Theoretical Investigation of In-Plane Hydrogen-Bonded Complexes of Ammonia with Partially Substituted Fluorobenzenes

Prashant Chandra Singh, Mohana Ray, and G. Naresh Patwari*

Department of Chemistry, Indian Institute of Technology Bombay, Powai, Mumbai 400 076, India

Received: December 29, 2006; In Final Form: February 8, 2007

Systematic investigation of in-plane hydrogen-bonded complexes of ammonia with partially substituted fluorobenzenes has revealed that fluorobenzene, difluorobenzene, and trifluorobenzene favor formation of cyclic complexes with a C−H···N−H···F−C binding motif. On the other hand, tetrafluorobenzene and pentafluorobenzene favor formation of linear C−H···N hydrogen-bonded complexes. The complete absence of exclusively linear N−H···F hydrogen-bonded complexes for the entire series indicates that C−F bond in fluorobenzenes is a reluctant hydrogen-bond acceptor. However, fluorine does hydrogen bond when cooperatively stabilized with C−H···N hydrogen bonds for the lower fluoro analogues. The propensity of fluorobenzenes to adapt to the C−H···N−H···F−C binding motif decreases with the progressive fluorination of the benzene ring and disappears completely when benzene ring is substituted with five or more fluorine atoms.

Introduction

The structure directing ability of weak intermolecular interactions, such as C−H···O and C−H···N hydrogen bonds, have been effectively used in organized self-assemblies and crystal engineering.[1−3] Similarly, in the case of partially fluorinated benzenes, it has been established that the C−H···F interactions influence the crystal structure.[4,5] However, the efficacy of organic fluorine to hydrogen bond has been a subject of debate and several authors based on structural database analysis have concluded that C−F group is an extremely poor hydrogen-bond acceptor.[6−11] Dunitz and Taylor have commented that, out of 5947 C−F bonds reported in the Cambridge Structural Database, only 37 were possibly involved in C−F···H hydrogen bonding and only in two cases the formation of hydrogen bond could be unambiguously established.[6]

Apart from crystal structures, the hydrogen-bonded complexes of water, methanol, and ammonia with partially fluorinated benzenes, viz., fluorobenzene,[12−14] 1,4-difluorobenzene,[12−14] and 1,2,4,5-tetrafluorobenzene,[15−17] have been investigated experimentally in the gas phase, along with computational studies. In the case of fluorobenzene−water system, two minima were identified theoretically: one with O−H···π hydrogen bond and the second an in-plane structure with water molecule acting both as a proton acceptor and a donor, resulting in a cyclic structure with O−H···F and C−H···O hydrogen-bonded contacts. Theoretically, both the π−bound and the in-plane structures were found to be equally stable. However, experimentally only the in-plane structure was observed, indicating that it is the lowest-energy configuration.[12] In the case of the 1,4-difluorobenzene−water complex only the in-plane structure, similar to fluorobenzene−water dimer, was found to be stable both theoretically and experimentally.[12] In the case of the 1,2,4,5-tetrafluorobenzene−water system, three isomers were observed at the MP2/6-31+G(*d*) level; however, once again only the in-plane cyclic structure was observed experimentally, in the gas phase.[15] Hydrogen-bonded complexes of methanol with fluorobenzene,[13] 1,4-difluorobenzene,[13] and 1,2,4,5-tetrafluorobenzene[16] have structures analogous to corresponding complexes with water, wherein the O−H group of methanol acts both as a donor and an acceptor resulting in the formation cyclic structure with C−H···O and O−H···F hydrogen bonds.

The hydrogen-bonded complexes of partially fluorinated benzenes with water and methanol have a common C−H···O−H···F−C structural motif leading to formation of cyclic complexes. Interestingly, the absence of exclusively linear in-plane O−H···F and/or C−H···O linear in-plane hydrogen-bonded complexes suggests that in the case of partially fluorinated benzenes the two sets of hydrogen bonds cooperatively stabilize the in-plane complexes.[18] On the other hand, hexafluorobenzene interacts with water via a O···π interaction, a reversal of the orientation relative to the water−benzene complex.[19,20] One of the notably interesting results in the case of hexafluorobenzene−water complex is the complete absence of in-plane O−H···F hydrogen boded species,[19−21] which is completely in contrast with the water complexes of partially fluorinated benzenes.[12−17]

At this stage, an interesting idea would be explore the formation of exclusively linear in-plane hydrogen-bonded complexes of partially fluorinated benzenes. To probe this point, we investigated complexes of ammonia with series of partially fluorinated benzenes, viz., fluorobenzene (FBz) 1,4-difluorobenzene (DiFBz), 1,3,5-trifluorobenzene (TriFBz), 1,2,4,5-tetrafluorobenzene (TetraFBz), and pentafluorobenzene (PentaFBz). The choice of ammonia for such an investigation can be rationalized on the basis of the fact that ammonia is a better hydrogen bond acceptor and a poor donor in comparison with water and methanol. This, we expect, will probably lead to formation of exclusively linear in-plane C−H···N hydrogen-bonded complexes.

