

Theoretical NMR study of the hydrogen bond and CH- π interactions in FH...Pyridine \perp X-benzene complexes

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Received on April 19, 2015

Accepted on Sep. 10, 2015

Abstract

NMR properties of the hydrogen bond and CH- π interactions in the FH...Pyridine \perp X-benzene complexes (where \perp denotes CH- π interaction and X = NH₂, OH, H, Cl, Br, and NO) have been investigated at the PBE1KCIS/6-311++G(d,p) level of theory. In addition to geometrical parameters, binding energies and Hammett constants, results of natural bond orbital (NBO) analyses are in good relationship with calculated NMR data (particularly with the two-bond ¹⁹F-¹⁵N spin-spin coupling constant ^{2h}J_{F-N}). Also, the relation between cooperativity energy (E_{coop}) and NMR data was considered. The results of this study led to better understanding of the NMR properties of the hydrogen bond and CH- π interactions in the complexes involved.

Keywords: CH- π interaction; Hammett constant; NBO; Coupling constant; Cooperativity energy.

Introduction

The CH- π interactions are weak noncovalent bindings between a C-H bond and π electron systems. These interactions play role in crystal packing, molecular conformations and the alignment of liquid crystals.^[1-3] Many experimental and theoretical studies have been afforded which support the existence of CH- π interactions.^[4-13]

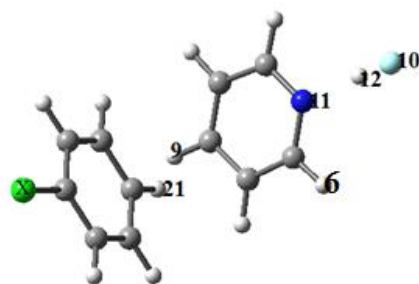
The contribution of the CH- π interactions in the binding of acetylcholine to its inhibitors was reported.^[14] Indeed, Wetmore and coworkers accentuate essential role for these interactions in the DNA repair process.^[15] The CH- π interactions play a major role in modeling the biological systems and take part, together with the π - π stacking interactions, in nucleobase-amino acid combinations.^[16] Few accurate ab initio calculations support the T-shaped orientations between the nucleobases and the aromatic side chains of amino acids which refer to the CH- π interactions.^[17-20]

Theoretical NMR studies have been performed to investigate the influence of trimer formation on one- and two-bond spin-spin coupling constants in complexes with X-H-Y hydrogen bond.^[21] Also, N-H...O=P hydrogen bonds have been examined using theoretical calculations.^[22]

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Theoretical NMR studies give good information about the relationship between energetic and NMR properties of the complexes involving benzene or substituted benzenes. Alkotra and Elguero reported theoretical NMR properties of the ortho and para-substituted benzenes. They compared their results with silabenzenes, pyridines and phosphabenzenes.^[23] Other authors investigated also the NMR properties of ternary complexes involving hydrogen bonds.^[24]

Cooperativity of the hydrogen bond and CH- π interactions has been previously reported and it was shown that there is a positive cooperativity between hydrogen bond and CH- π interactions in the modeled complexes formed from HF, pyridine and substituted-benzenes.^[25] In fact, complexes with electron-donating substituents show more cooperativity between hydrogen bond and CH- π interactions than those with electron-withdrawing ones. On the other hand, interplay between hydrogen bond and π -stacking interactions has been formerly considered in the modeled complexes formed from HF, pyridine and substituted-benzenes.^[26] Results obtained by these authors indicate cooperativity of interactions in the complexes where face-to-face aromatic and hydrogen bonding interactions coexist. The aim of the present work is to investigate the NMR properties of the FH...Pyridine \perp X-benzene complexes which encompass both hydrogen bond and CH- π interactions (see Scheme 1). We tried to find a relationship between the NMR data, particularly the two-bond $^{19}\text{F}-^{15}\text{N}$ spin-spin coupling constant $^{2h}J_{\text{F-N}}$, and the properties of the FH...Pyridine \perp X-benzene complexes. Results of this study help us understand better how the coexistence of the hydrogen bond and CH- π interactions in biological systems relates to energetic and geometrical properties of these systems. Also, energetic and NMR properties of FH...Pyridine||X-benzene complexes (where || denotes π -stacking interaction) were studied for the sake of comparison with the FH...Pyridine \perp X-benzene complexes.



