A Theoretical Investigation of Benzene−AlX_3 and Ethene−AlX_3 (X = H, F, Cl) Interactions

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The present report details the results of a high-level theoretical investigation of benzene−AlX_3 and ethene−AlX_3 (X = H, F, Cl) interactions. The binding energies, preferred modes of interaction of AlX_3 with benzene and ethene, and vibrational frequencies for these complexes have been evaluated at the MP2 level using basis sets ranging from the 6-31+G* to the much larger (6-311++G(2df,p) + diffuse(d,p)). In the lowest energy conformers of the benzene complexes, the Al atom is directly placed over one of the benzene carbons, while in the ethene complexes, the Al atom lies above the center of the π bond. The binding energies of both the benzene and ethene complexes of AlX_3 are dominated by electrostatic contributions, which is in contrast to the dominance of the electron correlation energy in the benzene−BX_3 complexes. A very sharp increase in the negative charge of the benzene carbon closest to the Al atom in the lowest energy conformers of the benzene complexes from −0.2 to −0.4 au points to an important role of activation of the aromatic ring by the Lewis acid in electrophilic aromatic substitution reactions.

Introduction

Several theoretical and experimental studies in the recent past have focused their attention on the role of the aromatic-π system in governing the structure and reactivity of complexes containing aromatic systems.[1−9] In nearly all these complexes, the electropositive groups which normally interact with the π-electron cloud are either hydrogen or cations (organic or metal).[1−8] While interactions involving the former result in weak van der Waals complexes, the latter are characterized by high binding energies dominated by electrostatic contributions. In continuation of a previous study,[10] wherein we focused our attention on the interactions of the π-electron cloud of the aromatic ring with systems containing neither a hydrogen nor a cation (boron-containing systems), the present study details the nature of interaction prevailing in the complexes of aromatic systems with AlX_3 (X = H, F, Cl).

Even though Lewis acids like AlX_3 (X = H, F, Cl) are extensively employed as catalysts in reactions involving aromatic systems,[11] neither experimental nor theoretical investigations have focused their attention on complexes of AlX_3 with π systems of any kind. Except for the complexes of AlX_3 with ammonia,[12,13] there have been relatively few investigations either experimental or theoretical of other complexes formed by AlX_3.[14−17] However, complexes formed by an aluminum atom with various organic molecules including benzene have attracted a lot of attention.[18,19] In this connection, a recent high-level theoretical investigation of the interaction of aluminum cation (Al^+) with benzene, pyridine, cyclopentadiene, pyrrole, and furan also merits mention.[20]

On the other hand, the AlX_3 monomers have been the focus of a number of experimental and theoretical studies.[21−25] These experimental studies include the infrared spectra of AlH_3[21] and the matrix infrared spectra of AlF_3 and $AlCl_3$.[22,23] Theoretical calculations at the second-order Möller−Plesset (MP2) and single and double excitation coupled cluster (CCSD) levels have been carried out by Schaefer and co-workers on AlH_3 and $AlCl_3$ in its monomeric and complexed states with ammonia.[12] The experimental investigations on AlH_3 also include theoretical calculations at the MP2 and CCSD levels.[21] There has also been a recent MP2 study of various aluminum monohalides by Frenking and co-workers.[24] AlF_3 has been the focus of a high-level theoretical study which included density functional theory (DFT), MP2, and CCSD methods.[25] The major differences in the monomeric and dimeric forms of AlF_3, $AlBr_3$, and AlI_3 has been the focus of a very recent experimental and theoretical investigation by Aarset et al.[26]

Therefore, the focus of the present theoretical investigation is a comparison of the geometries, binding energies, vibrational frequencies, and electronic properties of the minimal energy conformers of the C_6H_6−AlX_3 and the corresponding C_2H_4−AlX_3 systems. The preferred modes of interaction of AlX_3 with benzene have also been analyzed. In addition to a detailed comparison of the olefinic and benzene complexes of AlX_3, we also highlight the major differences with respect to the corresponding complexes of BX_3.[10] We illustrate these differences using the charge-decomposition analysis (CDA),[27] and natural bond orbital (NBO) partitioning schemes,[28] and the Laplacian of the electron density distribution.[29]

Computational Methods

Complete geometry optimizations at the MP2 level using the 6-31+G* basis set were carried out on different conformations of C_6H_6−AlH_3, C_6H_6−AlF_3, and C_6H_6−$AlCl_3$ shown in Figure 1. The corresponding C_2H_4 complexes are shown in Figure 2. Vibrational frequencies were then evaluated at the MP2/6-31+G* level on each of the above conformers to identify the real minimal energy structures. Each of these conformations was then subject to further geometry optimizations at the MP2 level using the 6-311++G** basis set. Single-point calculations were then carried out on all the MP2/6-311++G** optimized geometries using a very large basis set, MP2/6-311++G(2df,p) + diffuse(d,p) (abbreviated as MP2/6-311++G(3df,2p)). The exponents of the diffuse d basis functions for Al, C, F, and Cl

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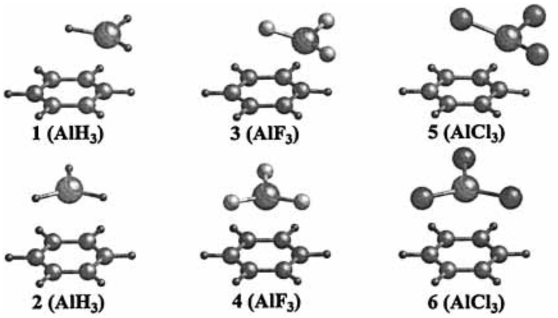

Figure 1. MP2/6-311++G** optimized structures of C_6H_6−AlH_3 (**1**, **2**), C_6H_6−AlF_3 (**3**, **4**), and C_6H_6−$AlCl_3$ (**5**, **6**).

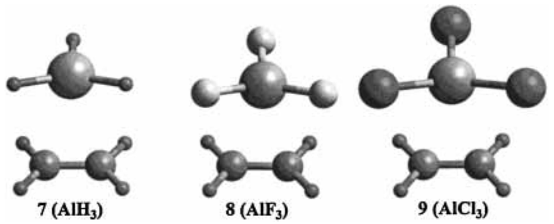

Figure 2. MP2/6-311++G** optimized structures of C_2H_4−AlH_3 (**7**), C_2H_4−AlF_3 (**8**), and C_2H_4−$AlCl_3$ (**9**).

are 0.0406, 0.0783, 0.2188, and 0.0938 respectively, and that of the diffuse p function for H is 0.188.

