Radiationless Decay Mechanism of Cytosine: An Ab Initio Study with Comparisons to the Fluorescent Analogue 5-Methyl-2-pyrimidinone

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The ultrafast radiationless decay mechanism of photoexcited cytosine has been theoretically supported by exploring the important potential energy surfaces using multireference configuration—interaction ab initio methods for the gas-phase keto-tautomer free base. At vertical excitation, the bright state is S1 (ππ*) at 5.14 eV, with S2 (nπ*) and S3 (nππ*) being dark states at 5.29 and 5.93 eV, respectively. Minimum energy paths connect the Franck—Condon region to a shallow minimum on the ππ* surface at 4.31 eV. Two different energetically accessible conical intersections with the ground state surface are shown to be connected to this minimum. One pathway involves N3 distorting out of plane in a sofa conformation, and the other pathway involves a dihedral twist about the C5–C6 bond. Each of these pathways from the minimum contains a low barrier of 0.14 eV, easily accessed by low vibronic levels. The path involving the N3 sofa distortion leads to a conical intersection with the ground state at 4.27 eV. The other pathway leads to an intersection with the ground state at 3.98 eV, lower than the minimum by about 0.3 eV. Comparisons with our previously reported study of the fluorescent cytosine analogue 5-methyl-2-pyrimidinone (5M2P) reveal remarkably similar conformational distortions throughout the decay pathways of both bases. The different photophysical behavior between the two molecules is attributed to energetic differences. Vertical excitation in cytosine occurs at a much higher energy initially, creating more vibrational energy than 5M2P in the Franck—Condon region, and the minimum S1 energy for 5M2P is too low to access an intersection with the ground state, causing population trapping and fluorescence. Calculations of vertical excitation energies of 5-amino-2-pyrimidinone and 2-pyrimidinone reveal that the higher excitation energy of cytosine is likely due to the presence of the amino group at the 4-position.

1. Introduction

The ability of DNA and RNA to absorb ultraviolet light without significant reaction or fluorescence is a property that is vital for life exposed to sunlight. This property has been given considerable experimental and theoretical attention in recent years,1 and it has been determined to be largely an intrinsic property of the nucleobases, which display extremely low fluorescent quantum yields and ultra-short excited-state lifetimes. Theoretical investigations into the structural and electronic properties but generally to display much longer fluorescence lifetimes. Theoretical investigations into the structural and similarities and differences with cytosine, focusing on the energetic and geometric changes involved with its fluorescence behavior. Understanding the photophysical behavior of an excited molecule requires accurate mapping of the potential energy surfaces (PESs), especially the singlet S1 surface. Kasha’s rule29 states that fluorescence will most likely originate from a population trapped on this surface. Trapping of the S1 population requires that the ci seams between this surface and the ground state surface must be too high in energy compared with the S1 minimum to be easily accessible or else the S1 population must be blocked from accessing this ci by an energy barrier sufficiently high to bind vibrational levels. In the case of 5M2P, we located two different ci seams between the S1 and the ground

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state surface, but they were too high in energy so trapping of the S1 population was shown to be possible; thus, fluorescence for 5M2P was supported theoretically.

We continue this study by presenting the results of MRCI calculations on the photophysical behavior of cytosine. Our goal is to theoretically identify the electronic and structural features needed to facilitate ultrafast radiationless decay of this base and to observe how they differ from 5M2P. While our report on 5M2P was to the best of our knowledge the first such analysis of that base, cytosine has received considerable theoretical attention.\(^8\)\(^\text{14,30}\) Ismail et al., using complete active space-self consistent field (CASSCF), reported a decay mechanism wherein the bright S2 ππ* population undergoes a state switching to the nOπ* surface, with a subsequent accessible channel to the ground state through a gs/n0π* ci.\(^7\) Also located was an energetically blocked gs/n0π* intersection, with considerable out-of-plane distortion at the intersection by N\(^3\).\(^1\) Merchán and Serrano-Andrés, by using complete active space with second-order perturbation theory (CASPT2) to include dynamical correlation, found S1 to be ππ* which crossed with the ground state surface.\(^8\) Other groups have located an accessible S0/S1 ci with C5/C6 diradical character and a commensurate twist around the C5—O6 bond. Sobolewski and Domcke located this channel in the cytosine—guanine base pair,\(^10\) and Tomic et al. located a similar distorted ci in isolated cytosine with density functional theory (DFT)/MRCI.\(^11\) Zgierski et al. also recently reported such a decay channel structure for cytosine from results of completely renormalized equation of motion coupled-cluster (CR-EOM-CCSD(T)) calculations of configuration interaction singles (CIS)-optimized geometries.\(^13\) With such a diverse and sometimes conflicting range of proposed mechanisms of the decay of excited cytosine, it is currently unclear which of these is more valid than the others. Indeed, a more accurate picture might actually be a combination of these mechanisms or even other mechanisms entirely. Additionally, some of these previous studies used methods that did not include dynamical correlation for calculating gradients. Dynamical correlation has been shown to be important for predicting the correct order of states and thus is critical when state crossings are involved.\(^8\) In this report, a comprehensive analysis of the pathways for the radiationless decay in cytosine is presented using MRCI methods for both the energies and the gradients, and they are compared with the results reported for the fluorescent analogue 5M2P. Detailed analysis of the differences in photophysical properties of the two molecules requires studies at the same high level of theory.

The methods used to study cytosine will be presented in section 2, including the theoretical treatments and software used. Then, in section 3, results will be discussed, including vertical excitation data, location of stationary points on the singlet-state adiabatic surfaces, ci, pathways connecting many of these points, and comparisons with 5M2P. Finally we will conclude and summarize in section 4.

2. Methods

The basis sets for all atoms were the double-ζ plus polarization (cc-pvdz) Gaussian basis sets of Dunning.\(^31\) Cytosine has 58 electrons in total, with 8 heavy atoms (N, O, and C), and 5 hydrogens. All calculations were carried out with no symmetry restrictions. Molecular orbitals (MOs) were obtained from a state-averaged multi-configuration self-consistent field (SA-MCSCF) procedure for the first four singlet states, unless otherwise specified. The five lowest singlet states arise from excitations of π, nO, and nO electrons to π* orbitals, and so the complete active set (CAS) of orbitals was chosen to be 7 π, 1 nO, and 1 nO, with a total of 12 electrons in 9 active orbitals. We denote this arrangement as (12, 9). In general, (n, m) denotes n electrons in m active orbitals. The CASSCF calculation generated 2520 reference configurations from this active space, which was used for all subsequent MRCI calculations presented here. The amino nitrogen lone pair was not treated as active in any of the calculations presented in this report.

