THE DARK SINGLET STATE AS DOORWAY STATE OF INTERSYSTEM CROSSING IN DNA MONOMERS.

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The excited state dynamics of 9-methylpurine (9MP) were studied with broadband transient absorption spectroscopy in the time regime from femtoseconds to 3 nanoseconds. Excitation of 9MP in aqueous solutions at 266 nm results in ultrafast internal conversion from the initially excited $S_2(\pi\pi^*)$ state to the S_1 state. Quantum chemical calculations that include bulk and explicit solvent interactions show that the S_1 state has significant $n\pi^*$ character. Population of the S_1 state is followed by intersystem crossing (ISC) to the $T_1(\pi\pi^*)$ state on a time scale of hundreds of picoseconds. Vanishingly small fluorescence yields were measured, supporting the dark character of the S_1 state as well as the high triplet yield in 9MP. Analogous experiments in acetonitrile show a decrease in the ISC lifetime by almost 50 % but an equally high triplet yield. The results presented in this work demonstrate the important role that the dark singlet state has in modulating the excited-state dynamics of DNA monomers in solution.