The zero-point vibrational energy (ZPVE) corrections were carried out using the zero-point vibrational energies evaluated at the MP2/6-31+G* level. Basis set superposition error (BSSE) corrections were carried out using the counterpoise method.[30] Since in case of benzene-containing complexes a 100% BSSE correction often underestimates the binding energies as compared to the experimentally evaluated quantities, we have often found it useful to employ a 50% BSSE correction.[31] In the case of the AlF_3 and $AlCl_3$ complexes, we believe that BSSE corrections would not be very useful because of (i) the very short Al−C_6H_6 or Al−C_2H_4 distances and (ii) the amount of charge transfer due to the near chemical bond-like situation. Such an argument of ours is in consonance with that of Schwenke and Truhlar,[32a] and Eggenberger et al.[32b] All calculations were carried out using a Gaussian-94 suite.[33]

NBO analysis was carried out for all the uncomplexed monomers AlH_3, AlF_3, and $AlCl_3$ and for all the benzene and ethene conformers to highlight the shifts in electron density upon complexation and also to evaluate the stabilization energies resulting due to such shifts in the electron density.[28] NBO's are the localized set of easily recognizable Lewis-like (σ and π bond, lone pair, and core) and non-Lewis (σ^* and π^* antibond and Rydberg) orbitals which are optimal in the sense of orthonormality and maximum occupancy of the Lewis set. It is important to point out one of the stellar features of the NBO method. Unlike most other charge-partitioning schemes, the NBO method is unaffected by the presence of diffuse functions in the basis set.[28]

Though several schemes are available to evaluate charge transfer in donor−acceptor complexes and the resulting energetic contributions, viz. Morokuma analysis,[34] constrained space orbital variation (CSOV) technique developed by Bagus et al.,[35] and the natural energy decomposition analysis (NEDA) scheme of Glendening and Streitwieser which is based on the NBO procedure,[36] we have found the CDA scheme of Dapprich and Frenking to be an extremely versatile, simple, and innovative approach to analyze charge transfer in terms of the easy to recognize molecular orbitals.[27] In the course of the discussion of our results, we show that both the NBO and CDA schemes give similar results (C_6H_6−AlF_3 being an exception) as regards the extent of charge transfer.

The CDA scheme, which closely espouses the Dewar−Chatt−Duncanson (DCD)[37] model of orbital mixing in donor−acceptor complexes, evaluates three terms: (i) the charge donation q_d given by the mixing of the occupied orbitals of the donor and the unoccupied orbitals of the acceptor; (ii) the back-donation q_b given by the mixing of the occupied orbitals of the acceptor and the unoccupied orbitals of the donor; (iii) the charge depletion from the overlapping area (charge polarization) q_r given by the mixing of the occupied orbitals of donor and acceptor. These terms are evaluated for each LCFO (linear combination of donor and acceptor fragment orbitals). Thus the CDA scheme is very useful for highlighting the most important orbitals which are responsible for the donor−acceptor interactions. In the case of the C_6H_6−AlX_3 complexes, we have benzene as the donor and AlX_3 as the acceptor. The CDA 2.1 program[38] was used in conjunction with the standard output of the MP2/6-31G* calculation to analyze the charge transfer in the C_6H_6−AlX_3 complexes within the CDA scheme.[39]

The Laplacian of the electron density distribution ($\nabla^2\rho(r)$ was evaluated using the AIMPAC program of Bader.[40] The Laplacian of the electronic charge density ($\nabla^2\rho(r)$) determines the reactivity of a molecular system because it determines where electronic charge is locally concentrated (where $\nabla^2\rho(r) < 0$) or locally depleted (where $\nabla^2\rho(r) > 0$).

All the AIM calculations were done on the MP2/6-31+G* optimized geometries with the AIMPAC series of programs using the MP2/6-31+G* wave functions as input. Contour plots were obtained using the MORPHY program of Popelier.[41]

Results and Discussion

In our earlier theoretical study on C_6H_6−BX_3 systems, we had carried out an elaborate conformational search at the MP2/6-31+G* level and obtained two low energy conformers possessing either a C_s or C_{3v} symmetry.[10] While the C_s symmetry conformer was the lowest energy structure (all positive vibrational frequencies), the C_{3v} conformer was a second-order saddle point structure (two imaginary frequencies). However, both these conformers exhibit a π type of interaction with benzene. In order to facilitate comparison with our earlier theoretical study on C_6H_6−BX_3 complexes,[10] we carried out calculations on both the C_s and C_{3v} conformers of the C_6H_6−AlX_3 complexes. Interestingly all the C_s conformers of the C_6H_6−AlX_3 complexes turn out to be the lowest energy structures (all positive vibrational frequencies). Since the C_{3v} conformers are all higher in energy (second-order saddle point structures) when compared to the corresponding C_s conformers, all subsequent discussions of the C_6H_6−AlX_3 complexes are limited to the features of the C_s conformers.

In case of the C_2H_4−AlX_3 complexes, the choice of the conformations on which the calculations were carried out, was governed by our earlier study on C_2H_4−BX_3 complexes.[10] The vibrational frequencies (all positive) confirm that the staggered C_s conformers wherein one of the Al−X bond is orthogonal to the C−C double bond are minimal energy structures of these complexes.

