Ab Initio Study of the Hydrogen Bonding between Pyrrole and Hydrogen Fluoride: A Comparison of NH···F and FH···π Interactions

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The structures, vibrational frequencies, and association energies of the NH···F and FH···π hydrogen-bonding complexes between pyrrole and hydrogen fluoride have been examined using the Hartree−Fock, Møller−Plesset (second order), and density functional theory. Full geometry optimization and energetics of these complexes are calculated using the 6-31G*, 6-31G**, 6-31+G*, 6-31+G**, 6-311G*, and 6-311++G** basis sets. The DFT calculations are carried out using the BLYP and B3LYP nonlocal exchange−correlation functionals. After BSSE (basis set superposition error) by the counterpoise (CP) method and ZPVE corrections, the association energies of the π-type and NH···F hydrogen-bonding complexes are calculated to be about 3.054 and 1.518 kcal/mol, respectively, at the MP4(SDTQ)/6-311++G**//MP2/6-31+G* level. The intermolecular interaction potential of the π-type hydrogen-bonding complex is also discussed.

Introduction

Hydrogen bonding is an important phenomenon in many chemical and biological systems, and hydrogen-bonding complexes have been extensively studied by a wide range of experimental techniques and calculations. A large number of molecules form hydrogen-bonding complexes in the form DH···A, where DH is a proton donor and A is a proton acceptor, which usually has lone-pairs or π electrons. Most of the studies focused on the former. A number of studies have dealt with complexes that contained π-type hydrogen bonds such as the complexes of benzene and halogens,[1] hydrogen halides,[2] water,[3] ammonia,[4] and alkanes.[5] We have measured the vibrational spectra of the self-association species of pyrrole, pyrazole, and imidazole and found that their π-type hydrogen-bonding dimers have NH stretching frequencies in the 3500−3300 cm^{-1} region. To understand how the dimers in pyrrole, pyrazole, and imidazole are associated through the π-type hydrogen bonding, we have investigated the interaction between the complex of pyrrole and hydrogen fluoride. Both pyrrole and hydrogen fluoride can be either proton donors or acceptors. Thus, there may exist two types of complexes between pyrrole and hydrogen fluoride with the NH···F and FH···π hydrogen bondings. M. Spoliti et al.[6] calculated the NH···F and FH···N hydrogen-bonding complexes between pyrrole and hydrogen fluoride with C_{2v} and C_s symmetry, respectively, and found that the interaction energies were −13 and −46 kJ/mol, respectively, at the HF/4-31G* level. However, since they did not fully optimize their geometries, further studies are needed.

The density functional theory (DFT) has been recognized as a very useful tool in the study of the extended systems because it is computationally less demanding for the inclusion of electron correlation. Recently, most DFT applications for intra- and intermolecular systems have been in the studies of molecular structures, vibrational frequencies, basicity, proton affinities, electron affinities, hydrogen-bonding energies, relative energies of conformational isomers, bond dissociation energies, internal rotations around a bond, and chemical reaction.[7] Few applications have been made to study the weak π hydrogen bondings.

In this study we have carried out both DFT and traditional ab initio calculations. The traditional ab initio calculations are performed at the Hartree−Fock and MP2 levels. In the DFT calculations we have used both the BLYP and B3LYP functionals. DFT calculations with these functionals have been found to yield accurate reaction energies for a wide range of processes,[8] but how well they are suited for describing the π hydrogen bondings is still unknown. In this work, the geometries, vibrational frequencies, and binding energies of the NH···F and FH···π hydrogen-bonding complexes between pyrrole and hydrogen fluoride are calculated. In addition, the potential surface of π-type hydrogen-bonding interaction are also calculated. The main aims here are to (i) compare the properties (i.e. geometries, vibrational frequencies of NH and HF stretching and binding energies) between NH···F and FH···π hydrogen-bonding complexes; (ii) investigate the basis set effect; and (iii) test the adequacy of DFT calculations.

Computational Methods

All the calculations have been performed with the GAUSSIAN94 program[9] using the 6-31G*, 6-31G**, 6-31+G*, 6-31+G**, 6-311G*, and 6-311++G** basis sets at the HF and MP2 levels. The same basis sets are used for the DFT calculations with two density functionals. In the first one, the exchange functional is of Becke (B), which includes a gradient correction,[10] and the correlation part is given by the gradient-corrected functional of Lee, Yang, and Parr (LYP).[11] In the second one, B3LYP is comprised of Becke's three-parameter exchange functional[12] and the Lee−Yang−Parr correlation functional.[11] The geometries are fully optimized by means of analytical gradients, and the vibrational frequencies were calculated in the harmonic approximation. The interaction energies of complexes were corrected by BSSE (basis set superposition error) using the counterpoise method[13] and ZPVE (zero-point vibrational energy).

Results and Discussions

A. Individual Molecules. The calculated geometries and vibrational frequencies for hydrogen fluoride and pyrrole are tabulated in Tables 1−5. The atomic numbering of pyrrole is

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TABLE 1: Computed Equilibrium Bond Length (Å) of Hydrogen Fluoride[a]

	6-31G*	6-31G**	6-31+G*	6-31+G**	6-311G*	6-311++G**
ab initio						
HF	0.911	0.901	0.913	0.902	0.897	0.897
MP2	0.934	0.921	0.941	0.918	0.927	0.912
DFT						
BLYP	0.945	0.937	0.949	0.939	0.936	0.933
B3LYP	0.934	0.925	0.938	0.928	0.925	0.922

[a] The experimental value is 0.92 Å, ref 11.