Methodology

The initial conformational search was performed at B3LYP/6-31G(d) level. The DiFBz−ammonia system resulted only in-

---

* To whom correspondence should be addressed. E-mail: naresh@chem.iitb.ac.in.

10.1021/jp0690087 CCC: $37.00

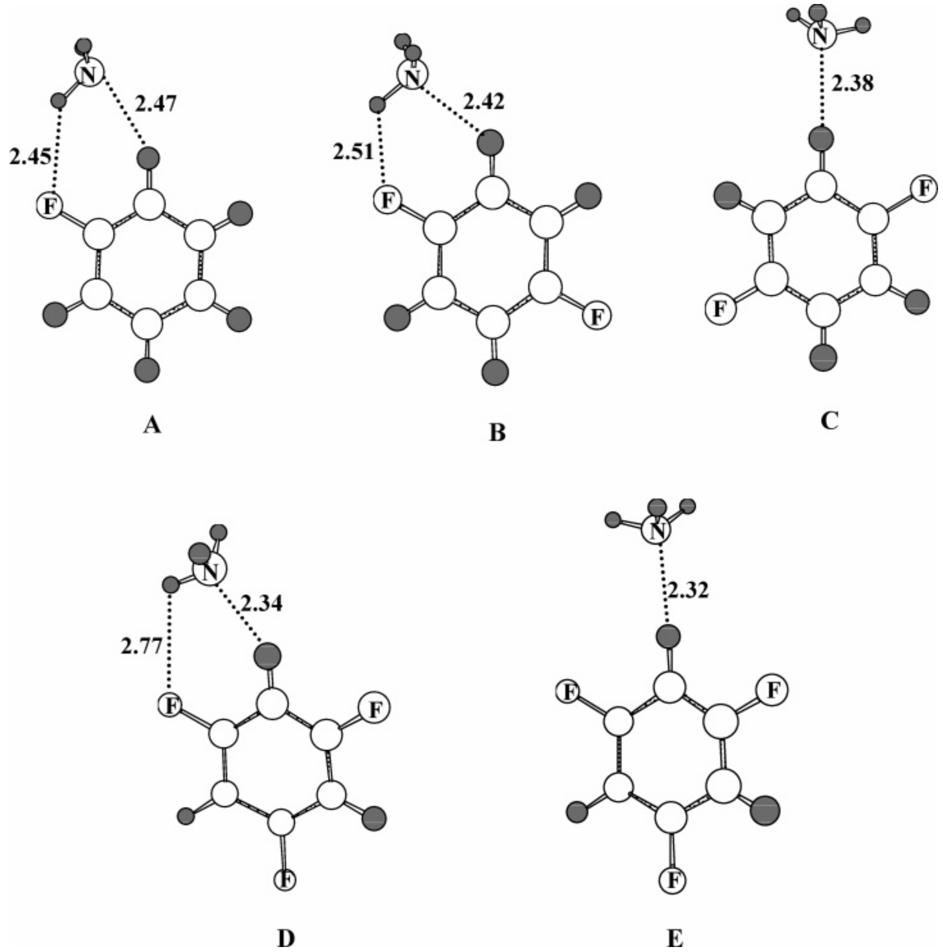

Figure 1. Structures of FBz−ammonia (A), DiFBz−ammonia (B, C), and TriFBz−ammonia (D, E) complexes optimized at the MP2/6-311++G(d,p) level of theory. The distances are given in angstroms.

plane complexes; however, for FBz, TriFBz, Tetra, and PentaFBz, both in-plane and π-bound structures were obtained. Since the primary objective of this report is to investigate in-plane hydrogen-bonded complexes, further calculations were carried out only on the in-plane structures. All the calculations reported here were carried out using 6-311++G(d,p) and aug-cc-pVDZ basis sets at DFT-B3LYP and MP2 levels of theory. The structures of the monomers and the complexes were optimized without any constraints and the nature of the stationary point obtained was confirmed by calculating the vibrational frequencies at the same level of theory. The interaction energy for the binary clusters was calculated using the following scheme[22,23]

$$\Delta E = \Delta E_{\mathrm{E}} + \Delta E_{\mathrm{BSSE}} + Z_{\mathrm{C}} \tag{1}$$

$$\Delta E_{\mathrm{E}} = E_{\mathrm{AB}}(\{\mathrm{AB}\}, G_{\mathrm{AB}}) - E_{\mathrm{A}}(\{\mathrm{A}\}, G_{\mathrm{A}}) - E_{\mathrm{B}}(\{\mathrm{B}\}, G_{\mathrm{B}}) \tag{2}$$

$$\Delta E_{\mathrm{BSSE}} = E_{\mathrm{A}}(\{\mathrm{A}\}, G_{\mathrm{A}}) - E_{\mathrm{A}}(\{\mathrm{B}\}, G_{\mathrm{AB}}) + E_{\mathrm{B}}(\{\mathrm{B}\}, G_{\mathrm{B}}) - E_{\mathrm{B}}(\{\mathrm{B}\}, G_{\mathrm{AB}}) \tag{3}$$

$$Z_{\mathrm{C}} = \mathrm{ZPVE}_{\mathrm{AB}} - \mathrm{ZPVE}_{\mathrm{A}} - \mathrm{ZPVE}_{\mathrm{B}} \tag{4}$$