Three different MRCI expansions were used for calculations. MRCI1 included only single excitation configuration state functions (CSFs) generated from the CAS orbitals, with the core 1s, σ orbitals and one oxygen lone pair remaining always frozen. This low-level expansion contained 637 560 CSFs and was used for single point calculations as well as location and frequency analysis of stationary points and ci searches.\(^33,34\) The next expansion, labeled MRCIστ1, incorporated dynamical correlation of the σ electrons with the π and nonbond electrons. It has been shown\(^35–39\) that dynamical correlation of core and active electrons is important in describing the excited states of organic π systems. Studies on aromatic and planar heteroatom systems that incorporate dynamical correlation with perturbation have supported this assertion, and it has been further shown that inclusion of σ — π correlation is important when studying the electronic structure and excited states of the nucleobases.\(^8,19,20,30,40,41\) For the MRCIστ1 expansion, only single excitation CSFs were included in the expansion, but the inclusion of excitations from the 14 σ orbitals and the second oxygen lone pair gave approximately 10 million CSFs. Is core orbitals were maintained as frozen. This expansion was used to refine MRCI1 single points and for a more accurate optimization of geometries such as important stationary points and ci. The third expansion used, labeled MRCIστ2, includes single excitations from the σ electrons and one oxygen lone pair plus single and double excitations from the CAS orbitals into the virtual orbitals. Double excitations dramatically increase the number of configurations in the expansion, with MRCIστ2 for this molecule having over 121 million CSFs. MRCIστ2 was only used for single point calculations of important geometries, and often only the first two states were allowed to converge, since our main focus was on the topology of the S1 surface.

Linear interpolation (LI) between important geometries was performed in order to quickly give qualitative information about state surface crossings and possible minima and barriers between equilibrated geometries. Calculations presented in this paper did not result in the rotation or translation of cytosine, only distortion, while maintaining the relative orientation as constant. The difference between the Cartesian coordinates of two geometries of interest was calculated, and several geometries were generated by adding this difference times a scaling factor from 0 to 1. This gives the energy profile for a molecular change corresponding to a single concerted motion of all atoms linearly between two geometries. The geometries generated along the LI path can then act as launching points for searches of gradient minima and barriers or can support a connection between
is a dark nπ* state with an oscillator strength of 0.001. This order of state character is conserved at all three levels of MRCI. Assigning orbital character to each excited state was challenging when using the CAS-MO basis set and the MRCI wave function coefficients, since the nonbonding MOs were quite mixed, and so were the resulting MRCI CSFs. A more absolute assignment was accomplished by analyzing the direction of the static state dipole moments and was also verified by the change in Mulliken charges for N3 and O8 compared with the Mulliken charges on these atoms for the S0 state. Because of the planarity of the ring, the orientation of the static state dipole can be approximated by its in-plane components. The dipole orientation angle is defined in Figure 1. The ground state has a dipole orientation of θ = 159.8° and a magnitude of 5.90 D. The dipole of the S1 state has an orientation of θ = 141°, and its magnitude is approximately twice that of S2 and S3 (4.33 D, compared with 2.32 D for S2 and 1.72 D for S3), showing that the charge on N2 and O8 has remained relatively fixed, as expected from a ππ* character. The state dipole for the S2 state reflects the loss of N3 charge with an orientation that is dominated by the carboxyl dipole (θ = 177°, as defined in Figure 1), and thus, S2 is assigned an nππ* character. The S1 state displays a dipole

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<th>S3</th>
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* All values are in electrons referred to the S0 of the minimized ground state at the MRCI level indicated. MRCI S0 energy for ground state in is -392.775 646 hartree. †f is the oscillator strength. ‡Italic numbers in parentheses are zero-point energy corrected energies in electronvolts. ‡Zaloudek et al. 49, Nir et al. 50 MRCI01 results for ground state in is -392.911 623 hartree. 44, 45 Indicates geometry was optimized at the MRCI01 level, otherwise the geometry used was optimized at the MRCI level. MRCI02 results for ground state in is -393.034 481 hartree.
TABLE 2: Selected Bond Lengths and Angles for Stationary Points and Conical Intersectionsa

|                  | R(S0) | R(S1)min | R(S2)lp(σpσa) | R(S3)lp2(σpσa) | R(S1)fmin | R(S2)fππ | R(S3)fππ
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<td>C2−C3</td>
<td>1.345</td>
<td>1.338</td>
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a Bond lengths are in Å, angles are in degrees, and geometries are optimized at the MRCI1 or MRCIσπ1 level, as indicated in the column heading for each geometry.

orientation of θ = 119°, reflecting a loss of charge from the oxygen, and so, this state is assigned an n(π*) character.

The assignment of the ππ* character to S1 in cytosine is supported almost universally in the literature by other researchers using a wide variety of theoretical methods such as CIS,13 CASPT2,30 quasi-degenerate second-order perturbation theory (QDPT2),13 DFT/MRCI,11 and early MRCI utilizing only several thousand CSFs.48 The assignments of character to the S2 and S3 ππ* states, however, are not generally consistent, with S2 being n(στπ*) and S3 being n(σπτ*) in some reports and reversed in others. Indeed, the results of our own multi-configuration self consistent field (MCSCF) calculations show S2 as n(στπ*) and S3 as n(σπτ*) when using MOs averaged over four states, but these assignments switch when the MOs are averaged over five states. It is clear, however, that in both of these cases the nonbond orbitals are quite mixed, with an assignment of n(στπ*) being given to a state that is mostly excitation from N3 but with a significant, although lesser, amount of excitation from N0 possible as well.

MRCI calculations on the ground state geometry using either of these two generated sets of MOs, however, consistently show S2 to be excitation from the N3 nonbond and show S3 as excitation from the C2−O6 bond.