TABLE 2: Computed Equilibrium Dipole Moment (D) of Hydrogen Fluoride[a]

	6-31G*	6-31G**	6-31+G*	6-31+G**	6-311G*	6-311++G**
ab initio						
HF	1.972	1.944	2.079	2.042	2.162	2.026
MP2	2.013	1.980	2.135	2.193	2.090	2.066
DFT						
BLYP	1.805	1.773	2.013	1.971	2.037	1.958
B3LYP	1.859	1.828	2.036	1.995	2.081	1.982

[a] The experimental value is 1.82 D; ref 12.

TABLE 3: Computed Equilibrium Vibrational Frequency (cm^{-1}) of Hydrogen Fluoride[a]

	6-31G*	6-31G**	6-31+G*	6-31+G**	6-311G*	6-311++G**
ab initio						
HF	4357.9	4492.6	4314.3	4471.8	4424.5	4493.2
MP2	4039.1	4191.2	3941.3	4093.2	4118.7	4199.0
DFT						
BLYP	3817.4	3926.8	3781.3	3910.8	3811.8	3941.6
B3LYP	3977.5	4087.8	3935.3	4071.5	3986.6	4099.4

[a] The experimental value is 3608 cm^{-1}; ref 13.

TABLE 4: Computed Equilibrium Bond Lengths (Å), Bond Angles (deg), Dipole Moments (D), and Rotational Constant (GHz) of Pyrrole

	HF	MP2	BLYP	B3LYP	expt[a]
			Bond Lengths		
N_2-C_1	1.363	1.373	1.388	1.376	1.370
C_2-C_3	1.358	1.383	1.390	1.378	1.382
C_3-C_4	1.427	1.418	1.434	1.425	1.417
N_1-H_1	0.992	1.011	1.016	1.008	0.996
C_2-H_2	1.070	1.081	1.087	1.081	1.076
C_3-H_3	1.071	1.082	1.089	1.082	1.077
			Bond Angles		
$\angle C_2N_1C_5$	109.5	110.2	109.8	109.8	109.8
$\angle N_1C_2C_3$	108.2	107.4	107.5	107.7	107.7
$\angle C_2C_3C_4$	107.1	107.5	107.5	107.4	107.4
$\angle H_1N_1C_2$	125.3	124.9	125.1	125.1	125.1
$\angle H_2C_2C_3$	130.6	131.4	131.5	131.3	130.8
$\angle H_3C_3C_2$	126.1	125.6	125.7	125.8	125.5
			Dipole Moments		
	1.895	1.917	1.896	1.901	1.740
			Rotational Constants		
A	9.2793	9.1514	8.9911	9.1335	8.9507
B	9.2036	8.9947	8.8616	9.0019	8.8899
C	4.6206	4.5362	4.4629	4.5336	4.4601

[a] Reference 14.

TABLE 5: Calculated Harmonic Vibrational Frequencies of Pyrrole Monomer[a]

		HF	MP2	BLYP	B3LYP	expt[b]	assignment[c]
1	a_1	3926(3553)	3648(3538)	3547	3670(3560)	3527	ν_{NH}
2	a_1	3473(3126)	3322(3189)	3201	3278(3185)	3148	ν_{CH}
3	a_1	3443(3099)	3302(3170)	3178	3262(3164)	3125	ν_{CH}
4	a_1	1648(1483)	1540(1478)	1470	1520(1474)	1470	ν_R
5	a_1	1548(1393)	1470(1411)	1389	1439(1396)	1391	ν_R
6	a_1	1264(1138)	1194(1146)	1142	1181(1146)	1148	ν_R
7	a_1	1161(1045)	1134(1088)	1073	1103(1070)	1074	δ_{CH}
8	a_1	1110(999)	1070(1027)	1012	1044(1013)	1018	δ_{CH}
9	a_1	968(871)	902(866)	873	899(872)	880	δ_R
10	a_2	946(851)	788(756)	828	872(846)	868	γ_{CH}
11	a_2	806(725)	633(608)	626	672(691)	712	γ_{CH}
12	a_2	679(611)	586(563)	609	630(611)	618	γ_R
13	b_1	966(869)	772(745)	772	818(793)	826	γ_{CH}
14	b_1	830(747)	707(679)	698	731(709)	720	γ_{CH}
15	b_1	684(616)	637(612)	619	641(622)	626	γ_R/γ_{NH}
16	b_1	484(436)	460(442)	397	447(434)	474	γ_{NH}/γ_R
17	b_2	3449(3104)	3317(3184)	3197	3278(3180)	3140	ν_{CH}
18	b_2	3417(3075)	3292(3160)	3166	3250(3152)	3116	ν_{CH}
19	b_2	1744(1570)	1599(1535)	1543	1599(1551)	1521	ν_R/δ_{NH}
20	b_2	1595(1436)	1520(1459)	1416	1474(1430)	1424	ν_R/δ_{NH}
21	b_2	1437(1293)	1337(1284)	1282	1322(1282)	1287	δ_{CH}/δ_{NH}
22	b_2	1253(1128)	1199(1151)	1136	1171(1136)	1134	δ_{NH}/δ_{CH}
23	b_2	1166(1049)	1094(1050)	1045	1079(1047)	1049	δ_{CH}/δ_{NH}
24	b_2	946(851)	879(844)	852	877(851)	863	δ_R

[a] Frequencies are in cm^{-1}, the values in parentheses are the scaled frequencies (see the text). [b] Reference 15. [c] ν, δ, and γ indicate the stretching, in-plane bending, and out-of-plane bending modes, respectively.

