Article

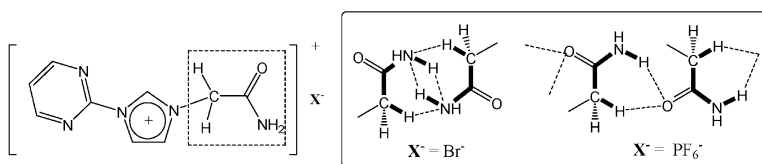# C−H- - -O Hydrogen Bonds in β-Sheetlike Networks: Combined X-ray Crystallography and High-Pressure Infrared Study

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C−H- - -O Hydrogen Bonds in β-Sheetlike Networks: Combined X-ray Crystallography and High-Pressure Infrared Study

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Abstract: Close interactions of the C^{α}−H- - -O type have been analyzed via X-ray crystallography and high-pressure infrared spectroscopy. The results demonstrate that the C^{α}−H- - -O interactions can offer an additional stability to the β-sheet formation. X-ray structural data suggest that while 1-acetamido-3-(2-pyrimidinyl)-imidazolium bromide exhibits a bilayer stacking, the PF_6^- salt reveals a β-sheetlike pattern. The appearance of the free-NH infrared absorption indicates that the conventional N−H- - -O or N−H- - -N hydrogen bonds do not fully dominate the packing for the PF_6^- salt. The high-pressure infrared study suggests that the C^{α}−H- - -O hydrogen bonds are the important determinants for the stability of the PF_6^- salt. This study also verifies that the imidazolium C−H stretching frequency shifts to a longer wavelength upon the formation of the C−H- - -O hydrogen bonds.

Introduction

Conventional hydrogen bonds, playing pivotal structural and functional roles, are one of the major features of biological macromolecule structures, while hydrogen atoms bound to nitrogen and oxygen atoms form classical hydrogen bonds with lone electron pairs on other oxygen and nitrogen atoms. In recent years, close interactions of the C−H- - -O type hydrogen bonds have been suggested in various organic compounds, but not much attention had been given to the potential significance of these bonds in biological macromolecules.[1−3] A notable exception is the recognized role of C^{α}−H- - -O bonds in biochemical systems.[4−9] The possibility of C−H- - -O hydrogen bonds contributing to the stability of protein structures has been addressed recently, suggesting that C−H- - -O hydrogen bonds

may act as an additional stabilizing factor.[4−9] Nevertheless, experimental evidences of C−H- - -O hydrogen bonds in biological macromolecules are notoriously difficult to obtain, mainly because the C−H- - -O interactions usually coexist with other strong hydrogen bonds making the contribution from C−H- - -O interactions difficult to be distinguished. To illustrate how C−H- - -O interactions disturb the strong O−H- - -O and N−H- - -O network in biologically related molecules, we probe the C−H- - -O interactions in a self-assembled β-sheetlike network, being held together by a bifurcated C^{α}−H- - -O(C)- - -H−N pattern, via high-pressure Fourier transform infrared (FTIR) in this study.

The C−H- - -O interaction is typically weak.[1−3] Nevertheless, strengths of the C−H- - -O interactions can be enhanced in protonated clusters or molecular aggregates containing charges.[10,11] Recent studies also suggested pressure as a variable to enhance the nature of C−H- - -O interactions.[12−15] In addition to charge and pressure effect, attention has been given to the occurrence of C^{α}−H- - -O-type hydrogen bonds in biological molecules.[5−9]

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The C^α is an activated carbon donor because it is bound to the electron-withdrawing amide N–H and C=O groups. Recently by using ab initio calculations, Scheiner et al. estimated the energy of the C^α–H- - -O hydrogen bond to be as much as 2.5–3.0 kcal/mol, being approximately one-half the energy of a conventional hydrogen bond.[16,17] However, the structural contribution of C^α–H- - -O hydrogen bond is still unclear, while the C^α–H- - -O interaction energy is suggested to be significant for providing stability and specificity in transmembrane helix interactions. We hope our high-pressure study on a self-assembled β-sheetlike network, being held together by a bifurcated C^α–H- - -O(C)- - -H–N pattern, will shed more light on the mechanism of C^α–H- - -O interactions in biological related molecules.