Geometries. In the absence of an experimental investigation of either the ethene−AlX_3 or the benzene−AlX_3 complexes, we compare the MP2/6-311++G** optimized geometries of the monomers to the experimentally determined bond lengths and then we discuss the changes in the monomer geometries in their complexed states. The experimentally determined C−C

TABLE 1: Binding Energies and Selected Distances of Benzene−AlX_3 Complexes[a]

	MP2/6-31+G*						MP2/6-311++G**						MP2/6-311++G(3df,2p)[b]					
	1 (C_s)	**2** (C_{3v})	**3** (C_s)	**4** (C_{3v})	**5** (C_s)	**6** (C_{3v})	**1** (C_s)	**2** (C_{3v})	**3** (C_s)	**4** (C_{3v})	**5** (C_s)	**6** (C_{3v})	**1** (C_s)	**2** (C_{3v})	**3** (C_s)	**4** (C_{3v})	**5** (C_s)	**6** (C_{3v})
$-\Delta E_e^N$	9.25	5.43	18.27	10.52	17.22	10.63	10.05	6.24	17.53	10.67	19.00	12.44	11.64	6.95	19.66	12.59	20.46	12.42
$-\Delta E_e^B$	5.87	2.00	11.91	5.41	7.90	3.35	6.92	3.65	11.36	4.93	8.48	3.68	9.06	5.15	14.24	8.07	13.16	6.90
$-\Delta E_e$	7.56	4.21	15.09	7.96	12.56	6.99	8.49	4.95	14.45	7.80	13.74	8.06	10.35	6.05	16.95	10.33	16.81	9.66
$-\Delta E_o$	5.20		13.10		10.82		6.13		12.46		12.00		7.99		14.96		15.07	
$-\Delta E_{cor}$	7.24	4.40	8.35	7.22	13.11	10.94	8.69	5.97	6.23	6.48	14.96	13.01	10.05	6.55	9.26	8.49	17.54	13.44
$-\Delta E_{es}$	7.81	6.74	31.19	25.07	20.64	14.02	6.73	6.45	24.93	20.68	16.23	12.23	6.87	6.65	25.83	21.42	17.04	12.96
$-\Delta H_{298}$	5.64		13.09		10.67		6.57		12.45		11.85		8.43		14.95		14.92	
$R_{Al-\Phi}$	2.562	3.285	2.314	2.808	2.347	3.227	2.571	3.172	2.324	2.782	2.352	3.139	(2.571)	(3.172)	(2.324)	(2.782)	(2.352)	(3.139)
R_{Al-X}	1.592	1.590	1.677	1.669	2.095	2.078	1.580	1.578	1.673	1.666	2.091	2.075	(1.580)	(1.578)	(1.673)	(1.666)	(2.091)	(2.075)
	1.597		1.682		2.105		1.584		1.677		2.100		(1.584)		(1.677)		(2.100)	

[a] All energies are in kcal/mol; distances are in Å. $-\Delta E_e^N$ and $-\Delta E_e^B$ represent the binding energies without and with basis set superposition error (BSSE) correction, respectively. ΔE_e is chosen to represent the mid value of ΔE_e^N and ΔE_e^B as upper and lower bounds, respectively. ΔE_0 is the ZPVE-corrected ΔE_e. ΔH_{298} is the enthalpy at 298.15 K and 1.0 atm. The frequencies for ZPE and thermal corrections were evaluated at the MP2/6-31+G* level. The electron correlation energy ΔE_{cor} is the value of the E_e (MP2) subtracted from E_e (HF) at the MP2-optimized geometry. ΔE_{es} is the electrostatic (charge−charge) interaction energy evaluated using NBO charges. $R_{Al-\Phi}$ and R_{Al-X} are the distances from aluminum to the benzene plane and the X (X = H, F, Cl), respectively. In the cases of **1**, **3**, and **5**, one X lies on the benzene plane while the other two equivalent X's are outside. [b] MP2/6-311++G(3df,2p)//MP2/6-311++G**.

and C−H bond lengths of 1.390 and 1.086 Å compare well with the calculated bond lengths of 1.399 and 1.086 Å for benzene.[42] On a similar note, the calculated Al−Cl bond length of 2.065 Å is well within the experimentally obtained distance of 2.06 ± 0.01 Å.[23a] However, the calculated Al−F bond length of 1.655 Å is slightly higher than the experimentally determined bond length of 1.631 Å.[22b] In the case of ethene, the theoretically predicted C−C and C−H bond lengths of 1.338 and 1.085 Å are in good agreement with the experimentally determined bond lengths of 1.339 and 1.085 Å.[43]

Upon complexation, there are significant changes in the geometries of the various monomers. Thus the Al−H bond length of 1.575 Å in the monomeric state increases to 1.578 Å in conformer and 1.580/1.584 Å in the conformer of the benzene−AlH_3 complex. A similar increase in the Al−F and Al−Cl bond lengths upon complexation is observed in conformers **3**−**6** of the benzene complexes. It can be seen that this increase is more in case of conformers **1**, **3**, and **5** than in conformers **2**, **4** and **6**. Interestingly in conformers **1**, **3**, and **5**, the Al−X bond lying over the benzene π cloud is shorter than the other two Al−X bonds. The increase in the monomer bond lengths of the benzene complexes is dwarfed by the large increases observed in case of the ethene complexes. Thus, this increase is more pronounced in case of the ethene−AlH_3 complex (**7**), with the Al−H bond length being 1.594/1.596 Å.

The benzene bond lengths show interesting variations in the various conformations. While there is no change in the C−C and C−H bond lengths in conformations **2** and **6**, there is a small increase in the C−C bond length and a small decrease in the C−H bond length in conformer **4**. Though the magnitude of this variation is extremely small, the binding energies (which would be discussed later) of conformer **3** reveal an interesting trend. In the case of conformers **1**, **3**, and **5**, there is substantial lengthening (1.405, 1.409, 1.410 Å in **1**, **3**, and **5**, respectively) of the C−C bond of benzene closest to the Al atom, as compared to the other C−C bonds (1.396−1.399 Å in case of all the three conformers). Similarly, there is a concomitant increase in the length of the C−H bond closest to Al atom. However, the magnitude of this increase, which is maximum in conformer **3**, is only 0.003 Å. The ethene C−C bond lengths show a gradual increase as one progresses from the ethene−AlH_3 (**7**) to ethene−$AlCl_3$ (**9**) complexes.