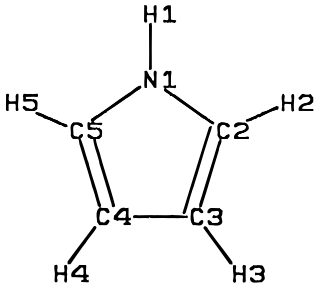

Figure 1. Atom numbering corresponding to the geometrical parameters of pyrrole in Table 4.

shown in Figure 1. In the case of hydrogen fluoride, all the calculations except BLYP/6-31G* and BLYP/6-31+G* yield bond lengths that deviate within 0.02 Å from the experimental value of 0.92 Å (see Table 1).[14] The calculated structures refer to equilibrium geometries, whereas experimentally deduced geometries are vibrational average structures. Therefore, all the calculated of H−F bond lengths are reasonable. Most of the calculations overestimate the dipole moment of hydrogen fluoride, especially at the Hartree−Fock and MP2 level. In Table 2, the calculated dipole moment, 1.805 D, using the BLYP/6-31G*, agrees well with the experimental value of 1.82 D.[15] The calculated dipole moments are affected by the basis set used. The use of diffuse functions on heavy atoms and polarization functions on hydrogen atoms yields larger and smaller dipole moments, respectively, and the use of a triple-split valence basis set increases the dipole moment significantly relative to that of the 6-31G* basis set. Table 3 lists the calculated harmonic frequencies of hydrogen fluoride. Compared with the experimental value of 3608 cm^{-1},[16] the DFT results agree better.

Table 4 shows the computed equilibrium geometry, dipole moment, and rotational constant of the pyrrole monomer using the 6-31G* basis set. The MP2 and B3LYP calculations give geometries, especially the bond lengths and rotational constants, in excellent agreement with experimental data.[17] Bond lengths are underestimated by the Hartree−Fock method and are overestimated by the BLYP theory. Bond lengths from the Hartree−Fock and DFT calculations deviate within 0.02 Å from the experimental values, and the bond angles deviate within 1° at all levels. So, the Hartree−Fock and BLYP calculations also give reasonable geometries of pyrrole. All calculations overestimate the dipole moment within 10% of the experimental value of 1.74 D.[17] The calculated harmonic vibrational frequencies of pyrrole using the 6-31G* basis set are listed in Table 5. The BLYP results are very close to experimental ones.[18] Hartree−Fock, MP2, and B3LYP results are larger than experimental values by about 11%, 4%, and 3%, respectively, on average. The values in parentheses are the scaled frequencies

TABLE 6: Intermolecular Parameters of the NH···F Complex between Pyrrole and Hydrogen Fluoride[a]

		6-31G*	6-31G**	6-31+G*	6-31+G**	6-311++G**
ab initio						
HF	R	3.077	3.075	3.176	3.191	3.199
	θ	104.5	104.5	127.3	130.7	138.0
	φ	157.2	157.2	165.7	167.3	171.2
	χ	2.6	2.5	5.2	2.4	2.8
MP2	R	2.984	2.977	3.053	3.082	3.095
	θ	99.2	99.2	121.2	127.5	134.7
	φ	160.0	160.1	164.4	169.6	175.0
	χ	0.2	0.4	0.4	1.7	0.8
DFT						
BLYP	R	2.95	2.953	3.075	3.143	3.147
	θ	92.5	93.4	104.5	123.7	127.7
	φ	160.1	160.0	157.5	166.5	169.6
	χ	1.3	1.3	1.3	1.3	1.8
B3LYP	R	2.935	2.938	3.088	3.103	3.102
	θ	95.0	96.1	122.9	123.5	125.2
	φ	158.8	159.0	167.4	167.2	165.2
	χ	0.2	0.1	6.0	0.4	6.6

[a] Distances in angstroms; angles in degrees.

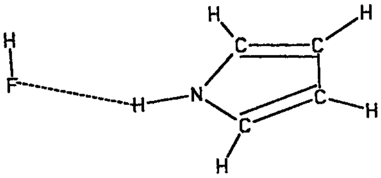

Figure 2. Structure of the NH···F hydrogen-bonding complex between pyrrole and hydrogen fluoride.

by factors of 0.90, 0.96, and 0.97 for Hartree−Fock, MP2, and B3LYP calculations, respectively. After scaling, the Hartree−Fock, MP2, and B3LYP also yield vibrational frequencies in close agreement with the experimental values. The calculated frequencies of in-plane modes (with a_1 and b_2 symmetry) are in general very close to experimental data, but some out-of-plane modes, for example, NH out-of-plane bending, have larger deviations from experimental ones.

