0.27	2.79	1.45	1.34	0
	VII	0.36	0.04	0.32	0.21	0.11	1	0.42	0.10	0.32	0.24	0.08	2
	VIII	0.25	0.03	0.22	0.18	0.04	2	0.33	0.12	0.21	0.26	-0.05	1
$C_2H_2 \cdots HF$	IX	2.99	0.13	2.86	1.29	1.57	0	2.95	0.25	2.70	1.26	1.44	0
	X	1.48	0.17	1.31	0.44	0.87	0	1.60	0.27	1.33	0.38	0.95	0

TABLE II. Interaction energies  $\Delta E$ , BSSE, counterpoise corrected interaction energies  $\Delta E^{\text{cp}}$  (kcal/mol) for the complexes at the DFT, MP2, and MP4 levels.

Complex	Level	Structure	6-31++G(d,p)			6-311++G(d,p)		
			$\Delta E$	BSSE	$\Delta E^{\text{cp}}$	$\Delta E$	BSSE	$\Delta E^{\text{cp}}$
$\text{C}_6\text{H}_6 \cdots \text{LiF}$	DFT	I	13.96	2.47	11.49	12.15	1.32	10.83
		IV	3.12	0.38	2.74	3.16	0.39	2.77
$\text{C}_2\text{H}_4 \cdots \text{LiF}$	MP2	I	17.78	6.67	11.11	...	...	...
		VI	10.59	1.55	9.04	8.85	0.50	8.35
	DFT	VII	2.45	0.36	2.09	2.43	0.34	2.09
		VI	11.34	3.21	8.13	10.13	2.41	7.72
	MP2	VII	2.79	0.75	2.04	2.72	0.66	2.06
$\text{C}_2\text{H}_2 \cdots \text{LiF}$	MP4//MP2	VI	11.41	3.28	8.13	10.31	2.55	7.76
		VII	2.88	0.86	2.02	2.80	0.73	2.07
		IX	10.62	1.44	9.18	8.92	0.43	8.49
	DFT	X	7.02	0.69	6.33	6.92	0.55	6.37
		XI	10.77	0.95	9.82	9.85	0.46	9.39
		IX	11.85	3.61	8.24	10.31	2.58	7.73
	MP2	X	7.07	1.21	5.86	6.96	1.08	5.88
		XI	11.54	2.80	8.74	10.64	2.25	8.39
		IX	11.94	3.58	8.36	10.49	2.61	7.88
		X	7.18	1.39	5.79	7.07	1.21	5.86
$\text{C}_6\text{H}_6 \cdots \text{HF}$	MP4//MP2	XI	11.72	2.82	8.90	10.88	2.28	8.60
		IX	4.47	1.06	3.41	4.29	1.08	3.21
		X	4.45	0.23	4.22	4.27	0.30	3.97
	DFT	X	1.68	0.29	1.39	1.72	0.32	1.40
		IX	4.60	1.31	3.29	4.41	1.26	3.15
$\text{C}_2\text{H}_4 \cdots \text{HF}$	MP2	X	2.00	0.65	1.35	2.01	0.70	1.31
		IX	4.53	1.33	3.20	4.33	1.27	3.06
	MP4//MP2	X	2.08	0.75	1.33	2.07	0.77	1.30
		X						

TABLE III. Selected MP2 structural parameters and Hartree-Fock frequencies for the monomers and complexes optimized with the 6-31++G(d,p) basis set.

Parameter <sup>a</sup>	Monomers <sup>b</sup>			LiF complexes							HF complexes				
	$\text{C}_6\text{H}_6$	$\text{C}_2\text{H}_4$	$\text{C}_2\text{H}_2$	I	IV <sup>d</sup>	VI	VII	IX	X	XI	II	III	VI	IX	X
$R_{\text{Z-F}}$	...	...	...	1.622	1.591	1.615	1.612	1.616	1.617	1.628	0.932	0.932	0.935	0.933	0.928
$R_{\text{X} \cdots \text{Z}}$	...	...	...	2.098	...	2.356	...	2.325	...	2.337	2.338	2.389	2.196	2.174	...
$R_{\text{C-C}}$	1.399	1.339	1.221	1.402	1.399	1.345	1.341	1.223	1.224	1.225	1.401	1.401	1.342	1.222	1.221
$R_{\text{C-H}}$	1.083	1.081	1.064	1.083	1.089	1.083	1.083	1.067	1.077	1.070	1.083	1.083	1.082	1.065	1.065
$R_{\text{F} \cdots \text{H(C)}}$	...	...	...	4.463	2.132	4.260	2.209	4.311	1.919	2.595	...	...	...	...	2.253
$\theta_{\text{X} \cdots \text{Z-F}}$	...	...	...	180.0	...	180.0	...	180.0	...	113.6	170.0	164.1	180.0	180.0	...
$\theta_{\text{H-C-C}}$	120.0	121.5	180.0	120.0	120.4	121.4	121.4	178.4	180.0	172.8	120.0	120.0	121.4	179.4	180.1
$\theta_{\text{F} \cdots \text{H-C}}$	...	...	...	...	180.0	...	180.0	...	180.0	...	...	...	...	...	173.7
$\theta_{\text{H} \cdots \text{F-Z}}$	...	...	...	...	180.0	...	180.0	...	180.0	...	...	...	...	...	133.5
$\nu_{\text{Z-F}}$	...	...	...	901	917	919	919	907	907	896	4402	4401	4352	4369	4458
$\nu_{\text{X} \cdots \text{Z}}$	...	...	...	142	...	163	...	175	...	301	79	79	106	108	...
$\nu_{\text{C-C}}$	1783	1830	2223	1773	1782	1815	1826	2210	2193	2204	1781	1781	1823	2216	2217
$\nu_{\text{C-H}}$	3374	3321	3693	3390	3368	3314	3295	3664	3658	3663	3380	3380	3321	3682	3685
$\nu_{\text{F} \cdots \text{H}}$	...	...	...	...	81	...	98	...	151	158	...	...	...	...	84

