

Research Article

Study of the Halogen Bonding between Pyridine and Perfluoroalkyl Iodide in Solution Phase Using the Combination of FTIR and ^{19}F NMR

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Halogen bonding between pyridine and heptafluoro-2-iodopropane (iso-C₃F₇I)/heptafluoro-1-iodopropane (1-C₃F₇I) was studied using a combination of FTIR and ^{19}F NMR. The ring breathing vibration of pyridine underwent a blue shift upon the formation of halogen bonds with both iso-C₃F₇I and 1-C₃F₇I. The magnitudes of the shifts and the equilibrium constants for the halogen-bonded complex formation were found to depend not only on the structure of the halocarbon, but also on the solvent. The halogen bond also affected the C_α-F (C-F bond on the center carbon) bending and stretching vibrations in iso-C₃F₇I. These spectroscopic effects show some solvent dependence, but more importantly, they suggest the possibility of intermolecular halogen bonding among iso-C₃F₇I molecules. The systems were also examined by ^{19}F NMR in various solvents (cyclohexane, hexane, chloroform, acetone, and acetonitrile). NMR dilution experiments support the existence of the intermolecular self-halogen bonding in both iso-C₃F₇I and 1-C₃F₇I. The binding constants for the pyridine/perfluoroalkyl iodide halogen bonding complexes formed in various solvents were obtained through NMR titration experiments. Quantum chemical calculations were used to support the FTIR and ^{19}F NMR observations.

1. Introduction

Halogen bonding, a noncovalent interaction between a halogen atom acting as an electron acceptor and an electron-rich Lewis base, has been known for nearly 150 years [1–6]. However, only recently has halogen bond started to attract wide-spread attention among scientists in a diversity of fields. Metrangolo and coworkers have reviewed the basic concepts as well as the major applications of the halogen bond [7, 8]. Examples include a wide range of applications in separation science, synthesis of liquid crystals and electronic materials, and the assembly of functional super molecules [9–18]. Recently, Meyer and Dubois [19] highlighted the application of halogen bonding to the synthesis of functional materials such as liquid crystal, nonlinear optical, magnetic conducting material, and halogen bonding based surface modification. A review by Beale et al. [20] provides an informative summary

of solution thermodynamics and applications of halogen bonding. Of particular importance are their presentations of detailed thermodynamic parameters measured for the halogen bonding systems made of organic donors and halogen anions in the solution phase and which emphasized their importance in the anion recognition. Erdélyi [21] reviewed the nature of halogen bonding in solution phase and summarized the techniques that have been used to study the halogen bond in solution.

Using a jet cooled molecular beam, combined with the Fourier-transform microwave spectroscopy, Legon has investigated the geometry and the stability of some halogen bonding complexes in the gas phase through the analysis of their rotational spectra [22, 23]. This research has allowed the detailed comparison of halogen and hydrogen bonding. It was pointed out that halogen bonds can be as strong as or slightly weaker than hydrogen bonds, depending on

the structures of the participating component molecules. While hydrogen bonds can adopt a variety of angles, halogen bonds are mostly linear relative to the halogen, the donor atom, and their covalently bonded substrates. This is due to the large electrostatic anisotropy of the halogen, which is highly localized along the extension of the carbon-halogen bond.

Halogen bond was first recognized in dihalide-containing complexes, but it is now understood that other halogen containing species can also act as electron acceptors [24–33]. When the halogens are bound to an electron-withdrawing moiety, the positive potential on the halogen atom is enhanced and the potential for halogen bonding is increased. In addition, halogen bonding ability increases with increasing the size of the halide because of the increase in the polarizability. Thus, iodine forms the strongest halogen bonds. For these reasons, perfluoroalkyl iodides have been often chosen to be the halogen donors in most halogen bonding studies. Fluorinated organoiodides have several scientific and industrial uses, including pharmaceuticals and nanoscience applications [34–39]. For example, halogen bond between perfluorobenzene iodide and pyridine containing molecules has recently been used to assemble gold nanoparticles [40].

As it is experimentally challenging to directly measure the strength of the halogen bond in a particular system, most research in the field has been focused on the geometry and structural impact. Like hydrogen bond [41, 42], halogen bond often leads to observable changes in the vibrational spectra of the participating molecules. Focusing on the halogen bond impact on the perfluoroalkyl iodide, Messina et al. [43] led the study of the systems between α , ω -diiodoperfluoroalkanes, and other electron donors using FTIR and Raman spectroscopy. According to the noisy light Coherent Anti-Stokes Raman Scattering Spectroscopy ($I^{(2)}$ CARS) [44], halogen bond between pyridine and perfluoroalkyl iodide causes the ring breathing vibration of pyridine to be blue shifted. The magnitude of the shift was comparable with that observed in the hydrogen bonding system between pyridine and water. Using FTIR and Raman spectroscopy, Van der Veken et al. [45–48] have studied the effect of halogen bond between CF_3X ($X = Cl, Br, I$) and various electron lone pair donors on the vibrations of the participants. The complexation enthalpies were determined based on the temperature dependence of the bond association constants. An *ab initio* calculation at the MP2/aug-cc-pVDZ(-PP) level was also performed to be compared with the spectroscopic observation. In addition to Raman and FTIR spectroscopy, ^{19}F NMR is another sensitive method to detect the halogen bond between perfluoroalkyl halides (PFC-iodide or bromide) and Lewis bases [49–52]. The change in the chemical shift upon halogen bonding was found to be the greatest on the alpha fluorine signals. Thus, both vibrational spectroscopy and ^{19}F NMR are useful tools for the investigation of halogen bond in solution.

Considering that halogen bond is one of the strongest noncovalent intermolecular forces, the thermodynamics in the halogen bonding formation have also been received attention. Fan and coworkers [44] studied the pyridine and perfluoroalkyl iodides. Their observations led to a hypothesis

that there existed some self-intermolecular halogen bond among iso- C_3F_7I molecules in the liquid phase, while this self-intermolecular halogen bond did not exist or at least was very weak for 1- C_4F_9I and 1- $C_6F_{13}I$.