The energies of S1, S2, and S3 at the MRCI1 level are respectively 5.10, 5.39, and 5.89 eV. At the MRCIσπ1 level, these energies are 4.94, 5.13, and 5.63 eV, reflecting a stabilization of about 0.2 eV for each state when σ−π correlation is included in the wave function. When the highest level of correlation is included at the MRCIσπ2 level, however, the energies destabilize somewhat to 5.14, 5.29, and 5.93 eV, respectively. Experimentally, crystalline cytosine, with corrections to approximate an isolated molecule, gives its maximum absorbance at 37 900 cm−1, or 4.70 eV.49 This translates into an error of 5.0−8.5% for MRCI. The next two bands, characterized as excitations from nonbond orbitals to the π*, had low intensity and were observed at 43 000 cm−1 and 45 400 cm−1, or 5.33 and 5.63 eV, making the error for MRCIσπ2 0.8% and about 5% for these states, respectively.

3.1.2. S1 Stationary Points. The S1 ππ* surface from vertical excitation leads through a mass-weighted gradient-directed path to a minimum, verified by frequency analysis,50 at 4.31 eV (MRCIσπ2). The zero-point energy corrected value is 4.16 eV which is 0.2 eV higher than the experimental 0−0 origin.51 Table 1 gives the first four energy levels for this geometry at the MRCI1 and MRCIσπ1 levels and the first two energies at the MRCIσπ2 level. Bond lengths and bond angles for this point are given in Table 2. This minimum will be called R(S1)min, and it is the global minimum at the MRCI1 and MRCIσπ1 levels. Its structure can be viewed in Figure 2b. The geometry of R(S1)min is compared with the geometry of R(S0), displays a stretching of the C2−O6 bond of about 0.1 Å, as well as a slight
two energies at the MRCI and N3 atom distorting out of plane. At this geometry, S2 is 0.3 eV higher than S1 (MRCI1) and is primarily nπ* in character with a lesser amount of ππ* mixing in. S3 is more than 1.5 eV higher (MRCI1) and is a n N 1 minima that is decoupled from the R e gap between (S 1 ) sp2,twist and the S1 energy of (S 1 ) min is as much as 0.3 eV, but the results of the higher correlation at the MRCI1 level are essentially pure n O orbital to the C 4 p orbital. If the ring was planar, this character would be assigned as ππ*, but with N3 being distorted significantly out of plane, this p orbital is for the most part decoupled from the π system. Likewise, pyramidalization of C4 has forced hybridization of its p orbital, and it is also decoupled from the π system. Thus, it is probably more accurate to characterize the state at this distorted geometry as an NVC4 diradical. S2 and S3 at this geometry are very high in energy, at 6.44 and 7.22 eV, respectively, at the MRCI1 level. These two states are essentially pure ππ* in character, and their energetic remoteness from S1 results in almost no ππ* mixing with the S1 state, as is seen by analysis of the MRCI wave function coefficients.

Three verified first-order saddle points were also located on the S1 surface at the MRCI1 level. The first four energies of these points at the MRCI1 and MRCI0 levels and the first two at the MRCI0 level are listed in Table 1, and its geometry can be viewed in Table 2 and Figure 2c. The ring in R(S1)′ min is also distorted out of the planarity of the ground state geometry, but rather than the butterfly fold displayed by R(S1)min, R(S1)′ min is distorted in a “sofa” or “envelope” conformation, with N3 puckered out of plane and the other five ring atoms remaining largely coplanar. Atom C4 is strongly pyramidalized, with the puckering out of plane and the other five ring atoms remaining relatively unpyramidalized. The barrier and is easily accessible by the S1 population at 4.46 eV at the MRCI0 level. It has an imaginary frequency of 318.91 cm−1. Its conformational distortion is the result of a dihedral twisting of the C3−C5 bond, with slight pyramidalization of those atoms. Its imaginary vector, shown in Figure 2e, is dominated by opposite out-of-plane motions of atoms H2 and H6 as the C3−C5 bond twists, and those two carbons pyramidalize somewhat. Because of this twisting about the C3−C5 bond, we label this region of S1 relative to R(S1)min the “twist” region.

At the MRCI1 and especially the MRCI0 level, the energy gap between R(S1)′ sp2,sofa and the S1 energy of (S 1 ) min is as is as much as 0.3 eV, but the results of the higher correlation at the MRCI0 level show that the topology of the S1 surface changes, and this energy barrier decreases. Indeed, when the most dynamical correlation is included in the wave function, the energy of (S 1 ) min raises by about 0.2 eV, and the MRCI0 energy of (S 1 ) sp2,twist is only about 0.15 eV higher than R(S1)min at 4.46 eV. This is only about a 3.5 kcal/mol barrier and is easily accessible by the S1 population at R(S1)min, which has excess vibrational energy from vertical excitation.

### 3.1.3. Conical Intersections
Conical intersections between energy surfaces provide an efficient channel for radiationless transitions and fluorescence quenching. The ci of cytosine that are important for its photophysics are presented here. Their energies, as well as the topography of their features, contribute to their role in the behavior of the photoexcited molecule. Other ci, less directly involved in the photophysics of cytosine, will also be presented in this section.

The topography of the potential PESs in the vicinity of ci can play a significant role in the efficacy of a ci to promote a nonadiabatic transition, as has been presented previously.52−59 For cytosine, which has a 33-dimensional coordinate space, the seam space, where two PESs I and J are degenerate, is spanned by 33 − 2 = 31 degrees of freedom, with the remaining two degrees of freedom being the branching coordinates, which lift the degeneracy linearly from the ci. These two branching coordinates are the tuning vector and the coupling vector53 and are denoted as g[I] and h[I], respectively, using Yarkony’s notation.52,57 g[I] is the energy difference gradient, and h[I] is the gradient of the coupling between states I and J. They are defined mathematically by

\[
g[I] = \frac{\partial}{\partial \mathbf{R}} [E_I - E_J] \tag{1}
\]

\[
h[I] = \left[ \Psi_I \frac{\partial H}{\partial \mathbf{R}} \Psi_J \right] \tag{2}
\]

where \(E_I\) and \(\Psi_I\) are the energy and eigenfunction of state I, respectively. The topography of the ci in the branching plane is given in terms of the parameters \(g, h, s_x, s_y\).52 The energies of the intersecting states I and J are then given by

\[
E_{IJ}(x,y) = s_x x + s_y y \pm \sqrt{(gx)^2 + (hy)^2} \tag{3}
\]

where \(x\) and \(y\) are displacements along the \(g[I]\) and \(h[I]\) directions, \(g\) and \(h\) are the slopes along those two directions, respectively,
and $s_x$ and $s_y$ give the tilt of the cone. These parameters are used here to characterize the topography of the $ci$ found.