<sup>a</sup>Bond lengths in Å, bond angles in degrees, and frequencies in  $\text{cm}^{-1}$ . Z=Li, H in LiF/HF, respectively. For structure numbering refer to Figs. 1 and 2.<sup>b</sup>MP2 LiF and HF bond lengths are, respectively, 1.609 and 0.927 Å. The corresponding Hartree-Fock frequencies of them are 928 and 4473  $\text{cm}^{-1}$ .<sup>c</sup>X, denotes the ring center in I, bond center in II, VI, IX, and XI, and carbon atom in III.<sup>d</sup>As MP2 values are not available for  $\text{C}_6\text{H}_6 \cdots \text{LiF}$  complex(IV) the corresponding DFT values are given.

TABLE IV. Natural bond orbital analysis for the LiF and HF complexes calculated at the HF/6-31++G(*d,p*) level.

Parameters	LiF complex				HF Complex			
	C <sub>6</sub> H <sub>6</sub> (I)	C <sub>2</sub> H <sub>4</sub> (VI)	C <sub>2</sub> H <sub>2</sub>		C <sub>6</sub> H <sub>6</sub>		C <sub>2</sub> H <sub>4</sub> (VI)	C <sub>2</sub> H <sub>2</sub> (IX)
			(IX)	(XI)	(II)	(III)		
$q_{CT}^a$ (a.u.)	0.014	0.018	0.010	0.004	0.003	0.003	0.009	0.006
Occupancy (a.u.)								
$\pi_{C=C}$	1.661	1.982	1.991	1.992	1.673, 1.659, 1.659	1.670, 1.661, 1.657	1.989	1.993
$\sigma^*(Z-F)$	0.029	0.031	0.023	0.019	0.003	0.003	0.009	0.006
$\Delta E^2$ (kcal/mol)								
$\pi_{C=C}, \sigma^*(Z-F)$	1.01	6.30	2.68	1.89	1.40	1.07, 0.11	4.56	3.46
		C <sub>6</sub> H <sub>6</sub> (IV)		C <sub>2</sub> H <sub>4</sub> (VII)		C <sub>2</sub> H <sub>2</sub> (X)		C <sub>2</sub> H <sub>2</sub> (X)
$q_{CT}^a$ (a.u.)		0.005		0.004		0.013		0.003
Occupancy (a.u.)								
$n_\sigma(F)$		1.996		1.996		1.994		1.999
$n_\pi(F)$		1.995		1.995		1.996		1.997
$\sigma(Z-F)$		1.989		1.990		1.984		1.999
$\sigma^*(C-H)$		0.013		0.010		0.018		0.008
$\Delta E^2$ (kcal/mol)								
$n_\sigma(F), \sigma^*(C-H)$		1.24		0.97		1.17		0.12
$n_\pi(F), \sigma^*(C-H)$		...		...		...		1.82
$\sigma(Z-F), \sigma^*(C-H)$		2.71		1.82		10.84		0.08

<sup>a</sup> $q_{CT}$  refers to the charge transferred from the  $\pi$  system to ZF(Z=H, Li) in structures I, II, III, VI, IX, and XI and from ZF to the  $\pi$  system in IV, VII, and X. For the structure numbering refers to Figs. 1 and 2. NBO occupancies for the monomers (i)  $\pi$  system.  $\pi_{C=C}$  and  $\sigma_{C-H}^*$  are, respectively, 1.663 and 0.010 for benzene, 1.999 and 0.008 for ethylene, and 1.999 and 0.006 for acetylene. (ii) Z-F  $n_\sigma(F)$ ,  $n_\pi(F)$ ,  $\sigma_{Z-F}$  and  $\sigma_{Z-F}^*$  are, respectively, 1.998, 1.995, 1.993, and 0.007 for LiF and 1.999, 1.999, 2.000, and 0.000 for HF.

geometries in ethylene and acetylene complexes have not been shown in the figure, as in both cases, they have been found not to be stable and converges on bond center geometries.

### 1. LiF complexes

Among the five structures (I–V) considered for the C<sub>6</sub>H<sub>6</sub>··LiF complex, I, IV, and V are found to be stationary points and II and III converged on I. Frequency calculations show that I and IV are stable forms and V is a second order saddle. In I, LiF approaches benzene along its C<sub>6</sub> axis with the Li atom pointing toward the ring and in IV the fluorine atom interacts with the benzene proton and this is consistent with the picture that emerges from the electrostatic potential map of benzene.

All three structures (VI–VIII) considered for the ethylene complex and the two structures (IX and X) considered for the acetylene complex are found to be stationary points. Frequency calculations reveal that VI and VII and IX and X are stable forms; VIII has turned out to be a first order saddle. Calculations with the 6-311++G(*d,p*) basis set have been performed for all the forms of ethylene and acetylene complexes. Change of basis set do not alter the surface features significantly.