Wherein, $E_X(\{Y\}, G_Z)$ denotes the electronic energy of X calculated with the basis set $\{Y\}$ at the geometry G_Z of X in the system Z and ZPVE_X is the zero-point vibrational energy of X. Further, according to Kim et al. 100% of basis set superposition error (BSSE) correction often underestimates the interaction energy and 50% correction is a good empirical approximation.[24] Therefore, we report the stabilization energies with 0, 50, and 100% BSSE correction. All the calculations were carried out using Gaussian 98.[25] To get more insights into the nature of interaction between ammonia and fluorobenzenes atoms in molecules (AIM) analysis was carried out using AIM 2000 package.[26]

Results and Discussion

The in-plane hydrogen-bonded complexes of partially fluorinated benzenes with ammonia can be classified into two sets. The first one has cyclic structure with C−H⋯N−H⋯F−C binding motif, in which both fluorobenzenes and ammonia act as hydrogen bond donors as well as acceptors. The second set has linear structure with a C−H⋯N hydrogen bond, wherein the fluorobenzenes act as donors and the ammonia as an acceptor. The FBz−ammonia system, at all the four levels of theory, converges only into a cyclic structure with C−H⋯N−H⋯F−C binding motif. Figure 1A depicts the structure calculated at MP2/6-311++G(d,p) level of theory. The gross features at all the four levels of theory are similar to that shown in Figure 1A, with the N−H⋯F hydrogen-bonded distance shorter than the C−H⋯N distance. Table 1 lists the relevant intermolecular geometrical parameters for all the complexes and Table 2 lists the binding energies. For all the complexes, the binding energies at B3LYP level are considerably lower than those obtained at MP2 level, which can be attributed to significant contribution of dispersion to the total stabilization energy.

TABLE 1: Optimized C−H···N, N−H···F Distances (Å) and C−H···N, N−H···F Angles (Deg) for Various Hydrogen-Bonded Complexes of Fluorobenzenes with Ammonia

		FB	DiFB		TriFB		TetraFB		PentaFB
		cyclic	linear	cyclic	linear	cyclic	linear	cyclic	linear
B3LYP	C−H···N	2.51	2.40	2.45	2.34		2.30		2.28
6-311++G(d,p)	∠C−H···N	146.8	175.3	149.8	179.9		179.5		178.9
	N−H···F	2.47		2.59					
	∠N−H···F	115.9		114.9					
B3LYP	C−H···N	2.54	2.42	2.47	2.38		2.32		2.30
aug-cc-pVDZ	∠C−H···N	147.1	175.6	150.8	179.4		179.5		178.9
	N−H···F	2.49		2.64					
	∠N−H···F	115.5		113.9					
MP2	C−H···N	2.47	2.38	2.42	2.32	2.34	2.28		2.27
6-311++G(d,p)	∠C−H···N	146.8	179.9	148.0	173.6	150.7	178.6		177.4
	N−H···F	2.45		2.51		2.77			
	∠N−H···F	115.7		115.5		114.5			
MP2	C−H···N	2.44		2.40		2.35		2.32	2.26
aug-cc-pVDZ	∠C−H···N	145.8		146.8		148.1		149.4	160.2
	N−H···F	2.37		2.42		2.55		2.63	3.14
	∠N−H···F	114.6		114.3		114.3		113.3	108.7

TABLE 2: Stabilization Energies (kJ mol^{-1}) of Linear and Cyclic Complexes of Partially Fluorinated Benzenes with Ammonia at the B3LYP and MP2 Levels of Theory