It has been long believed that the magnitude of the vibrational frequency shift in the hydrogen bonded complex is proportional to the strength of the hydrogen-bond [53]. In other words, the magnitude of the vibrational frequency shift is correlated with the complexation enthalpies. It is reasonable to apply the same principle to the halogen bond. Therefore, FTIR results provide information about enthalpy change in the halogen bond formation. On the other hand, ^{19}F NMR titration experiments provide information about binding constants and thereby changes in the Gibbs free energy during halogen bond formation. As a result, the comparison between the FTIR and ^{19}F NMR results makes it possible to derive the contribution of entropy to the halogen bond formation.

Using the combination of ^{19}F NMR and theoretical calculations, Sarwar and coworkers [52] examined the thermodynamics of halogen bonding in iodoperfluoroarenes involved solution system with respect to substituent, structural, and solvent effects. The experimental results were compared with the density functional theory (DFT) calculations [52] in order to be able to model the supermolecular interactions for drug design.

Whether in a liquid phase binary system or in solution, halogen bonding may play very important roles in defining the structure of the liquid and solution. Inspired by previous work, the present paper seeks to determine if halogen bond exists among molecules of perfluoroalkyl iodides. Based on the hypothesis by Fan et al. [44], the intermolecular halogen bond among iso- C_3F_7I molecules, a secondary iodide, should be stronger than those formed among molecules of primary iodides (e.g., 1- C_4F_9I , 1- $C_6F_{13}I$). In order to test this argument, the present work uses a combination of FTIR and ^{19}F NMR to quantify the halogen bonding between pyridine and iso- C_3F_7I /1- C_3F_7I in various solvents. First, the strength of halogen bond is compared between pyridine/iso- C_3F_7I and pyridine/1- C_3F_7I . Second, for the same halogen bonding system, the strength is compared in different solvents. Third, a series of dilution experiments were performed using both FTIR and ^{19}F -NMR to gather evidence of intermolecular self-halogen bond. Finally, the thermodynamics of the halogen bond for the system between pyridine and perfluoroalkyl iodides in solution phase was studied using the combination of the results from FTIR and ^{19}F NMR measurements.

2. Experimental Section

2.1. Chemicals and Regents. All reagents and solvents were purchased from commercial houses. All solvents were purchased as anhydrous or used immediately after dispensing from a solvent purification system.

2.2. FTIR and ^{19}F NMR Measurement. FTIR spectra were recorded on a PerkinElmer Paragon 500 FTIR spectrometer. All the measurements were carried out at the room

temperature, and the corresponding solvents were used to record the background spectra. A liquid sample holder with a NaCl windows was used, and the resolution of the FTIR spectrometer was set at 1 cm^{-1} during experiments. ^{19}F NMR spectra were recorded on a Varian 400MR 400 MHz High-Field Superconducting NMR spectrometer. 1.00 M KF solution in D_2O was used in each measurement as an external reference for ^{19}F NMR.

2.3. Theoretical Calculations. All computations were performed with the Gaussian 03 or Gaussian 09 [54, 55] suite of programs. The interaction energies and geometrical parameters in solution phase were computed using the DFT method with the functional M052X and the aug-cc-pVDXZ basis set for all atoms except iodine, where a pseudopotential was required (aug-cc-pVDXZ-PP) [56]. Geometry optimizations for monomer and dimer of iso- $\text{C}_3\text{F}_7\text{I}$, 1- $\text{C}_3\text{F}_7\text{I}$, as well as the hydrogen bonding complex between iso- $\text{C}_3\text{F}_7\text{I}/1\text{-C}_3\text{F}_7\text{I}$ and CHCl_3 in vacuum phase were performed with density function theory (DFT) using 3-21G-B3LYP, CalcAll, and the tight convergence criteria. The calculations of ^{19}F NMR were performed using the optimized geometry.

3. Result and Discussion

3.1. Comparison of Halogen Bonding Strength and Solvent Effect between Pyridine/Iso- $\text{C}_3\text{F}_7\text{I}$ and Pyridine/1- $\text{C}_3\text{F}_7\text{I}$. According to previous work using $\text{I}^{(2)}\text{CARS}$, halogen bond between pyridine and perfluoroalkyl iodides in the liquid phase binary system led the ring breathing vibration frequency of pyridine blue shift by 7.8, 7.6, and 9.7 cm^{-1} for 1- $\text{C}_4\text{F}_9\text{I}$, 1- $\text{C}_6\text{F}_{13}\text{I}$, and iso- $\text{C}_3\text{F}_7\text{I}$, respectively [44]. Using FTIR, the present work showed similar impact of halogen bond between pyridine and iso- $\text{C}_3\text{F}_7\text{I}/1\text{-C}_3\text{F}_7\text{I}$ in the solution phase. The ring breathing vibration of pyridine was found to be blue shifted on the formation of halogen bonding complex with iso- $\text{C}_3\text{F}_7\text{I}$ and 1- $\text{C}_3\text{F}_7\text{I}$. According to Table 1, the blue shift of $9 \pm 1\text{ cm}^{-1}$ observed for pyridine/iso- $\text{C}_3\text{F}_7\text{I}$ in acetonitrile (0.4 M) is comparable with the shift observed for the same donor/receiver in the binary system. The difference in the magnitude of blue shift between liquid binary system and the solution phase is caused by the solvent rather than the concentration of the solute. As shown in Table 1, for the same solvent, the ring breathing vibration of pyridine shows greater blue shift for the pyridine/iso- $\text{C}_3\text{F}_7\text{I}$ system than that for the pyridine/1- $\text{C}_3\text{F}_7\text{I}$ system. This indicates that pyridine forms stronger halogen bond with iso- $\text{C}_3\text{F}_7\text{I}$ than with 1- $\text{C}_3\text{F}_7\text{I}$ regardless of the solvent used. This is also consistent with the ^{19}F NMR results by Metrangolo et al. [49, 50] using perfluoroalkyl iodide involved in a halogen bonding system where secondary iodide invariably was found to give larger change in the F chemical shift than a primary iodide. It was pointed out [57] that perfluorinated chains were stronger electron-withdrawing residues and more sterically demanding than fluorine atoms. Consequently, the carbon connected to iodine in iso- $\text{C}_3\text{F}_7\text{I}$ is more electropositive than the carbon connected to iodine in 1- $\text{C}_3\text{F}_7\text{I}$. The same principle can be applied to the liquid phase binary system described by Fan et al. [44].