Earlier reports on LiF complexes<sup>6,9</sup> with different bases show that LiF always prefer cyclic forms and lithium bonding is more angular than hydrogen bonds. To test this possi-

bility structures I, VI, and IX, that have lithium bonds, respectively, in benzene, ethylene, and acetylene have been optimized allowing the fluorine atom to move around in the vertical plane passing through the carbon atoms; the lithium atom is retained in its position. Such optimizations have shown that there are no cyclic forms observed in benzene and ethylene complexes. But in the acetylene case a bent structure XI is found to be stable. Here Li interacts with the acetylene  $\pi$  electrons while the acetylene proton is electrostatically attracted by the fluorine atom of LiF. XI is found to be the most stable conformation of the C<sub>2</sub>H<sub>2</sub>··LiF complex.

### 2. HF complexes

Full geometry optimizations at the Hartree–Fock level show that the PES of the C<sub>6</sub>H<sub>6</sub>··HF complex has five stationary points, I–V as noted in the Fig. 1. Frequency calculations reveal that structure I is a second order saddle, III–V are first order saddles, and II alone is the equilibrium structure, an observation markedly different from the C<sub>6</sub>H<sub>6</sub>··LiF complex and earlier predictions.<sup>18–20</sup> As the imaginary frequency of III is very low and the complexation energy of III is very close to that of II, they have been reoptimized with basis set 6-311++G(*d,p*) and frequency calculations with this basis set show that both II and III are minima.

Contrastingly, the PESs of C<sub>2</sub>H<sub>4</sub>··HF and C<sub>2</sub>H<sub>2</sub>··HF complexes have similar features as that of corresponding LiF complexes; VI–X are found to be stationary points; fre-

quency calculations show that T-shaped structures of both the complexes VI and IX are stable and the structures with the bifurcated hydrogen bonding in ethylene (VIII) is a second order saddle. The structure with the secondary hydrogen bond, VII turns out to be a first order saddle, while X is a stable form. Optimizations and frequency calculations with 6-311++G(*d,p*) basis set also predict the same; VI is again confirmed to be a minimum and VII and VIII are found to be second and first order saddles, respectively. The bent or resting structure for the HF complex has not been considered, as was done with LiF, because the hydrogen bond prefers almost a linear geometry and this does not allow the fluorine to get closer to the base protons in space and form a bent structure. If HF is placed above acetylene in a resting geometry with the hydrogen atom of HF centered on the triple bond, the fluorine atom is found to be near to the carbon atom and such a disposition is electrostatically repulsive and therefore unstable.

The PES searches of the HF/LiF complexes of benzene, ethylene, and acetylene reveal the following: while LiF and HF prefer totally different interaction geometries with benzene, both form complexes with similar geometries with ethylene and acetylene. LiF favors the face center geometry but HF prefers bond and atom center geometries with benzene. LiF and HF complexes with ethylene and acetylene assume the T-shape geometry in full agreement with experiment. Additionally, LiF forms complexes with benzene, ethylene, and acetylene through secondary hydrogen bonding interaction where the fluorine atom of LiF interacts with the proton of the  $\pi$ -system. But in HF complexes only the acetylene complex is found to have such a secondary hydrogen bonded form stable. Such differential preferences of proton and lithium for the interaction with the  $\pi$  system seem to have a very interesting origin and this will be revealed through various analyses in the following sections.

## B. Energetics

Complexation energies, BSSE, ZPEC, and corrected complexation energies computed at the HF level are compiled in Table I. Table II lists, the complexation energies, BSSE and BSSE corrected complexation energies computed at the DFT, MP2, and MP4 levels. ZPE corrections at the MP2, DFT levels could not be provided as calculations of frequencies at the MP2, DFT levels are computationally more demanding. For the same reason MP4 single point energies on MP2 geometries for benzene complexes are not reported.

### 1. LiF complexes

LiF complexes of benzene, ethylene, and acetylene are mainly of two types; one in which the complex is stabilized by the  $\pi$ -lithium interaction and in the other that is stabilized by the hydrogen bonding interaction involving the protons of  $\pi$  systems and the fluorine atom of LiF. Only in the acetylene complex there exists a conformation in which the LiF molecule interacts almost in a resting position.

The binding energies calculated at the HF, DFT, and MP2 levels show that in all the three complexes  $\pi$ -lithium bonded structures (I, VI, and IX) are more stable than their

respective  $\pi$ -hydrogen bonded structures (IV, VII, and X). This reveals that the  $\pi$ -lithium bonding interaction is stronger than the hydrogen bonding interaction involving the protons of the  $\pi$ -system. In I, VI, and IX, LiF aligns vertically on the  $C_6$  axis in benzene,  $C_2$  axis in ethylene and acetylene, respectively, with the lithium atom pointing downward toward the  $\pi$  system. In benzene it is called face center geometry and in ethylene and acetylene it is noted as bond centered structures or T-shape geometry. The order of stability among the  $\pi$ -lithium bonded structures is found to be I>IX>VI. BSSE and ZPE corrected binding energies of these complexes show that the benzene complex is more stable while the other two vary very little in stability. The above trend is repeated in all the levels. One interesting observation here is that the order of stability does not correspond with the order of HOMO values of the  $\pi$  bases and this is indicative of the fact that charge transfer interaction is not the dominant force in the  $\pi$ -lithium interaction. This clearly brings out the major contribution of electrostatic force to the above interaction. It has already been shown<sup>30</sup> that the lithium bonding interaction derives its stability more from the ion-multipole interaction and the present context is evidence for such stabilization with the  $\pi$ -lithium acceptor.