Although the points reported in this work are minima on the seam hypersurface, it is not suggested that actual nonadiabatic dynamics occurs only at these points. Indeed, it has been shown that, depending on the accessibility of the seam relevant to the reaction pathways and on the initial wavenumber conditions, extended or narrow ranges of the seam may be important to the dynamics. The present study focuses on whether these seams are energetically accessible to enable radiationless decay that will compete with radiative fluorescence. The minimum energy point then serves as the lower bound. If there is not enough energy available to access that point, then there is definitely not enough energy to access the energetically higher regions on the seam. A quantitative discussion that would provide vibrational distributions, rates, and quantum yields would require dynamics and the description of a larger part of the seam. This is beyond the scope of the present work.

3.1.3.1. $R_e(c01)_{sofa}$ and $R_e(c01)_{twist}$. The ability of cytosine to undergo ultrafast radiationless decay depends on several factors, one of which is the ability of the excited $S_1$ population to energetically access an intersection with the ground state. Thus, the location of the $S_0$-$S_1$ seams is crucial to predicting the photophysical behavior of the molecule. Two such seams, corresponding to the two different kinds of conformational distortion compared with $R_e(S_1)_\text{min}$, as described earlier, were located in cytosine. Both have $S_0$/$S_1$ minimum energies approximately equal to or lower than the minimum on the $S_0$ surface, depending on the level of correlation included, and $S_0$ for each corresponds to the ground state closed-shell PES. The minimum energy points on the $ci$ seams are labeled $R_e(c01)_{sofa}$ and $R_e(c01)_{twist}$. Figure 3 shows their geometries, and Figure 4 shows the branching vectors at these $ci$. Energies are listed in Table 1 for all three levels of correlation, and bond and angle data are listed in Table 2. $R_e(c01)_{sofa}$ has a bond very similar to $R_e(S_1)_{\text{min}}$ and $R_e(S_1)_{\text{sp2,sofa}}$, with N1 distorted out of plane in a sofa conformation and strong C1 pyramidalization. Its energy is 4.10 eV at the MRCI1 level. Optimizing the MRCI1 geometry at the MRCI0x1 level increases the energy to 4.41 eV, and when higher correlation at the MRCI0x2 is included, this geometry gives an $S_0$ energy of 4.09 eV and an $S_1$ energy of 4.45 eV. The average of these energies is 4.27 eV, which is lower in energy than $R_e(S_1)_{\text{min}}$. $R_e(S_1)_{\text{sp1,sofa}}$ or $R_e(S_1)_{\text{sp2,sofa}}$. The highest barrier between this $ci01$ and the $R_e(S_1)_{\text{min}}$ is only 3.5 kcal/mol. Thus, population from vertical excitation should have clear access to this $ci01$, making this $ci$ a viable channel for ultrafast radiationless decay of the excited population to the ground state. The character of the $S_1$ state at this $ci$ is virtually the same as that of $R_e(S_1)_{\text{min}}$, a diradical with excitation primarily from the distorted N1 p orbital (shown in Figure 5c) to the hybridized orbital on the pyramidalized C1 atom (shown in Figure 5d). The topology of this $ci01$ is shown in Figure 5a, and cone parameters are given in Table 3. It is tilted and relatively symmetric.

It should be noted here that $R_e(c01)_{sofa}$ is conformationally very similar to a $ci01$ found in cytosine by Ismail et al. and also Merchán and Serrano-Andrés. The authors assigned closed-shell/nvC^+ character to this $ci01$, but while it was energetically favored compared with the $S_1$ minimum, CASSCF or CASPT2 gave a substantial barrier on that region of the $S_1$ surface. MRCI does give a barrier separating $R_e(S_1)_{\text{min}}$ from $R_e(c01)_{sofa}$, but it is small.
Another $S_0$–$S_1$ seam involving the ground state surface was located in cytosine with MRCI. This $ci$, labeled $R_{ci}(c|01)_{twist}$, displays conformational distortion primarily as a result of a 114.8° dihedral twist around the $C_5$–$C_6$ bond, as well as some pyramidalization of those atoms, with the rest of the ring atoms following this primary distortion. Its character is best described as $n^\pi_*$, with primary excitation from the $p_z$ orbitals on $C_7$, $N_1$, and $O_6$ to the $C_5$ $p_z$ orbital, as shown in Figures 5c and 5d. $N_1$ is somewhat out of plane and is pyramidalized. $R_{ci}(c|01)_{twist}$ has an $S_0/S_1$ average energy of 3.98 eV at the MRCI$\alpha\alpha_2$. Given that the energy at this level of theory for the saddle point separating this $ci01$ from the global MRCI$\alpha\alpha_2$ minimum is less than 0.20 eV above the minimum, this $ci01$ not only is energetically accessible by a vibrationally excited $S_1$ population but also is the energetically favored channel to the ground state surface, being about 0.3 eV lower than that of the minimum or $R_{ci}(c|01)_{sofa}$. The topography for this $ci$, shown in Figure 5b, displays a vertical $ci$, which is the ideal topography for efficient nonadiabatic transitions from an upper to a lower adiabatic surface, in this case $S_1$ to $S_0$. Marian et al. and also Zgierski located a similar energetically accessible $ci01$ using DFT/ MRCI, also having a $C_5$–$C_6$–$H_6$ dihedral angle only about 10° more than our results from MRCI.

Experimentally, it has been shown that cytosine retains its subpicosecond lifetime in a low pH environment. It has been argued that $N_3$ should be protonated in this case, thus removing the pyramidalized amino nitrogen. Both of these $ci$ could serve to funnel higher energy populations onto the $\pi^\pi*$ surface.