B. Hydrogen-Bonding Complexes between Pyrrole and Hydrogen Fluoride. The geometries of hydrogen-bonding complexes between hydrogen fluoride and pyrrole are optimized with the 6-31G*, 6-31G**, 6-31+G*, 6-31+G**, 6-311G*, and 6-311++G** basis sets at Hartree−Fock, MP2, BLYP, and B3LYP levels. The vibrational frequencies are also calculated.

1. NH···Complex. The calculated values of the intermolecular geometrical parameters of the NH···F hydrogen-bonding complex are listed in Table 6. The parameters R, θ, φ, and χ are the distance between N and F, the angle of H−F···H, the angle of F···H−N, and the dihedral angle of NH···FH, respectively (see Figure 2). We find that the MP2, BLYP, and B3LYP calculations yield similar geometries. The use of polarization functions on the hydrogen atoms has little effect on the geometry, but the use of diffuse functions on heavy atoms causes a noticeable change of geometry. The hydrogen-bonding distance R and the bonding angle θ increase significantly at all levels when diffuse functions on heavy atoms are used. The calculations with the 6-31G* and 6-31G** basis sets show that the complex prefers the tetrahedral structure and the lone-pairs of the F atom are contracted around the atomic center, whereas the calculations with diffuse functions on heavy atoms show that F has more diffusive lone-pairs. This indicates that the sp^3-like character of the lone-pair electrons in the F atom has been decreased by the use of the diffuse functions on heavy atoms, which causes the increase of θ. The other possibility is that the calculations with diffuse functions on heavy atoms favor the dipole−dipole interaction between pyrrole and hydrogen fluoride. Therefore, the bonding angle θ increases significantly when diffuse functions on heavy atoms are used. There is no energy minimum of the NH···F hydrogen-bonding complex at all levels with the 6-311G* basis set. Table 7 shows the interaction energy of the NH···F hydrogen-bonding complex between pyrrole and hydrogen fluoride. ΔE is the energy difference between the dimer and monomers without BSSE and ZPVE corrections. The single-point energies of the monomers and the NH···F hydrogen-bonding complex are obtained at the 6-311++G** geometry using the 6-311G* basis set at all levels. ΔE clearly depends on the choice of the basis set and decreases remarkably when the diffuse functions on heavy atoms are used. DFT calculations with the 6-31G* and 6-31G** basis sets yield very large BSSEs, about 3−4 kcal/mol, for this system, whereas the calculations using the basis sets with diffuse functions on heavy atoms reduce BSSE to within 0.4 kcal/mol. MP2 and Hartree−Fock calculations also yield smaller BSSEs when the diffuse functions on heavy atoms are used. These results show that the calculation with a more flexible basis set decreases BSSE. After BSSE and ZPVE corrections, ΔE_f is in the range between 1.2 and 1.7 kcal/mol at all levels. The B3LYP gives a ΔE_f similar to that of MP2. To judge which method gives more reasonable results, we also calculated the single-point energy to estimate the interaction energy of the NH···F hydrogen bonding at the MP4(SDTQ)/6-31+G* and MP4(SDTQ)/6-311++G** levels with the MP2/6-311++G** geometry. ΔE, ΔE_{cp}, and ΔE_f of the former are 3.535, 2.461, and 1.518 kcal/mol, and those of the latter are 3.750, 2.620, and 1.677 kcal/mol, respectively. ΔE_f is also affected by the basis set used at the MP4 level. With the same basis set, the MP2 and B3LYP calculations are in agreement with MP4 calculations. All the MP2 and B3LYP calculations except using the 6-311G* basis set give a close agreement with MP4 calclations. Hartree−Fock also yields a reasonable result when the diffuse functions on heavy atoms are used, whereas the BLYP calculations underestimate ΔE_f. Since BSSE is always overestimated,[19] the

TABLE 7: Interaction Energy of the NH···F Complex between Pyrrole and Hydrogen Fluoride (kcal/mol)[a]

		6-31G*	6-31G**	6-31+G*	6-31+G**	6-311G*[b]	6-311++G**
HF	$-\Delta E$	3.854	3.902	2.519	2.450	3.444	2.577
	$-\Delta E_{cp}$	2.309	2.296	2.265	2.271	2.821	2.263
	$-\Delta E_f$	1.303	1.279	1.482	1.505	2.062	1.529
MP2	$-\Delta E$	5.707	5.642	3.732	3.524	4.615	3.502
	$-\Delta E_{cp}$	2.740	2.627	2.661	2.640	3.290	2.520
	$-\Delta E_f$	1.587	1.499	1.681	1.739	2.347	1.578
BLYP	$-\Delta E$	6.607	6.642	2.460	2.402	4.851	2.514
	$-\Delta E_{cp}$	2.586	2.479	2.169	2.128	3.038	2.153
	$-\Delta E_f$	1.368	1.335	1.283	1.308	2.121	1.235
B3LYP	$-\Delta E$	6.130	6.169	2.802	2.742	4.892	2.835
	$-\Delta E_{cp}$	2.809	2.741	2.476	2.481	3.340	2.476
	$-\Delta E_f$	1.599	1.617	1.654	1.679	2.486	1.593

[a] $\Delta E = E(\text{complex}) - E(\text{pyrrole}) - E(\text{hydrogen fluoride})$. $\Delta E_{cp} = \Delta E - \text{BSSE}$. $\Delta E_f = \Delta E_{cp} - \Delta\text{ZPVE}$ (ZPVE(complex) − ZPVE(pyrrole) − ZPVE(hydrogen fluoride)). [b] At the 6-311++G** geometry; see the text.