It is appropriate to compare, from the earlier work, the binding energies of the related complexes here. Fujii and co-workers<sup>28</sup> have compared the HF/6-31G binding energy of the  $C_6H_6 \cdots Li^+$  complex 36.1 kcal/mol with the experimental value 37.9 kcal/mol. Del Bene and co-workers<sup>30</sup> have reported the MP2/6-31G\*/HF/3-21G binding energies of  $Li^+$  complexes of ethylene and acetylene, respectively, as 23.2 and 23.6 kcal/mol. DFT/6-31G(2*d,2p*) binding energy of the  $C_2H_4 \cdots Li$  complex has been reported<sup>27</sup> to be 2.16 kcal/mol. The above results indicate two points (i) benzene complex is quite stronger of all the three and the binding energies of ethylene and acetylene complexes are lower and lie closely in energy; of the two, the acetylene complex is slightly more stable. BSSE and ZPE corrected binding energies of LiF complexes of the  $\pi$  bases employed here show the same trend; (ii) they show the range in which the stability of LiF complexes should fall. This is in view of the fact that LiF complexes will have intermediate stability compared to  $Li^+$  and Li atom complexes as shown earlier. This prediction is also in good agreement with our results.

A different order of stability is observed if the structures of the three complexes (IV, VII, X) that are stabilized by secondary hydrogen bonding interaction alone are considered. HF, MP2, DFT binding energies show the same trend in the stability order and it is found to be X>IV>VII. The acetylene complex is found to be the most stable. This is understandable from the fact that the protons in acetylene are attached to  $sp$  hybridized carbon and are more acidic compared to benzene; ethylene protons that are attached to  $sp^2$  carbon and are less acidic. A more acidic proton can naturally form a stronger hydrogen bond. Though the protons involved in the complexation in IV and VII are attached to  $sp^2$  carbons the charge developed on the benzene carbon on account of charge transfer is delocalized in the aromatic system while the charge developed on the ethylenic carbon is delocalized only to the next carbon atom. This accounts for

the increased stability of the benzene complex IV compared to ethylene complex VII. In addition to the  $\pi$ -lithium bonded (IX), hydrogen bonded (X) structures, the  $C_2H_2 \cdots LiF$  complex has an additional structure (XI) and this is found to be the most stable among the three. Interestingly, this structure has both types of interaction and hence the stability is found to be higher. Attempts to get similar structures in benzene and ethylene complexes show that there are no such stable forms. This occurs in the acetylene complex due to two factors; one, the tendency of Li to form cyclic structures and the next, the proximal disposition of the fluorine atom to the acetylenic proton in space in this complex.

The trends observed in the binding energies of the different structures of these complexes remain the same at all the levels and with both basis sets. BSSE values are lower at the HF, DFT levels and higher in the MP2, MP4 levels as observed earlier and as expected. Inclusion of the correlation at the MP2 level increases the binding energy while the correlation correction at the MP4 level is not all that significant. DFT binding energies are also higher. ZPE corrections done at the HF level is around 1 kcal/mol in all the complexes. The change of the basis set from double-zeta to triple-zeta decreases the  $\pi$ -lithium bond strength and increases the hydrogen bond strength.

## 2. HF complexes

HF forms complexes with acetylene and ethylene with T-shaped geometry similar to LiF but with benzene the preference of HF is totally different; only bond centered (II) and atom centered (III) structures are stable. HF assumes oblique orientation over the C–C bond and over the carbon atom of the benzene ring. This clearly indicates that the forces that are involved in the  $\pi$ -hydrogen bonding interaction is different from that in the  $\pi$ -lithium bonding interaction. II and III have more or less the same binding energy, 1.88 kcal/mol. The change of the basis set does not result in significant change but inclusion of the electron correlation has increased the binding energy. Cheney and co-workers<sup>18,20</sup> have reported both  $C_{6v}$  and  $C_s$  geometry at the 3-21G\* level. At 3-21G\* optimization both symmetric  $C_{6v}$  and symmetric  $C_s$  structures turned out to be stationary points as it appears in our case, but they have not performed the frequency calculations to characterize the stationary points. They assumed both as minima. Frequency calculations done at the HF level in our case clearly revealed that the  $C_{6v}$  structure I is a second order saddle and only II and III are minima. Bredas and Street<sup>19</sup> have considered five interaction geometries for the  $C_6H_6 \cdots HF$  complex and performed optimizations at the HF/3-21G level and they have done single point HF/6-31G\* and MP2/6-31G\* calculations on HF/3-21G geometries. They have reported binding energies etc. for  $C_{6v}$  and  $C_s$  and secondary hydrogen bonded structures. They have also assumed that the symmetric structure is a minimum. Bredas and Street<sup>19</sup> have reported that the complexation energy of II is slightly higher than that of III at all the levels employed; the reported binding energies are higher and this is in view of the 3-21G basis set used for optimization. The magnitude of our computed binding energy shows that  $\pi$ -hydrogen bonds are weaker in general and weaker than  $\pi$ -lithium bonds in

particular. If the stability of the HF complexes are examined the following trends are noted. Uncorrected and BSSE corrected binding energies follow the same order of strength, ethylene>acetylene>benzene at the HF, DFT, and MP2 levels. If ZPE correction is also included HF binding energies show the order benzene>acetylene>ethylene. The trends observed at the higher levels are consistent with the experimental values reported by Andrews and his group<sup>14</sup> and with the theoretical predictions by Pople and co-workers<sup>17</sup> and Bredas and Street.<sup>19</sup> Nelson and co-workers<sup>40</sup> have correlated empirically the electric dipole moment induced upon complexation with the strength of the interaction. They have found that the induced dipole moments of the complexes increase in the order ethylene>acetylene>benzene, and therefore the binding energies should also follow the same order. This trend is in good agreement with our DFT and MP2 binding energies. In the  $C_2H_2 \cdots HF$  complex alone the form X that has the weak secondary hydrogen bonding interaction is found to be stable. The binding energies of IX and X show that the  $\pi$ -hydrogen bond is stronger than the secondary hydrogen bond.

