We address possible relaxation mechanisms of electronically excited DNA oligomers with a combined quantum mechanics/molecular mechanics (QM/MM) approach. Using long-range corrected density functional theory (LRC-DFT), we show that charge transfer (CT) states between neighboring nucleobases appear at energies just above optically bright $1\pi\pi^*$ excitonic states in aqueous solution. In double stranded DNA systems, both intrastrand and interstrand CT states are observed. It has been hypothesized that excitonic states may decay via a conical intersection into a CT state on a subpicosecond timescale. The proximity in energy of such states in our calculations appears consistent with this claim. Assuming that such a non-radiative mechanism occurs, we investigate subsequent relaxation of CT states by constructing and optimizing the geometry of model CT systems with constrained density functional theory (CDFT). We find that CT states relax in double stranded DNA through proton transfer across Watson-Crick base pairs with little to no energy barrier. Furthermore, the ground state energy shifts upwards along this reaction coordinate to nearly the same as that of the proton coupled charge transfer state, creating the possibility for a non-radiative pathway to the ground state.