2P141 Solvent effects on the tautomerization of isocytosine investigated by infrared spectroscopy and quantum chemical calculations

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Introduction. The tautomerism of pyrimidine and purine bases has been studied extensively because it directly affects the base-pairing in DNA. To understand the spontaneous and induced mutagenesis caused by the tautomerization of DNA bases, it is necessary to investigate the stabilization of the keto tautomers in solutions. In the present work, effects of solvents on the tautomeric stabilization of isocytosine and its model compound have been investigated using Fourier transform infrared (FT-IR) spectroscopy coupled with quantum chemical calculations. First of all, we have to clarify the assignments of the IR bands observed for the solutions of isocytosine by the aid of quantum chemical calculations.

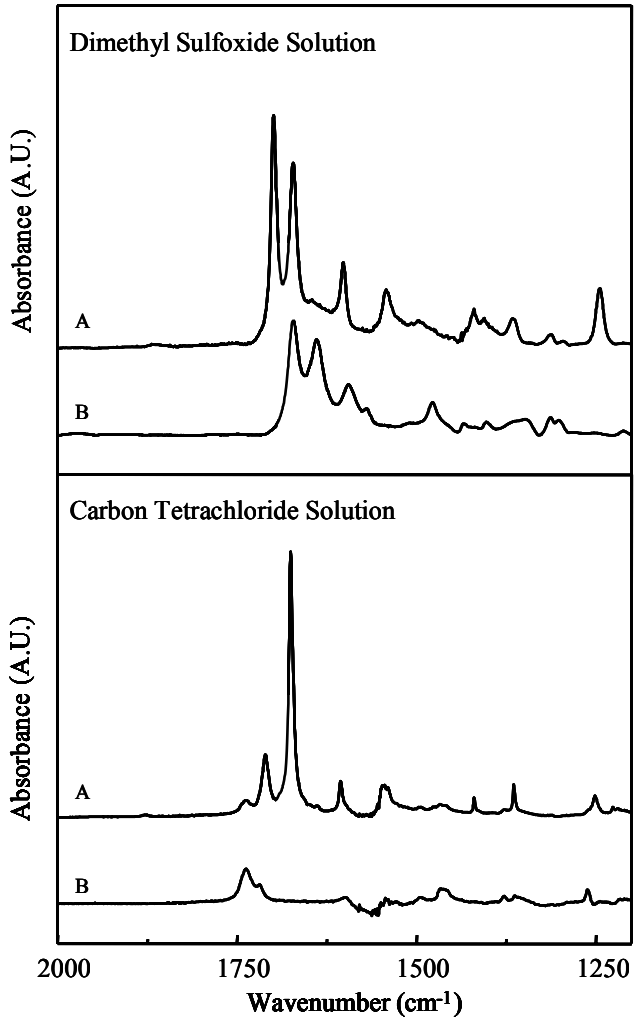

Figure 1 IR spectra of 4(3H)-pyrimidinone (A) and isocytosine (B) in dimethyl sulfoxide (upper) and carbon tetrachloride (lower) solutions.

Experiment. IR spectra of isocytosine and 4(3H)-pyrimidinone were measured in several organic solvents using either attenuated total reflection (ATR) or transmission liquid cells. All IR spectra were recorded on a Nicolet 6700 spectrometer equipped with a mercury cadmium telluride (MCT) detector at a resolution of 1 cm^{-1} and 256 number-of-scans. Subtraction of the solvent spectrum was performed for all samples.

Calculation. Structural optimizations of isocytosine and 4(3H)-pyrimidinone were performed with *ab initio* molecular orbital methods at the Hartree-Fock (HF) and the Møller-Plesset second perturbation (MP2) levels and with a density functional theory (DFT) method employing GAUSSIAN 03 program. The optimized structures were calculated for isolated and dimer molecules. In order to compare the calculated frequencies and intensities with the experimentally observed one, IR spectra of the molecules were simulated, assuming that the band shapes and bandwidth are Lorenzian and 5 cm^{-1},