There has emerged in the recent literature some controversy as to whether the formation of C–H- - -O interactions causes changes in the C–H stretching frequency and the equilibrium C–H length that are opposite in sign to those observed in conventional hydrogen bonds.[1–3,18–21] As we know, the vibrational modes undergo a red frequency shift and accompanying intensification upon formation of the conventional hydrogen bond via N–H- - -O or O–H- - -O interactions. However, in a number of cases, the C–H- - -O interactions lead to the shortening of the bridging C–H bond, not the lengthening that is generally considered a typical feature of hydrogen bonds.[2,3] Two schools of thought have emerged in trying to explain the physical basis for blue-shifted C–H frequencies. As suggested by Hobza et al.,[2] the blue-shifting C–H- - -O may be attributed to the electron density transfer from the proton acceptor to the remote part of the proton donor. Therefore, the blue-shifting C–H- - -O interactions were labeled as anti-H-bonds. On the other hand, Scheiner et al. performed ab initio calculations to determine whether the two contrasting behaviors can be traced to different patterns of electron density shifts within the complex or they are associated with very different geometrical perturbations within the proton donor molecules.[3,21] In contrast to Hobza et al.,[2] no fundamental distinctions between the two sorts of interactions were concluded by Scheiner et al.[21] The controversy arises mainly because of the difficulty in observing the perturbed C–H stretching bands due to the weakness of C–H- - -O interactions. There has been evidence that the C–H- - -O interactions can be dramatically enhanced in the presence of high pressure.[12–15] We hope this pressure-dependent study will shed light on the controversy.

Generally, vibrational studies were performed at ambient pressure and mostly at room temperature to analyze the functioning of biologically related molecules, while interest in pressure as an experimental variable has been growing in physicochemical studies of biochemical and biological systems. Recently the combination of high pressure and spectroscopic methods is beginning to map the conformational landscapes of biological related molecular complexes.[12–15] The use of pressure allows one to change, in a controlled way, the intermolecular interactions without the major perturbations produced by

changes in temperature or chemical composition. In addition to being an important thermodynamic variable, pressure can be used to as a valuable means of triggering and investigating the folding and unfolding transition of large molecules such as proteins. To assess the effects concerning how C^α–H- - -O interactions disturb the conventional hydrogen bond networks, the present article describes the application of a high-pressure method to monitor the changes in structures of a β-sheetlike network based on 1-acetamido-3-(2-pyrimidinyl)-imidazolium cation.

Experimental Methods

1-Acetamido-3-(2-pyrimidinyl)-imidazolium bromide was synthesized from the reaction of 2-pyrimidinyl-imidazole (2.00 g, 13.7 mmol) with 2-bromoacetamide (1.89 g, 13.7 mmol) in CH_3CN (150 mL).[22] After refluxing for 12 h, the precipitated powder was collected and recrystallized from methanol to give a white product with a yield of 75%. The PF_6^- salt was obtained from the bromide salt (1 g, 3.5 mmol dissolved in methanol) by a simple metathesis reaction with an equivalence of NH_4PF_6 (0.69 g, 4.2 mmol in methanol).[22,23] A white precipitate was formed. After filtration this precipitate was washed by H_2O/MeOH several times. Recrystallization from CH_3CN gave a white product with a yield >80%. The X-ray structure analysis exhibits a self-assembled β-sheetlike network in 1-acetamido-3-(2-pyrimidinyl)-imidazolium hexafluorophosphate.[22] The samples were diluted with KBr powder to reduce the IR absorption. Infrared spectra of the mixed samples were measured on a Perkin-Elmer Fourier transform spectrophotometer (model Spectrum RXI) with a LITA (lithium tantalate) mid-infrared detector. A diamond anvil cell (DAC) of Merril-Bassett design, with a diamond culet size of 0.6 mm, was used for generating pressures to approximately 3 GPa. Two type IIa diamonds were used for mid-infrared measurements. The sample was contained in a 0.3-mm-diameter hole in a 0.25-mm-thick stainless steel gasket mounted on the diamond anvil cell. The infrared beam was condensed by a 5X beam condenser manufactured by Perkin-Elmer onto the sample in the diamond anvil cell. Typically a resolution of 4 cm^{-1} was chosen (data point resolution of 2 cm^{-1}). For each spectrum typically 1000 scans were co-added. Moreover, the absorption spectra of DAC were measured first and subtracted from those of the samples to remove the absorption of diamond anvils.