	linear [C−H···N]			cyclic [C−H···N H···F−C]		
	E^a	E^b	E^c	E^a	E^b	E^c
FBz						
B3LYP/6-311++G(d,p)				5.6	4.0	4.8
B3LYP/Aug-CC-PVDZ				5.1	3.2	4.1
MP2/6-311++G(d,p)				11.5	5.7	8.5
MP2/aug-cc-pVDZ				12.5	6.9	9.7
DiFBz						
B3LYP/6-311++G(d,p)	7.3	5.0	6.2	7.1	5.3	6.2
B3LYP/Aug-CC-PVDZ	6.6	4.5	5.5	6.4	4.3	5.3
MP2/6-311++G(d,p)	12.7	6.6	9.6	13.6	8.3	11.0
MP2/aug-cc-pVDZ				13.4	7.6	10.5
TriFBz						
B3LYP/6-311++G(d,p)	9.3	6.7	8.0			
B3LYP/Aug-CC-PVDZ	8.1	5.9	7.0			
MP2/6-311++G(d,p)	14.4	7.5	10.9	15.2	8.7	11.9
MP2/aug-cc-pVDZ				14.7	8.9	11.8
TetraFBz						
B3LYP/6-311++G(d,p)	12.2	9.3	10.8			
B3LYP/Aug-CC-PVDZ	10.6	8.4	9.5			
MP2/6-311++G(d,p)	16.2	8.8	12.5			
MP2/Aug-CC-PVDZ				16.9	10.8	13.9
PentaFBz						
B3LYP/6-311++G(d,p)	13.3	10.5	11.9			
B3LYP/Aug-CC-PVDZ	11.6	9.2	10.4			
MP2/6-311++G(d,p)	17.9	10.6	14.3			
MP2/Aug-CC-PVDZ	17.8	11.4	14.6			

[a] No BSSE correction. [b] 100% BSSE correction. [c] 50% BSSE correction.

The DFBz−ammonia system also converges to a cyclic complex with C−H···N−H···F−C binding motif at all the four levels of theory, and Figure 1B depicts the structure obtained at MP2/6-311++G(d,p) level. However, in comparison with the FBz−ammonia complex, a reversal of N−H···F and C−H···N distances was observed, uniformly for all foursets of calculation. Additionally, the emergence of the linear C−H···N hydrogen-bonded complexes was also observed for the DFBz−ammonia system (Figure 1C) at all levels of theory, with an exception of MP2/aug-cc-pVDZ level. The comparable binding energy for both linear and cyclic complexes indicates that the strengthening C−H···N interaction is at the expense of the N−H···F interaction. On the experimental front, Vaupel et al. have recently reported that the out-of-plane N−H···π configuration is preferred for the FBz−ammonia complex, while in-plane configuration is preferred for the DiFBz−ammonia complex.[14] The switching of binding from out-of-plane configuration to in-plane configuration going from FBz to DiFBz is unique to ammonia binding and has not been observed either for water or methanol. Contrary to FBz and DiFBz, the complexes of TriFBz have neither been reported experimentally nor theoretically. The DFT-B3LYP level calculations yield only the linear C−H···N hydrogen-bonded complexes in the case of the TriFBz−ammonia system, while both cyclic and linear structures were observed at MP2/6-311++G(*d,p*) level, shown in parts D and E of Figure 1, respectively. The MP2/aug-cc-pVDZ level for the TriFBz−ammonia system converges only onto a cyclic structure. Experimental evidence is awaited to shed light on the exact structure, whether it is linear or cyclic.

Figure 2A shows the structure of the TetraFBz−ammonia

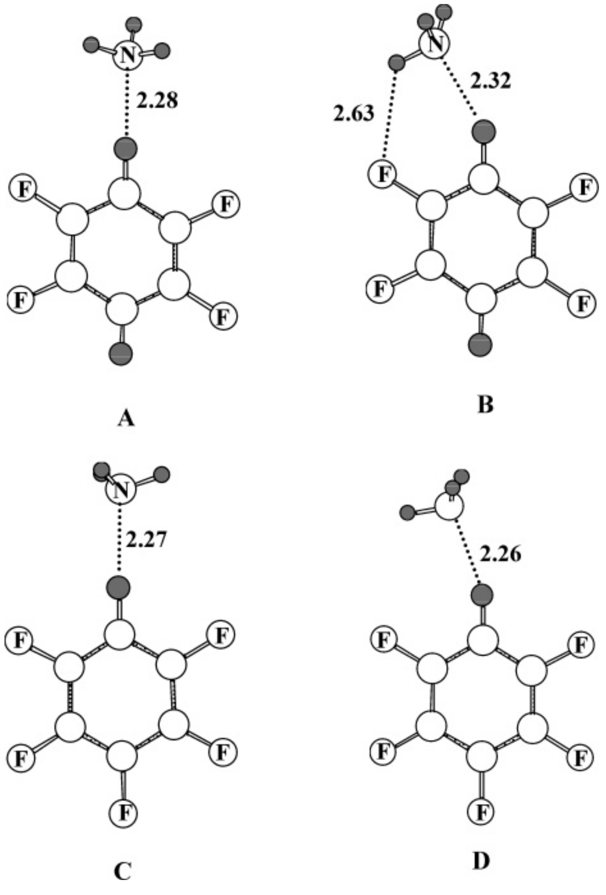

Figure 2. Structures of TetraFBz−ammonia (A, B) and PentaFBz−ammonia (C, D) complexes. A,C and B,D were calculated at the MP/6-311++G(d,p) and MP2/aug-cc-pVDZ levels of theory, respectively. The distances are given in angstroms.