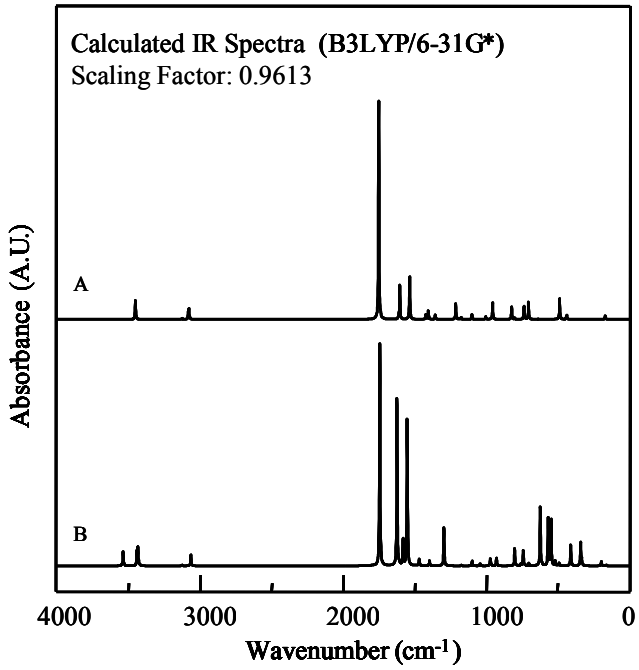

Figure 2 Simulated IR spectra of 4(3H)-pyrimidinone (A) and isocytosine (B) obtained by B3LYP/6-31G* method.

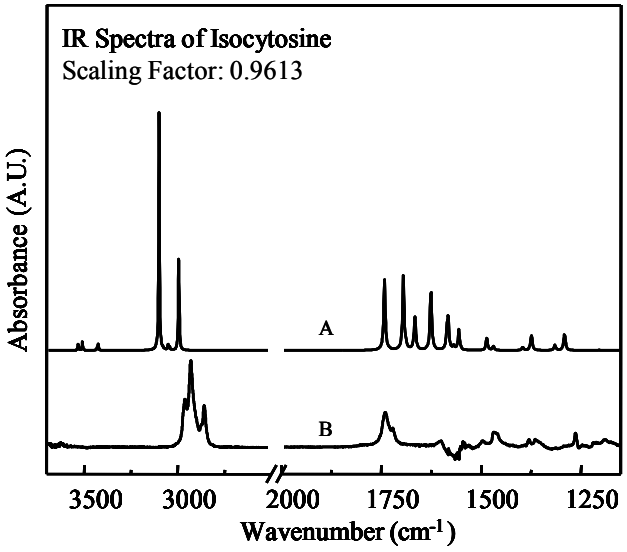

Figure 3 Simulated IR spectrum of isocytosine keto-dimer obtained by B3LYP/6-31G* method (A) and IR spectrum of isocytosine in carbon tetrachloride solution (B).

respectively.

Results and Discussion. Figure 1 shows the experimentally observed IR spectra of isocytosine (iCyt) and 4(3H)-pyrimidinone (4(3H)Pyr) in dimethyl sulfoxide (DMSO) and carbon tetrachloride (CCl_4) solutions in the 2000-1200 cm^{-1} spectral region. The concentrations of the iCyt and 4(3H)Pyr in DMSO are 10 mM and 20 mM, respectively, while those in CCl_4 are less than 0.5 mM because their solubilities in CCl_4 are very low. It can be seen that substantial differences in band shapes and peak positions are observed in the region of 1750-1650 cm^{-1} where bands due to the C=O stretching vibrations appear. The calculated IR spectra of iCyt and 4(3H)Pyr in their keto forms at the B3LYP/6-31G* level are demonstrated in Figure 2. The calculated IR frequencies and intensities of the C=O vibrations (~1745 cm^{-1}) for iCyt and 4(3H)Pyr are very close to each other. Therefore, the spectral variations shown in Figure 1 may indicate the deviation from the near-normal vibrations of the C=O groups of the samples in the organic solvents. Figure 3 shows the calculated IR spectrum of one of the isocytosine keto-dimers. The calculated dimer-spectrum exhibits relatively strong bands around 3000 cm^{-1}, similar to the spectrum observed for iCyt in CCl_4 solution. These strong bands are attributed to the vibrations of the N-H groups involved in the H-bonding interactions result from the dimer formation.