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Comparative study of radiationless deactivation mechanisms in cytosine and 2,4-diaminopyrimidine

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ABSTRACT

We present a comparative computational CASPT2 and CC2 study of the deactivation mechanisms of electronically excited cytosine (Cyt) and 2,4-diaminopyrimidine (DAPy). A number of S_1/S_0 conical intersections exhibiting N—H bond elongation were optimized. These conical intersections are accessible from the Franck–Condon region along $^1\pi\sigma^*$ excited-state reaction paths. We also focus on the phototautomerism of DAPy and propose the photoinduced dissociation-association (PIDA) mechanism for this process. Supplementary experimental results on the UV irradiation of DAPy in acetonitrile solution show tautomerization to imino tautomers. By analyzing differences in the photophysics of the nucleobase Cyt and its analogue DAPy, this study provides new insight into the varying degrees of photostability between nucleobases and their close analogues.

1. Introduction

The five nucleobases are constituents of nucleic acids. They carry out fundamental biological functions involving transcription and encoding of genetic information. At the same time, they are dominant chromophores in biological structures. The nucleobases are exceptionally photostable compounds and protect the macromolecules of nucleic acids from mutations caused by the damaging influence of UV light [1–3].

The gas-phase UV-absorption maximum of the pyrimidine nucleobase cytosine (Cyt) was found at 4.28 eV (290 nm) and was assigned to a $\pi \rightarrow \pi^*$ electronic transition [4]. Several spectroscopic studies of aqueous solutions of Cyt have found absorption maxima at 4.65, 5.44, and 6.29 eV [5–8], while in acetonitrile solution four maxima have been observed at 4.54, 5.19, 5.79, and 6.20 eV, of which the last two are most intensive [6,8]. It has been found that the most stable form in acetonitrile solution is the amino-oxo tautomer (see Scheme 1) [6]. Various spectroscopic techniques such as the measurement of excited-state lifetimes [9], resonant two-photon ionization [10,11], and time-resolved spectroscopy [12–14] have been used in the past 15 years to elucidate further aspects of the photophysics of Cyt. Several computational studies on the vertical excitation energies and the UV-absorption behavior of Cyt have been presented as well [15–18].

A structurally close analogue of Cyt is 2,4-diaminopyrimidine (DAPy, see Scheme 1). Together with xanthine this compound can form a "rare base pair" that matches the Watson–Crick model. Such a DAPy—xanthine base pair can be enzymatically incorporated into DNA, which can provide nonstandard sequence "tags" in oligonucleotides used for diagnostic applications, expand the versatility of experiments for the in-vitro evolution of nucleic acids, and assist in obtaining self-replicating oligonucleotides as models for the origin of life [19–21]. The resonant two-photon ionization spectrum of DAPy in the gas phase has shown four independent N-H signals, which hints at the presence of the diamino tautomer [22]. Its excitation energy was estimated to be 4.27 eV. A much longer excited-state lifetime than expected for a radiationless deactivation was observed (estimated on a timescale of 10 ps to 1 ns). This suggests that sizable barriers have to be overcome before the internal-conversion domain can be reached [22].

As shown previously in a number of examples, structural modification of the nucleobases can drastically affect their degree of photostability [2,23–30]. Substitution of certain functional

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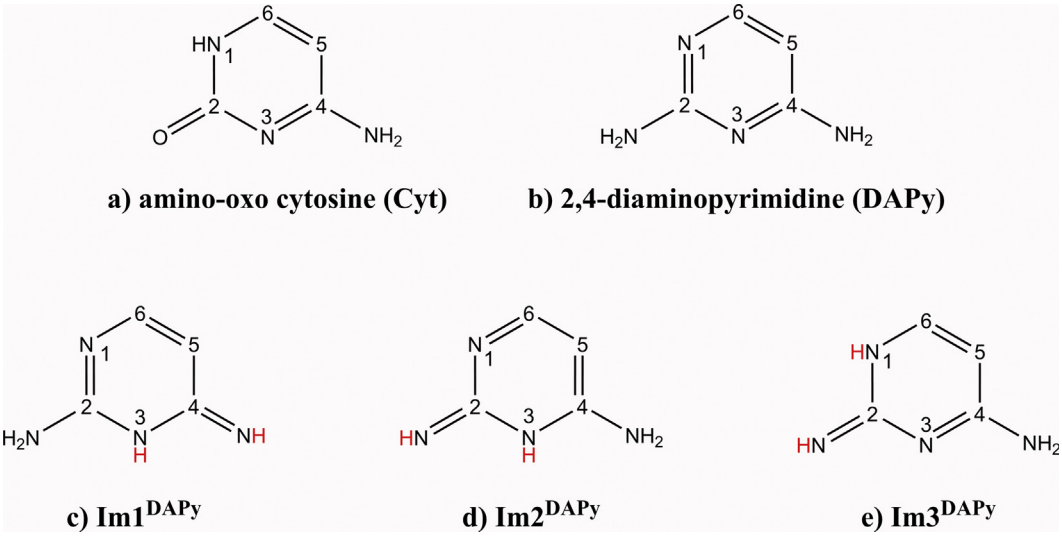

Scheme 1. Structural formulas of (a) the keto tautomer of Cyt, (b) the diamino tautomer of DAPy and (c–e) its imino tautomers: (c) $Im1^{DAPy}$, (d) $Im2^{DAPy}$, (e) $Im3^{DAPy}$.

groups of the aromatic rings can also affect the excited-state lifetimes and hinder radiationless deactivation. The canonical structures of the two compounds under study herein are depicted in Scheme 1.