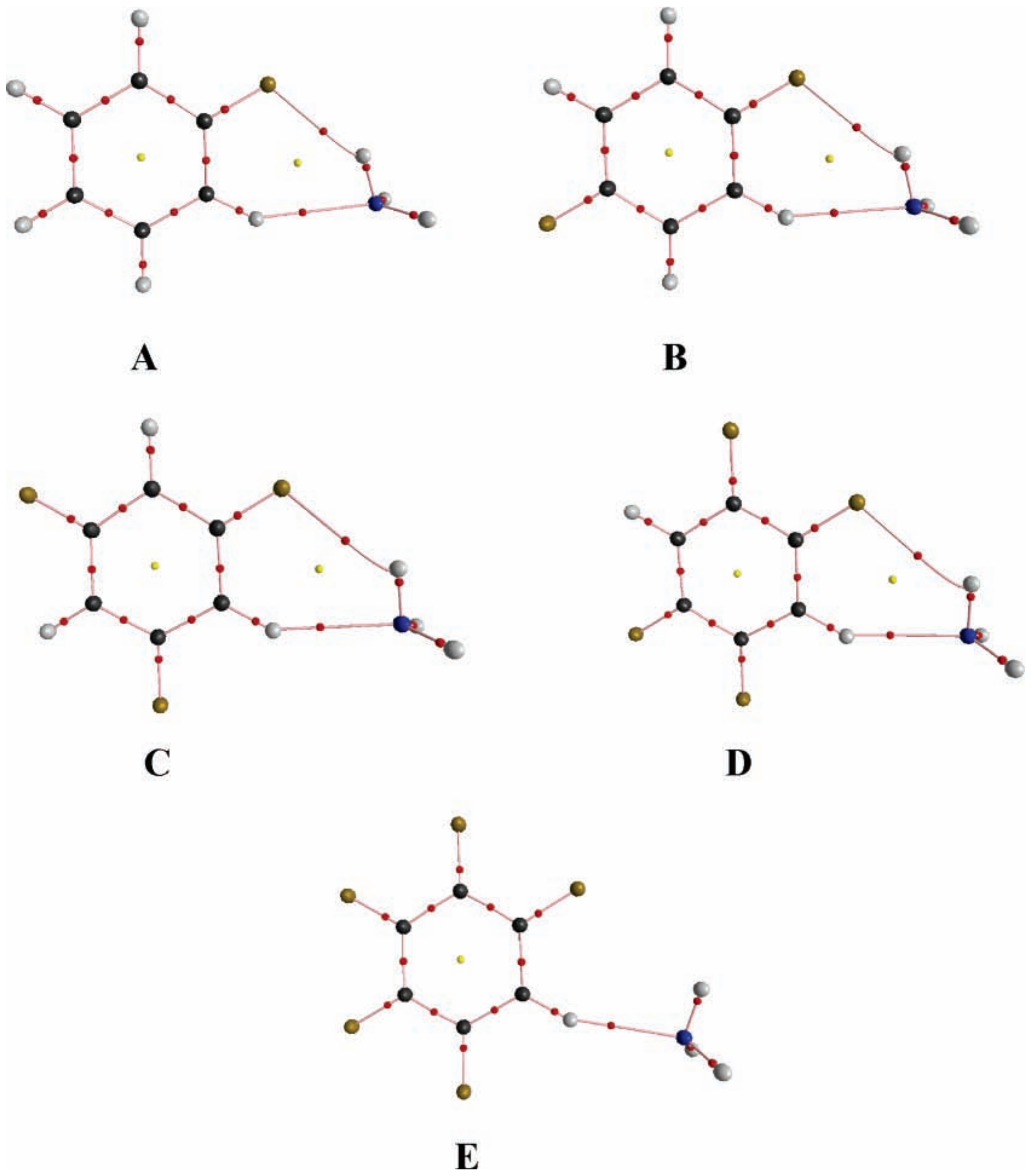

Figure 3. Molecular graphs of complexes of ammonia with (A) FBz, (B) DiFBZ, (C) TriFBZ, (D) TetraFBz, and (E) PentaFBz calculated for MP2/aug-cc-pVDZ level optimized structures. Both (3,−1) BCPs and (3,+1) RCPs are shown.