FH...Pyridine \perp X-benzene complexes

X = NH₂, OH, H, Cl, Br, and NO

Scheme 1: The FH...Pyridine \perp X-benzene complexes involving both hydrogen bond and CH- π interactions.

Computational methods

All geometries were optimized at the MP2/6-31G** level of theory with Gaussian09 program package.^[27] Keyword nosymm was used to obtain perpendicular T-shaped geometries for the FH...Pyridine \perp X-benzene complexes. Frequency

computations have been performed on optimized geometries to verify the ground states of these geometries. The binding energies of all complexes were calculated with correction for the basis set superposition error (BSSE) using the Boys-Bernardi counterpoise technique.^[28] Also, single point energy calculations have been performed on the optimized structures at the MP2/6-311++G** level of theory. The NMR calculations were performed using SPINSPIN keyword on the structures optimized at the MP2/6-31G** level of theory using the PBE1KCIS/6-311++G** level since PBE1KCIS has a good performance for weak interactions.^[29] The total coupling constants ${}^2\text{J}_{\text{F-N}}$ and ${}^3\text{J}_{\text{H-H}}$ have been evaluated as the sum of paramagnetic spin-orbit (PSO), diamagnetic spin-orbit (DSO), Fermi-contact (FC) and spin-dipole (SD) terms. FC, SD, DSO, and PSO components of spin-spin coupling constant are related to electronic and bonding features of the molecules. Previous investigations concentrated on the FC coupling mechanism because it is the easiest to analyze and understand and a basic physical understanding of this mechanism dates to decades ago. The SD coupling mechanism requires occupied and unoccupied non-s orbitals. For C-C bonds, the SD term results primarily from the (positive) one-orbital π contributions, which arise from π - π^* excitations. Small contributions are also given by pseudo- π orbitals. The positive SD terms increase with the bond order of the C-C bond. The PSO coupling mechanism requires occupied as well as unoccupied non-s orbitals at the coupling nuclei. In the case of coupling between two first row atoms, the PSO mechanisms occur typically in π systems and systems containing heteroatoms with lone pairs. The isotropic PSO term results from several factors. In the way the PSO coupling mechanism becomes clear, it is possible to relate it to bond order, π -strength, electronegativity and the magnetizability of a bond. Since the DSO term is always relatively small, the DSO coupling mechanism was so far the least interesting and therefore also the least investigated mechanism. However, the degree of smallness of the DSO term is a direct indicator of the anisotropy of the charge distribution centered at the coupling nuclei and is thus a representative of bond polarity and the electronegativity difference between the two atoms. Detailed mechanisms of spin-spin coupling constants have been reported by many authors.^[30-33] Additionally, isotropic values of the proton shielding tensor have been considered. The isotropic shielding values are denoted as σ_{iso} where $\sigma_{\text{iso}} = 1/3 (\sigma_{11} + \sigma_{22} + \sigma_{33})$ and σ_{ii} values are the principal tensor components. The population analysis has been performed by the natural bond orbital (NBO) method^[34] at the MP2/6-31G** level using NBO program implemented under Gaussian09 program package.^[27] The NBO study clarifies the role of orbital interactions, mainly charge transfers, by considering all possible interactions between filled donor and empty acceptor NBOs and estimating their energetic weights by second-order perturbation theory. For each donor NBO (i) and acceptor NBO (j), the donor-acceptor interaction energy $E^{(2)}$ is estimated as:

$$E^{(2)} = -q_i \frac{F(i, j)^2}{e_j - e_i} \quad \text{eq.1}$$

Where q_i is the orbital occupancy, e_i , e_j are diagonal elements and $F(i,j)$ is an off-diagonal NBO Fock matrix element.