BSSE values are found to be lower at the HF and DFT levels and comparatively higher at the MP2 and MP4 levels. ZPE corrections for the HF complexes are slightly more in the case of acetylene and ethylene whereas it is less for benzene when compared to their LiF complexes. The change of basis set from double-zeta to triple-zeta increased BSSE slightly and correspondingly decreased the binding energy. DFT, MP2, and MP4 levels show higher binding energies compared to the HF level. The comparison of binding energies of LiF and HF complexes reveal that  $\pi$ -lithium bonds are definitely stronger than the  $\pi$ -hydrogen bonds. The secondary hydrogen bonding interaction is also found to be stronger in LiF complexes than in HF complex. HF and LiF show a reverse order of stability for their complexes with benzene, ethylene, and acetylene. Complexes with the  $\pi$ -electron donors are relatively weaker than those with the ( $n + \pi$ ) and  $n$  donors.

## C. Structure and bonding

Complexation leads to changes that are significant only in selected structural parameters of the monomers and introduces new bonding parameters in the region of intermolecular contact. Selected MP2 parameters and Hartree–Fock frequencies of the monomers and complexes are listed in Table III. For the above analysis the data obtained with 6-31++G( $d,p$ ) are considered.

### 1. LiF complexes

In the lithium bonded structures (I, VI, and IX) the LiF molecule is most symmetrically disposed around the  $\pi$  system with the Li atom pointing vertically downward toward the  $\pi$  bases. Such an orientation reveals two things: (1) the electrostatic interaction dominates and especially the ion–dipole interaction contributes mainly to stabilization; (2) charge migrates from the  $\pi$  orbitals to the  $\sigma^*$  orbital of LiF. The calculated X $\cdots$ Li distance in all three complexes is in the range of 2.0–2.4 Å and this shows that  $\pi$ -lithium bonds are stronger. It should be noted here that relative strengths of

lithium and hydrogen bonds could not be straightforwardly correlated through intermolecular distances in lithium and hydrogen bonds and this is in view of the fact that the intermolecular distance in lithium bonds have been reported to be significantly larger than in hydrogen bonds due to the inner closed shell in the lithium atom.<sup>26</sup> But among lithium complexes such distance should correlate with the strength of the interaction. This distance is the shortest in the benzene complex and follows the order  $C_2H_4 > C_2H_2 > C_6H_6$ . The above order is in good agreement with the computed interaction energies of the complexes. A different trend in  $\nu_{X...Z}$  is an indication of the role played by the electrostatic forces in stabilizing the complexes.

Expectedly, the Li–F bond length has increased on complexation and the increase is found to be slightly greater in the benzene complex while it is more or less same in the ethylene and acetylene complexes. The lowering of  $\nu_{Z-F}$  observed in complexes also indicate this. The geometrical parameters of benzene and ethylene are not altered much due to complexation except a slight increase in C–C bond length. But changes have been observed in almost all the structural parameters in the  $C_2H_2 \cdots LiF$  complex. Computed  $\nu_{C-C}$  and  $\nu_{C-H}$  also reflect the same. This is the consequence of a few structural parameters sharing the whole perturbation. In the acetylene complex C–C and C–H bonds undergo elongation and C–C–H bond angles slightly decrease. The acetylene protons are slightly moved away from the molecular axis in a direction that is opposite to the approach of LiF towards acetylene as reported in the  $C_2H_2 \cdots HF$  complex.<sup>22</sup> Such a bending reveals that  $\pi$ -lithium bonding interaction has led to rehybridization of the carbon from  $sp$  to  $sp^2$  to a smaller degree. Similar rehybridization should be observable in the ethylene complex where the ethylene carbon atoms should undergo pyramidalization ( $sp^2$  to  $sp^3$ ) to a smaller extent and thus push the ethylenic protons out of the molecular plane. But such changes are too small to be observable in ethylene as well as in benzene.

The hydrogen bonded forms IV, VII, and X have characteristically shorter F $\cdots$ H distances (Table III). Acetylene protons, being more acidic than benzene and ethylene protons, have a stronger interaction as reflected through C–H bond length changes on complexation in these complexes. The variation in the structural parameters is greater in the acetylene complex compared to the other two. This is also evident from  $\nu_{F...H}$  listed in Table III. The Li–F bond lengthens on complexation and correspondingly  $\nu_{Li-F}$  decreases. The C–C bond of acetylene lengthens but there is no change of the C–C–H bond angle observed earlier. Contrastingly the C–C–H bond angles in benzene and ethylene change by 1°.

Unlike benzene and ethylene, acetylene is found to have yet another stable form XI on complexation with LiF; the form that is more stable than  $\pi$ -lithium (IX) and hydrogen bonded (X) forms, has a resting type or bent structure with the Li atom is placed at 2.4 Å above the  $C\equiv C$  bond. On optimization the lithium atom is found to move slightly away from the midpoint of the  $C\equiv C$  bond and towards one carbon atom and F is lying above the C–H bond. The  $X \cdots Li$  distance in XI is therefore found to be more than in X though

the  $\pi$ -lithium bond is stronger in XI. The  $X \cdots Li-F$  angle and  $F \cdots H$  distance show that there occurs a strong interaction between the fluorine atom and acetylenic protons but the geometrical dispositions of fluorine, proton, and carbon atoms are such that there is no hydrogen bond formation between F and H. But the  $\nu_{F...H(C)}$  shows it to be otherwise. The changes in the C–H bond length and C–C–H angle are slightly greater in XI than in IX.