TABLE 1: The magnitudes of the frequency blue shift in the ring breathing vibration of pyridine on the formation of halogen bonding with iso- $\text{C}_3\text{F}_7\text{I}/1\text{-C}_3\text{F}_7\text{I}$ in various solvents (the concentrations of pyridine and perfluoroalkyl iodide are 0.2 M in all the solutions).

Solvent	Iso- $\text{C}_3\text{F}_7\text{I}$	1- $\text{C}_3\text{F}_7\text{I}$
Cyclohexane	$8 \pm 1\text{ cm}^{-1}$	$6 \pm 1\text{ cm}^{-1}$
Hexane	$8 \pm 1\text{ cm}^{-1}$	$6 \pm 1\text{ cm}^{-1}$
Chloroform	$5 \pm 1\text{ cm}^{-1}$	$4 \pm 1\text{ cm}^{-1}$
Acetone	$9 \pm 1\text{ cm}^{-1}$	$7 \pm 1\text{ cm}^{-1}$
Acetonitrile	$9 \pm 1\text{ cm}^{-1}$	$6 \pm 1\text{ cm}^{-1}$

For the same system, the magnitude of the frequency blue shift depended on the solvents used. The magnitude of shifts seems to be associated with the polarity of the solvent as well as the potential competitive intermolecular interactions between solvent molecules and the halogen bonding precursors (Table 1). Chloroform, acetone, and acetonitrile can all provide an electron lone pairs for the potential halogen bond with perfluoroalkyl iodides. On one hand, chloroform has been observed to form hydrogen bonds with pyridine [42]. Moreover, chloroform can potentially form hydrogen bonds with the fluorine in perfluoroalkyl iodide [58]. The combination of these effects may explain the smallest blue shift of ring breathing vibration of pyridine in chloroform among all the solvents used. Except for chloroform, the ring breathing vibration of pyridine in its halogen bonding complexes with perfluoroalkyl iodides shows larger blue shifts in polar solvents, indicating that the halogen bonding complexes between pyridine and perfluoroalkyl iodides can be stabilized by the polar solvents.

3.2. Impact of Halogen Bonding on Iso- $\text{C}_3\text{F}_7\text{I}$. The halogen bond between pyridine and a perfluoroalkyl iodide not only leads to the vibration frequency shift in pyridine molecule but also affects the vibrations of the perfluorocompounds. Previous research [43] indicated that the C-I stretching and $\text{C}_\alpha\text{-F}$ stretching vibration frequency experienced a red shift while a perfluoroalkyl iodide is engaged in halogen bonding. When the iso- $\text{C}_3\text{F}_7\text{I}$ was mixed with pyridine solution in cyclohexane, the infrared spectra were recorded. Figure 1 shows that in cyclohexane solution, the vibration of iso- $\text{C}_3\text{F}_7\text{I}$ at 1113 cm^{-1} and 1168 cm^{-1} were both red shifted on the formation of halogen bond with pyridine. Based upon quantum mechanical frequency calculations, we assigned the vibration of iso- $\text{C}_3\text{F}_7\text{I}$ observed at 1113 cm^{-1} to the $\text{C}_\alpha\text{-F}$ stretching involved vibration (predicted to come $\sim 1106\text{ cm}^{-1}$). The vibration at 1168 cm^{-1} was assigned to the $\text{C}_\beta\text{-F}$ stretching involved vibration (predicted to come at 1165 cm^{-1}). Calculations (DFT and MP_2), performed by Valerio et al., indicated that the halogen bond between NH_3 and CF_3I led to the elongation of C-F bond. This was attributed to charge-transfer involving antibonding LUMO orbitals in the CF_3I molecule [57]. This explains why the frequency of $\text{C}_\alpha\text{-F}$ stretching exhibited some red shift when the iodine in iso- $\text{C}_3\text{F}_7\text{I}$ is engaged in the halogen bond with pyridine. The frequency red shift observed the for $\text{C}_\beta\text{-F}$ involving stretching indicated that the fluorine connected to C_β might play certain roles in the

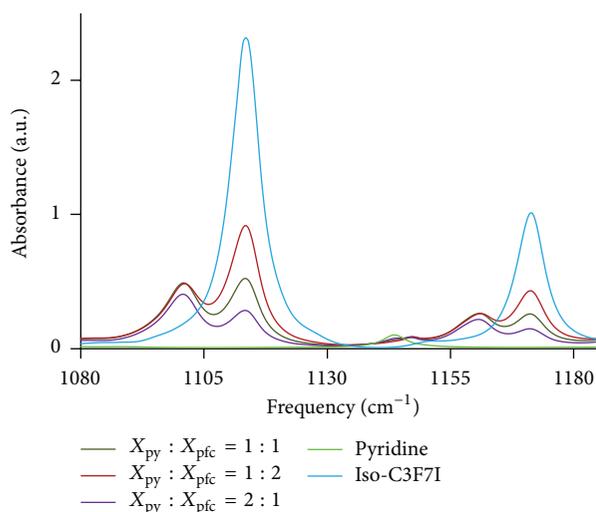


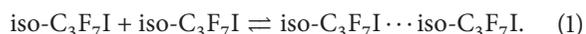
FIGURE 1: FTIR absorbance of C_{α} -F stretching involved vibration in iso- C_3F_7I upon the formation of halogen bonding with pyridine in cyclohexane (X_{py} and X_{pfc} denote the molar fractions of pyridine and that of iso- C_3F_7I).

halogen bonding complexes. Similar shift patterns about C_{α} -F were observed for the systems acetone/iso- C_3F_7I , triethylamine/iso- C_3F_7I , and acetonitrile/iso- C_3F_7I in cyclohexane, indicating that acetone, acetonitrile, and triethylamine can form halogen bond with iso- C_3F_7I . However, the mixture of chloroform and iso- C_3F_7I did not show the red shift in the C_{α} -F stretching vibration. This suggests that the halogen bond between iso- C_3F_7I and $CHCl_3$ is weaker than both halogen bond between iso- C_3F_7I and iso- C_3F_7I and the hydrogen bond between iso- C_3F_7I and $CHCl_3$.