Results and discussion

The interaction energy (ΔE) for each FH...Pyridine \perp X-benzene complex is defined as the difference between the energy of complex and the energies of the three individual monomers:

$$\Delta E = E_{FH \dots pyridine \perp X - benzene} - (E_{HF} + E_{pyridine} + E_{X - benzene}) \quad \text{eq.2}$$

The computed binding energies and the most important structural parameters of the FH...Pyridine \perp X-benzene complexes are presented in Table 1. It should be noted that the negative value of the interaction energy ($-\Delta E$) is considered as binding. On the other hand, the cooperativity energy (E_{coop}) for each ternary complex is defined as the difference between the interaction energy of that complex and the interaction energies of all possible binary complexes which exist in that structure:

$$E_{coop} = \Delta E_{FH \dots pyridine \perp X - benzene} - (\Delta E_{HF \dots pyridine} + \Delta E_{pyridine \perp X - benzene} + \Delta E_{FH \dots X - benzene}) \quad \text{eq.3}$$

Table 1: The binding energies (in kcal mol⁻¹) for the FH...Pyridine \perp X-benzene and Pyridine \perp X-benzene complexes, N11...H12 distances, H12-F10 bond lengths and the distance from the X-benzene plane to H9 (in Å) for the FH...Pyridine \perp X-benzene complexes calculated at the MP2/6-31G** level of theory.

X	$r_{(N11 \dots H12)}$	$r_{(H12-F10)}$	$r_{(H9 \dots \pi)}$	$-\Delta E^a$	$-\Delta E^b$	$-E_{coop}$
NH ₂	1.7259	0.9467	2.28	12.73, 20.24	1.94, 6.50	0.66
OH	1.7281	0.9464	2.31	12.24, 19.42	1.59, 5.85	0.51
H	1.7295	0.9461	2.30	12.17, 19.46	1.62, 5.97	0.43
Cl	1.7322	0.9457	2.38	11.81, 19.62	1.40, 6.27	0.28
Br	1.7321	0.9458	2.32	11.77, 19.50	1.34, 6.12	0.29
NO	1.7332	0.9465	2.34	11.58, 18.64	1.23, 5.38	0.22

^a Calculated for ternary complexes.

^b Calculated for binary complexes.

The italic values refer to MP2/6-311++G(d,p) level of theory.

Cooperativity energies (E_{coop}), which reflect synergetic effects between CH- π interaction and hydrogen bond in the above mentioned complexes, are given in Table 1. As can be seen, electron-donating substituents lead to higher binding energies and higher cooperativity effects than electron-withdrawing ones. This result is in agreement with the obtained geometrical parameters which indicate that the shortest $r_{N \dots H}$ distance corresponds to the complex with X=NH₂ while the H-F bond length in this complex is the longest one. The H-F bond length in the free molecule HF is 0.88 Å computed at the MP2/6-31G** level. Obviously, complexation leads to elongation of the H-F bond in comparison to the free HF molecule.

The relationship between calculated NMR data and binding energy values is discussed in the following section. As a consequence of diamagnetic anisotropy, each proton in a molecule is shielded from the applied magnetic field to an extent that depends on the electron density surrounding it.^[35] In the FH...Pyridine⊥X-benzene complexes, the electron-donating or the electron-accepting character of the substituent X influences the electron density surrounding the hydrogen atom in para position relative to X in the benzene ring (H₂₁) and, also, the hydrogen of pyridine (H₉) which interacts with the X-benzene. The results show that the isotropic values of the proton shielding tensor (IS) of H₂₁ in the ternary FH...Pyridine⊥X-benzene complexes are smaller compared to those in the binary Pyridine⊥X-benzene complexes and the X-benzene monomers (Table 2). The substituents X lead also to an increase in the IS (H₂₁) values of the ternary FH...Pyridine⊥X-benzene complexes compared to the unsubstituted complex (X=H). On the contrary, the value of IS (H₉) for X=H is higher than those for other substituents in the ternary FH...Pyridine⊥X-benzene complexes. The results show that complexes with higher IS (H₂₁) values have relatively high binding energies. On the other hand, the IS (H₉) values of the ternary complexes are lower than those in the binary Pyridine⊥X-benzene complexes and in the pyridine monomer. Also, the substituents X lead to a decrease in the IS (H₉) values of the ternary FH...Pyridine⊥X-benzene complexes compared to X=H (Table 2). The results presented in Table 2 indicate that there is a good relationship between the difference of the IS (H₉) values of the ternary FH...Pyridine⊥X-benzene complexes and those of the binary Pyridine⊥X-benzene ones, ΔIS (H₉), and the binding energy values: the smaller ΔIS (H₉), the higher is the binding energy. Thus, the IS values of H₉ which contribute to the CH-π interaction influences the binding energy values in the FH...Pyridine⊥X-benzene complexes.

