NONRADIATIVE DECAY IN A SERIES OF CYTOSINE DERIVATIVES IN ROOM- TEMPERATURE AQUEOUS SOLUTION

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The lowest excited singlet states formed in the DNA and RNA bases by UV absorption have subpicosecond lifetimes in aqueous solution at room temperature. Ultrafast internal conversion by the bases minimizes the probability of photochemistry, providing nucleic acids with a high degree of photostability. In order to better understand the factors responsible for rapid nonradiative decay, we have been studying the photophysics of a series of cytosine derivatives by femtosecond transient absorption spectroscopy. The measurements indicate that subtle chemical substitutions profoundly alter the excited-state dynamics. Interestingly, the modified cytosines all have longer S1 lifetimes, suggesting that natural selection may have maximized the rate of nonradiative decay in the naturally occurring base.