One of the notable geometrical features of the benzene−AlX_3 interaction is the location of the AlX_3 moiety. It can be seen that in conformers **1**, **3**, and **5**, the Al atom is directly placed over one of the carbon atoms and is extremely close to the benzene π plane (2.571, 2.324, and 2.352 Å for **1**, **3**, and **5**, respectively). Therefore, one can expect a near chemical-bond situation. However, we subsequently show that such a situation, without endangering the aromaticity of the benzene, has a profound influence on the charge distributions of the carbons of benzene. The close approach of AlX_3 and C_6H_6 in conformers **1**, **3**, and **5**, together with the concomitant charge transfer (to be discussed in detail later on), results in the pyramidalization of AlX_3 ($\angle$X−Al...C = 98°−106°). A similar situation is observed in the ethene−AlX_3 interaction with the Al−C═C distances ranging from 2.373 Å in conformer (C_2H_4−AlF_3) to 2.482 Å in conformer **7** (C_2H_4−AlH_3). A comparison of the location of the Al atom in the lowest energy conformers of both the ethene and benzene complexes indicates that Al is more closer to the benzene π ring than to the ethene double bond. These short Al−C distances in the C_6H_6−AlX_3 and C_2H_4−AlX_3 complexes should be visualized in the context of the extremely short Al−N distances which exist in $AlCl_3$−NH_3 and AlH_3−NH_3 adducts.[12] In $AlCl_3$−NH_3, the experimental Al−N distance of 1.996 ± 0.019 Å is close to the theoretically predicted distance of 2.027 Å, obtained at the MP2 level using the double-ζ polarization (DZP) basis set.[12c]

Conformer **4** exhibits a curious trend with regard to the intermolecular AlX_3 to distance. This is in sharp contrast to our expectation of a gradual increase in this distance as one proceeds from (**2**) to (**4**). Such a contrast was also observed in the interaction of BF_3 with C_6H_6 the BF_3−C_6H_6 intermolecular distance (3.250 Å) being shorter than those in BH_3−C_6H_6 (3.250 Å) and BCl_3−C_6H_6 (3.470 Å).[10] We believe that this contrast could be due to an increased orbital overlap between the **2**a″ orbital of AlF_3 (which is entirely composed of the fluorine p(π) orbitals) and the **2**b_{1u} orbital of benzene. Such an optimum overlap is not feasible in case of AlH_3 (H does not have p orbitals) and $AlCl_3$ (Cl has 3p orbitals which are lower in energy as compared to the fluorine 2p orbitals).

Binding Energies. The binding energies of both the C_6H_6 and C_2H_4 complexes of AlX_3, shown in Tables 1 and 2, display interesting binding characteristics. In the case of the C_6H_6 complexes, the C_s conformers are invariably more stable than the corresponding C_{3v} conformers by about 3 kcal/mol (AlH_3) and about 6−7 kcal/mol (AlF_3 and $AlCl_3$). The BSSE and ZPVE corrected MP2/6-311++G(3df,2p) binding energies of the

TABLE 2: Binding Energies and Selected Distances of Ethene−AlX_3 Complexes[a]

	MP2/6-31+G*			MP2/6-311++G**			MP2/6-311++G(3df,2p)[b]		
	7	**8**	**9**	**7**	**8**	**9**	**7**	**8**	**9**
	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)	(C_s)
$-\Delta E_e^N$	10.42	17.86	14.63	10.38	16.51	14.97	12.50	18.67	17.35
$-\Delta E_e^B$	7.63	13.51	8.40	7.98	12.56	8.19	10.74	15.25	12.79
$-\Delta E_e$	9.02	15.68	11.51	9.18	14.53	11.58	11.62	16.96	15.07
$-\Delta E_0$	6.47	13.90	9.69	6.63	12.75	9.76	9.07	15.18	13.25
$-\Delta E_{cor}$	5.07	4.39	6.50	5.73	2.44	7.14	7.08	4.96	9.87
$-\Delta E_{es}$	7.10	20.28	12.83	5.66	14.52	8.82	5.82	15.20	9.33
$-\Delta H_{298}$	7.15	14.00	9.80	7.31	12.85	9.87	9.75	15.28	13.36
$R_{Al-C=C}$	2.485	2.364	2.440	2.482	2.373	2.432	(2.482)	(2.373)	(2.432)
R_{Al-X}^c	1.594	1.678	2.099	1.581	1.674	2.093	(1.581)	(1.674)	(2.093)
	1.596	1.678	2.097	1.583	1.673	2.092	(1.583)	(1.673)	(2.092)

[a] All energies are in kcal/mol; distances are in Å. $-\Delta E_e^N$ and $-\Delta E_e^B$ represent the binding energies without and with BSSE correction, respectively. ΔE_e is chosen to represent the mid value of ΔE_e^N and ΔE_e^B as upper and lower bounds, respectively. ΔE_0 is the ZPE-corrected ΔE_e. ΔH_{298} is the enthalpy at 298.15 K and 1.0 atm. The frequencies for ZPE and thermal corrections were evaluated at the MP2/6-31+G* level. The electron correlation energy ΔE_{cor} is the value of the E_e (MP2) subtracted by E_e (HF) at the MP2 optimized geometry. ΔE_{es} is the electrostatic (charge−charge) interaction energy evaluated using NBO charges. $R_{Al-C=C}$ and R_{Al-X} are the distances from aluminum to the midpoint of the C═C bond of ethene and the X (X = H, F, Cl), respectively. [b] MP2/6-311++G(3df,2p)//MP2/6-311++G**. [c] First distance occurs twice, second occurs once.

C_6H_6−AlX_3 complexes indicate that conformer **5** (C_6H_6−$AlCl_3$) exhibits the largest binding energy ($\Delta E_0 = 15.07$ kcal/mol) as compared to either conformer **1** (C_6H_6−AlH_3) or, (C_6H_6−AlF_3). However, it can be seen that the relative binding energies of conformers **3** and **5** are very much dependent on the kind of basis set employed. The binding energy exhibited by conformer (14.96 kcal/mol) contrasts sharply with our earlier study on C_6H_6−BX_3,[10] wherein it was observed that the C_6H_6−BF_3 complex is the most weakly bound as compared to either C_6H_6−BH_3 or C_6H_6−BCl_3.[13] The BSSE and ZPVE corrected binding energies of C_6H_6−BH_3, C_6H_6−BF_3, and C_6H_6−BCl_3 at the MP2/6-311++G(3df,2p) level were 4.76, 3.29, and 5.89 kcal/mol, respectively.[10] The binding energies of the C_2H_4−AlX_3 complexes indicate that the C_2H_4−AlF_3 conformer has the highest binding energy (15.18 kcal/mol) as compared to either C_2H_4−AlH_3 or C_2H_4−$AlCl_3$.