While the vibration of iso- C_3F_7I was significantly affected by halogen bond, the FTIR spectra of various 1- C_3F_7I halogen bonding systems did not show similar shifts. We suggest that the vibrations of 1- C_3F_7I are not as sensitive as those of iso- C_3F_7I to halogen bond formation, as discussed below.

3.3. Dilution of Iso- C_3F_7I with Various Solvents. The effect of halogen bonding on the C_{α} -F stretching involved vibration of iso- C_3F_7I does not provide direct evidence for the intermolecular self-halogen bonding among the molecules of iso- C_3F_7I . Therefore, the dilution experiments with some halogen bonding inactive solvents were performed.

The intermolecular self-halogen bond between two iso- C_3F_7I molecules can be expressed with the following equation (1), where one molecule uses its iodine atom and the other uses its alpha fluorine atom to form the halogen bond:



The dilution test will cause the equilibrium above to shift to left; that is, the amount of iso- C_3F_7I engaged in the self-halogen bond will decrease and the amount disengaged from the self-halogen bond will increase upon dilution. The dilution test was performed first with cyclohexane, and the results were summarized in Figure 2. According to the geometry optimization calculations for iso- C_3F_7I in vacuum (DFT/3-21GB3LYP/CalcAll), the vibration absorption at $\sim 900 \text{ cm}^{-1}$

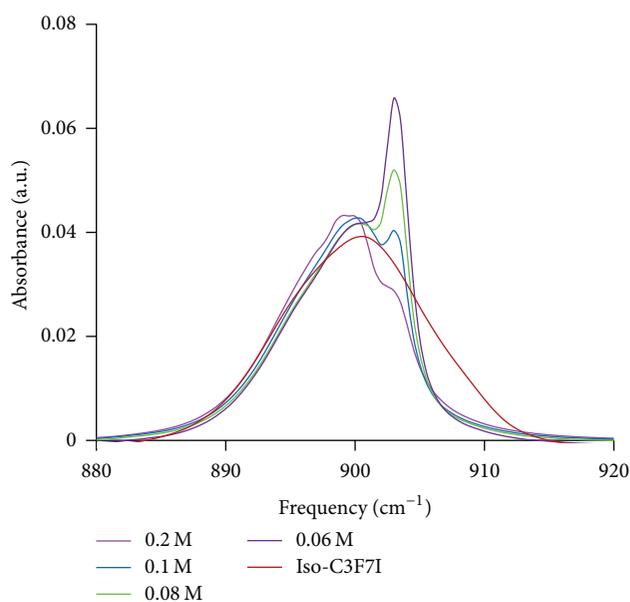


FIGURE 2: FTIR absorbance of C_{α} -F bending involved vibration in iso- C_3F_7I upon dilution with cyclohexane.

shown in Figure 2 is a C_{α} -F bending involved vibration. This peak is very broad in pure iso- C_3F_7I , resolving into two components as the dilution was carried out. Moreover, the component at higher frequency becomes more intense as the dilution proceeds. A theoretical calculation was performed for a dimer of iso- C_3F_7I in vacuum. The results showed that the C_{α} -F bending involved vibration at $\sim 900 \text{ cm}^{-1}$ split into two (899.95 cm^{-1} and 905.08 cm^{-1}). The one at the lower frequency corresponds to the C_{α} -F engaged in the halogen bonding, and the one at the higher frequency is correlated with the C_{α} -F free of the halogen bonding. This is perfectly consistent with the observation in Figure 2. As the dilution proceeds, the amount of nonhalogen bonded C_{α} -F increases and leads to a relative intensity increase of the component at the higher frequency.

Figure 3 shows dilution of iso- C_3F_7I in various solvents. Both acetone and acetonitrile form halogen bonds with iso- C_3F_7I ; consequently the spectra in these solvents show primarily isolated fluorocarbon with little or no indication of self-halogen bond. Hexane, on the other hand, does not have a significant influence on the equilibrium between the self-halogen bonded complex and the isolated iso- C_3F_7I . As a result, the dilution with hexane exhibited mainly the C_{α} -F bending vibration in an aggregation of iso- C_3F_7I . In chloroform, the C_{α} -F bending involved vibration peaked at the same position with that in hexane. This suggests that chloroform formed a hydrogen bond with the alpha fluorine in iso- C_3F_7I . The hydrogen bond between iso- C_3F_7I and chloroform is supported by the geometry optimization calculation for the iso- C_3F_7I -chloroform system in vacuum.

The vibrational spectra of 1- C_3F_7I were not only insensitive to the halogen bond between 1- C_3F_7I and various halogen bonding acceptors, they were also insensitive to the dilution tests. Theoretical calculation suggests that the self-halogen bond in vacuum between two 1- C_3F_7I molecules

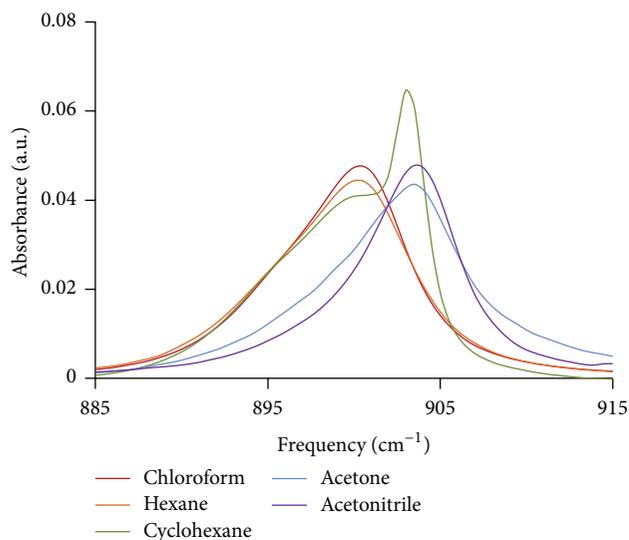


FIGURE 3: FTIR absorbance of C_{α} -F bending involved vibration in iso- C_3F_7I upon dilution with various solvents (the concentrations of iso- C_3F_7I in various solvents are 0.06 M).