Two additional $ci$ seams were located in cytosine. The MRCI$\alpha_1$-optimized geometries are shown in Figure 3; energies are listed in Table 1; and bonds and angles are listed in Table 2. Cone parameters are listed in Table 3. An $S_2$–$S_1$ minimum energy point on the $n^\pi_*/n^\sigma_*$ seam was found at 4.84 eV (MRCI, Table 1). This $ci$ is named $R_{ci}(c|01\prime)$. The geometry is planar, although the amino $N_3$ is pyramidalized. The crossing of the $n^\sigma_*/n^\pi_*$ states changes the character of the $S_2$ state, and thus the change in the mixing of the character of state $S_2$ with $S_1$ is possibly responsible for the barriers located on the $S_1$ surface. The remaining $ci$ located for cytosine is a $c|01\prime$, named $R_{ci}(c|01\prime\prime)$ located at 4.74 eV (MRCI$\alpha_1$), but it is a stationary point on the $\pi^\pi*/n^\pi_*$ seam with neither of the states having a closed-shell character. The closed-shell state is at 5.29 eV. The geometry of this $ci$ resembles the $ci$ found by Merchán and Serrano-Andrés, although the two states in their case were gs/ $\pi^\pi*$. Since $S_1$, $S_2$, and $S_3$ are very close in energy, the order of state characters could be very sensitive to the level of correlation used in the calculations.

3.1.3.2. Other Conical Intersections. Additional $ci$ were located in cytosine. Their energies are below vertical excitation. Although they are not encountered here in a direct mechanism of the $S_1$ surface deactivation, they could be accessed if the system absorbs higher energy photons, or they may be indirectly involved in the excited-state dynamics of cytosine. Two $ci$ seams between the $S_1$ and the $S_2$ states were found. Their energies are presented in Table 1; their bond lengths and bond angles are listed in Table 2; the values of the cone parameters presented in eq 3 are listed in Table 3; and the optimized geometries are shown in Figure 3. One of these geometries, labeled $R_{ci}(c|12)$ at 4.21 eV (MRCI$\alpha_1$), is the lowest energy point on a $S_1$–$S_2$ seam found for cytosine, and it has $n^\sigma_*/\pi^\pi_*$ character which is reflected in a 0.13 Å increase in the $C_2$–$O_6$ bond length. This $ci$ is close to planar with a slight chair-like conformational distortion, angling $C_4$ and the amino $N_7$ above the plane while angling $N_1$ slightly below the plane. This is clearly seen in the side view shown in Figure 3. Most interesting is the fact that all the bond and angle values of this $ci$ are very closely matched with those of $R_{ci}(S_1)_{min}$, indicating its proximity to that minimum. The second $ci12$, labeled $R_{ci}(c|12\prime)$ at 4.64 eV (MRCI$\alpha_1$), was located by optimizing the $S_1$–$S_2$ crossing seam from vertical excitation. The energies of $S_1$ and $S_2$ are very close upon vertical excitation, and thus the $S_1$–$S_2$ seam is easily accessed. This $ci$ has $n^\sigma_*/\pi^\pi_*$ character. The geometry at the minimum energy point on the seam has approximately $C_1$ symmetry, except for the pyramidalized amino nitrogen. Both of these $ci$ could serve to funnel higher energy populations onto the $\pi^\pi*$ surface.

Figure 7 shows the accessibility of the two gs/$\pi^\pi*$ $ci$ presented in the previous section, $R_{ci}(c|01)_{sofa}$ and $R_{ci}(c|01)_{twist}$, from $R_{ci}(S_1)_{min}$. $R_{ci}(S_1)_{min}$ is connected to the two saddle points, $R_{ci}(S_1)_{sp,sofa}$ and $R_{ci}(S_1)_{sp,twist}$, corresponding to two different conformational changes. The figure shows these two conformational change directions, “twist” and “sofa”, from $R_{ci}(S_1)_{min}$ on the $S_1$ surface, along with the rest of the first five energy levels calculated at the MRCI$\alpha_1$ level. The figure is several combined energy plots between optimized geometries described in previous sections. The vertical lines correspond to these optimized geometries, shown under the plot, which are con-
nected within each region. The energies for $R_e(S_i)_{min}$ are shown in the center of the plot with energy pathways along the sofa direction to the right (regions A–D) and in the twist direction to the left (regions A′–C′).

In the sofa direction, $R_e(S_i)_{min}$ is connected to the $ci$ through two saddle points and a second minimum. Region A shows $N^3$ distorting out of plane in a sofa fashion to $R_e(S_i)_{p1,sofa}$. The $S_1$ region around this saddle point is too flat to effectively sample via the gradient, but LI shows no additional barriers or minima on the $S_1$ surface in region A. $S_2$ here is $\pi\pi^\ast$ and is rising in energy. This is reflected in the carbonyl compressing from the minimum to $R_e(S_i)_{p1,sofa}$. $S_1$ is $\pi\pi^\ast$ in this region and is falling in energy. $S_4$ is a second $n\pi^\ast$ state. In region B from $R_e(S_i)_{p1,sofa}$ to $R_e(S_i)_{p2,sofa}$, the amino is going more out of plane with the ring, and $C_4$ is starting to pyramidalize at $R_e(S_i)_{p2,sofa}$. This region is also very flat, and so LI was used to connect these two saddle points, showing no additional features between them. An avoided crossing can be seen at the geometry of $R_e(S_i)_{p1,sofa}$ between $S_2$ and $S_1$, resulting from the $S_2/S_1 ci$ described earlier. Further pyramidalizing $C_4$ in this way leads to $R_e(S_i)'_{min}$ (region C) with the $S_1$ character primarily an $N^3/C^4$ diradical. $S_2$ to $S_4$ in this region are rising steeply to greater than 6 eV, resulting in little mixing of the nonbond character into the $S_1$ state from $R_e(S_i)'_{min}$ and onward in this direction. Further distortion in the same fashion (region D) eventually leads to the sofa $R_e(ci01)_{sofa} ci$. This region was also sampled with LI. The character of $R_e(S_i)'_{min}$ and $R_e(ci01)_{sofa}$ are both described as $N^2/C^4$ diradicals.