Table 2: The isotropic values of the proton shielding tensor (in ppm) for hydrogen in para position relative to the substituent X (H₂₁) and the hydrogen of pyridine which contributes to the CH-π interaction (H₉), calculated at the PBE1KCIS/6-311++G** level of theory.

X	IS ^a	IS ^b	IS ^c	IS ^d	IS ^e	ΔIS (H ₉)	-ΔE ^a
NH ₂	24.78	24.62	24.60	26.70	26.64	0.068	12.73
OH	24.89	24.17	24.15	27.13	27.07	0.061	12.24
H	33.38	23.89	23.87	27.30	27.24	0.055	12.17
Cl	24.12	24.38	24.38	26.81	26.69	0.119	11.81
Br	23.93	24.10	24.08	27.09	27.00	0.090	11.77
NO	24.35	23.93	23.92	25.49	25.38	0.115	11.58

^a Values of IS (H₂₁) in the X-benzene monomers, ^b Values of IS (H₂₁) in the binary complexes, ^c Values of IS (H₂₁) in the ternary complexes, ^d Values of IS (H₉) in the binary complexes and ^e Values of IS (H₉) in the ternary complexes. Value of IS (H₉) in pyridine is 24.33 ppm.

As mentioned above, the interaction of HF with pyridine in the FH...Pyridine⊥X-benzene complexes changes the N...H distance and the H-F bond length in these complexes. The results show that there is a linear correlation between the two-bond ^{19}F - ^{15}N spin-spin coupling constant ${}^{2h}J_{\text{F}_{10}\text{-N}_{11}}$ values and the $r_{\text{N}\dots\text{H}}$ distances in the FH...Pyridine⊥X-benzene complexes as depicted in Figure 1. As can be seen, the increase in the coupling of the $^{19}\text{F}_{10}$ and $^{15}\text{N}_{11}$ atoms is accompanied by a decrease in the $r_{\text{N}\dots\text{H}}$ distances. Moreover, the relation between ${}^{2h}J_{\text{F-N}}$ and the binding energy is showed in Figure 2 where it can be seen how the coupling between the $^{19}\text{F}_{10}$ and $^{15}\text{N}_{11}$ atoms makes a positive effect on the binding energies of the FH...Pyridine⊥X-benzene complexes. The two-bond ^{19}F - ^{15}N spin-spin coupling constant ${}^{2h}J_{\text{F}_{10}\text{-N}_{11}}$ has four FC, SD, PSO and DSO components, the values of which are reported in Table 3. Obviously, the FC component is the most important component of the two-bond spin-spin coupling constant ${}^{2h}J_{\text{F}_{10}\text{-N}_{11}}$.

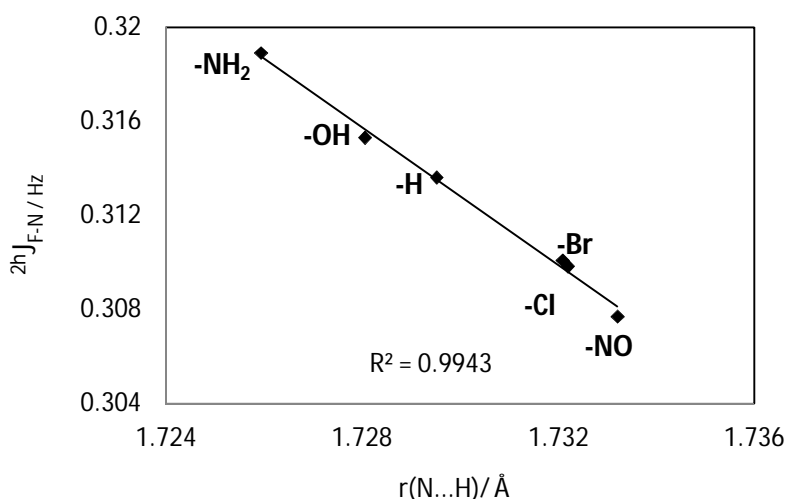


Figure 1: Relationship between ${}^{2h}J_{\text{F}_{10}\text{-N}_{11}}$ and $r_{\text{N}\dots\text{H}}$ distances in the FH...Pyridine⊥X-benzene complexes.