(3.68 kcal/mol) is weaker than that between two iso- C_3F_7I molecules (4.86 kcal/mol). In addition, while there is only one alpha fluorine in iso- C_3F_7I , there are two in 1- C_3F_7I . We suggest that this further decreases any impact that the weaker halogen bond might have on the $C-F_{\alpha}$ bending frequency, rendering it undetectable in the FTIR spectrum at the present resolution.

3.4. ^{19}F NMR Dilution Experiments. The ^{19}F NMR spectra of both iso- C_3F_7I and 1- C_3F_7I were collected in various solvents. A sealed capillary tube filled with KF/D_2O solution and placed in the NMR sample tube was used as an internal reference for each measurement. The ^{19}F NMR spectrum of iso- C_3F_7I is straightforward. While a triplet at -79 ppm represents the resonance of fluorine in the CF_3 group, the pentet at -153 ppm is the resonance of the alpha fluorine. Two triplets at -83 ppm and -122 ppm and nonets at -67 ppm were identified in the ^{19}F NMR spectrum of 1- C_3F_7I . The assignment of this spectrum is rather tricky. Generally, the coupling constant J_{ij} decreases dramatically as the number of chemical bonds separating nuclei i and j increases. In the case of 1- C_3F_7I , however, the alpha fluorine shows a strongest coupling with the gamma fluorine in CF_3 group [59]. When combined with the coupling of the beta fluorine in CF_2 group, the resulting nonet was assigned as the alpha fluorine (the fluorine germinal to iodine) resonance. On the other hand, the coupling constant $J_{\beta\alpha}$ is much larger than the coupling constant $J_{\beta\gamma}$. Thus, the beta fluorine appears as triplet at -122 ppm [59].

The dilution of iso- C_3F_7I and 1- C_3F_7I was performed in hexane, cyclohexane, chloroform, acetone, and acetonitrile. The ^{19}F NMR spectra were collected over the concentration range of 0.04 M to 4 M. The plot of $\Delta\delta = \delta_{\text{solution}} - \delta_{\text{pure iso-}C_3F_7I/1-C_3F_7I}$ versus the concentration in hexane, cyclohexane, chloroform, acetone, and acetonitrile is shown

in Figures 4, 5, 6, 7, and 8, respectively. In all the solvents, the chemical shift of beta and gamma fluorine showed a consistent upfield shift of NMR frequency upon dilution. In the dilution with hexane, the chemical shift of all alpha, beta, and gamma fluorine displayed a similar trend. In the dilutions with other solvents, the change in the chemical shift of alpha fluorine(s) exhibited a different trend from that of beta and gamma fluorine. While the upfield shift of beta and gamma fluorine upon dilution can be attributed to the impact of screening constant σ_0 , determined mainly by the regular solvent effect, the trend in the chemical shift of alpha fluorine indicates that the local diamagnetic screen constant σ_d is responsible for the shielding parameter change of the alpha fluorine upon dilution.

The local diamagnetic screen constant σ_d depends on the electronic structure in the immediate vicinity of the fluorine atom, so the chemical shift in the ^{19}F NMR signal should experience the greatest change if the fluorine atom directly participates in the halogen bond or is next to the halogen bonding donor iodine. Previous work on ^{14}N NMR indicated that the donation of the electron lone pair by nitrogen in the halogen bond relationship led to more shielding of nitrogen [49]. Similarly, the alpha F, when involved in self-halogen bond as an electron lone pair donor, will be subject to more shielding. This is consistent with the results from theoretical calculations (NMR calculations for a dimer in vacuum, based on the optimized geometry), which showed that the fluorine engaged in halogen bonding is more shielded than the fluorine free of halogen bonding. The difference in the shielding parameters between the F involved in halogen bond and the F free of halogen bond is similar for iso- C_3F_7I and 1- C_3F_7I . This also explains the similar results observed in ^{19}F NMR dilution tests between iso- C_3F_7I and 1- C_3F_7I . The unified dilution trends among fluorine chemical shifts in the dilution with hexane indicated that dispersion forces were insufficient to break down the self-halogen bonded complex. On the other hand, cyclohexane provides stronger dispersion forces, because the ring shape allows for a larger area of contact. Thus, the dilution of both 1- C_3F_7I and iso- C_3F_7I using cyclohexane leads to the dissociation of self-halogen bonded complex. As the dilution proceeded, more alpha fluorine disengaged the halogen bonding and became less shielding, leading to a downfield shift of the NMR frequency. This downfield shift because of the dissociation of self-halogen bonding complex counteracted the up-field shift from the general dilution effect. As a result, the $\Delta\delta$ ($\Delta\delta = \delta_{\text{solution}} - \delta_{\text{pure 1-}C_3F_7I}$ or $\Delta\delta = \delta_{\text{solution}} - \delta_{\text{pure iso-}C_3F_7I}$) values for the alpha fluorine in both 1- C_3F_7I and iso- C_3F_7I are smaller than those of beta and gamma fluorine when they are diluted with cyclohexane.