The pathways connecting $R_e(S_i)_{min}$ to $R_e(ci01)_{twist}$ are presented in Figure 7 to the left of $R_e(S_i)_{min}$ in regions A′–C′. The distortion in this direction is that of a twisting about the $C_5$–$C_6$ bond, and this motion leads to the saddle point $R_e(S_i)_{p2,twist}$ (region A′), where the imaginary vector is precisely this $C_5$–$C_6$ twisting. The plot in this region is a mass-weighted gradient-directed pathway from the saddle point $R_e(S_i)_{p2,twist}$ to $R_e(S_i)_{min}$. $S_2$ in this region is $n\sigma\pi^\ast$, which is rising as the system evolves from $R_e(S_i)_{min}$ toward $R_e(S_i)_{p2,twist}$. Commensurately, the carbonyl bond is compressing in this direction, from 1.30 Å at $R_e(S_1)_{min}$ to 1.22 Å at the saddle point. $S_3$ in region A′ is $n\sigma\pi^\ast$ mixed with $\pi\pi^\ast$, which crosses $S_2$ near the geometry of the $S_1$ saddle point. $S_4$ is a second $\pi\pi^\ast$ state in this region. Further twisting of the $C_5$–$C_6$ bond (region B′) leads from the barrier downhill to a very flat region of $S_1$, where the gradient is almost zero, to an intermediate geometry, shown at the border of regions B′ and C′. Attempts to locate a stationary point here were unsuccessful, as the system tends to go toward the $S_0$–$S_1$ seam with the routine we use for this purpose, and indeed linearly interpolating from this geometry to the twist $R_e(ci01)_{twist}$ (region C′) gives an essentially flat but slightly downhill path to the $ci01$. In regions B′ and C′, $S_2$ to $S_4$ are all mixed character of $n\sigma\pi^\ast$, $n\pi\pi^\ast$, and $\pi\pi^\ast$, and all three are around 6 eV or higher and not significantly influencing the character of $S_1$, which is $\pi\pi^\ast$ and quite delocalized throughout the entire path from $R_e(S_i)_{min}$ to $R_e(ci01)_{twist}$. At the $ci$, the $H_5$–$C_5$–$C_6$–$H_6$ dihedral angle has increased to 114.8°, and $N^1$ is somewhat out of plane and pyramidalized. Similar to the energies in the sofa region, energies calculated at the MRCI$\pi\tau$2 level for geometries in the twist region give the barrier at $R_e(S_i)_{p2,twist}$ as only about 0.15 eV higher than the minimum on the $S_1$ surface and so is not considered large enough to impede the highly vibrationally excited $S_1$ population from reaching $R_e(ci01)_{twist}$. Furthermore, a small barrier is consistent with the experimental observations of a break-off of the resonance-enhanced multiphoton ionization (REMPI) spectrum close to the 0–0 origin.\textsuperscript{51} Significantly, as was previously mentioned, the MRCI$\pi\tau$2 energy of this $ci01$ is about 0.3 eV lower than the global MRCI$\pi\tau$2 minimum, further supporting this $ci$ as the energetically favored channel for radiationless decay of photoexcited cytosine. Gradient directed paths on $S_0$ from both $R_e(ci01)_{sofa}$ and $R_e(ci01)_{twist}$ lead to the equilibrium ground state geometry.

**3.2. Comparisons between Cytosine and 5M2P.** We reported a detailed ab initio analysis of the fluorescence mechanism of 5M2P, a fluorescent cytosine analogue, the structure of which is shown in Figure 1.\textsuperscript{28} Our interest in this DNA base analogue is in the differences and similarities 5M2P has compared to cytosine. In this section, we will discuss many
of the structural and electronic similarities and differences between these two bases.

Figure 8 shows the MRCI results from that previous study on 5M2P, along with results for cytosine at the same level of theory. Energetically, it can be seen that the initial vertical excitation for cytosine is 5.14 eV, while for 5M2P it is only 4.37 eV, lower by about 0.8 eV. The S1 energies away from excitation for cytosine is 5.14 eV, while for 5M2P it is only

The initial vertical excitation excitation creates more excess vibrational energy in cytosine than in 5M2P. In 5M2P, there exists a low-energy minimum at 3.92 eV, which is below the energetically lowest c01 by about 0.3 eV, low enough to bind vibrational states and eventually fluoresce. In cytosine, this portion of the S1 surface, toward the c01, contains a small barrier but is essentially flat all the way to the c01, so this, by contrast, constitutes a viable radiationless decay channel. Cytosine has a second low-energy decay channel to the ground state as well, the twist c01, while the geometrically similar twist c01 for 5M2P is about 0.4 eV above the global minimum on the S1 surface. Thus, excluding any structural comparisions, MRCI supports efficient radiationless decay in cytosine but not in 5M2P, on the basis of these energy differences.

Interestingly, the S0 energy in the sofa region differs significantly for the two bases, with that of 5M2P remaining about 3 eV below the S1 energy for the region from R(S1)min to R(S1)'min and only then rising steeply to meet S1 at the sofa c01. By contrast, S0 for cytosine rises continually in its sofa region, and it is only about 1 eV lower than S1 at R(S1)'min. It can be argued that for cytosine S0 intersects with S1 earlier along the minimum energy path on the S1 surface, crossing at a geometry more similar to that of R(S1)'min.