The radiationless deactivation mechanisms of the excited states of Cyt have been extensively investigated at different levels of theory using both static explorations of the excited-state potential-energy surfaces and nonadiabatic molecular-dynamics simulations [2,3,24,26,27,29,31–46]. It has been well documented that Cyt deactivates in a radiationless manner to the ground state via S_1/S_0 conical intersections along a variety of excited-state reaction paths [2,3,24,26,27,29,31–46]. In contrast, DAPy has not been as intensively studied, thus significantly less is known about its photostability compared to other pyrimidine bases. The nonadiabatic photodynamical surface-hopping simulations of Nachtigallová et al. have shown that the additional amino group, which is present in DAPy in contrast to Cyt, blocks part of the ring-puckering modes involved in ultrafast deactivation [47]. On the other hand, it does not alter the excited-state lifetime of DAPy significantly, because other ultrafast relaxation pathways are available. The simulated UV spectrum of DAPy has a single broad band with the origin at 4.46 eV and a maximum at 5.10 eV. These authors have also shown that the excitation energy influences the dynamics of DAPy, the degree of ring-puckering, and the variety of structures by which the system relaxes to the ground state. They have also found that the excited-state lifetime is longer by about 50% when the excitation energy is 4.6–4.7 eV in comparison to 5.0–5.1 eV or 5.1–5.6 eV. If the excitation energy is at the band maximum or higher, it allows the system more time for a suitable adjustment of all coordinates to reach the conical intersection. The most common conical intersections involved in the radiationless deactivation of DAPy have been found to be characterized by twisting of the N1—C6 and C5—C6 bonds and by puckering of atoms N1 and C6 [47]. The systematic investigation of the photophysics and the photochemistry of nucleobase analogues such as DAPy is essential for understanding why nature "has chosen" selected nucleobases such as Cyt as constituents of nucleic acids [2].

A mechanism for phototautomerization that explains the formation of tautomers through excited states was proposed by Sobolewski: in the so-called photoinduced dissociation-association (PIDA) mechanism, the tautomerization is driven by a $\pi\sigma^*$ excited-state reaction path [48–50]. This mechanism involves the photodissociation of an X—H bond (e.g. N—H) and the subsequent association of the H atom to another H-accepting center, both steps of which occur in an excited state. The $\pi\sigma^*$ excited state plays a key role in H-atom detachment and proton-transfer processes in a variety of molecular systems [51,52]. In general, each X—H bond can harbor a $\pi\sigma^*$ state where the σ^* orbital exhibits antibonding character with respect to that X—H bond. At short X—H bond lengths typically found for a ground-state equilibrium geometry, a $\pi\sigma^*$ state usually presents as a $\pi \rightarrow$ Rydberg state or at least as an excited state with a strong Rydberg character. Upon elongation of the respective X—H bond, the spatial extent of the σ^*/Rydberg orbital shrinks and the Rydberg character thus decreases until the orbital can be classified as a compact antibonding orbital. Electronic excitation to a $\pi\sigma^*$ state can lead to X—H photodissociation due to the repulsive character of the electronic state with respect to elongation of the X—H bond.

In Cyt, however, the PIDA mechanism and alternative mechanisms for phototautomerization are overshadowed at room temperature by internal conversion through ring-puckered conical intersections [2,3,24,26,27,29,31–46]. At low temperatures, on the other hand, amino–imino tautomerization processes have been observed for Cyt [14] and 1-methylcytosine [53] in an argon matrix after irradiation with UV light of wavelengths shorter than 311 nm (for Cyt) and 308 nm (for 1-methylcytosine). These processes cannot be explained by the PIDA mechanism due to high energy barriers found for Cyt and 1-methylcytosine along this mechanistic reaction path. An alternative mechanism for phototautomerization has been presented by Li and Blancafort for 1-methylcytosine [54] and by Triandafillou and Matsika for Cyt [44]. This mechanism involves the ring-puckered conical intersections driving the radiationless deactivation via S_1/S_0 internal conversion, which were found to be connected along a barrierless reaction path to a transition state for ground-state tautomerization [54,44].

Another competing photochemical mechanism that has been widely studied is the photocyclodimerization of pairs of nucleobases [55,56]. Roca-Sanjuán et al. have shown that the formation of the cyclobutane dimer occurs through an S_1/S_0 conical intersection along the excited-state reaction path of the $^1\pi\pi^*$ excited state in a barrierless manner [57]. Such investigations have not been presented for DAPy so far.

The present comparative study focuses on the radiationless deactivation mechanisms in Cyt and DAPy. We aim to unravel the differences in the degree of photostability between these two compounds and elucidate the phototautomerization of DAPy via the PIDA mechanism. This comparison may provide insight into the