complex optimized at the MP2/6-311++G(d,p) level, which exhibits a linear C−H···N hydrogen-bonded interaction between TetraFBz and ammonia. The two DFT-B3LYP level calculations also yield similar linear structures. However, only a cyclic complex was obtained at the MP2/aug-cc-pVDZ level, shown in Figure 2B. Mikami's group has reported the IR spectra of the TetraFBz−ammonia complex in the C−H stretching region, which indicates the formation of an in-plane complex.[17] However, from the IR spectrum it is not clear whether the structure of the complex is linear or cyclic. The IR spectrum in the N−H stretching region is required to determine the exact structure. In the case of PentaFBz, a linear complex was observed at the MP2/6-31++G(d,p) level, shown in Figure 2C, while a quasilinear complex was observed at MP2/aug-cc-pVDZ level, shown in Figure 2D. Once again, no prior reports exist in the literature on complexes of PentaFBz, and this is the first such report. Finally, in the case of the hexafluorobenzene−ammonia system no in-plane hydrogen-bonded structure was observed, similar to the hexafluorobenzene−water complex.[19,20]

The bonding pattern for ammonia complexes of all the five partially substituted fluorbenzenes optimized at MP2/aug-cc-pVDZ level were analyzed by the topographical study of electron density using the AIM approach.[27] In the present case the critical points of electron density distribution were obtained, characterized by the rank and trace of the Hessian matrix. A (3,−1) bond critical point (BCP) with a positive Laplacian for the electron density distribution at the BCP indicates the noncovalent interaction.[28,29] Figure 3 shows the molecular graphs of electron density for MP2/aug-cc-pVDZ optimized structures for complexes of ammonia with all the five fluorobenzenes. These calculations reveal the presence of (3,−1) BCP between both the C−H···N and the N−H···F contacts, indicating the presence of two sets of hydrogen bonds for the complexes of FBz, DiFBz, TriFBz, and TetraFBz with ammonia. Table 3 lists the values of the electron density and Laplacian of the electron density at the BCPs, values of which are in the range acceptable for hydrogen bonds.[29] Additionally, a (3,+1) ring critical point (RCP) was observed outside the benzene ring, indicating the presence of a C−H···N−H···F−C cyclic binding motif. On the other hand, in the case of PentaFBz only one BCP for the

TABLE 3: Topological Parameters[a] at the BCPs for C−H···N and N−H···F Contacts Calculated at the MP2/aug-cc-pVDZ Level for the Ammonia Complexes with Various Fluorobenzenes

	C−H···N						N−H···F					
	$\rho(r_c)$	$\Delta^2\rho(r_c)$	G_c	V_c	H_c	ϵ	$\rho(r_c)$	$\Delta^2\rho(r_c)$	G_c	V_c	H_c	ϵ
FBz	0.0111	0.0331	0.0077	−0.0071	0.0006	0.0601	0.0083	0.0359	0.0081	−0.0072	0.0009	0.0359
DiFBz	0.0120	0.0353	0.0083	−0.0077	0.0006	0.0433	0.0075	0.0338	0.0075	−0.0065	0.0010	0.0550
TriFBz	0.0136	0.0396	0.0093	−0.0087	0.0006	0.0177	0.0057	0.0286	0.0060	−0.0048	0.0012	0.1425
TetraFBz	0.0145	0.0418	0.0098	−0.0092	0.0006	0.0142	0.0049	0.0259	0.0052	−0.0040	0.0013	0.2351
PentaFBz	0.0160	0.0460	0.0107	−0.0099	0.0008	0.0023						

[a] All entries are in atomic units except ϵ, which is dimensionless.