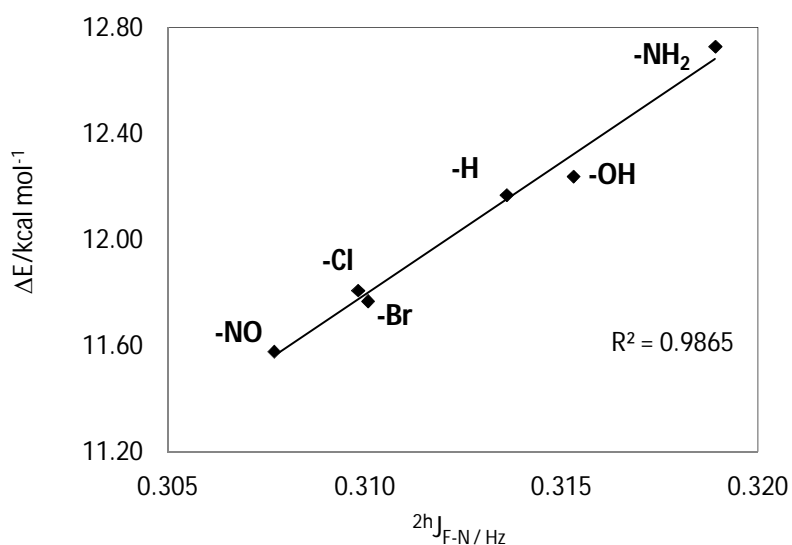


Figure 2: Binding energy versus ${}^{2h}J_{\text{F}_{10}\text{-N}_{11}}$ for the FH...Pyridine⊥X-benzene complexes.

Table 3: The coupling constant ${}^{2h}J_{F_{10}-N_{11}}$ and its components (in Hz) for the FH...Pyridine⊥X-benzene complexes, calculated at the PBE1KCIS/6-311++G** level of theory.

X	FC($\times 10^2$)	SD($\times 10^1$)	PSO($\times 10^0$)	DSO($\times 10$)	J($\times 10^{-2}$)
NH ₂	0.311	0.123	-0.520	0.564	0.319
OH	0.307	0.123	-0.500	0.564	0.315
H	0.306	0.122	-0.498	0.560	0.314
Cl	0.302	0.122	-0.487	0.566	0.310
Br	0.302	-0.121	-0.482	0.572	0.310
NO	0.141	0.122	-0.470	0.563	0.307

To study the effect of the electronic properties of substituent X on the coupling between the ${}^{19}F_{10}$ and ${}^{15}N_{11}$ atoms, a correlation between the corresponding Hammett constants (σ) and the values ${}^{2h}J_{F_{10}-N_{11}}$ was considered. As can be observed in Figure 3, a linear relationship with a good correlation coefficient between ${}^{2h}J_{F_{10}-N_{11}}$ and the σ_{para} values was obtained. Thus, the electron-donating and electron-withdrawing nature of substituent X represents an important factor that affects the coupling constants between different atoms in the complexes involving these substituents.