Results and Discussion

1-Acetamido-3-(2-pyrimidinyl)-imidazolium bromide exhibits a bilayer stacking and is depicted in Figure 1. The carbonyl group orients opposite to the imidazolium ring, thus ruling out any possibility of internal hydrogen bonding. The ionic layer is constructed by a hydrogen-bonding network through the interactions between the bromide anions and the acetamido-functionalized imidazolium cations. As the Br$^-$ was replaced by the PF_6^- anion, two interesting hydrogen-bonding patterns are observed in Figure 2. First, the carbonyl O atom of the amide groups forms hydrogen bonds both with a C^α–H proton and a N–H proton from the neighboring acetamide group to generate a one-dimensional catemer, cf., Figure 2. It is instructive to note that this bifurcate C^α–H- - -O(C)- - -H–N pattern is analogous to that of the β-sheets reported. The second hydrogen-bonding pattern is a cyclic ring formed between the pyrimidyl and imidazolium groups through C–H- - -N hydrogen-bonding interactions, cf., Figure 2. The X-ray structure analysis also exhibits that the C^2–H proton of the imidazolium cation forms C^2–H- - -O=C interaction in Figure 2. In our previous study,

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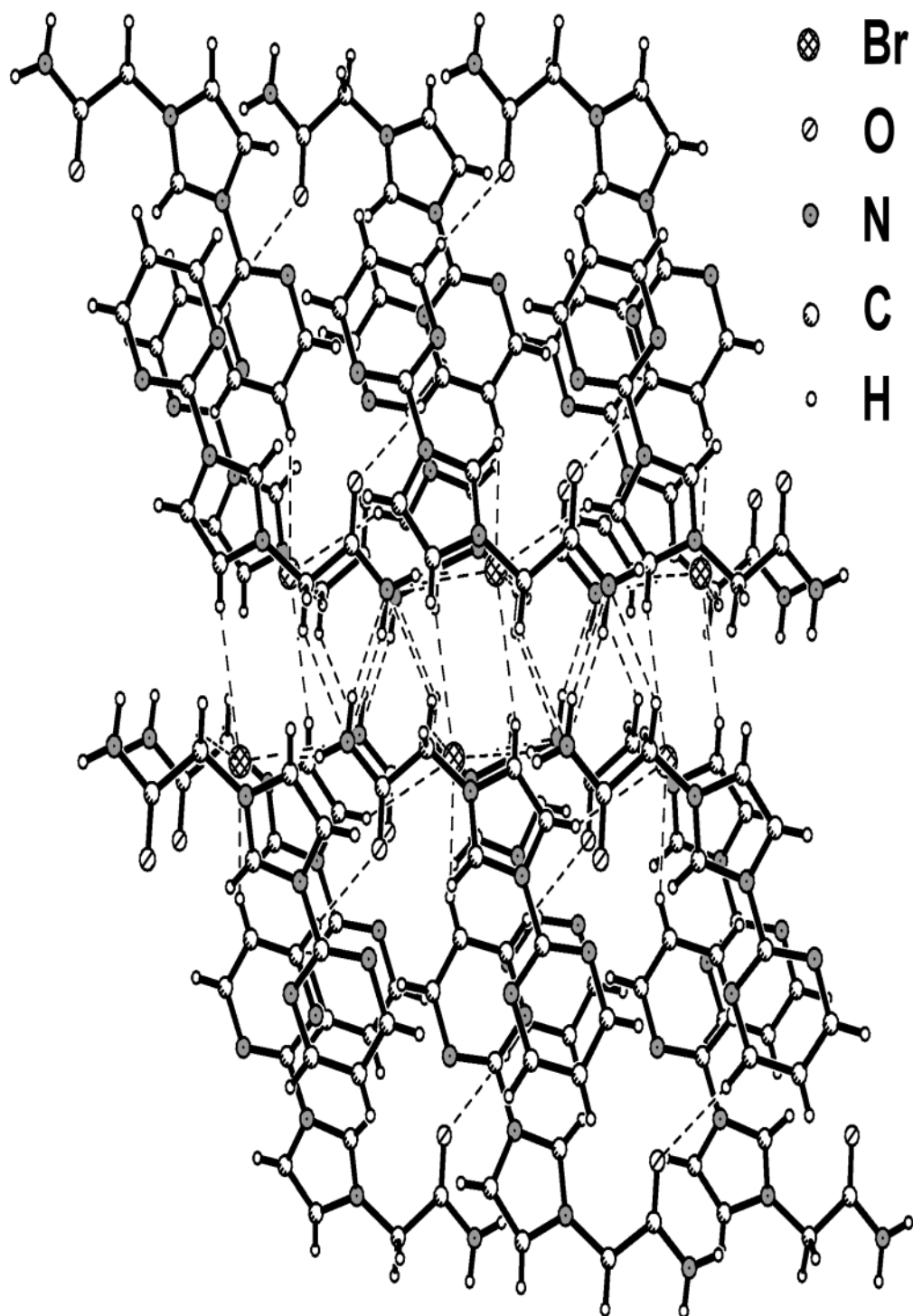(21) Scheiner, S.; Kar, T. *J. Phys. Chem. A* **2002**, *106*, 1784.