As for the dilution with chloroform, it was proposed earlier and by theoretical calculation that chloroform formed hydrogen bond with alpha fluorine in iso- C_3F_7I . Additionally, our calculations showed that hydrogen bonds can also be formed between the alpha fluorine in 1- C_3F_7I and chloroform. Moreover, formation of hydrogen bond made the alpha fluorine less shielding, causing a downfield shift of the NMR

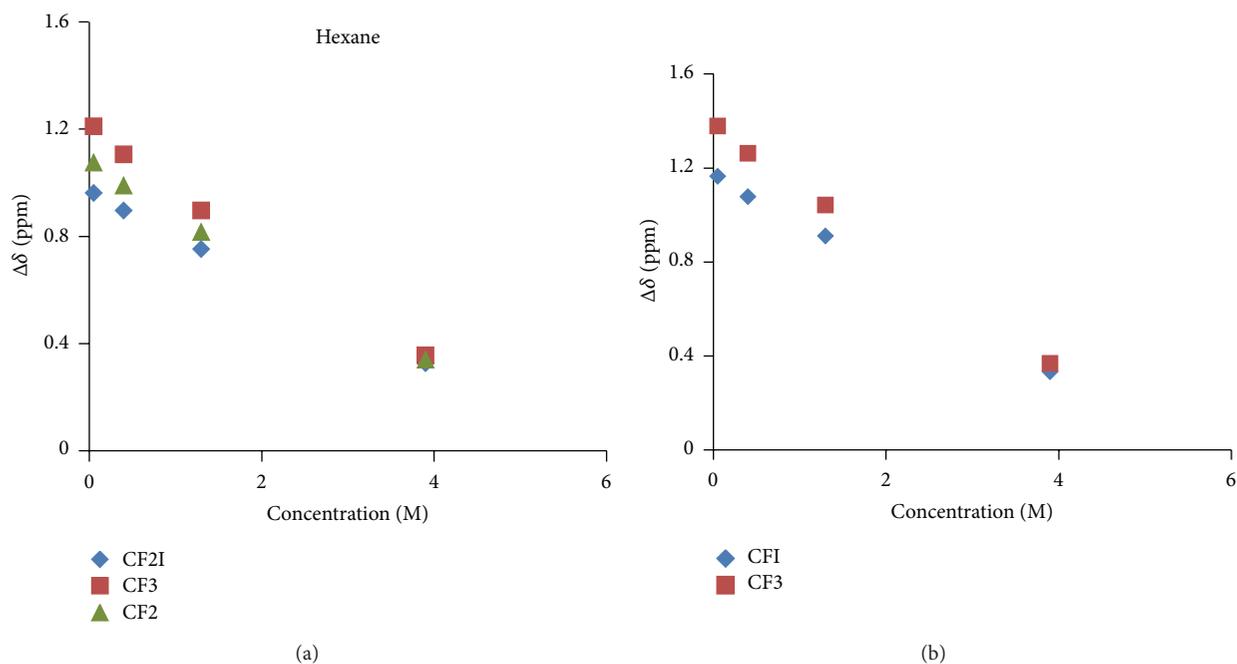


FIGURE 4: Change in the chemical shift of ¹⁹F in the perfluoroalkyl iodides upon dilution with hexane (from Figure 4 to Figure 8, the upper panel is for 1-C₃F₇I, the lower panel is for iso-C₃F₇I, $\Delta\delta = \delta_{\text{solution}} - \delta_{\text{pure 1-C}_3\text{F}_7\text{I}}$ for 1-C₃F₇I, and for iso-C₃F₇I, $\Delta\delta = \delta_{\text{solution}} - \delta_{\text{pure iso-C}_3\text{F}_7\text{I}}$).

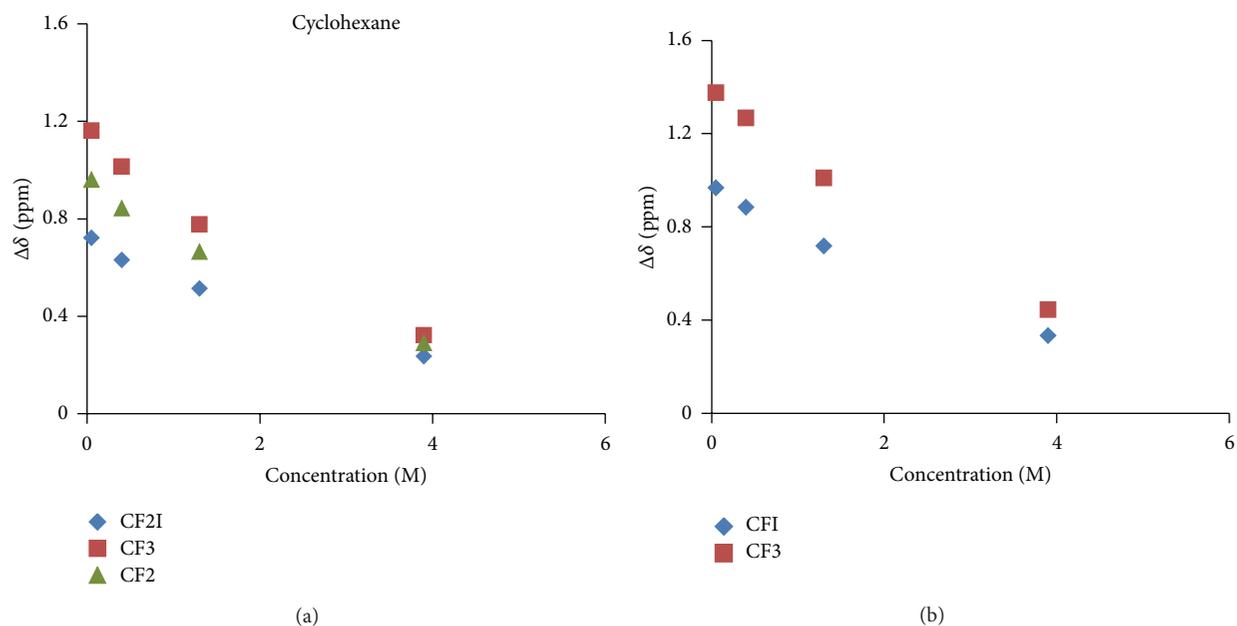


FIGURE 5: Change in the chemical shift of ¹⁹F in the perfluoroalkyl iodides upon dilution with cyclohexane.

frequency. The same effect is brought by the dissociation of self-halogen bonded complex. As a result, the ¹⁹F NMR dilution tests in chloroform showed some similar alpha fluorine trend to the ones in cyclohexane. In the ¹⁹F NMR study of 2'-F-2'-deoxyarabinoflavoproteins [60], the chemical shift of fluorine moves to a higher frequency when the fluorine atom donated its electron lone pair in hydrogen bond.