TABLE 8: Interaction Energy of the Linear NH···F Complex between Pyrrole and Hydrogen Fluoride (kcal/mol)[a] at the C_{2v} Symmetry

	HF		MP2		BLYP		B3LYP	
method	ΔE	ΔE_{cp}	ΔE	ΔE_{cp}	ΔE	ΔE_{cp}	ΔE	ΔE_{cp}
6-31G*	3.036	2.295	4.242	2.792	4.075	2.364	4.109	2.655
6-31+G**	2.300	2.174	3.200	2.479	2.076	1.890	2.425	2.247

[a] $\Delta E = E(\text{complex}) - E(\text{pyrrole}) - E(\text{hydrogen fluoride})$. $\Delta E_{cp} = \Delta E - \text{BSSE}$.

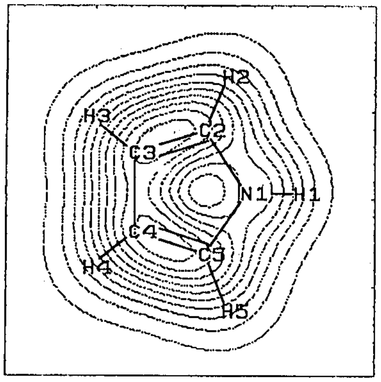

Figure 3. Contour of the π-electron density 2 Å above the ring plane of pyrrole.

interaction energy of the NH···F complex between pyrrole and hydrogen fluoride should be larger than 1.518 kcal/mol.

Besides the calculations of the minima of the NH···F hydrogen-bonding complex, we also calculate the interaction energy of the NH···F hydrogen-bonding complex at the C_{2v} symmetry, which confirmed the linearity of NH···FH, at Hartree–Fock, MP2, BLYP, and B3LYP levels with the 6-31G* and 6-31+G** basis sets. All levels show that there exist two imaginary frequencies, corresponding to the intermolecular in-plane and out-of-plane vibrational modes. Table 8 shows the interaction energies without and with BSSE correction. Comparing to those given in Table 7, the interaction energy differences (after BSSE correction) between the equilibrium geometry and the C_{2v} geometry are within 0.2 kcal/mol at all levels, except BLYP calculations. The C_{2v} geometry favors the dipole–dipole interaction, whereas the equilibrium geometry favors higher order multipole interactions. By comparing the interaction energies of the equilibrium geometry and the C_{2v} geometry of the NH···F hydrogen-bonding complex, we find that high-order multipole interactions play a crucial role in the NH···F hydrogen bonding between pyrrole and hydrogen fluoride.

2. FH···π Complex. Pyrrole as a proton acceptor forms FH···π hydrogen bonding with hydrogen fluoride through the π-electron system of pyrrole. We plot the contour of the π-electron density 2 Å above the ring plane of pyrrole in Figure 3. This figure shows that the region above C_3 and C_4 has a large population of π electrons. From the Mulliken population analysis, we find that the N atom has the largest negative charge. Locating the bonding region of pyrrole is an interesting problem. First, we guess that the π hydrogen bonding is formed between C_3 and C_4. However, most of the calculated results reveal that in the π-type complex the hydrogen end of the H–F bond points toward C_3 of pyrrole, whereas the calculations at the Hartree–Fock and MP2 levels without diffuse functions on heavy atoms (6-31G*, 6-31G**, and 6-311G* basis sets) show that it points toward the middle of the C_3–C_4 bond. Table 9 shows the intermolecular parameters of the fully optimized geometry of this π-type complex at all levels. R, θ, and χ are the distance between C_3 or the middle of C_3–C_4 and F (the shortest distance between the pyrrole ring and F), the bisect angle of the H–F axis and the C_2 axis of pyrrole, and the dihedral angle of FH···NH, respectively (see Figure 4). We find that DFT yields a structure similar to that of MP2 except χ. DFT yields a larger χ. It seems that DFT calculations result in a larger repulsion between electrons, because the larger the distance between F and N, the larger χ is. The Hartree–Fock calculations yield a larger R than that of MP2 calculations, but similar θ and χ. The calculations with the 6-31G* and 6-31G** basis sets yield similar results at all levels, whereas the calculations with the diffuse functions on heavy atoms give larger θ and χ. This indicates that the calculations with the diffuse functions on heavy atoms result in a larger repulsion between electrons and a longer distance between F and N. For example, the HF/6-31G* and HF/6-31+G* calculations yield distances between F and N of 3.375 and 3.735 Å, respectively. The triple-split valence basis sets comparing to the double-split valence basis sets have no noticeable effect. Table 10 shows the interaction energy of the FH···π complex between hydrogen fluoride and pyrrole. Without BSSE and ZPVE corrections, the calculated ΔE at the

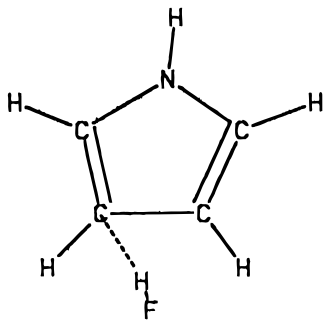

Figure 4. Structure of the NH···π hydrogen-bonding complex between pyrrole and hydrogen fluoride.