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Figure 1. Molecular packing of the bilayer structure of 1-acetamido-3-(2-pyrimidinyl)-imidazolium bromide viewed along the layer interface. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-153355.

we reported the use of high-pressure infrared technique to characterize a self-assembled triple helical spine based on the acetamido functionalized pyrazinyl-imidazolium hexafluoro-phosphate salt.[12] In this work, we employ the same technique to demonstrate that C^{α}−H- - -O interactions can offer additional stability to the formation of β-sheets.

Figure 3a and b show the infrared absorption of the Br⁻ salt and PF₆⁻ salt, respectively, obtained at room temperature and ambient pressure in the region of N−H and C−H stretching vibrations. The free N−H stretching mode shows an absorption

at 3481 cm⁻¹, cf., Figure 3b, while the bands in the region of 3200−3400 cm⁻¹ can be attributed to hydrogen-bonded N−H vibrations, cf., Figure 3a and b. To facilitate the interpretation of the experimental spectra, ab initio calculations, performed at the B3LYP/6-31G* level, were carried out using the Gaussian 98 program package.[24] Harmonic vibrational frequencies were obtained from analytical second derivatives and were scaled with a single factor (0.945). As shown in Table 1, we examined the frequencies and absorption intensities of the monomer cation and have compared them to the experimental data obtained at
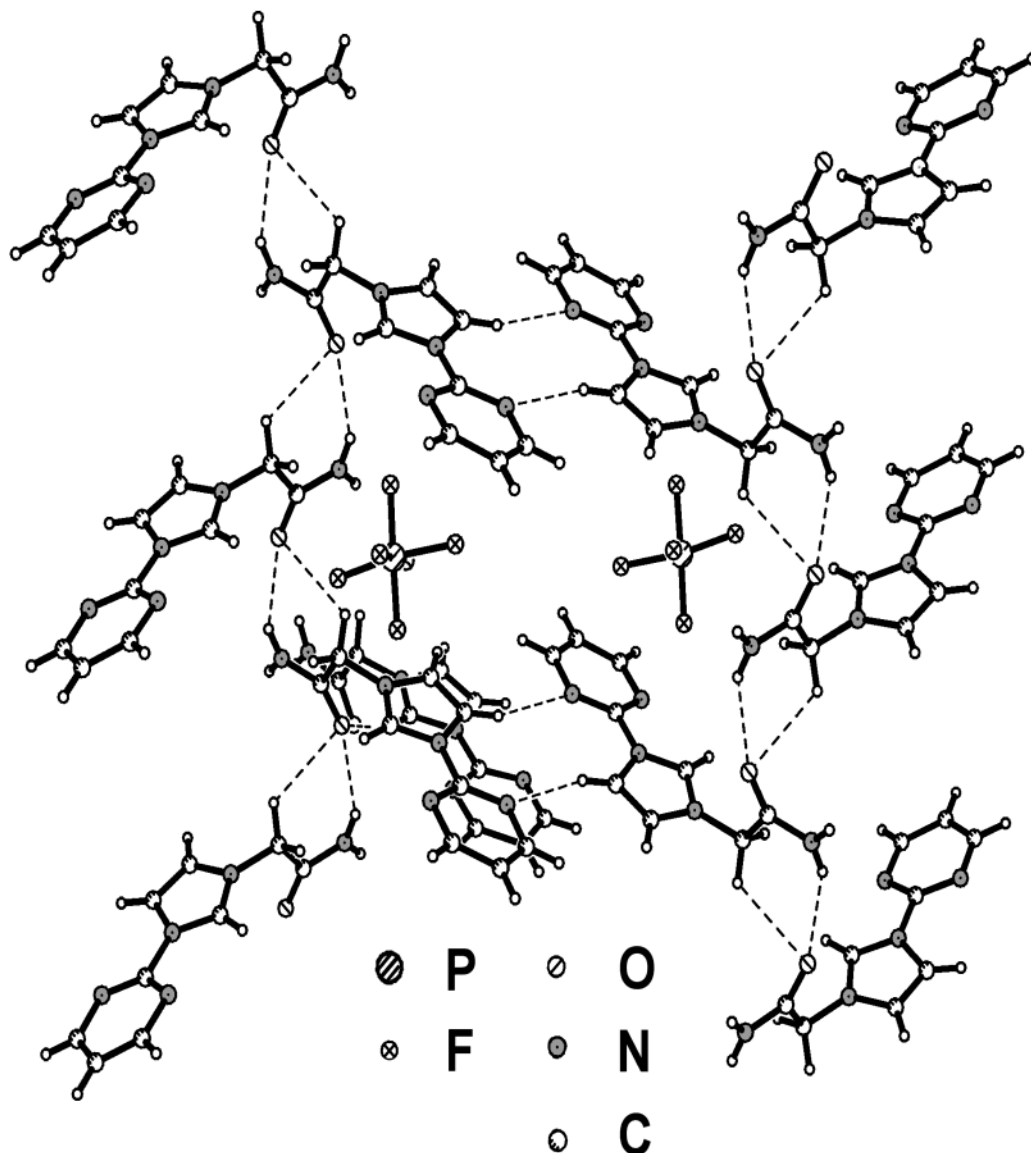
Figure 2. β-sheet type catemer of the PF_6^- salt formed by C–H- - -O and N–H- - -O hydrogen bonding and a cyclic ring formed between the pyrimidinyl and imidazolium group through C–H- - -N hydrogen-bonding interactions in a motif of graph set $R_2^2(10)$. Crystallographic data have been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC-153356.