While the dilution was performed using acetone and acetonitrile, the solvent molecules are not only able to dissociate the self-halogen bonded complex, but also to form halogen bond with the iodine in both iso-C₃F₇I and 1-C₃F₇I. Both of these effects make the alpha fluorine less shielding and a larger downfield shift of the NMR frequency. As a result, the $\Delta\delta$ value became negative upon dilution.

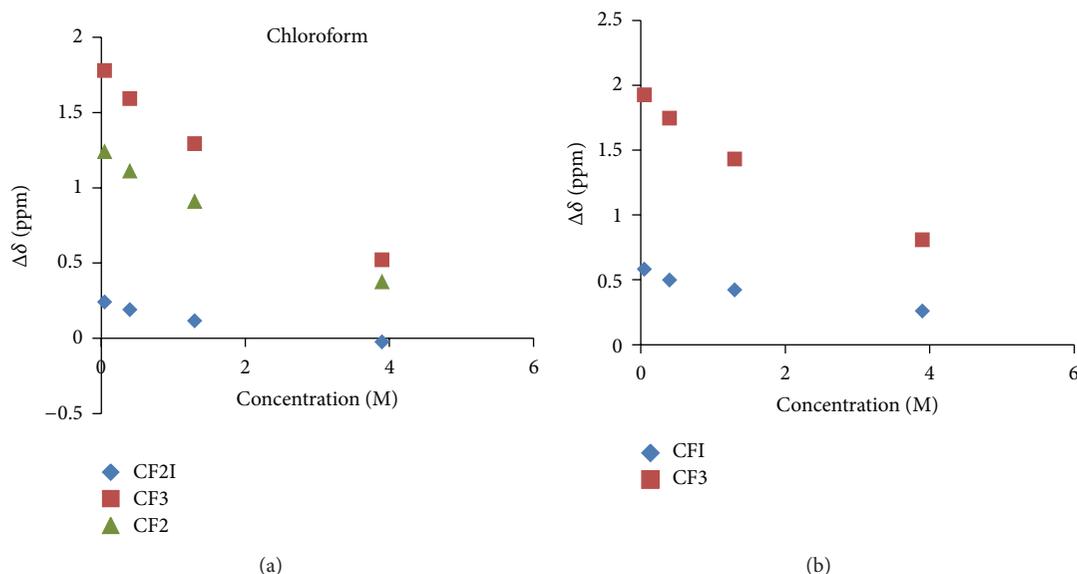


FIGURE 6: Change in the chemical shift of ^{19}F in the perfluoroalkyl iodides upon dilution with chloroform.

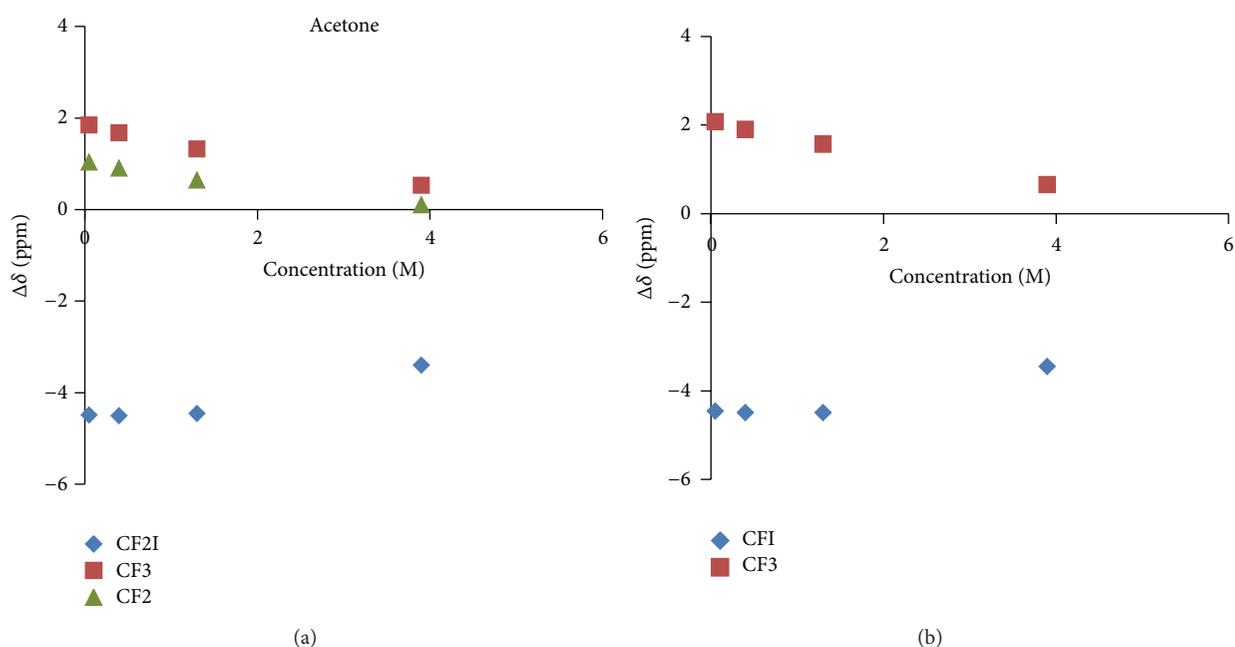


FIGURE 7: Change in the chemical shift of ^{19}F in the perfluoroalkyl iodides upon dilution with acetone.

3.5. ^{19}F NMR Titration and the Halogen Bonding Association Constants for Pyridine/Iso- $\text{C}_3\text{F}_7\text{I}$ (1- $\text{C}_3\text{F}_7\text{I}$) in Various Solvents. ^{19}F NMR titration experiments were performed to determine the equilibrium constants for the halogen bonding complex formed between pyridine and perfluoroalkyl iodides in various solvents (Table 2). These data indicate that the association between pyridine and perfluoroalkyl iodides is more favorable in nonpolar solvents such as hexane and cyclohexane. According to Table 1, the halogen bond formed between pyridine and perfluoroalkyl iodides caused the largest blue shift of pyridine ring breathing vibration in acetone. However, the halogen bonding association constants obtained in acetone

and acetonitrile are among the lowest values. In Table 1, the magnitudes of the frequency shift in the ring breathing vibration of pyridine are greater in polar solvents than those in nonpolar solvents. This indicates that the enthalpy change for the halogen bonding formation is more negative in polar solvents than in non-polar solvents. On the other hand, in Table 2, the halogen bonding association constants are greater in nonpolar solvents than those in polar solvents. In other words, the changes in Gibbs free energy are more negative in nonpolar solvents than those in polar solvents. The only way to rationalize this observation is to consider the contribution of entropy change in the formation of halogen bonds.

