Excited-state deactivation of 5-vinyluracil: Effects of π-π conjugation and intramolecular hydrogen bond C—H···O=C

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ABSTRACT

The excited-state decay mechanisms of 5-vinyluracil (5VU) are explored by using a combination of experimental and theoretical methods. The effects of vinyl substituent, including the π-π conjugation effect and intramolecular hydrogen bond, are discussed. 5VU comprises the conformers 5VUA and 5VUB at ground state, with and without an intramolecular hydrogen bond C—H···O=C, respectively. The steady-state absorption and fluorescence spectra of 5VU are significantly red-shifted with respect to that of uracil. The time-resolved experimental results show that the excited-state decays of 5VU can be described by using three time constants: 2.26 ps, 13.45 ps and 4.66 ns. The decay pathways of 5VU obtained with the linearly interpolated internal coordinate method, predict that the two shorter lifetimes of 2.26 ps and 13.45 ps are attributed to 5VUB, and that the longest lifetime of 4.66 ns is attributed to 5VUA.

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1. Introduction

The excited-state behaviors of DNA/RNA bases, together with their nucleosides and nucleotides, have attracted great interest in the domain of photophysics and photochemistry [1–22]. In particular, the RNA base uracil (U) and DNA base thymine (T) have gained considerable attention for their important roles in living organisms and their different excited-state deactivation [17–34]. It was reported that there are two lowest singlet excited electronic states in the Franck-Condon (FC) region, one is bright state $^1\pi\pi^*$ (hereafter referred to as S_π) and the other is dark state $^1n\pi^*$ (hereafter referred to as S_n) [20,27–29]. The ultrafast nonradiative decay pathway is found via a conical intersection (CI) between the S_π state and the ground state S_0. This CI structure involves six-membered ring puckering and the out-of-plane deformation of the 5-substituent [21,27,28,30]. In addition, the fluorescence decay pathway of T can be described with a bi-exponential function [28,30,31].

With the purpose of providing further insights into the ultrafast nonradiative deactivation mechanism of U and T, the effects of substituents are thus explored extensively [27–41]. The results revealed that 5-substituted compounds show increasingly complex behavior and exhibit long excited-state lifetimes. For example, 5-fluorouracil (5FU) [27–29,33–36] and 5-aminouracil (5AU) [38–40] are widely studied. For 5FU, which is a drug used in cancer treatment [36], the fluorine atom is a strong electron acceptor. For 5AU, the amino is a strong electron donor and may conjugate with the pyrimidine ring in the p-π type. However, the effects of substituents on the excited-state behavior of U derivatives are far from being fully understood despite the availability of numerous studies.

To clarify the effects of the intrinsic properties of 5-substituents on the excited-state deactivation of U, we reported the experimental and theoretical studies on the singlet excited-state deactivation of 5-vinyluracil (5VU). The vinyl conjugates with the pyrimidine ring in the π-π type. Such interaction is seldom reported. In addition, 5VU comprises two conformers at ground state, namely, 5VUA and 5VUB (Fig. 1). 5VUA exhibits a weak intramolecular hydrogen bond C—H···O=C, whereas 5VUB does not. It is well known that hydrogen bonds play an important roles in excited-state deactivation of chromophores [42–44]. However, only a few reports have explored the effect of this type of hydrogen bond on excited-state deactivation. In the present work, we found that C—H···O=C shows an important effect on the excited-state deactivation of 5VU.

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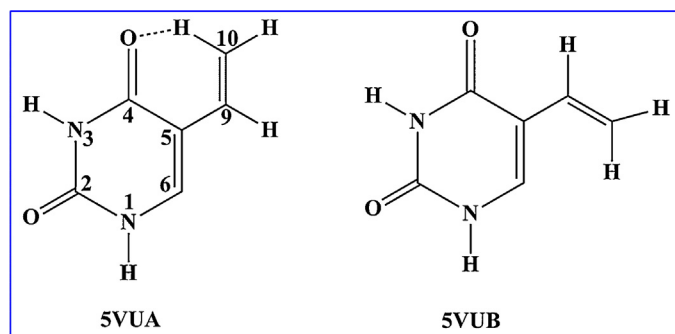
Fig. 1. Two conformers of 5VU: 5VUA and 5VUB with and without an intramolecular hydrogen bond C—H···O=C, respectively.

2. Experimental methods

All compounds (U, T and 5VU) were purchased from Tokyo Chemical Industry without further purification. The compounds were dissolved in a phosphate buffer solution (pH = 7.0), prepared with 0.1 M sodium dihydrogen phosphate and 0.1 M disodium hydrogen phosphate. In addition, 1 mM solutions for the femtosecond time-resolved transient absorption spectra were used, and 0.1 mM solutions were utilized for the fluorescence emission spectra. Solute concentrations were adjusted to produce an absorbance that was less than or equal to ~0.5 in a 1.0 cm quartz cell for the steady-state UV/Vis absorption spectra.