TABLE 9: Intermolecular Parameters of the FH···π Complex between Pyrrole and Hydrogen Fluoride[a]

		6-31G*	6-31G**	6-31+G*	6-31+G**	6-311G*	6-311++G**
ab initio							
HF	R	3.306	3.317	3.310	3.331	3.259	3.337
	θ	66.3	66.1	82.6	82.3	63.6	80.7
	χ	4.8	4.7	17.1	17.0	1.2	16.4
MP2	R	3.16	3.157	3.163	3.147	3.077	3.137
	θ	58.8	58.8	75.8	75.4	63.1	77.0
	χ	4.8	2.7	13.6	13.8	0.0	13.4
DFT							
BLYP	R	3.113	3.103	3.105	3.112	3.065	3.084
	θ	57.6	58.1	88.9	89.2	62.7	88.2
	χ	11.6	13.9	24.8	23.8	19.1	23.3
B3LYP	R	3.082	3.075	3.09	3.09	3.069	3.101
	θ	61.0	60.5	89.3	88.9	64.1	87.9
	χ	19.1	18.9	24.0	24.1	14.6	23.1

[a] Distances in angstroms; angles in degrees.

TABLE 10: Interaction Energy of the FH$\cdots\pi$ Complex between Pyrrole and Hydrogen Fluoride (kcal/mol)[a]

		6-31G*	6-31G**	6-31+G*	6-31+G**	6-311G*	6-311++G**
HF	$-\Delta E$	5.678	5.450	4.958	4.597	6.184	4.651
	$-\Delta E_{cp}$	4.459	4.371	4.410	4.306	4.538	4.158
	$-\Delta E_f$	3.070	3.084	3.126	2.930	3.083	2.833
MP2	$-\Delta E$	8.819	7.783	7.608	6.915	8.816	6.982
	$-\Delta E_{cp}$	4.836	4.521	5.516	5.215	4.750	5.170
	$-\Delta E_f$	3.316	3.094	3.816	3.619	3.104	3.222
BLYP	$-\Delta E$	6.968	6.768	6.340	5.851	7.962	5.803
	$-\Delta E_{cp}$	3.967	3.745	5.615	5.410	4.449	5.516
	$-\Delta E_f$	2.471	2.413	4.142	3.974	2.971	3.766
B3LYP	$-\Delta E$	7.325	7.076	6.531	6.063	8.126	6.053
	$-\Delta E_{cp}$	4.844	4.622	5.854	5.664	5.038	5.446
	$-\Delta E_f$	3.353	3.254	4.294	4.182	3.530	4.000

[a] $\Delta E = E(\text{complex}) - E(\text{pyrrole}) - E(\text{hydrogen fluoride})$. $\Delta E_{cp} = \Delta E - \text{BSSE}$. $\Delta E_f = \Delta E_{cp} - \Delta\text{ZPVE}(\Delta\text{ZPVE}(\text{complex}) - \text{ZPVE}(\text{pyrrole}) - \text{ZPVE}(\text{hydrogen fluoride}))$.

HF/6-31G* level is 5.68 kcal/mol, which is larger than the ΔE of 4.07 kcal/mol of the π complex between hydrogen fluoride and benzene at the same level.[20] This can be explained by the fact that the π-electron density above the ring plane of pyrrole is larger than that of benzene and the population of π electrons above the pyrrole ring is more localized than that of benzene. With BSSE and ZPVE corrections, ΔE_f's depend on the methods and basis sets used; the use of diffuse functions on heavy atoms yields a larger ΔE_f and the use of polarization functions on hydrogen atoms yields a smaller ΔE_f except at the Hartree−Fock level. The Hartree−Fock calculations yield $\Delta E_f \approx 3.1$ kcal/mol with the 6-31G*, 6-31G**, 6-31+G*, and 6-311G* basis sets. The MP2 calculations with the 6-31G*, 6-31G**, and 6-311G* basis sets yield nearly the same ΔE_f. However, with the diffuse functions on heavy atoms, MP2 calculations yield a larger ΔE_f. The DFT calculations with the diffuse functions on heavy atoms yield slightly larger values of ΔE_f than MP2. As for the calculations of the NH$\cdots$F complex, we also use MP4(SDTQ)/6-31+G*//MP2/6-311 ++G** and MP4(SDTQ)/6-311++G**//MP2/6-311 ++G** to estimate the interaction energy. With both the BSSE and ZPVE correction, we obtain ΔE_f's of 3.422 and 3.054 kcal/mol. The MP2 yields a close agreement with MP4 with the same basis sets.