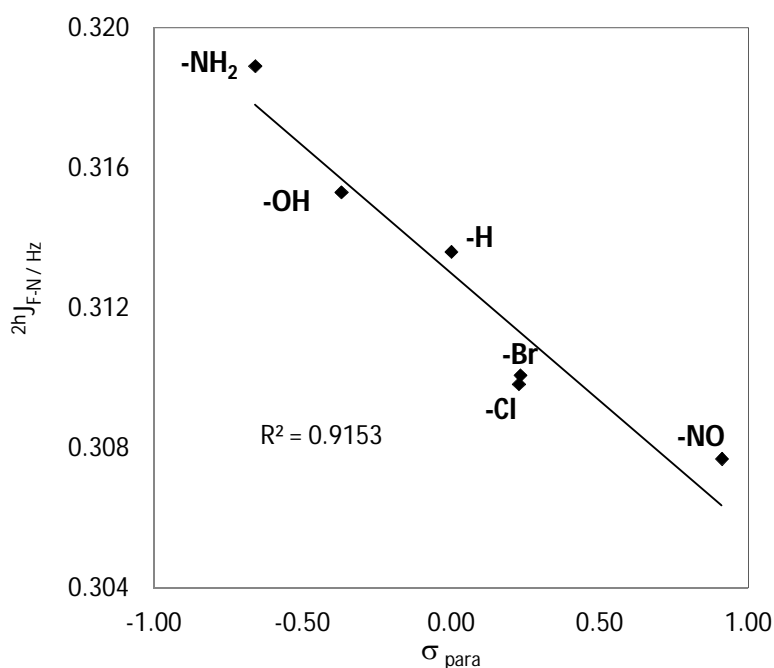


Figure 3: Relationship between the ${}^{2h}J_{F_{10}-N_{11}}$ values and the Hammett constants of the substituents X in the FH...Pyridine⊥X-benzene complexes.

The H₁₂ atom contributes to the hydrogen bond interaction between HF and pyridine in the ternary FH...Pyridine⊥X-benzene complexes. In each complex there is a coupling between H₁₂ and the H₆ hydrogen atom of the pyridine ring. The values of the coupling constant ${}^3J_{H_{12}-H_6}$ and its components are reported in Table 4. As can be observed, the most important component of ${}^3J_{H_{12}-H_6}$ is DSO. To investigate the effect of coupling between H₁₂ and H₆ on the binding energy of the FH...Pyridine⊥X-benzene

complexes, a correlation between ${}^3J_{H_{12}-H_6}$ and ΔE was considered. The results indicate that an increase in the values of ${}^3J_{H_{12}-H_6}$ is to some extent accompanied by an increase in the binding energy of the FH...Pyridine \perp X-benzene complexes (with the exception of X=Br). Thus, the coupling of atom H₁₂, which contributes to the hydrogen bond interaction, with atom H₆ may be important in the variation of the ΔE values in the above mentioned complexes.

Table 4: The coupling constant ${}^3J_{H_{12}-H_6}$ and its components (in Hz) for the FH...Pyridine \perp X-benzene complexes calculated at the PBE1KCIS/6-311++G** level of theory.

X	FC($\times 10$)	SD($\times 10$)	PSO($\times 1$)	DSO($\times 10$)	J($\times 1$)
NH ₂	0.234	-0.190	-0.285	0.304	0.319
OH	0.215	-0.200	-0.288	0.312	0.315
H	0.257	-0.206	-0.269	0.285	0.314
Cl	-0.057	-0.101	-0.017	0.247	0.310
Br	0.150	-0.178	-0.263	0.349	0.310
NO	0.209	-0.205	-0.304	0.331	0.307

The order of the ${}^3J_{H_{12}-H_6}$ values in the FH...Pyridine \perp X-benzene complexes is as: NO < H < Cl < OH < NH₂ < Br. As can be seen, complexes with electron-donating substituents have higher ${}^3J_{H_{12}-H_6}$ values than those with electron-accepting substituents. Thus, the electron-donating character of substituent X helps to have a better coupling between atoms H₁₂ and H₆ in these complexes. It seems that the electron-donating nature of Br leads to a better coupling between atoms H₁₂ and H₆, while its electron-accepting nature leads to less interaction of Br-benzene with Pyridine...HF and thus to lower binding energy value for the FH...Pyridine \perp Br-benzene complex. The results indicate that the increase in the ${}^3J_{H_{12}-H_6}$ values goes with a decrease in the $r_{N...H}$ distance and also with an increase in the E_{coop} values of the FH...Pyridine \perp X-benzene complexes (with the exception of X=Br).

Population analysis has been performed using the NBO method ^[34] on the optimized FH...Pyridine \perp Br-benzene complexes at the MP2/6-31G** level of theory. The results reveal that there is a good relation between calculated donor-acceptor $E^{(2)}$ interaction energies and ${}^{2h}J_{F-N}$ values. As seen in Figure 4, the increase of $E^{(2)}$ for the transition $n \rightarrow \sigma^*_{HF}$ (where n refers to the lone pair of pyridine) is accompanied by an increase in the ${}^{2h}J_{F-N}$ value. In fact, the increase of $E^{(2)}$ interaction energies leads to a decrease in the $r_{N...H}$ distances. Thus, the strength of the electronic transitions from pyridine to the HF molecule has influence on the values of the two-bond ${}^{19}F-{}^{15}N$ spin-spin coupling constant ${}^{2h}J_{F-N}$.