Conformational similarities between these two bases on excited-state surfaces began to reveal themselves when stationary points on the S1 surface of cytosine were being calculated. Both molecules are planar in the ground state, and both excite their bright state and then evolve easily to a local minimum on the S1 ππ* surface. The distortion that takes place to reach this minimum for each molecule is very closely matched, both in bond and angle values, as well as the butterfly fold of the ring out of planarity. Overlaid plots of bond and angle values of the two bases are included in Supporting Information (Figure S1-1) for the geometries discussed in this paper and those reported previously for 5M2P. These plots illustrate that both bases display strikingly identical geometries on the excited-state surfaces, including S1→S2 intersections, S2→S3 intersections, and the MRCI S1 minimum. Indeed, it is clear from these two studies that these two bases have almost identical conformations, on both bright and dark surfaces, along pathways from vertical excitation on down to R(S1)'min. Both bases fold along the C4=N1 axis in a butterfly fashion, although 5M2P folds by several degrees more than cytosine. Features of the S1 surface after this butterfly minimum, although structurally very similar, are just different enough to make up what appear to be the dominant differences that ultimately separate the photophysical behavior of these two bases. Both, at the MRCI level, have a barrier on the S1 surface where the sofa-type distortion begins, with N3 predominantly leaving coplanarity with the other five ring atoms, and beyond this barrier, both bases have a second local minimum where the sofa distortion is more pronounced, R(S)'min. It is at the barrier that the two bases start to show differences in their bond and angle values. Beyond this second minimum, 5M2P must distort much further to reach the geometry of the c01, whereas the difference in geometry in cytosine between the second minimum and the c01 is much smaller. Electronically, the two molecules display somewhat different character at this c01. Cytosine displays strong diradical character at C4, while 5M2P displays more delocalized ππ* character. This is refected in the N3→C4 bond lengths for the two bases in this region, with that of 5M2P shorter and more double bond in character than that of cytosine, which stretches from 1.423 to 1.462 Å in the region from R(S)'min to the sofa c01. This is likely due to π donation from the amino group, which maintains a distance from C4 shorter than a C=N single bond throughout this region. The greater π overlap in 5M2P translates into a larger higher occupied molecular orbital—lowest unoccupied molecular orbital (HOMO–LUMO) gap, thus, increasing
the energy of the S1 surface and the gap between S0 and S1 in this region. Similarly, the N3–C4 bond stretching seen in cytosine in this region could also explain the higher energy of S0 compared with that of 5M2P and could contribute to the smaller energy gap.

Twisting about the C5–C6 bond for both molecules can eventually lead to the twist ci01 intersection with the ground state. However, in the case of 5M2P, this ci geometry is too high in energy to be a viable decay channel, and the atoms C5 and C6 are somewhat less pyramidalized than those in cytosine. The MOs involved with the S1 character of both the cytosine and the 5M2P twist ci01 are similarly delocalized. A saddle point analogous to cytosine’s $R_{ci}(S1)_{sp, twist}$ was located in the twist region of 5M2P, with an almost identical distortion to that of cytosine. Bond lengths and bond angles for the ring atoms are compared in a plot in Figure SI-1. The MRCl energies for this 5M2P saddle point are $S0 = 1.67$ eV, $S1 = 3.86$ ($\pi\pi^*$), 5.26 ($n_0\pi^*$), and 5.85 eV ($n_0\pi^*$), with an $S0/S1$ gap of about 2.2 eV. At the same level of theory, the gap between $S0$ and $S1$ energies for $R_{ci}(S1)_{sp, twist}$ is 2.1 eV or 0.1 eV less than that of 5M2P. Perhaps more important is the fact that for 5M2P the twist ci01 is about 0.3 eV higher than this saddle point, while for cytosine the ci is lower in energy than the saddle point at all levels of theory. Thus, like the sofa region, 5M2P must destabilize energetically in order to reach degeneracy between $S0$ and $S1$, while cytosine actually stabilizes. Further investigations into the reasons why the two bases display dramatically different energies at this ci are currently in progress.

The initial higher excitation energy of cytosine compared with that of 5M2P is likely to be an important factor in the different photophysical decay mechanisms of these two bases. To probe the reason behind this higher initial excitation, two additional bases were studied at the MRCl level: 2-pyrimidinone (2P) and 5-amino-2-pyrimidinone (5A2P). Vertical excitation energies for the optimized ground state structure of 2P were almost matched with 5M2P at 4.65 ($n_0\pi^*$), 4.69 ($\pi\pi^*$), and 5.38 eV ($n_0\pi^*$), with the same ordering of states. Thus, the methyl on 5M2P has almost no role in the energies or character of its excited states. The results of 2P also imply that the amino group on cytosine is necessary for its higher vertical energies. However, when the amino group is moved to the 5-position in 5A2P, the vertical excitation energies are also almost matched with 5M2P, including ordering of the states, at 4.62, 4.66, and 5.33 eV, showing that the amino has almost no effect at C5. This indicates a $\pi$–resonance interaction of the amino group in cytosine with the ring, which is supported by two important geometrical differences between the ground state structures of cytosine and 5A2P: in cytosine, the amino group is oriented so that its lone pair is almost perpendicular to the ring plane, and the C4–N7 bond is 1.38 Å, shorter than the average C–N single bond (about 1.47 Å); in ground state 5A2P, the amino group is rotated about 90° to the ring, and the C5–N7 bond length is 1.42 Å. This shows that the amino group in 5A2P is essentially decoupled from the ring $\pi$ system and is not included in the overall $\pi$ resonance of the ring. Thus, we propose that the presence and position of the amino group on the ring is critical to the higher excitation energy of cytosine, and it is largely due to $\pi$ donation from the amino nitrogen lone pair into the ring. Further investigations into the details of the role of the amino group in the photophysics of cytosine are currently in progress.

Besides the energetic arguments detailed above, a comparison of the photophysical behaviors of cytosine and 5M2P will benefit from an analysis of the nonadiabatic coupling $33,52,62,63$ between $S1$ and $S0$ for each base at geometries close to each of the two $S0$–$S1$ seams presented in this study: sofa and twist. The nonadiabatic coupling vector $f$ for transitions between two adiabatic PESs $I$ and $J$ is defined in eq 4:

$$f(I) = \sum_{ij} R_{ij} \phi_j (I)$$

where $\phi_j = \sum_i C_i^j \phi_i$ is the MRCI expansion for state $I$ in the basis of CSFs $\phi_i$, and $R_{ij}$ is the transition density matrix between state $J$ and state $I$. By calculating the magnitude of $f$ for geometries on the $S1$ surface close to $R_{ci}(S1)_{sofa}$ and $R_{ci}(S1)_{twist}$ for both cytosine and 5M2P, a qualitative comparison of the probabilities of nonadiabatic transitions from $S1$ to $S0$ can be made for the two bases in these two regions of $S1$.