## 2. HF complexes

Benzene forms a complex with HF only through  $\pi$ -hydrogen bond; no secondary hydrogen bonded forms are found to be stable. In the  $\pi$ -hydrogen bonded form, unlike LiF, HF prefers positions of lower symmetry, a bond center or an atom center in benzene for the interaction. Such preference of proton interaction with symmetric bases has also been reported.<sup>30</sup> Asymmetric structures have also been proposed by the HOMO-LUMO interaction model and CNDO results.<sup>25</sup> Baiocchi and co-workers<sup>12</sup> have performed a molecular beam electric resonance technique study of the  $C_6H_6 \cdots HF$  complex and reported a symmetric average structure with the hydrogen end of HF pointing toward benzene and the hydrogen atom is placed at a distance of 2.25 Å from the benzene plane. The large amplitude motions present in this complex made it difficult for them to determine the equilibrium structure. Later Andrews and co-workers<sup>14</sup> have studied the IR spectrum of the  $C_6H_6 \cdots HF$  complex in the argon matrix and based on the observation of one degenerate HF librational mode they have proposed the symmetric  $C_{6v}$  structure for the complex. Calculation reveals further that the interaction geometry is fairly guided by the electrostatics with charge transfer playing a less dominant role. This is also in accordance with the earlier observation that in hydrogen bonded complexes electrostatic forces contribute more than the charge transfer interaction. Though bond centered (II) and atom centered (III) structures are found to be equally stable, the geometry around the intermolecular contact— $X \cdots H$  distance and  $H \cdots H-F$  angle—are characteristically different. It should also be noted that HF takes up an oblique orientation above the benzene ring and this shows that the proton interacts, at least, mildly with other  $\pi$  bonds or carbon atoms.

Similar to LiF complexes, HF forms  $\pi$ -hydrogen bonded complexes with the T-shaped geometry with ethylene and acetylene; this is in full agreement with the experimental data available for the HF complex.<sup>10,11</sup> HF takes up a vertical orientation. On complexation, characteristically H–F bond lengthens and C–C and C–H bonds undergo mild changes; correspondingly  $\nu_{H-F}$  decreases. Shorter  $X \cdots H$  distances are observed. The  $X \cdots H$  distance decreases in the order  $C_6H_6 > C_2H_4 > C_2H_2$  and this appears to correlate with C–C bond orders 1.5:2.0:3.0. One would normally expect that shorter the intermolecular bond distance, stronger the complex. But the trend in the  $X \cdots H$  distance in these complexes does not agree with the order found in complex binding energies ( $C_2H_4 > C_2H_2 > C_6H_6$ ) but  $\nu_{X...Z}$  reflect the same trend. The change in the weak intermolecular bond distance here probably reflect a change in the spatial extent of the charge distribution in the  $\pi$  systems rather than a change in the

magnitude of the interaction energy. The experimentally observed<sup>41,42</sup>  $X \cdots H$  distances in ethylene and acetylene complexes 2.22 and 2.19 Å correlate well with MP2  $X \cdots H$  distances.

No significant changes in the geometry of the  $\pi$  systems have been noted due to complexation except slight distortion of linearity of acetylene. The  $X \cdots H-F$  angle in these complexes shows that HF assumes a vertical orientation with ethylene and acetylene—a contrary arrangement of oblique orientation with benzene. It is puzzling to note that HF assumes different orientations in the benzene complex, compared to it in ethylene and acetylene complexes. Perhaps the answer lies at the orbital origin of  $\pi$ -hydrogen bonds in these systems and will be discussed in the following section. In addition to  $\pi$ -hydrogen bonded form acetylene has yet another form of  $C_2H_2 \cdots HF$  complex; a form that is stabilized by the secondary hydrogen bond (X). The geometry of this complex reveals that it is weaker than the  $\pi$ -hydrogen bonded form (IX). In X,  $C-H \cdots F$  is not perfectly linear.

The geometry of LiF and HF complexes with benzene, ethylene, and acetylene indicate that (i) the  $\pi$ -Li/ $\pi$ -H interactions though weak mainly stabilize the complex. In the  $C_6H_6 \cdots HF$  complex HF assumes an oblique orientation and both bond centered and atom centered geometries are equally favorable but exhibit slightly different structural features. (ii) Lithium, unlike proton, prefers the most symmetrical site for the interaction. (iii) The  $C_2H_2 \cdots LiF$  complex assumes a unique resting geometry where  $\pi$ -lithium and  $F \cdots H$  attractive interactions are operative. Acetylene suffers perceptible changes in geometry on complexation. (iv) There is reasonable agreement between the available experimental bond parameters of the HF complexes with MP2 values.

#### D. Analysis of interactions

NBO analysis has been performed on Hartree–Fock wave functions of the stable forms with the 6-31++G(d,p) basis set. Computed orbital occupancies of the monomers, the quantum of charge transferred from donor to the acceptor  $q_{CT}$ , occupancies of the frontier MOs, and  $\Delta E^2$ , the second order perturbation energy lowering due to the interaction of the donor and acceptor orbitals in the complexes are collected in Table IV.

