Photophysical investigations of the canonical nucleobases that make up DNA and RNA show that in room-temperature solvents, their excited states decay with (sub)picosecond lifetimes ($\tau = 0.3\text{-}2\text{ ps}$). The apparent generality of ultrafast excited-state deactivation in the canonical nucleobases has led to the hypothesis that nucleobases are molecular survivors of the harsh UV environment on the early Earth before the emergence of life. However, we have recently shown that jet-cooled cytosine (Cyt) and its derivatives exhibit much longer lifetimes (e.g. $\tau = 930\text{ ps}$ for 1-ethylcytosine) when excited at or closely above the $S_1(\pi\pi^*)$ electronic origins. Only above 500 cm$^{-1}$ vibrational excess energy in the $S_1(\pi\pi^*)$ state does internal conversion sets in, the lifetimes of higher-lying vibronic levels decreasing to <20 ps. We now prove that the internal conversion mechanism involves twisting of the C5-C6 double bond in the $S_1(\pi\pi^*)$ state by chemically “clamping” this bond in 5,6-trimethylene-cytosine (5,6-TMCyt), see (c,d) below. The clamped 5,6-TMCyt has a lifetime of $\tau = 3.2\text{ ns}$ at its 0-0 band, and the onset of internal conversion increases to 4300 cm$^{-1}$ above the electronic origin. The availability of 5,6-TMCyt and similar derivatives with longer lifetimes allows to investigate the UV spectra and determine excited-state lifetimes of cytosine-water clusters, Cyt$\cdot$(H$_2$O)$_n$.

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