A major difference in the binding of benzene or ethene with BX_3 and AlX_3 is that in the AlX_3 complexes, electrostatic interactions have a dominant contribution to the binding energy, while in the BX_3 complexes, the correlation energy (ΔE_{cor}) is dominant. Thus the C_6H_6−AlX_3 complexes conform to the general behavior of donor−acceptor complexes (i.e., electrostatic interactions dominate the binding energy) with some notable exceptions.

Earlier theoretical studies on the binding of to NH_3 have obtained a CCSD/DZP ZPVE corrected binding energy of 26.5 kcal/mol.[12b] However, the study of the interaction of with NH_3 has not been reported at the same level of theory. Nevertheless, comparisons made at lower levels of theory seem to indicate that the B−N bond in BH_3−NH_3 is stronger than the Al−N bond in AlH_3−NH_3 by 10 kcal/mol.[12,13] On the other hand, comparisons using the local spin density (LSD) and nonlocal spin density (NLSD) approximations in the density functional methods indicate that the B−N bond is 5.1 kcal/mol stronger than the Al−N bond.[13a] The higher strength of the B−N bond has been attributed to the increased Lewis acid strength of B as compared to Al,[44] which governs the formation of a dative bond between the empty p orbital of B or Al and the lone pair of nitrogen. In light of the above, it is interesting to compare the binding energies of AlH_3 and BH_3 with C_6H_6 or C_2H_4. The MP2/6-311++G(3df,2p) binding energy (corrected for BSSE and ZPVE) of C_6H_6−BH_3 is 4.76 kcal/mol. On the other hand, a similarly corrected MP2/6-311++G(3df,2p) binding energy of C_6H_6−AlH_3 is 7.99 kcal/mol which is not smaller but much greater than that of C_6H_6−BH_3. This implies that purely on the basis of Lewis acidity and basicity, one cannot explain the binding energies of C_6H_6 or C_2H_4 with BH_3 and AlH_3.

Vibrational Frequencies. The relative trends and shifts in vibrational frequencies are important in understanding the structure and energetics of van der Waals complexes.[10,45] It is interesting to examine whether these vibrational frequencies are useful aids in understanding the intricacies of these donor−acceptor complexes. Though experimental vibrational frequencies are not available for the benzene−AlX_3 and ethene−AlX_3 complexes, the vibrational frequency shifts of all the C_s conformers of the C_6H_6−AlX_3 and C_2H_4−AlX_3 complexes with respect to the frequencies in their monomeric states are shown in Tables 3 and 4.

The six vibrational frequencies in AlX_3 evolve from three stretching and three bending modes. It can be seen from Table 3 that the red shifts of the stretching modes are more pronounced in the case of the AlF_3 complexes. However, in the case of the symmetric stretching mode (ν_3), there is a continuous decrease in the red shift as one progresses from AlH_3 to $AlCl_3$. A similar trend is observed for the antisymmetric stretching mode (ν_1) in the case of the BX_3 complexes.[10]

It can be seen from Table 4 that all the modes of benzene exhibit significant blue shifts when compared to the monomeric benzene. However, it can be seen that one of the C−H stretching modes (ν_5) exhibits marked red shifts in cases of C_6H_6−AlF_3 and C_6H_6−$AlCl_3$. This red shift can be readily understood when one takes into account the increase in the C−H bond length closest to the AlX_3 moiety. We believe that this red shift could be used as an important experimental aid to examine the effects of complexation with AlX_3 compounds on benzene. It is of interest to note that a similar red shift is observed in the C−H frequencies of the C_2H_4−AlF_3 and C_2H_4−$AlCl_3$ complexes given in Table 4. The out-of-plane bending modes, on the other hand, reveal important similarities with the corresponding BX_3 complexes. Thus the complexes exhibit more pronounced blue shifts than either the AlH_3 or $AlCl_3$ complexes, which is similar to what is observed in the case of the BX_3 complexes. However, while C_6H_6−BF_3 is the most weakly bound of the C_6H_6−BX_3 complexes, C_6H_6−AlF_3 is the most strongly bound among the C_6H_6−AlX_3 complexes. Thus, bending modes cannot be said to be reliable indicators of the binding energies. However our recent studies on C_6H_6−H_2O and C_2H_4−H_2O complexes seem

TABLE 3: Comparison of the Frequencies of the Stretching and Bending Modes of AlH_3, AlF_3, and $AlCl_3$ and Their Frequency Shifts in the Complexed States along with the van der Waals Modes at the MP2/6-31+G* Level[a]

mode	AlH_3	$C_2H_4-AlH_3$	$C_6H_6-AlH_3$	AlF_3	$C_2H_4-AlF_3$	$C_6H_6-AlF_3$	$AlCl_3$	$C_2H_4-AlCl_3$	$C_6H_6-AlCl_3$
stretching									
ν_1	2003[288]	−42[218]	−35[176]	949[207]	−50[186]	−62[93]	646[206]	−41[179]	−45[149]
ν_2	2003[288]	−47[128]	−54[128]	949[207]	−56[150]	−69[123]	646[206]	−46[154]	−62[148]
ν_3	1993[0]	−39[276]	−49[291]	681[0]	−18[44]	−22[65]	399[0]	−5[20]	−8[56]
bending									
ν_4	731[400]	20[593]	7[498]	301[156]	20[239]	2[287]	210[45]	23[87]	3[143]
ν_5	818[244]	−22[182]	−8[212]	244[40]	−8[17]	2[20]	154[10]	8[5]	4[6]
ν_6	818[244]	−24[182]	−34[162]	244[40]	−9[25]	−9[3]	154[10]	3[3]	1[5]
van der Waals[b]									
τ_z		101[0]	64[0]		34[0]	91[0]		60[1]	98[0]
b_{ip}		234[1]	95[0]		120[3]	88[1]		111[3]	86[0]
τ_{op}		328[6]	135[0]		133[1]	47[0]		118[2]	45[0]
s_z		196[9]	156[37]		226[6]	207[3]		188[10]	177[1]
ϕ_{ip}		446[1]	411[1]		223[5]	132[1]		229[3]	109[1]
ϕ_{op}		483[15]			417[1]	125[0]		400[20]	104[0]

[a] All frequencies are in cm^{-1}. IR intensities (km/mol) are enclosed in brackets adjacent to the frequency shifts. [b] The van der Waals mode definitions are given in ref 45.