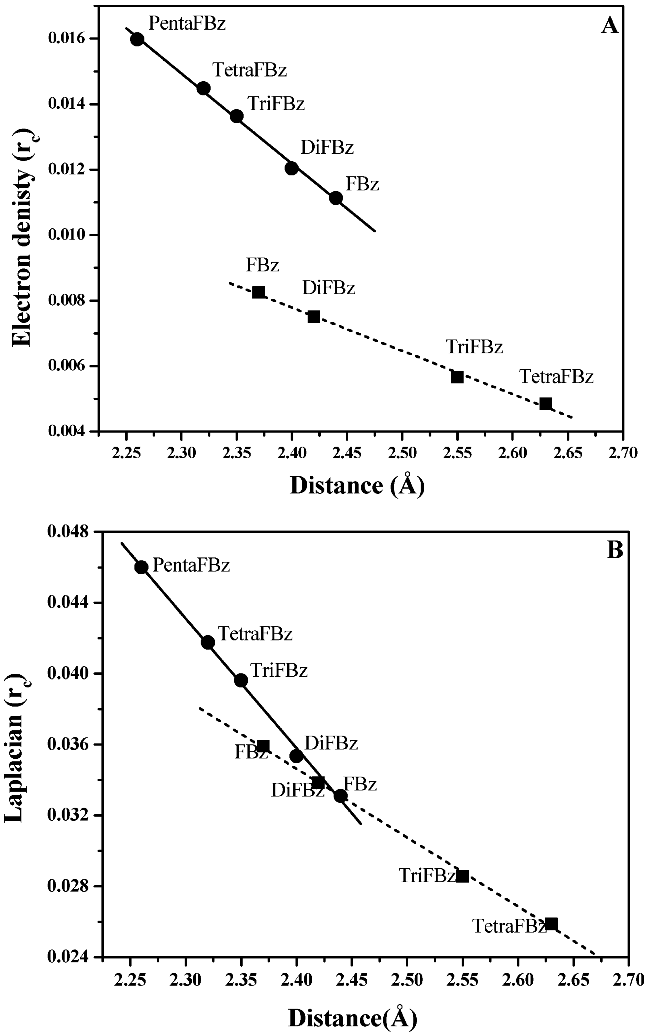

Figure 4. (A) Plot of electron density at the BCPs for C−H···N (●; solid line) and N−H···F (■; dashed line) contacts vs hydrogen bond distance. (B) Plot of the Laplacian at the BCPs for C−H···N (●; solid line) and N−H···F (■; dashed line) contacts vs hydrogen bond distance. Note the reversal of the trend between the two correlations.

C−H···N contact was observed, and the RCP completely absent, which indicates the formation of a quasilinear C−H···N hydrogen-bonded complex. Parts A and B of Figure 4 show the plots of electron density at the BCP and the Laplacian of the electron density at the BCP vs the C−H···N/N−H···F hydrogen bond distance, respectively. Both, the electron density at the BCP and the Laplacian of the electron density at the BCP, increase for the C−H···N interaction linearly with progressive fluorination; on the other hand they decrease linearly for the N−H···F interaction. To get further insights into the nature of interactions, electronic energy density (H_c), and its components, the local one electron kinetic energy density (G_c), and the local potential energy density (V_c), for the charge distribution at the BCPs for C−H···N and N−H···F contacts were calculated, which are also listed in Table 3. The electronic energy density H_c at the BCPs is positive for both C−H···N and N−H···F contacts, which indicates interaction between closed shell systems, dominated by the kinetic energy term.[28] Further, the bond ellipticity (see Table 3) for the C−H···N contacts decrease with increase in fluorination, which confirms the propensity of fluorobenzenes to from linear C−H···N hydrogen-bonded complexes with increase in number of fluorine atoms. Another interesting observation that can be made from the molecular graphs depicted in Figure 3 is the curvature of the bond path connecting N−H···F interaction, which increases with fluorination and eventually breaks in the case of pentaFBz. This observation is in line with the increase in bond ellipticity for the N−H···F contacts down the series (see Table 3). All the above observations imply, in a straightforward manner, that progressive fluorination favors the C−H···N hydrogen-bonded interaction at the expense of N−H···F interaction.

One of the most striking features of these calculations is the complete absence of linear N−H···F hydrogen-bonded complexes through the entire series, which glaringly points to the fact that the organic fluorine is a reluctant hydrogen-bond acceptor. The present calculations clearly demonstrate that FBz exclusively forms cyclic complex at all levels of theory, while only linear/quasilinear complexes were observed for PentaFBz. For DFBz, TriFBz, and TetraFBz there is clear shift in tendency to form linear complexes from cyclic complexes with increase in fluorination. Progressive fluorination leads to shortening and strengthening of C−H···N hydrogen-bonded interaction at the expense of the N−H···F interaction. This implies that the successive fluorination decreases the ability of fluorobenzenes to adapt to the C−H···N−H···F−C binding motif, which completely disappears in the case of PentaFBz. Extrapolating, one would expect that hexafluorobenzene would not form any in-plane hydrogen-bonded complexes due to lack of C−H group, which indeed is the case. The most important inference that can be made from these calculations is that the C−F bond completely looses ability to hydrogen bond when benzene is substituted with five or more fluorine atoms. Coincidentally, this is exactly the number of fluorine atoms required to remove the vibronic structure in the gas-phase absorption spectra of fluorobenzenes, which has been attributed to the mixing of the σ and π molecular orbitals in higher fluoro analogues of benzene.[30]

Conclusions

The in-plane hydrogen-bonded complexes of a series of fluorosubstituted benzenes with ammonia were investigated using ab initio calculations. The binary complexes of the lower fluoro analogues, FBz, DiFBz, and TriFBz, preferentially adapt to a cyclic structure with C−H···N−H···F−C binding motif. The stability of such cyclic complexes due to cooperativity of C−H···N and N−H···F hydrogen bonds. It was observed that increase in fluorination strengthens the C−H···N hydrogen bond at the expense of N−H···F hydrogen bond. The N−H···F hydrogen bond completely disappears in the case of the PentaFBz−ammonia system, which forms a linear C−H···N hydrogen-bonded complex. On the other hand, linear N−H···F hydrogen-bonded complexes were completely absent, which reinforces the point out that organic fluorine is a reluctant hydrogen bond acceptor. Substitution at least five C−H units of benzene with C−F units is essential for the complete disappearance of N−H···F hydrogen bond.

Acknowledgment. Financial support from CSIR (Grant No. 01(1902)/03/EMR-II) and BRNS (Grant No. 2004/37/5/BRNS/398) are gratefully acknowledged. Authors wish to thank Prof. H. B. Singh for his valuable comments.