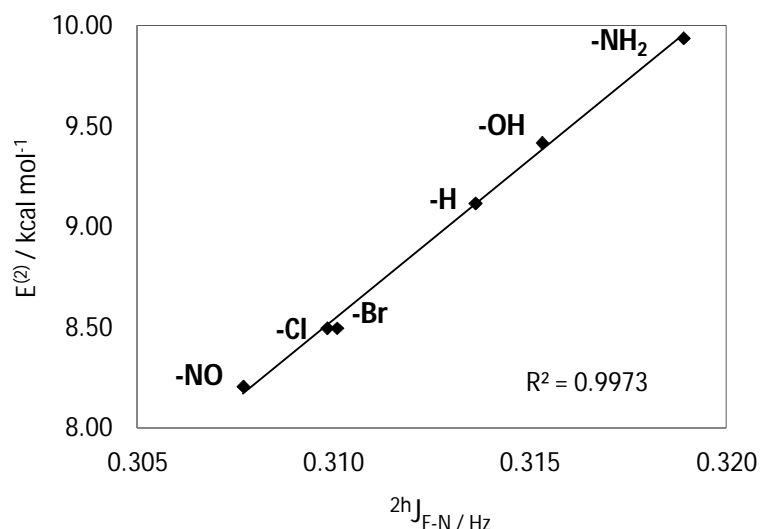


Figure 4: Donor-acceptor $E^{(2)}$ interaction energies for the transition $n \rightarrow \sigma^* \text{HF}$ versus ${}^2hJ_{F-N}$ values.

To connect the NMR data to synergetic effects in the complexes studied, a correlation between ΔIS (H_9) and E_{coop} values was considered. As can be observed in Figure 5, complexes with smaller ΔIS (H_9) have higher E_{coop} values. In fact, pyridine contributes in both hydrogen bond and CH- π interactions in the ternary complexes and has less IS (H_9) values than in the binary complexes in which this molecule takes part showing only CH- π interaction. Consequently, the existence of hydrogen bond between pyridine and HF in the ternary complexes moves the IS (H_9) values and can direct the magnitude of the binding energy values and also synergetic effects in the FH...Pyridine-X-benzene complexes.

In a previously published work by A. Ebrahimi et al., the cooperativity of π -stacking and hydrogen bond interactions has been considered.^[26] However, the NMR properties of the above interactions were not studied. Herein, the FH...Pyridine||X-benzene complexes were optimized at the MP2/6-31G** level of theory for the sake of comparison with the FH...Pyridine-X-benzene complexes. The results show that the binding energies of the FH...Pyridine-X-benzene complexes are larger than those for the FH...Pyridine||X-benzene ones. The order of binding energies (in kcal mol^{-1}) for the FH...Pyridine||X-benzene complexes is NH_2 (1.93) < Cl (2.83) < H (3.68) < OH (8.22) < NO (8.27) < Br (8.82). As can be seen, complexes with electron-withdrawing substituents have larger binding energies than those with electron-donating ones. Also, the NMR properties of the π - π stacking and hydrogen bond interactions in the FH...Pyridine||X-benzene complexes were calculated and presented in Table 5. These data were compared with the NMR properties of the CH- π and hydrogen bond interactions in the FH...Pyridine-X-benzene complexes. The results indicate that in the case of X= NH_2 , H, and Cl, the FC component was found to be the most important component of ${}^2hJ_{F10-N11}$ in the FH...Pyridine||X-benzene complexes, whereas the PSO

component was found to be the most important component of ${}^2\text{h}J_{\text{F10-N11}}$ in these complexes in the case of X= OH, NO, and Br. Moreover, the increase of ${}^2\text{h}J_{\text{F10-N11}}$ values of the FH...Pyridine||X-benzene complexes was found to be accompanied by an increase in the ΔE values. As a result, the increase in the ${}^2\text{h}J_{\text{F10-N11}}$ values for both FH...Pyridine \perp Br-benzene and FH...Pyridine||X-benzene complexes was found to be accompanied by an increase in the binding energies of these ternary complexes.

