2A3b Dimerization and tautomerization of 4(3H)-pyrimidinone in solutions investigated by infrared spectroscopy and quantum chemical calculations

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Introduction. The dimerization and tautomerization of pyrimidine and purine bases have been studied extensively because it directly affects the base-pairing in DNA. In the present work, the dimerization of 4(3H)-pyrimidinone (4(3H)Pyr) has been investigated using infrared (IR) spectroscopy coupled with quantum chemical calculations. The tautomerism of 4(3H)Pyr in various solvents is also discussed.

Experiment and Calculation. IR spectra of 4(3H)Pyr were measured in several organic solvents using either ATR or transmission liquid cells. All spectral acquisitions were performed using 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 measured spectra. Structural optimizations of 4(3H)Pyr 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 and vibrational frequencies were calculated for isolated and dimer molecules of 4(3H)Pyr.

Results and Discussion. Figure 1 (A)-(C) shows the IR spectra of 4(3H)Pyr calculated at the B3LYP/6-31G* level in the monomer, ring dimer, and chain dimer forms, respectively. The observed IR spectrum of 4(3H)Pyr in carbontetrachloride (CCl_4) solution (D) exhibits the spectral bands of both the monomer and dimer forms for 4(3H)Pyr. The simulated IR spectra at the B3LYP/6-31G* level satisfactorily reproduce the experimentally observed IR spectrum of 4(3H)Pyr in CCl_4 solution. The structural optimization also indicates that the ring dimer is much more stable than the chain dimer. Therefore, we concluded that the ring dimer and monomer co-exist in the CCl_4 solution.

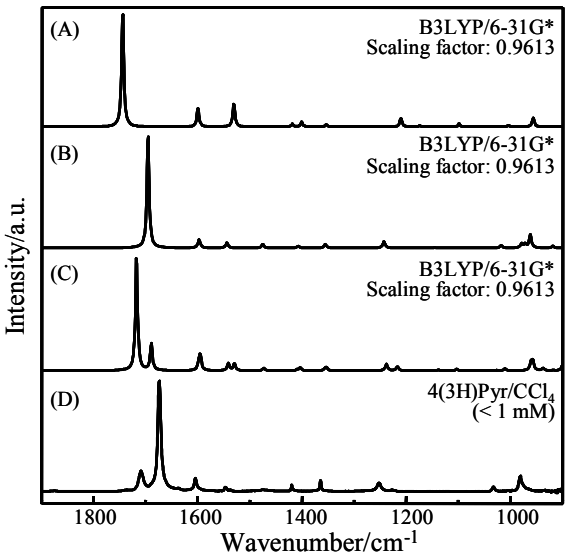

Figure 1 IR spectra of 4(3H)Pyr (A) monomer, (B) ring dimer, and (C) chain dimer calculated at the B3LYP/6-31G* level, and an observed IR spectrum of 4(3H)Pyr in carbontetrachloride solution (D).