3. *The Comparison of NH$\cdots$F- and FH$\cdots\pi$-Type Interactions*. NH$\cdots$F and FH$\cdots\pi$ complexes have different hydrogen bond lengths, interaction energies, and shifts of vibrational frequencies relative to that of individual molecules. The hydrogen bond length of the NH$\cdots$F complex is shorter than that of the FH$\cdots\pi$ complex, because lone-pair electrons are more contracted than π electrons. The basis sets with diffuse functions on heavy atoms increase the hydrogen bond length of the NH$\cdots$F complex by about 0.1 Å at all levels, but have no evident effect on another complex. As for the changes of the geometry of the pyrrole ring, all the calculations show that the C−N and C_2-C_3 bond lengths slightly decrease and increase, respectively, in both complexes, whereas the C_3-C_4 bond length increases in the FH$\cdots\pi$ complex, but decreases in the other complex, which can be understood by the fact that in the FH$\cdots\pi$ complex pyrrole donates electrons through the part of the ring near the C_3-C_4 bond, thus decreasing the double-bond character of C_3-C_4. It is surprising that the interaction energy of the NH$\cdots$F complex is much smaller than that of the FH$\cdots\pi$ complex, which can be explained by the fact that the hydrogen fluoride is a good proton donor, but a poor proton acceptor. The basis sets with diffuse functions on heavy atoms decrease the BSSE of the interaction energy, especially for the NH$\cdots$F complex.

Table 11 shows the harmonic vibrational frequencies of the HF and NH stretching modes of monomers and complexes. The HF and NH stretching modes of complexes are all red-shifted relative to that of the monomer. In the FH$\cdots\pi$ complex, hydrogen fluoride is a proton donor. The HF stretching frequency is red-shifted significantly, and its IR absorption intensity increases remarkably. The NH stretching mode has the same trend but to a lesser extent. In the NH$\cdots$F complex, the shifted frequencies of HF and NH stretching modes do not differ too much, but the IR absorption intensity of the NH stretching mode (proton donor part) increases more significantly than that of the HF stretching mode. It is well-known that the absorption intensity and the vibrational frequency shift of the AH stretching mode in the hydrogen complex (AH$\cdots$B) are augmented with the increase of atomic charge and charge flux of the AH bond. The variations of the vibrational frequency and absorption intensity of the AH stretch mode in the FH$\cdots\pi$ complex are more prominent than that of the NH$\cdots$F complex. This is consistent with the calculated interaction energies of the complexes.

TABLE 11: Calculated Harmonic Vibrational Frequencies (cm^{-1}) and IR Intensities (km/mol) of HF and NH Stretching Modes in the Pyrrole−Hydrogen Fluoride Complexes and Pyrrole and Hydrogen Fluoride Monomers[a]

		HF	MP2	BLYP	B3LYP
free	ν_{HF}	4358(141)	4039(91)	3817(39)	3977(62)
	ν_{NH}	3926(83)	3685(73)	3547(34)	3670(49)
NH$\cdots$F complex	ν_{HF}	4325(173)	3991(73)	3779(63)	3938(90)
	ν_{NH}	3910(219)	3656(279)	3484(278)	3617(277)
FH$\cdots\pi$ complex	ν_{HF}	4237(437)	3906(414)	3629(440)	3780(496)
	ν_{NH}	3920(97)	3678(86)	3545(43)	3666(61)

[a] The values in parentheses are the IR intensities.

C. The Potential Surface of the FH$\cdots\pi$ Complex. The amount of energy for hydrogen fluoride to move around on top of the benzene ring is very small. To move from above the center of the ring to on top of the middle of one of the benzene carbon−carbon bonds was calculated to cost only about 0.4 kcal/mol.[20] Thus, the potential surface is quite flat for the π-type hydrogen bonding. We have considered several configurations of the π-type complex of pyrrole and hydrogen fluoride, as shown in Figure 5. For the case where the hydrogen fluoride molecule is perpendicular to the pyrrole molecular plane, the acidic hydrogen points toward (a) the middle of the pyrrole C_3-C_4 bond, (b) atom C_2, and (c) the N atom. We have also considered the case where the acidic hydrogen fluoride is parallel to the N−H bond of pyrrole, i.e. case d. The interaction energies of these cases are listed in Table 12. At the HF/6-31G* level, we find that the potential surface has local minima in cases a and c, as inferred from the vanishing imaginary parts of the calculated vibrational frequencies. The other two cases have nonvanishing imaginary parts of frequencies. The MP2/6-31G*//HF/6-31G* calculations yield that ΔE_{cp} (with BSSE correction only) for the case a is the same as that for the case where the acidic H points toward C_3. This indicates that the acid can move freely from the top of C_3 to the C_4 of pyrrole. ΔE_{cp} for cases

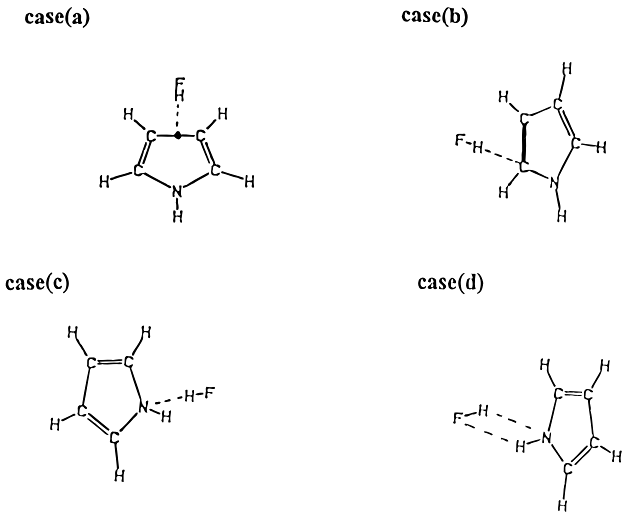

Figure 5. Sketches of the pyrrole−hydrogen fluoride complex configurations, for cases a−c where the hydrogen fluoride molecule is perpendicular to the pyrrole molecular plane with the acidic hydrogen pointing toward (a) the middle of the pyrrole C_3−C_4 bond, (b) atom C_2, and (c) the N atom and (d) where the acidic hydrogen fluoride is parallel to the N−H bond of pyrrole.