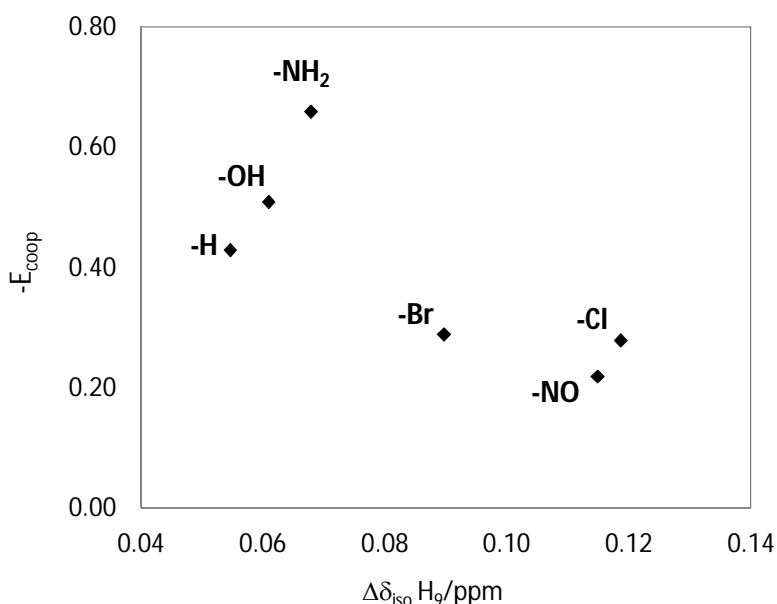


Figure 5: Correlation between $\Delta\text{IS} (\text{H}_g)$ and E_{coop} values.

Table 5: The coupling constant ${}^2\text{h}J_{\text{F10-N11}}$ and its components (in Hz) for the FH...Pyridine||X-benzene complexes.

X	FC($\times 10^{-1}$)	SD($\times 10^{-1}$)	PSO($\times 10^{-1}$)	DSO($\times 10^{-1}$)	J($\times 10^{-1}$)
NH ₂	-0.271	-0.006	0.010	0.795	-0.169
OH	-0.167	0.108	0.236	0.764	0.184
H	-0.277	-0.006	0.101	0.797	-0.175
Cl	-0.285	-0.007	0.099	0.808	-0.184
Br	-0.176	0.107	0.238	0.775	0.177
NO	-0.170	0.100	0.235	0.771	0.173

Conclusions

The present work investigates the NMR properties of the hydrogen bond and CH- π interactions in the FH...Pyridine \perp X-benzene complexes. The results show that there is a good relationship between $\Delta\text{IS} (\text{H}_g)$ and the binding energy. A linear correlation was observed between the two-bond ${}^{19}\text{F}$ - ${}^{15}\text{N}$ spin-spin coupling constant ${}^2\text{h}J_{\text{F10-N11}}$ and the $r_{\text{N}\dots\text{H}}$ distances. The most important component of ${}^2\text{h}J_{\text{F10-N11}}$ in the FH...Pyridine \perp X-benzene complexes is thereby the FC component. A linear relationship with a good correlation coefficient between ${}^2\text{h}J_{\text{F10-N11}}$ and the Hammett

constants of the substituent X in the FH...Pyridine⊥X-benzene complexes was obtained.

When compared with the FH...Pyridine||X-benzene complexes, the binding energy of the corresponding FH...Pyridine⊥X-benzene complexes was found to be larger. The most important component of $^{2h}J_{F_{10}-N_{11}}$ in the FH...Pyridine||X-benzene complexes was found in the case of X= NH₂, H, and Cl to be the FC component whereas in the case of X= OH, NO, and Br, the PSO component was found to be the most important component. The coupling between the $^{19}F_{10}$ and $^{15}N_{11}$ atoms makes a positive effect on the binding energies of both the FH...Pyridine⊥X-benzene and the FH...Pyridine||X-benzene complexes.

Acknowledgment

We thank The Research Consul of University of Zabol for financial support.

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