Following the MRCI method $33,59$ and given the conformational similarities the two bases exhibit for $S1$ geometries discussed in this study, the magnitude of $f$, $|f|$, was calculated for geometries in two regions for each base: points linearly interpolated between $R_{ci}(S1)_{S0,min}$ and $R_{ci}(S1)_{S0,max}$ and also points linearly interpolated between $R_{ci}(S1)_{sofa}$ and $R_{ci}(S1)_{twist}$. Figure 9 shows plots of $|f|$ in bohr$^{-1}$ as a function of the N3–C4 bond length, R(N3–C4), for the sofa region and shows $|f|$ as a function of the $X$–C5–C6–H6 dihedral angle in the twist region (where $X = H$ for cytosine and $X = CH_2$ for 5M2P). It can be seen that in the twist region (regions C′ and D′, Figure 7) the values for $|f|$ for the two bases follow almost identical trends and magnitudes from the saddle point to the vicinity of the twist ci01 ($|f|$ at the intersection itself is infinity, but the value for the dihedral angle at the twist ci01 for each base is given on the x axis for reference). This implies that the nonadiabatic transition probabilities close to the twist ci01 for each base are about equal, and so the energetic accessibility differences at the twist ci01 for the two bases are likely to be the dominant factor in how the $S1$ population of each base behaves in this region of $S1$. In the sofa region (region D, Figure 7), however, cytosine displays about a factor of 10 more coupling compared with the same region in 5M2P, even for geometries very close to the sofa ci01. The reason for this is that in the sofa region of cytosine the $S0$ PES is much higher than in 5M2P, making the gap between $S1$ and $S0$ much smaller in cytosine, as discussed above. Since the first term of the right-hand side of eq 4 is the dominant term, $f$ varies almost linearly with the inverse of $\Delta E_{01}$, and so this smaller energy gap in cytosine dramatically increases $|f|$ in this region compared with the energy gap in 5M2P. Thus, both the S1 energetic differences and the resulting coupling differences are important contributions in this region for the photophysical behavior differences between cytosine and 5M2P.

The large derivative coupling in this region of cytosine generates higher nonadiabatic transition rates and indicates that the sofa ci01 seam extends close to the minimum energy pathway for cytosine in the sofa region. It has been shown before that the position of the ci seam relative to the minimum energy pathway can have an effect on the nonadiabatic dynamics producing radiationless transitions either in an extended region of the seam or just close to the minimum energy point $50,61$

4. Conclusions and Summary

The ultrafast radiationless decay of photoexcited cytosine has been supported theoretically with the MRCl calculations presented in this paper. Initial absorption of a UV photon excites the ground state system to $S1$, the bright $\pi\pi^*$ state at 5.14 eV.
The $S_1$ surface has a minimum at 4.31 eV which exhibits stretching of the carbonyl by about 0.1 Å and exhibits folding of the ring slightly in a butterfly fashion along the N$_3$/C$_4$ axis. Two $ci$ seams have been located which are connected to the $S_1$ minimum through barriers of about 0.15 eV. Pathways connecting the $S_1$ minimum to the sofa $ci01$ seam show a lower second barrier and a second minimum. At this geometry, the system is described best as an N$_3$/C$_4$ diradical on the ground state surface. The $ci$ between $S_1$ and the closed-shell $S_0$ surface has a geometry almost identical to the minimum and energy of 4.27 eV. Excess vibrational energy of the $S_1$ population from vertical excitation, about 0.8 eV above the global minimum, assures that the population can efficiently reach this $ci01$, making this $ci$ an effective channel for ultrafast decay to the ground state. The $S_1$ minimum at 4.31 eV, is also connected to a second $ci01$ seam. In this second pathway, the so-called twist direction, cytosine twists dihedrally about its C$_5$-C$_6$ bond, creating considerable ring distortion out of plane. This pathway, like the sofa direction, has a low barrier of 0.15 eV, compared with the global minimum. Twisting motion of the C$_5$-C$_6$ bond leads to a second $ci$ with the ground state, lower in energy compared with the $ci$ located in the sofa region of $S_1$. This $ci$ has an energy of 3.98 eV, which is about 0.3 eV lower than the global minimum or the sofa $ci01$, making this the more energetically favored $ci01$. Thus, we have shown that cytosine has two viable channels for ultrafast radiationless decay of its photoexcited state to the ground state surface. Experimentally bi-exponential decay signals, by time-resolved photoelectron spectra and femtosecond multiphoton ionization, support the idea of more than one decay channel.$^{54,65}$

Results of cytosine were compared with our previously published results of its fluorescent analogue, 5M2P. Comparisons of the important bonds and angles of these two bases revealed striking matches in the geometrical distortions along virtually all excited-state surfaces. As well, in 5M2P, the $S_1$ system was shown to be connected to both a sofa- and twist-distorted $ci01$, with geometrical similarity compared to cytosine especially matched in the twist $ci01$ region. However, 5M2P is excited only to about 4.4 eV, leading to less excess vibrational energy in the $S_1$ population, while cytosine is excited initially to 5.14 eV, leading to a more vibrationally excited $S_1$ population. 5M2P was also shown to stabilize to an $S_1$ minimum at least 0.3 eV below the energies of the two located $ci$ with the ground state surface, thus trapping the $S_1$ population and enabling fluorescence from the longer-lived $S_1$ population. Comparing the calculated vertical excitation energies for 5M2P and cytosine to those for 2-pyrimidinone revealed that the 5-methyl has at most minimal electronic effect on the vertical excitation energies of 5M2P and revealed that the lack of the 4-amino group seems to be the source of the major differences in the photophysics of 5M2P and cytosine. Comparing the excitation energy of cytosine to the vertical excitation energies and geometry of ground state 5-amino-2-pyrimidinone, which displayed energies very close to those of 5M2P, indicates that the initial higher excitation energy of cytosine is likely due to resonance of the 4-amino with the ring $\pi$ system, which is not present when the amino is at C$_5$. In addition to the role of the amino group as a proton donor in a base pair interaction with guanine, results of this study also implicate its role in the high vertical excitation energy of cytosine, as well as its enhancement of nonadiabatic coupling in the vicinity of one of its $S_0$/$S_1$ seams. Both of these effects can promote radiationless decay of photoexcited cytosine. Further investigations into the details of these important structural and electronic factors are currently in progress.

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Supporting Information Available: A complete table of bond lengths and angles, as well as plots comparing values of bond lengths and angles in cytosine and 5M2P, for all geometries discussed in this study. This material is available free of charge via the Internet at http://pubs.acs.org.
References and Notes