Absorption spectra were measured at room temperature on a Perkin-Elmer Lambda 35 double-beam UV–vis spectrophotometer. Fluorescence spectra were obtained at room temperature on a HORIBA Jobin Yvon Fluoromax-4 spectrofluorometer, with a Xenon lamp and 1.0 cm quartz cells. In the fluorescence lifetime measurements, a time-correlated single photon counting (TCSPC) method was employed on the 5VU solution by exciting the sample using a pulse laser (295 nm, NanoLED) at a 1 MHz repetition rate with a bandpass of 10 nm.

Femtosecond time-resolved transient absorption experiments were carried out on aqueous solutions of 5VU using a classical pump-probe setup with 100 fs UV pump pulses with a center wavelength of 260 nm, as described elsewhere [45,46]. The spot size of the probe pulse was 3–4 times smaller than that of pump pulse. The polarizations of the pump and probe pulses were adjusted to the magic angle to eliminate reorientational dynamics. The pump and probe pulses were focused and crossed in a free-flowing cell of the solution under study to avoid photodamage. All measurements were carried out at room temperature. Transient absorption signals were recorded with a charge-coupled device together with a chopper. The induced absorbance change (ΔOD) was recorded versus the time delay between the pump and probe pulses. ΔOD is defined as the sample absorbance at the probe wavelength in the presence of the pump pulse minus the absorbance at the same wavelength with the pump pulse blocked.

Transient absorption signals were fitted to a sum of exponentials by using our implementation of a global, nonlinear curve fitting program based on LabVIEW. The fitting function was analytically convoluted with a Gaussian that best represents the instrument response function.

3. Computational details

In this study, all the calculations were performed on the Gaussian 09 package [47]. The structures of U, T and 5VU were of diketo form, which is the most stable form in the electronic ground state [27,30,35].

The ground-state and excited-state geometry optimizations were located at the PBE0/6-31G+(d,p) and TD-PBE0/6-31+G(d,p) levels, respectively. The exchange-correlation hybrid functional PBE0 is widely used in the excited-state studies of U and its derivatives [27,30,35,39,40,48] and could provide a good description with respect to the experiment. All the equilibrium geometries of the ground and excited states were checked through frequency calculations, which turned out to be all positive. The polarizable continuum model (PCM) [30,35,39,40] was used to simulate the bulk solvent effects on the electronic states. The default integral equation formalism (IEF)-PCM in Gaussian was used in the calculation of the ground states, and the excited states and vertical excitation energies (VEEs) were computed at the linear response (LR)-PCM/TD-PBE0/6-31+G(d,p) level. Due to the state-specific (SS)-PCM/TD-PBE0 implementation allows for a more accurate determination of static and dynamic solvent effects on optical spectra [40], the absorption and emission energies, which are shown in supporting information (SI), were computed at the (SS)-PCM/TD-PBE0/6-31+G(d,p) level. We should note that IEF-PCM and LR-PCM are rewritten consistently into PCM for simplification in the following.

The CIs between S_π and S_0 in the gas phase with an out-of-plane deformation of the 5-substituent were located at the CASSCF (12,9)/6-31+G(d,p) level [49] for U, T and at the CASSCF(16,12)/6-31+G(d,p) level for 5VU. Then decay pathways were calculated with the linearly interpolated internal coordinate (LIIC) method between the S_π equilibrium geometries and the CIs at the PCM/TD-PBE0/6-31+G(d,p) level.

4. Results and discussion

4.1. Steady-state absorption and fluorescence spectra

The steady-state UV/Vis absorption and fluorescence spectra of U, T and 5VU in a room-temperature aqueous solution at pH = 7.0 are shown in Fig. 2. The corresponding features are summarized in Table S1 (SI). The normalized fluorescence spectrum of U shown in the inset of Fig. 2(b) was obtained from a previous report [30]. As shown in Fig. 2 and Table S1, the absorption and fluorescence spectra of T exhibit a slight red shift with respect to that of U, whereas 5VU exhibits a large red shift with respect to U. Furthermore, the fluorescence intensity of 5VU is much stronger than that of U and T.

4.2. Time-resolved excited-state deactivation

To better understand the effect of vinyl on the excited-state deactivation of 5VU, we obtain the time-resolved fluorescence spectra and transient absorption spectra of 5VU in an aqueous solution.

The fluorescence decay behaviors of 5VU at five different wavelengths (370, 380, 390, 400 and 410 nm), as shown in Fig. 3, are obtained with the TCSPC method in a room-temperature aqueous solution. The fluorescence decays of 5VU obviously depend on the detected wavelength and slow down with an increase in wavelength. These characteristics may result from the existence and equilibrium of the two 5VU conformers (5VUA and 5VUB) in the excited state. All of the fluorescence decays are fitted with bi-exponential functions, and the corresponding lifetimes are about 18 ps and 4.66 ns. However, the lifetime of 18 ps is shorter than our instrument resolution (~200 ps). Thus, the relatively short lifetime is obtained from the following femtosecond time-resolved transient absorption experiments.

Fig. 4 shows the femtosecond time-resolved transient absorption spectra of 5VU in a room-temperature aqueous solution. A broad and strong transient absorption from 500 nm to 700 nm is