ambient pressure, i.e., Figure 3a and b. Prominent IR bands in Figure 3a are assigned to the stretching bands of CH_2 (2850–3025 cm^{-1}), pyrimidinyl C–H (six-membered ring, 3025–3100 cm^{-1}), imidazolium C–H (five-membered ring, 3100–3200 cm^{-1}), and hydrogen-bonded N–H vibration (3200–3400 cm^{-1}). A general agreement between calculations, cf., Figure 3c, and observations, cf., Figure 3a, is reached, although the observed spectrum, cf., Figure 3a, reveal the red shifts of N–H stretching frequencies due to the hydrogen bonding of Br⁻- - -H–N and N- - -H–N.

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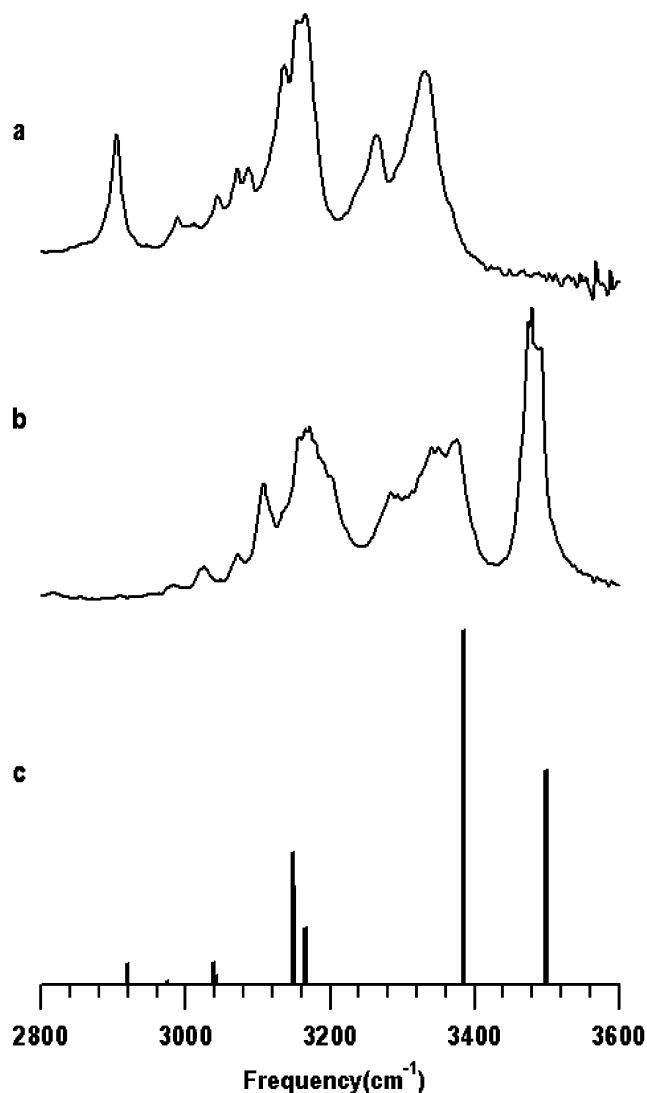
As the Br⁻ was replaced by PF_6^-, cf., Figure 3b, the additional feature appeared at 3481 cm^{-1} in Figure 3b, is attributed to a free-NH stretching vibration. The appearance of the free-NH infrared absorption in Figure 3b is interesting. This result suggests that the conventional N–H- - -O or N–H- - -N hydrogen bond does not fully dominate the packing in the PF_6^- salt.[12] As revealed in Figure 3a, the two absorption bands in the fundamental C^α–H stretching region located at 2904 and 2989 cm^{-1} for the Br⁻ salt are shifted to 2982 and 3025 cm^{-1} in Figure 3b for the PF_6^- salt. Substantial changes in the intensities of these C^α–H bands are also observed between the two different salts. To rationalize the experimental observations, C^α–H- - -O hydrogen bonding is suggested to be one of the dominant stabilization contributions in Figure 3b. It is likely that the hydrogen-bonding patterns in this rich hydrogen-bonding donor environment are determined by the relative hydrogen-bonding acceptor strength of the Br⁻, PF_6^-, and carbonyl O atom. For the Br⁻ salt, the Br⁻ anion is a stronger hydrogen bond acceptor than the carbonyl O atom, so that the Br⁻ anion