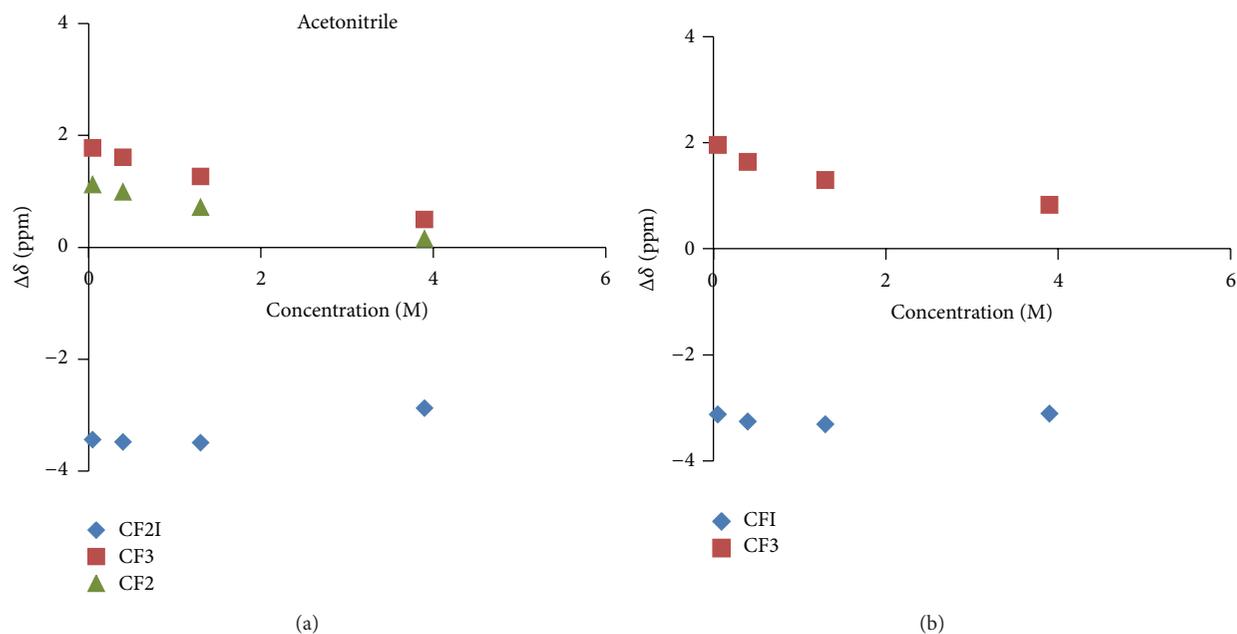


FIGURE 8: Change in the chemical shift of ^{19}F in the perfluoroalkyl iodides upon dilution with acetonitrile.

The overall entropy change in the formation of halogen bond between pyridine and perfluoroalkyl iodides in different solvents depends on whether the molecules of perfluoroalkyl iodides stay as an aggregation through self-halogen bond or isolated through hydrogen/halogen bonding with solvent molecules. In the non-polar solvents like cyclohexane and hexane, where perfluoroalkyl iodides mostly stay as an aggregation, the formation of halogen bond between pyridine and perfluoroalkyl iodides results in a significant increase in entropy. In polar solvents like chloroform, acetone, and acetonitrile, where both perfluoroalkyl iodides and pyridine have tendency to form halogen or hydrogen bond with solvent molecules, the formation of halogen bond between pyridine and perfluoroalkyl iodides does not necessarily lead to an increase in entropy and sometimes can even lead to an entropy decrease. After all, in the nonpolar solvents, the contribution from the positive entropy change compensates or even overrides the less negative enthalpy change in the formation of halogen bond between pyridine and perfluoroalkyl iodides. Thus, the overall larger halogen bonding association constants were observed in the nonpolar solvents than in the polar solvents.

4. Conclusion

The combination of FTIR and ^{19}F NMR indicated that intermolecular self-halogen bond among the molecules of iso- $\text{C}_3\text{F}_7\text{I}$ and 1- $\text{C}_3\text{F}_7\text{I}$ is present in several solvents. The halogen bond between pyridine and perfluoroalkyl iodide not only affects some of the vibrational frequencies of pyridine but also impacts the vibrational frequencies of iso- $\text{C}_3\text{F}_7\text{I}$. As an electron lone pair donor, the alpha fluorine in perfluoroalkyl iodides is more shielded when it is engaged in the halogen bond, but less shielded when it is engaged

TABLE 2: Halogen-bonding association constants for pyridine/iso- $\text{C}_3\text{F}_7\text{I}$ and pyridine/1- $\text{C}_3\text{F}_7\text{I}$ systems in various solvents.

Solvent	Iso- $\text{C}_3\text{F}_7\text{I}$	1- $\text{C}_3\text{F}_7\text{I}$
Cyclohexane	21.5 ± 5.4	10.2 ± 2.0
Hexane	13.0 ± 2.7	8.4 ± 1.7
Chloroform	3.8 ± 0.9	2.6 ± 0.7
Acetone	3.1 ± 0.8	1.9 ± 0.6
Acetonitrile	3.6 ± 0.8	2.4 ± 0.6

in hydrogen bonding. The halogen bonded complexes of pyridine and perfluoroalkyl iodides, though stronger in polar solvents, showed significantly lower association constants in acetone and acetonitrile than in non-polar solvents such as hexane and cyclohexane. The entropy change makes a favorite contribution to the halogen bond between pyridine and perfluoroalkyl iodides in the non-polar solvent such as hexane and cyclohexane.

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