TABLE 4: Calculated MP2/6-31+G* Vibrational Frequency Shifts of the Stretching and Bending Modes of Benzene and Ethene in Their Complexed States[a]

mode[b]	C_6H_6	$C_6H_6-AlH_3$ (**1**)	$C_6H_6-AlF_3$ (**3**)	$C_6H_6-AlCl_3$ (**5**)
stretching				
ν_1	3242.7	8.2	14.6	14.6
ν_{12}	3233.7	12.5	20.9	21.4
ν_{12}	3233.7	6.4	13.1	12.7
ν_{15}	3218.6	13.7	22.2	21.9
ν_{15}	3218.6	5.1	11.4	10.2
ν_5	3208.9	1.8	−10.1	−15.9
out-of-plane ring bending				
ν_{19}	882.4	56.4	95.1	89.4
ν_{19}	882.4	29.4	62.7	42.0
ν_7	862.5	42.5	81.3	61.1
ν_{11}	831.2	38.2	73.9	62.8
ν_{11}	831.2	16.1	25.5	18.9
ν_4	673.8	21.4	38.0	35.5

mode[b]	C_2H_4	$C_2H_4-AlH_3$ (**1**)	$C_2H_4-AlF_3$ (**3**)	$C_2H_4-AlCl_3$ (**5**)
stretching				
ν_5	3315.3	11.0	8.6	10.3
ν_9	3291.0	13.3	11.6	14.1
ν_1	3221.2	0.1	−5.2	−3.4
ν_{11}	3204.3	7.0	3.0	5.1
ν_2	1704.8	−24.9	−26.3	−28.1
out-of-plane ring bending				
ν_7	982.6	58.0	101.0	94.4

[a] All frequencies are in cm^{-1}. [b] The fundamental modes are numbered according to Herzberg (ref 52).

to indicate that these bending modes are more reliable indicators of the exchange repulsion energies.[46]

Theoretically evaluated frequencies of the van der Waal modes cannot be directly compared with the experimentally determined frequencies. But the relative trends are more reliable and informative. Therefore, the theoretically evaluated frequencies of the van der Waals modes of these complexes are shown in Table 3. One of the interesting van der Waals modes, which reflects the ease with which the van der Waals complex dissociates, is the stretching mode s_z. It can be seen that it in a way reflects the binding energies exhibited by the $C_6H_6-AlX_3$ complexes.

Charges and Electronic Structure. The Weinhold's natural population analysis (NPA)[27] charges work extremely well, even when diffuse functions are employed in the basis sets. The NPA charges of all the atoms of the monomers in their uncomplexed and complexed states are listed in Table 5.

The partial charge on Al is more positive in the case of AlF_3 as compared to both AlH_3 and $AlCl_3$. While the positive charge on Al in AlX_3 (monomeric and complexed states) follows the trend ($AlF_3 > AlCl_3 > AlH_3$), the positive charge on B in BX_3 follows the trend ($BF_3 > BH_3 > BCl_3$) in the monomeric state and ($BF_3 > BCl_3 > BH_3$) in the complexed state. More interestingly, though BF_3 and AlF_3 exhibit similar trends in terms of the positive charge on B and Al, electrostatic energies are dominant only in case of the $C_6H_6-AlF_3$ complex. The bonding of Al and X (F, Cl) in AlF_3 and $AlCl_3$ monomers merits special mention because it has a bearing on the charge profiles of their complexes with benzene or ethene. We illustrate this aspect by showing the NBO occupancies of the Al 3s and 3p orbitals in Table 6. It can be seen that in the monomeric states, the p_z orbital is partially filled. Second, it can be seen that the electron occupancies on the other orbitals are also quite low, which can be easily understood, given the high electronegativity of both F and Cl.

Though the charges on Al exhibit small changes upon complexation in conformers **2**, **4**, and **5**, the changes in the charges in conformers **1**, **3**, and **5** indicate that there is a charge

TABLE 5: MP2/6-311++G(3df,2p)-NBO Charges for All Complexes

	C_6H_6/C_2H_4	AlH_3	C_6H_6−AlH_3		C_2H_4−AlH_3	AlF_3	C_6H_6−AlF_3		C_2H_4-AlF_3	$AlCl_3$	C_6H_6−$AlCl_3$		C_2H_4−$AlCl_3$
			1	**2**	**7**		**3**	**4**	**8**		**5**	**6**	**9**
partial charges													
q_{Al}		1.25	1.11	1.24	1.04	2.27	2.17	2.25	2.16	1.46	1.36	1.48	1.34
q_X		−0.42	−0.39, −0.40	−0.42	−0.39, −0.38	−0.76	−0.75, −0.76	−0.76	−0.76, −0.75	−0.49	−0.49, −0.50	−0.50	−0.49, −0.50
q_C	−0.20/−0.36		−0.31[b] −0.18 to −0.19	−0.21	−0.37		−0.41[b] −0.16 to −0.18	−0.21	−0.39		−0.39[b] −0.16 to −0.17	−0.21	−0.37
q_H	0.20/0.18		0.23[c] 0.21−0.22	0.21	0.21		0.25[c] 0.21−0.23	0.22	0.22		0.26[c] 0.21−0.23	0.21	0.22
p{π} population at Al		0.01	0.08	0.02	0.13	0.12		0.13	0.16	0.23		0.23	0.29
charge transfer from C_6H_6/C_2H_4 to AlX_3			0.09	0.02	0.11		0.10	0.03	0.11		0.13	0.02	0.14

[a] First charge occurs once, second occurs twice. [b] Charge of carbon closest to the aluminum atom. The charges of the remaining carbon atoms are within the range given below it. [c] Charge of hydrogen closest to the aluminum atom. The charges of the remaining hydrogen atoms are around the range given below it.

transfer from benzene to AlX_3. Thus, the order of decrease in the positive charge on Al in these conformers is nearly the same (0.14 e in C_6H_6−AlF_3 and 0.10 e in C_6H_6−$AlCl_3$ and C_6H_6−AlF_3). It can easily be seen from Table 6 that the total charge gained by the Al valence orbitals in conformers **1**, **3**, and **5** is nearly equal to the decrease in the positive charge in Al. It can also be correlated to the charge transfer from benzene to both (0.10 e) and (0.13 e) in these conformers.