TABLE 12: Molecular Energies (hartrees) and Interaction Energies (kcal/mol) of the FH···π Complexes between Pyrrole and Hydrogen Fluoride

	E (hartrees)	$-\Delta E$	$-\Delta E_{cp}$
	HF/6-31G*//HF/6-31G*		
(a)	−308.819 809 8	5.678	4.460
(b)	−308.817 868 7	4.460	3.554
(c)	−308.816 598 6	3.663	2.827
(d)	−308.816 332 1	3.496	1.893
	MP2/6-31G*//HF/6-31G*		
(a)	−309.672 709 9	7.735	5.527
(b)	−309.670 230 3	6.179	4.471
(c)	−309.668 687 2	5.211	3.560
(d)	−309.668 500 1	5.093	2.570

b and c are 1.056 and 1.967 kcal/mol smaller, respectively. From MP2/6-31G*//HF6-31G* calculations, we find that the barrier for the acidic hydrogen to move from the global minimum to another local minimum (see Figure 5c) is about 2 kcal/mol, which is much larger than 0.4 kcal/mol for the hydrogen fluoride to move from the C_{6v} position to above the middle of the benzene carbon−carbon bond.[21] This can be explained by the fact that the π electrons of pyrrole are more localized than those of benzene. The potential surface of this π-type hydrogen bonding is fairly flat, since the binding energy changes by only 1.056 and 1.967 kcal/mol when the acidic hydrogen fluoride moves over a large distance from C_3 to C_2 and N, respectively. The distances between acid hydrogen and pyrrole are 2.34, 2.34, and 2.26 Å, respectively, in Figure 5a−c, with the HF/6-31G* geometry. The equilibrium acidic hydrogen positions above C_2, C_3, C_4, and C_5 are nearly in the same plane. The N atom has the largest negative charge, as indicated by a shorter distance between acidic hydrogen and pyrrole shown in Figure 5c. The last case, shown in Figure 5d, has two hydrogen bonds, NH···F and FH···N. This is a saddle point, because it has a nonvanishing imaginary part of the frequency at the HF/6-31G* level. The H···N and H···F distances are the same, 2.81 Å, which is larger than those between acidic hydrogen and pyrrole in Figure 5a−c. Relative to case c, the angle of FH···N is changed and the binding energy drops by about 1 kcal/mol. Since the attraction between acidic hydrogen and pyrrole nitrogen is decreased due to the elongation of the H···N distance from 2.26 to 2.81 Å and the repulsion between acidic fluorine and pyrrole nitrogen is increased due to the shortening of the F···N distance from 3.18 to 2.96 Å, the binding energy of case d is still about 1 kcal/mol smaller than that of case c.

Conclusion

Hartree−Fock, second-order Møller−Plesset, and DFT calculations have been performed for NH···F and FH···π hydrogen-bonding complexes between pyrrole and hydrogen fluoride.

The position of the F atom is optimized to be 3.1−3.2 Å away from atom C_3 of pyrrole in the π complex and 2.9−3.1 Å away from the N atom in the NH···F complex at the MP2 and DFT(BLYP and B3LYP) levels. Most of the calculations demonstrate that the acidic hydrogen points toward atom C_3 of pyrrole in the optimized geometry of the π complex and the optimized angle between monomer axes in the NH···F complex is close to the tetrahedral angle, which is not close to the best angle for dipole−dipole interaction. The intraction energy with BSSE and ZPVE corrections of the π complex is about 2 times that of the NH···F complex, which is larger than that of the π complex between hydrogen fluoride and benzene. The increase of the IR absorption intensity and red shift of the stretching mode (the proton donor part) of FH in the π complex are much larger than those of NH in the NH···F complex. Calculations for various positions of hydrogen fluoride of the π-type complex of pyrrole and hydrogen fluoride indicate that the potential surfaces of the π-type hydrogen bonding are quite flat.

It has already been demonstrated that the use of polarization functions on hydrogen atoms has little effect on the geometries and hydrogen-bonding energies of these two complexes. The addition of diffuse functions on heavy atoms, however, changes the relative orientation between monomers significantly in these complexes and increases the correlation energy in the π complex. In addition, the use of diffuse functions on heavy atoms greatly reduces BSSE, especially in the DFT calculations.

DFT calculations yield geometries and interaction energies (with the diffuse functions on heavy atoms) similar to MP2 and excellent vibrational frequencies. Especially, B3LYP caculations give geometries, dipole moments, vibrational frequencies of individual molecules and complexes, and the interaction energy of the NH···F hydrogen-bonding complex in good agreement with those of MP2 calculations. Since DFT is computationally much more efficient, it is an important method for studying hydrogen-bonding problems.

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