a

b

c

Frequency(cm⁻¹)

Figure 3. Experimental infrared spectra of (a) the Br⁻ salt and (b) the PF$_6$⁻ salt, respectively, obtained at ambient pressure and (c) the ab initio-calculated stick diagram of monomeric cation.

Table 1. Ab Initio Calculated Vibrational Frequencies (cm⁻¹) and Intensity of the Monomer of 1-Acetamido-3-(2-pyrimidinyl)-imidazolium Cation[a]

frequency (cm⁻¹)[a]	intensity	assignment
3500	63.8	asym. NH$_2$ stretching
3386	105.4	sym. NH$_2$ stretching
3166	16.8	sym. CH stretching (5)
3151	29.3	asym. CH stretching (5)
3149	39.2	C^{2}H stretching (5)
3070	0.0006	CH stretching (6)
3042	2.8	CH stretching (6)
3039	6.9	CH stretching (6)
2975	1.4	asym. CH$_2$ stretching
2919	6.2	sym. CH$_2$ stretching

[a] Frequency scaled by 0.945.

dominates the packing in the crystal structure. For the PF$_6$⁻ salt, the carbonyl oxygen atom seems to be a stronger hydrogen acceptor than the PF$_6$⁻ anion, such that the C$^\alpha$−H- - -O=C hydrogen bonding turns out to be one of the dominant stabilization contributions in the crystal packing. There were some evidences that C$^\alpha$−H- - -O appears to be a compensatory mechanism to provide stability to the β-sheets,[9] while a
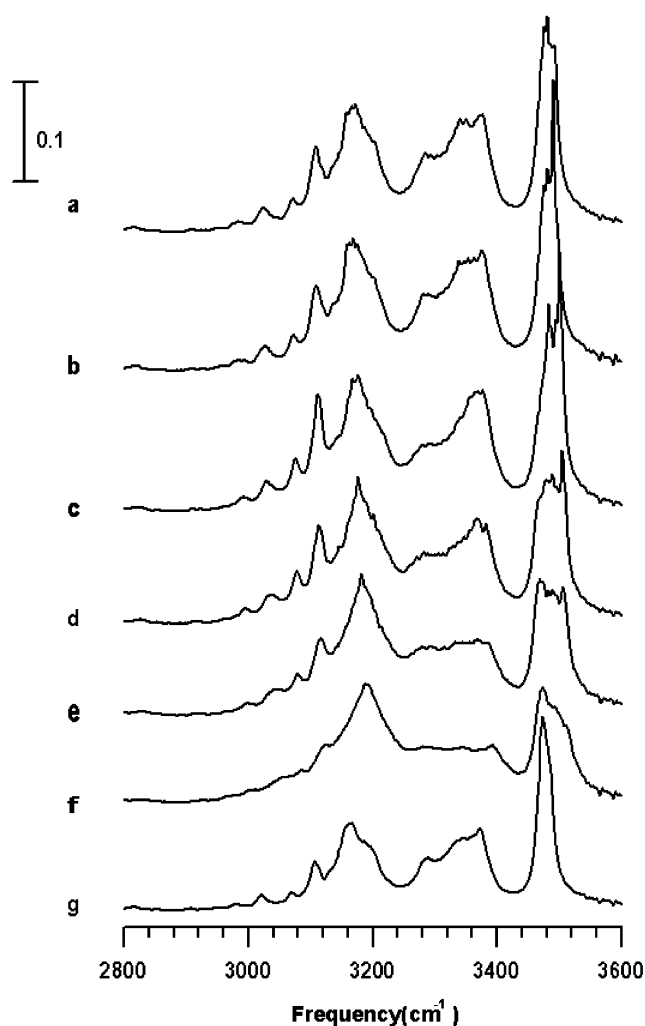
Frequency(cm⁻¹)