Given this charge transfer, it is of interest to gain a deeper understanding of the role of each benzene molecular orbital (MO). However, in the case of complex interactions, it is an extremely difficult task to identify the contributions of individual molecular orbitals. Even though orbital mixing itself is not the origin of binding interactions, the mixing of the fragment molecular orbitals in a way reflects the electronic interactions of the fragments. To obtain a qualitative interpretation of the results of these high-level ab initio calculations, we have used the CDA approach of Frenking and co-workers. The results of the CDA scheme which has been employed to highlight the contributions of each individual molecular orbital in the charge transfer observed in conformers **1**, **3**, and **5** of the C_6H_6−AlX_3 complexes are listed in Table 6. It can be seen that there is a general consonance of the results of the CDA and NBO analysis as regards the charge transfer. The absolute values, however, do not match because of the different partitioning schemes employed in these methods. In particular, the NBO analysis and CDA scheme seem to differ on the amount of charge transfer (q_d) observed in the case of C_6H_6−AlF_3. This is because CDA distinguishes between charge donation (q_d) and repulsive polarization (q_r), while the NBO analysis gives the cumulative charge donation. This point can be understood when one observes the value of the repulsive polarization (q_r) term in Table 6. It can be seen that it is lowest in case of C_6H_6−AlF_3. The utility of the CDA scheme, however, lies in distinguishing the individual orbital contributions. In all the cases, the major charge donation from benzene to AlX_3 emerges from a single orbital. This orbital is incidentally the HOMO-1 orbital of these complexes, whose contribution to the total charge donation (q_d) can be seen in Table 6. This orbital is obtained as a result of an interaction of the occupied benzene $1e_{1g}$ orbital and one of the unoccupied orbitals of AlX_3 (e″ in the case of $AlCl_3$). The $1e_{1g}$ orbital of benzene is incidentally one of the degenerate HOMO's of the benzene monomer.

It is interesting to examine the effects of complexation with AlX_3 on the charges of benzene. The fact that significant but profound changes occur in the charges of benzene is reflected in Table 5. The benzene carbon closest to the aluminum atom has more negative charge when compared to the remaining five carbon atoms in conformers **1**, **3**, and **5**. A simultaneous increase in the positive charge on the hydrogen atom attached to this carbon can also be seen.

Though a number of theoretical studies have delved into the electronic structure of donor−acceptor van der Waals complexes,[47] the exact nature of donor−acceptor bonds is still ambigious. In our earlier study on the C_6H_6−BX_3 complexes, we found that the interaction of aromatic-π system with the empty p_z orbital of boron significantly contributes to the interaction energy in the case of C_6H_6−BH_3 from an analysis of the energetic contributions of various terms using the second-order perturbation theory. A similar analysis carried out on the C_6H_6−AlX_3 complexes reveals that the energetic contribution of the π-p_z orbital interaction in C_6H_6−AlF_3 is far less than the other two complexes and moreover contrasts with the binding energy. Second, the charge transfer observed in C_6H_6−AlF_3

TABLE 6: MP2/6-311++G(3df,2p)-NBO Occupancies of the Al Valence Orbitals in the Monomeric and Complexed States along with the Results of the CDA Analysis

NBO orbital	AlH_3	$C_6H_6-AlH_3$ (**1**)	AlF_3	$C_6H_6-AlF_3$ (**3**)	$AlCl_3$	$C_6H_6-AlCl_3$ (**5**)
3s	0.83	0.82	0.25	0.27	0.53	0.54
$3p_x$	0.44	0.48	0.16	0.17	0.34	0.34
$3p_y$	0.44	0.48	0.16	0.17	0.34	0.36
$3p_z$	0.01	0.08	0.12	0.17	0.23	0.29
total	1.72	1.87	0.69	0.78	1.44	1.53
q_d (total)		0.14		0.06		0.26
q_b (total)		−0.01		0.02		−0.01
q_r (total)		−0.14		−0.13		−0.22
q_d (HOMO-1)		0.08		0.11		0.14

[a] The descriptions of the various charge components are listed in the text.

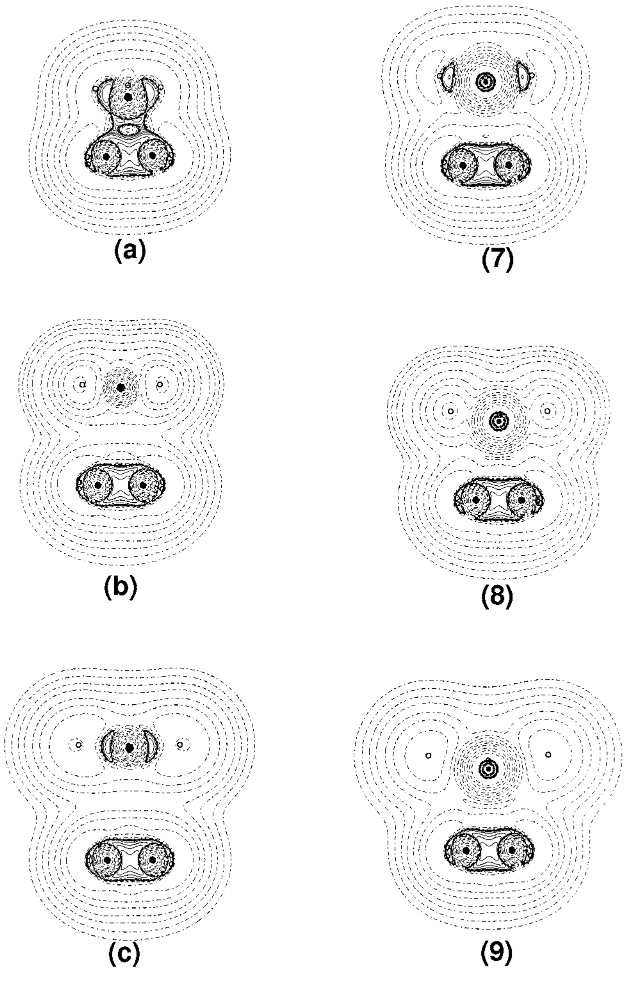

Figure 3. Contour plots of the Laplacian ($\nabla^2\rho(r)$) of the $C_2H_4-BX_3$ and $C_2H_4-AlX_3$ complexes. The solid lines indicate regions of charge concentration ($\nabla^2\rho(r) < 0$). (a) $C_2H_4-BH_3$, (b) $C_2H_4-BF_3$, (c) $C_2H_4-BCl_3$; (**7**) $C_2H_4-AlH_3$, (**8**) $C_2H_4-AlF_3$, (**9**) $C_2H_4-AlCl_3$.