References and Notes

(1) Jeffrey, G. A. *An Introduction to Hydrogen Bonding*; Oxford University Press: New York, 1997.

(2) Desiraju, G. R.; Steiner, T. *The Weak Hydrogen Bond in Structural Chemistry and Biology*; Oxford University Press: Oxford, 1999.

(3) Desiraju, G. R. *Acc. Chem. Res*. **2002**, *35*, 565. (b) Desiraju, G. R. *Chem. Commun*. **2005**, *24*, 2995.

(4) Thalladi, V. R.; Weiss, H. C.; Blaser, B.; Boese, R.; Nangia, A.; Desiraju, G. R. *J. Am. Chem. Soc*. **1998**, *120*, 8702.

(5) Dunitz, J. D.; Schweizer, W. B. *Chem.*−*Eur. J*. **2006**, *12*, 6804.

(6) Dunitz, J. D.; Taylor, R. *Chem.*−*Eur. J*. **1997**, *3*, 89.

(7) Howard, J. A. L.; Hoy, V. J.; O'Hagan, D.; Smith, G. T. *Tetrahedron*. **1996**, *52*, 12613.

(8) Shimoni, L.; Glusker, J. P. *Struct. Chem.* **1994**, *4*, 383.

(9) Murray-Rust, P.; Stallings, W. C.; Monti, C. T.; Preston, R. K.; Glusker, J. P. *J. Am. Chem. Soc*. **1983**, *105*, 3206.

(10) O'Hagan, D.; Rzepa, H. S. *J. Chem. Soc., Chem. Commun*. **1997**, 645.

(11) Frohlich, R.; Rosen, T. C.; Meyer, O. G. J.; Rissanen, K.; Haufe, G. *J. Mol. Struct.* **2006**, *787*, 50.

(12) Tarakeshwar, P.; Kim, K. S.; Brutschy, B. *J. Chem. Phys.* **1999**, *110*, 8501.

(13) (a) Buchhold, K.; Reimann, B.; Djafari, S.; Barth, H. D.; Brutschy, B.; Tarakeshwar, P.; Kim, K. S. *J. Chem. Phys.* **2000**, *112*, 1844. (b) Djafari, S.; Barth, H. D.; Buchold, K.; Brutschy, B. *J. Chem. Phys.* **1997**, *107*, 10573.

(14) Vaupel, S.; Brutschy, B.; Tarakeshwar, P.; Kim, K. S. *J. Am. Chem. Soc*. **2006**, *128*, 5416.

(15) Venkatesan, V.; Fujii, A.; Ebata, T.; Mikami, N. *Chem. Phys. Lett.* **2004**, *394*, 45.

(16) Venkatesan, V.; Fujii, A.; Ebata, T.; Mikami, N. *J. Phys. Chem. A* **2005**, *109*, 915.

(17) Venkatesan, V.; Fujii, A.; Mikami, N. *Chem. Phys. Lett.* **2005**, *409*, 57.

(18) Ziołkowski, M.; Grabowski, S. J.; Leszczynski, J. *J. Phys. Chem. A* **2006**, *110*, 6514.

(19) Gallivan, J. P.; Dougherty, D. A. *Org. Lett.* **1999**, *1*, 103.

(20) Danten, Y.; Tassaing, T.; Besnard, M. *J. Phys. Chem. A* **1999**, *103*, 3530.

(21) Patwari, G. N.; Lisy, J. M. *J. Phys. Chem. A* **2003**, *107*, 9495.

(22) Boys, S. F.; Bernardi, F. F. *Mol. Phys*. **1970**, *19*, 553.

(23) Grabowski, S. J.; Sadlej, A. J.; Sokalski, W. A.; Leszczynski, J. *Chem. Phys.* **2006**, *327*, 151.

(24) Kim, K. S.; Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145.

(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *GAUSSIAN 98*, revision A.11.1.1; Gaussian, Inc.: Pittsburgh, PA, 2001.

(26) Biegler-Konieg, F.; Schonbohm, J.; Bayles, D. *J. Comput. Chem.* **2001**, *22*, 545.

(27) Bader, R. F. *Atoms in Molecules: A Quantum Theory*; Oxford University Press: Oxford, UK, 1990.

(28) (a) Matta, C. F.; Castillo, N.; Boyd, R. J. *J. Phys. Chem. A* **2005**, *109*, 3669. (b) Matta, C. F.; Castillo, N.; Boyd, R. J. *J. Phys. Chem. B* **2006**, *110*, 563.

(29) Koch, U.; Popelier, P. L. A. *J. Phys. Chem.* **1995**, *99*, 9747.

(30) Zgierski, M. Z.; Fujiwara, T.; Lim, E. C. *J. Chem. Phys*. **2005**, *122*, 144312.