Figure 4. IR spectra of the PF$_6$⁻ salt in region of C−H and N−H stretching vibration modes under the pressure of (a) ambient, (b) 0.3 GPa, (c) 0.9 GPa, (d) 1.5 GPa, (e) 1.9 GPa, (f) 2.3 GPa, (g) released to ambient, respectively.

correlation between C$^\alpha$−H- - -O and N−H- - -O hydrogen bonds was proposed.[5−9]

To understand the mechanism of C$^\alpha$−H−O hydrogen bonding, high-pressure IR study were employed. Figure 4 shows the infrared spectra of the PF$_6$⁻ salt under the pressure of ambient (curve a), 0.3 GPa (curve b), 0.9 GPa (curve c), 1.5 GPa (curve d), 1.9 GPa (curve e), 2.3 GPa (curve f) and back to ambient (curve g). The profile changes of the free N−H stretching mode at ∼3481 cm⁻¹ may reflect the weak interactions between the N−H and PF$_6$⁻ anions, as indicated by the X-ray structure analysis. It is instructive to note that the possibility of pressure-induced transformation in the structure should not be excluded under the pressure above 1.5 GPa, cf. Figure 4e and f. Nevertheless, no significant changes in the infrared absorption spectra were observed after the pressure was released, cf., Figure 4a and g.

The pressure dependence of the C$^\alpha$−H modes was plotted as Figure 5a and b and Figure 5c, obtained from the PF$_6$⁻ salt and the Br⁻ salt, respectively. To determine the correct band center, the peaks were analyzed by fitting Gaussian functions. As revealed in Figure 5a and b, the C$^\alpha$−H modes of the PF$_6$⁻ salt were blue-shifted by increasing the pressure, while the absorption frequencies of the C$^\alpha$−H modes of the Br⁻ salt, cf.,

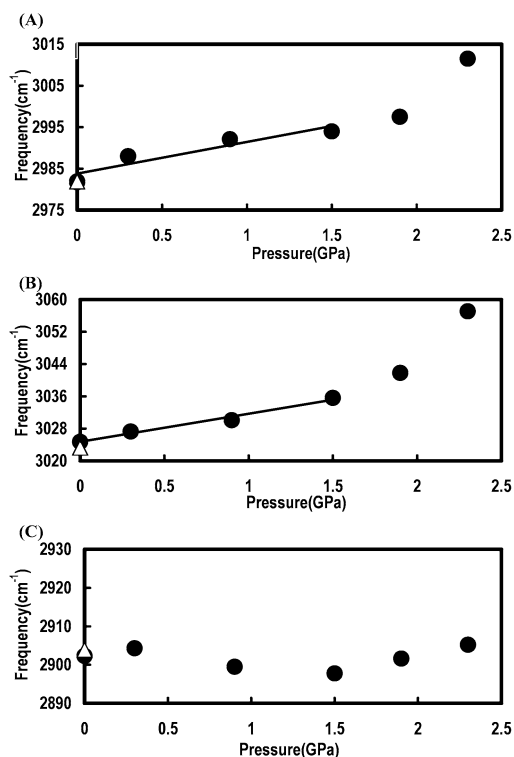**Figure 5.** Pressure dependence of the C^α–H modes obtained from the PF_6^- salt (a and b) and the Br^- salt (c), respectively. The triangles denote the frequency position upon pressure release to ambient.
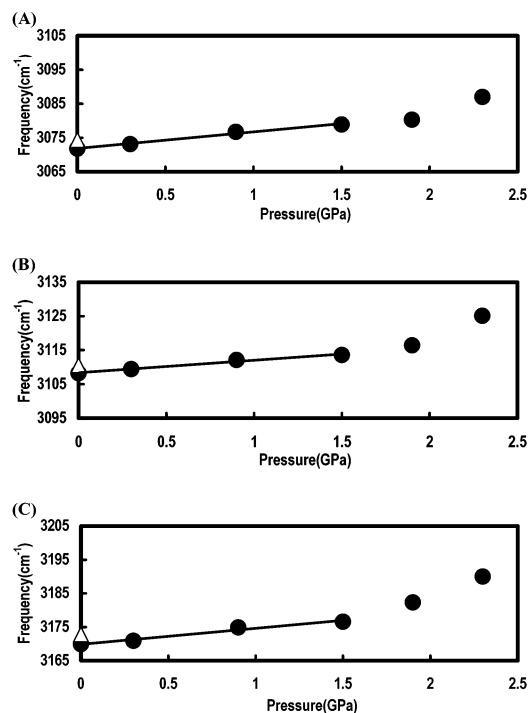

Figure 6. Pressure dependence of the (a) 3072, (b) 3108, and (c) 3170 cm^{-1} bands corresponding to C–H stretching modes of pyrimidinyl and imidazolium rings of the PF_6^- salt. The triangles denote the frequency position upon pressure release to ambient.