##### 1. LiF complexes

In the  $\pi$ -lithium bonded structures (I, VI, and IX) the  $\pi$  system acts as the donor and LiF as the acceptor and in the secondary hydrogen bonded forms (IV, VII, and X) LiF acts as the donor and the  $\pi$  system accepts the electron. Therefore NBO analysis of these two groups of complexes are discussed separately. The  $C_2H_2 \cdots LiF$  complex has an additional form XI—the most stable among the three forms IX, X, and XI—stabilized by both the  $\pi$ -lithium interaction and the  $F \cdots H$  attraction. This will be of course treated as a separate case as similar forms are not observed in benzene and ethylene complexes.

Orbital occupancies and  $\Delta E^2$  values for the  $\pi$ -lithium bonded structures show that  $\pi_{C=C}$  orbitals of the  $\pi$  system and  $\sigma^*(LiF)$  are involved in the charge transfer process. On complexation,  $\pi$  orbital occupancies decreased marginally

and that of  $\sigma^*(LiF)$  increased considerably.  $Q_{CT}$  values indicate that the charge is transferred from the  $\pi$  system to LiF and in the order  $C_2H_4 > C_6H_6 > C_2H_2$  and the  $\Delta E^2$  values are in the order  $C_2H_4 > C_2H_2 > C_6H_6$ . But the complex binding energies of I, VI, and IX is in the order  $C_6H_6 > C_2H_2 > C_2H_4$ . Usually, when charge transfer forces alone stabilize a complex  $q_{CT}$  and  $\Delta E^2$  will be proportionately higher, the stronger the complex. Absence of such a trend here in these complexes clearly shows clear dominance of electrostatic interaction and its varying contribution to each complex and to each form.<sup>6</sup> Such a trend is characteristic of hydrogen and lithium bonding situations. It is true that charge transfer interactions do play a role here but what is more interesting is that electrostatics is dominating and seems to decide the orbitals involved in the charge transfer process. It manifests itself through the preference of interaction geometry. This aspect is clearly brought out from the analysis of complex molecular orbitals.

Benzene has three  $\pi$  orbitals,  $a_{2u}$  and  $e_g$  and the  $a_{2u}$  orbital hereafter referred as  $\pi_1$  is nondegenerate and is a lower energy molecular orbital; the doubly degenerate  $\pi$  orbitals  $e_g$  hereafter referred to as  $\pi_2$  and  $\pi_3$  are the HOMOs. More specifically  $\pi_2$  refers here to the MO that has a node passing through the C–C bonds and  $\pi_3$  refers to that molecular orbital whose node passes through two carbon atoms. Obviously  $\pi_1$  does not have a node at all. NBO analysis that gives a localized picture treats  $\pi_1$ ,  $\pi_2$ , and  $\pi_3$  equally and shows as all of them participate equally in the charge transfer in the  $C_6H_6 \cdots LiF$  complex. If the *ab initio* wave functions are closely examined it clearly reveals that it is purely  $\pi_1$  that donates electrons to  $\sigma^*(LiF)$ ;  $\pi_1$  is preferred though it is low lying than  $\pi_2$  and  $\pi_3$  for symmetry reasons. This surprising observation is in full accordance with the guiding principle of FMO interactions. We have already mentioned that LiF assumes the most symmetric orientation in view of the increased stabilization from the ion–dipole interaction and in this orientation  $\pi_1$  will have an increased constructive overlap with LiF antibond orbitals. Participation of the  $\pi_1$  orbital is more evident from the increased stabilization of  $\pi_1$  over  $\pi_2$  and  $\pi_3$  in the complex.

In the hydrogen bonded structures IV, VII, and X, the  $q_{CT}$  value decreases in the order  $C_2H_2 > C_6H_6 > C_2H_4$  and parallels the trend in the complex binding energies and this shows that the charge transfer plays a more dominant role in this hydrogen bonding situation. Of course the additional stabilization due to electrostatic force is not ruled out. Orbital occupancies and  $\Delta E^2$  values indicate that both  $n_\sigma$  of fluorine and the bond pair LiF donate electrons to the C–H antibond orbitals in the  $\pi$  system; occupancies of  $n_\sigma(F)$  and  $\sigma(Li-F)$  decrease marginally while that of  $\sigma^*(C-H)$  increases.  $\Delta E^2$  values confirm the mixed donation of  $n_\sigma(F)$  and  $\sigma(Li-F)$  and reveals that  $\sigma(Li-F)$  increasingly donate than  $n_\sigma(F)$ .

The  $C_2H_2 \cdots LiF$  complex has the most stable form XI that is stabilized by the  $\pi$ -lithium bond and  $F \cdots H$  attractive interaction. We have seen that the  $F \cdots H$  distance is too high to consider it a weak hydrogen bond.  $Q_{CT}$  and  $\Delta E^2$  values of XI is lower than the T-shaped form IX though the former is stronger than the latter. This again proves this form derives

its stability more from the electrostatic interaction than from the charge transfer interaction.

## 2. HF complexes

HF complexes of benzene, ethylene, and acetylene stabilize through  $\pi$ -hydrogen bonds II, III, VI, and IX. Unlike LiF complexes, the secondary hydrogen bonded form is found to be stable only in the acetylene complex. There is no equivalent form for XI either. As the  $C_6H_6 \cdots HF$  complex assumes an asymmetric ( $C_s$ ) form the three  $\pi$  orbitals show up different occupancies. Occupancy of one  $\pi$  orbital increases while the other two decreases. In both II and III one  $\pi$  bond will be directly involved in donation but the other two  $\pi$  orbitals flow the electrons towards it as it is a delocalized  $\pi$  system. As it happened in the  $H_2CO$  complex<sup>6</sup> where C–H bond electrons are mobilized towards the donor center oxygen atom, the donating  $\pi$  orbital here should gain electrons at the expense of the other two. In the  $\pi$ -hydrogen bonded forms of the ethylene and acetylene complexes, the occupancies of  $\pi$ -orbitals decrease and  $\sigma^*(H-F)$  increases as expected.  $Q_{CT}$  and  $\Delta E^2$  values decrease in the order  $C_2H_4 > C_2H_2 > C_6H_6$  and it exactly matches the order in complex binding energies. This confirms that the charge transfer interaction is more pronounced and determines the stability order—a notable point of contrast between hydrogen bonding and lithium bonding situations.