(which is less than that observed in $C_6H_6-AlCl_3$) is not commensurate with its binding energy which is dominated by electrostatic interactions. Jonas et al. in their theoretical study on the interactions of with Me_3N made similar observations.[24b] What they found was that even in the absence of covalent contributions, Me_3N was very strongly bound to (binding energy of 49.3 kcal/mol). They concluded that $Me_3N-AlCl_3$ was mainly held by electrostatic interactions.

In order to visualize and analyze the major differences of the nature of bonding in the BX_3 and AlX_3 complexes, we calculated the Laplacian of the electron density distribution $\nabla^2\rho(r)$ of the $C_2H_4-BX_3$ and $C_2H_4-AlX_3$ complexes. Figure 3 shows the contours of the Laplacian in the plane containing the (Al or B atom) and the two carbon atoms of ethene. The deformation of the charge concentration at the ethene carbon atoms is most pronounced in case of the $C_2H_4-BH_3$ complex with the area of charge concentration ($\nabla^2\rho(r) < 0$, solid lines) being shifted toward the boron atom. A similar observation was made by Fau and Frenking recently.[48] However, in the $C_2H_4-BF_3$ and $C_2H_4-BCl_3$ complexes, the charge is more concentrated in the immediate vicinity of the ethene molecule. Such a situation also prevails in the AlX_3 complexes, with the charge being more localized over the ethene carbon atoms. These results seem to indicate that the strong binding energies observed in case of the $C_2H_4-AlX_3$ complexes are entirely dominated by electrostatic interactions with charge transfer having a minor role. This aspect is confirmed by the dominant contributions of the electrostatic energies (ΔF_{es}) to the binding energy. On the other hand, $C_2H_4-BF_3$ and $C_2H_4-BCl_3$ emerge as weak van der Waals complexes in contrast to the covalent nature of the $C_2H_4-BH_3$ complex.

Implications. Given these results on the geometries, energies, and charges of the complexes of benzene with Lewis acids like AlH_3, AlF_3, and $AlCl_3$, it would be of interest to understand the chemical implications of this theoretical study. It can be seen from the charges given in Table 5 that there is a significant increase in the negative charge of one of the benzene carbons as compared to the other carbons. We believe that this increase in the negative charge (or nucleophilicity) would ease an electrophilic attack on this particular benzene carbon as a result of a significant lowering in the activation energy. Furthermore, the increase in the positive charge on the hydrogen attached to this carbon would facilitate its departure after an attack by an electrophile. In an earlier paper of ours,[49] we had evaluated the binding energies of a Lewis acid ($AlCl_3$) with a proelectrophile like CH_3Cl and C_6H_6 to be about 3.33 and 19.00 kcal/mol, respectively. Moreover the Al−C distance in $CH_3Cl-AlCl_3$ and $C_6H_6-AlCl_3$ are 3.300 and 2.352 Å. Thus, in the absence of any external source of energy, the Lewis acid−aromatic ring interactions are very strong. Additionally, the free energy of association of benzene in the liquid state is only about 5 kcal/mol.[50] This implies that these interactions have a significant role of activation of the aromatic ring in electrophilic aromatic substitution reactions (in particular Friedel−Craft's reaction)[51] and can also be expected to prevail in the condensed phase.

It is of interest to note that these charge effects are not limited to these Lewis acids. Thus, in an experimental and theoretical study of Sriniwas et al. on the interaction of Si^+ with C_6H_6, the Si^+ cation is directly placed over one of the benzene carbons.[3a] They also report a large increase in the negative charge of the benzene carbon, which lies directly under the Si^+ cation.

Conclusions

Using high-level ab initio calculations, the binding energies, geometries, vibrational frequencies, charges of C_6H_6−AlX_3 (X = H, F, Cl) complexes have been evaluated at the MP2 level using fairly large basis sets. The ZPVE and BSSE corrected binding energies of benzene−AlX_3 (X = H, F, Cl) complexes (8−15 kcal/mol) are significantly higher than the corresponding binding energies of benzene−BX_3 complexes (3−6 kcal/mol). This tight binding is also reflected in the very short AlX_3 to benzene distances exhibited by the lowest energy conformers of these complexes. Though these binding energies are significantly lower than those involving the binding of a metal cation or an organic cation with benzene, we believe that they are the highest for a neutral compound (uncharged species) binding to benzene. Therefore, while the benzene−BX_3 complexes are predominantly bound by weak van der Waals forces, the benzene−AlX_3 complexes can be said to be bound by weak chemical bonds. The domination of the binding energies of these complexes by electrostatic forces, which is in sharp contrast to that observed in benzene−BX_3 complexes, gives credence to our point.

Though very small changes are observed in the geometries of the monomers in the lowest energy conformers of these complexes, it is interesting to note that the AlX_3 moiety lies directly over one of the benzene carbons. This is similar to that observed in the case of benzene−BX_3 complexes. These low-energy conformers of the benzene−BX_3 complexes are characterized by a significant charge transfer which is reflected in the HOMO-1 orbitals of these complexes. This HOMO-1 orbital of these complexes is formed from the combination of one of the benzene HOMO's and an unoccupied orbital of AlX_3.

The most interesting facet of the interaction of AlX_3 compounds with benzene is the charge reorganization induced on the benzene atoms as a result of complexation. The significant increase in the negative charge on the carbon atom closest to AlX_3 and a concomitant increase in the positive charge of the hydrogen atom attached to this carbon have significant implications on the role of AlX_3 compounds as catalysts in electrophilic aromatic substitution reactions. While an increase in the negative charge on the carbon facilitates an attack by an incipient electrophile, an increase in the positive charge on the hydrogen facilitates its exit after the electrophile is bound. Thus, it would be interesting to experimentally examine this unusual but vital role of Lewis acids (AlX_3 compounds in this case) in electrophilic aromatic substitution reactions.

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