Figure 5c, varied only slightly red-shifted in frequency ($p < 1.5$ GPa). The existence of insensitivity to pressure in the C^α–H modes of the Br^- salt, cf., Figure 5c, shows that the application of external pressure in this experiment hardly alters the C^α–H bond lengths of the Br^- salt. The major changes induced by the pressure are the changes in intermolecular distances. The empty space, i.e., free volume, is decreased upon increasing the pressure. The frequencies of the C^α–H modes of the PF_6^- salt, increase linearly with increasing pressure. Slopes (dν/dP) of 7.6 cm^{-1}/GPa (Figure 5a) and 7.0 cm^{-1}/GPa (Figure 5b) were obtained by plotting variation of ν against variation of P below the pressure of 1.5 GPa. Nevertheless, the pressure-induced frequency-shifts of the C^α–H modes are relatively large under the pressure above 1.5 GPa, cf., Figure 5a and b. This may indicate a pressure-induced structural transformation above the pressure of 1.5 GPa. The increase in the C–H stretching frequencies with pressure, cf., Figure 5a and b, is contrasts to the general trend observed in the strong hydrogen bonded systems having O–H- - -O and C=O- - -H interactions.[25-27] For instance, an increase in pressure shortens and strengthens the intermolecular hydrogen bond in ice VII, while the length of intramolecular OH bonds increases as the pressure is increased.[25-27] In the C–H- - -O hydrogen bonding, the C–H acts as the proton donor. This type of hydrogen-bonding interaction is, in general, rather weak compared to the conventional hydrogen bond. A blue shift of the C–H stretching frequency and a shortening of the C–H bond are characteristic for the C–H- - -O interactions. Extensive theoretical and experimental

investigations have been carried out in the recent literature to identify the strength and directionality of these relatively weak interactions.[1-3,28-31] A possible explanation has been proposed is that the C–H hydrogen is pushed toward the carbon by the oxygen atom due to modification of C–H- - -O interactions upon increasing the pressure. The possibility that pressure might change the anharmonic nature of the potential well should not be excluded.

Figure 6 illustrates the pressure dependence of the 3072, 3108, and 3170 cm^{-1} bands corresponding to the C–H stretching modes of pyrimidinyl and imidazolium rings of the PF_6^- salt, while the frequencies of the C–H modes increase linearly with slope of 4.9 cm^{-1}/GPa (Figure 6a), 3.7 cm^{-1}/GPa (Figure 6b), and 4.7 cm^{-1}/GPa (Figure 6c), respectively, under the pressure below 1.5 GPa. The X-ray structure analysis exhibits that the C^2–H, C^4–H, and C^5–H protons of the imidazolium cation form C^2–H- - -O=C, C^4–H- - -N, and C^5–H- - -F–P interactions, respectively, while the pyrimidinyl C^4–H forms the C–H- - -F–P interaction with the PF_6^- anions. The blue shift in frequency observed in Figure 6 may be due to the modification of the C–H- - -O, C–H- - -N and C–H- - -F contacts upon compression. On the basis of the infrared results, we conclude that the 3108 cm^{-1} band should be attributed to the C^2–H stretching mode of the imidazolium cation. Interestingly, in comparison to the results of ab initio calculations, i.e., 3149 cm^{-1} for C^2–H stretching mode and the experimental spectrum of the Br^- salt, i.e., Figure 3a, a red shift ($\sim$ 41 cm^{-1}) of the imidazolium C^2–H stretching frequency was observed upon the formation of the C–H- - -O hydrogen bond, cf., Table 1.[16]

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Conclusions

In this work, we show that the diversity of the crystal structures may be used in the design of supramolecular architectures and materials with special properties. When the anion is bromide, a novel bicyclic dimer is formed in which the amido NH_2 groups serves as hydrogen bond acceptors; when the anion is PF_6^-, a β-sheet type of amide catemer via C^α−H- - -O and N−H- - -O hydrogen bonds is formed. The present analysis clearly shows that C^α−H- - -O hydrogen bonds can offer an additional stability to the β-sheet network and act as a compensating factor to disturb the formation of strong N−H- - -O hydrogen bonding. This finding implies the importance of the C^α−H- - -O hydrogen bonds in biological systems. The high-pressure measurements also verify that when C^2−H- - -O=C hydrogen bonds are formed, there is a red shift of the imidazolium C^2−H stretching frequency.

Supporting Information Available: X-ray crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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