More interesting information comes out if one looks at the interacting donor and acceptor orbitals by examining the wave functions of the complex. The occupancies of the  $\sigma^*(H-F)$  and  $q_{CT}$  values are much closer for II and III as the binding energies do. But the donating orbitals differ, it is  $\pi_1$  and  $\pi_3$  in II and  $\pi_1$  and  $\pi_2$  in III.  $\Delta E^2$  shows that one  $\pi$  orbital interacts in II but a careful examination of the wave function reveals that both  $\pi_1$  and  $\pi_3$  orbitals interact. NBO orbital occupancies show that in III one  $\pi$  orbital dominantly donates while another  $\pi$  orbital weakly participates in the interaction. The third  $\pi$  orbital is not at all perturbed. This also shows up in  $\Delta E^2$  values. A closer look at the wave function shows that  $\pi_1$  and  $\pi_2$  orbitals are the interacting MOs in III. II and III therefore involve one degenerate  $\pi$  orbital each for donation besides  $\pi_1$  and are equivalent forms. The oblique orientation of HF shows the interaction of the proton with all other carbon atoms electrostatically and this would have led to this limited participation of  $\pi_1$  orbital in the charge transfer along with  $\pi_2$  and  $\pi_3$  in III and II. Slight contraction of the C–H bond length is also observed and this is a consequence of the C–H bond electron being pulled towards the donor orbitals, as found in  $H_2CY \cdots Z-F$  ( $Y=O, S, Se; Z=H, Li$ ) complexes.<sup>6</sup>

Only  $C_2H_2 \cdots HF$  has the secondary hydrogen bonded form (X) and the NBO analysis shows the following.  $Q_{CT}$  and  $\Delta E^2$  values indicate the weak nature of the interaction. A mixed donation from  $n_\sigma(F)$ ,  $n_\pi(F)$ , and  $\sigma(H-F)$  with greater participation of  $n_\pi(F)$  is observed;  $\sigma^*(C-H)$  orbital accepts the charge. It should be noted here that the involvement of  $n_\pi(F)$  in donation makes the intermolecular weak bond angular. This should be contrasted with the LiF complex (X) and in that the LiF bond pair is donated preferably over  $n_\sigma(F)$ .

NBO and direct analysis of wave functions have made it possible to unambiguously fix the origin of various interactions that stabilize the LiF and HF complexes of benzene, ethylene, and acetylene. Surprising and at the same time more interesting observation here is the involvement of different  $\pi$  orbitals of benzene in I, II, and III and the role of electrostatic and charge transfer interactions in deciding the geometry and stability of the complexes. Ethylene and acetylene do not present such diverse situations—in both LiF and HF complexes the T-shaped geometry is favored. The notable feature here is that the electrostatic interaction favors a particular interaction geometry and the geometry decides the participating MOs for interaction. Though electrostatic interactions contribute substantially over the charge transfer interaction in both the lithium and hydrogen bonding situation, the influence of the electrostatic interaction is more in the former than in the latter.

## IV. CONCLUSIONS

We summarize the following conclusions from our theoretical investigations:

- (i) Computed binding energies, in full agreement with experimental data, and frequency calculations indicate that the most stable structures of the HF complexes of ethylene and acetylene are T-shaped as observed earlier and the  $C_6H_6 \cdots HF$  complex assumes bond-centered or atom-centered geometry in total contrast with earlier predictions.
- (ii) In the most stable form LiF assumes a T-shaped geometry with ethylene and acetylene as HF does but with benzene, unlike HF, it prefers the symmetric  $C_{6v}$  face centered geometry.
- (iii) BSSE and ZPE corrected binding energies show that  $\pi$ -lithium and  $\pi$ -hydrogen bond energies fall in the range 7.0–10.0 kcal/mol and 1.5–2.0 kcal/mol, respectively, and are weaker. Secondary hydrogen bonds that stabilize certain other conformations of these complexes are weaker still. BSSE is generally lower for HF and DFT levels and higher for the MP2 level. No significant changes are observed with the change of basis set.
- (iv) LiF complexes are stronger than the Li atom complexes but they are weaker than  $Li^+$  complexes. This indicates the role of the electrostatic interaction that plays in lithium bonding.
- (v) While LiF forms stronger complex with benzene compared to ethylene and acetylene, HF shows a reverse trend.
- (vi) Experimental geometric parameters of the HF complexes correlate well with MP2 results.
- (vii) The stability order and quantum of charge transfer in these complexes indicate that though lithium and hydrogen bonds derive stability from electrostatic and charge transfer forces, lithium bonds have a more dominant contribution from the electrostatic interaction than hydrogen bonds do. In these complexes electrostatic forces decide the favorable geometry and the geometry decides the orbitals that participate in

charge transfer. In the benzene complex, LiF prefers the most symmetric site for interaction where HF chooses a nonsymmetric location. Surprisingly, this difference in the geometry changes the interacting donor orbital; it is  $\pi_1$  in the (LiF) complex and  $\pi_1$  and  $\pi_2$  or  $\pi_1$  and  $\pi_3$  in the HF complex.

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