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Ultraviolet absorption induces hydrogen-atom transfer in G·C Watson-Crick DNA base pairs in solution

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Abstract: Ultrafast deactivation pathways bestow photostability on nucleobases and hence preserve the structural integrity of DNA following absorption of ultraviolet (UV) radiation. One controversial recovery mechanism proposed to account for this photostability involves electron-driven proton transfer (EDPT) in Watson-Crick base pairs. We report the first direct observation of the EDPT process after UV excitation of individual guanine-cytosine (G·C) Watson-Crick base pairs by ultrafast time-resolved UV-visible and mid-infrared spectroscopy. We tracked the formation of an intermediate, biradical species (G[·H]·C[+H]) with a lifetime of 2.9 ps. The majority of these biradicals return to the original G·C Watson-Crick pair, but up to 10 % of the initially excited molecules instead form a stable double hydrogen atom transferred photoproduct G^{*}·C^{*}. Observation of these sequential EDPT mechanisms across intermolecular hydrogen bonds confirms an important and long debated pathway for deactivation of photoexcited base pairs, with possible implications for the UV-photochemistry of DNA.

For over fifty years, the role of inter-strand proton or hydrogen atom transfer in double helix DNA has been debated as a possible precursor for mutagenesis and carcinogenesis.^[1] However, recent theoretical studies postulated that ultrafast inter-strand electron-driven proton transfer (EDPT) instead contributes to the prevention of mutagenic photolesions in DNA excited by absorption of solar ultraviolet (UV) radiation.^[2] Rapid relaxation processes such as the proposed EDPT pathway render DNA intrinsically photostable^[3] and reduce the need for enzyme driven repair^[4] of photo-damage. Despite extensive prior study of DNA photophysics, the question of whether UV-induced EDPT is active in Watson-Crick (WC) base pairs remains contentious and contradictory experimental results have been published.^[2a, 5] In duplex DNA, recent reports suggest that both intra-strand interactions between “vertically” stacked nucleobases attached to the same sugar-phosphate backbone, and inter-strand interactions between “horizontally” WC-paired bases might contribute to the photochemistry of double-stranded DNA.^[6] A hybrid of the two processes may also occur; Zhang *et al.* invoked inter-strand proton transfer after intra-strand electron transfer,^[5d] but considered purely inter-strand EDPT to be unlikely on the

basis of QM/MM calculations on duplex DNA.^[7] The vertical π -stacking interactions can also promote photo-induced formation of long-lived excimers,^[6] but whether these excimers initiate or suppress proton transfer reactions is unresolved.

Here, we report use of ultrafast time-resolved optical spectroscopy, in both the UV-visible and mid-infrared (IR) spectral regions, to track the decay dynamics of an ensemble of individual UV-excited G·C WC base pairs (1) in solution. The results, summarized in **Fig. 1**, show direct evidence for the involvement of EDPT in the deactivation dynamics of the G·C WC pair. Observation in a solution of G·C dimers excludes any possible participation of excimer states induced by π -stacking. After UV excitation of G·C in chloroform, a single hydrogen atom transfers within 40 fs with a quantum yield of $\Phi_{\text{biradical}} \geq 0.6$, forming an intermediate, biradical species (G[·H]·C[+H]), which either recovers to the original G·C WC pair or decays to generate a “stable” (within the 1.3 ns timeframe of our measurements) double hydrogen atom transferred photoproduct (G^{*}·C^{*}). This work provides the most compelling evidence to date for the involvement of EDPT driven relaxation in individual WC base pairs and identifies the mechanism through which this process proceeds.

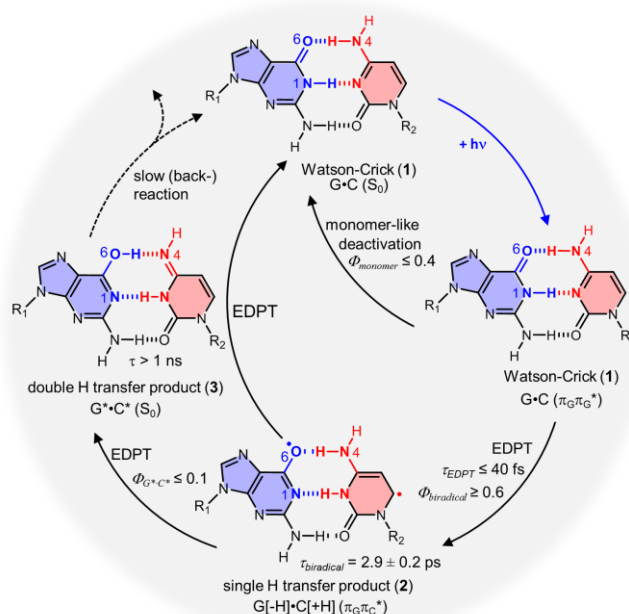


Figure 1. Deactivation mechanism of electronically excited G·C Watson-Crick base pairs (1). After UV excitation of the guanine (blue) moiety, electron-driven proton transfer (EDPT) along the central hydrogen bond occurs within 40 fs, and the resulting G[·H]·C[+H] biradical (2) lives for 2.9 ps. This intermediate undergoes a second EDPT, which either returns it to the original ground state Watson-Crick structure or leads to the G^{*}·C^{*} tautomer (3). The G^{*}·C^{*} tautomer is stable for > 1 ns, although its eventual fate is unknown. Alternatively, the initially excited G·C molecules can follow monomer-like deactivation pathways. The quantum yields (Φ) correspond to 260-nm excitation.

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Time-resolved electronic absorption spectroscopy (TEAS) and time-resolved vibrational absorption spectroscopy (TVAS) measurements of the G-C base pair were performed with equimolar solutions of silyl-protected guanosine (G) and (deoxy)cytidine (C) in chloroform (experimental details are given in the Supporting Information, SI). In this aprotic solvent, the G and C mixtures exist predominantly in the WC conformation.^[5c, 8] Moreover, chloroform provides a reasonable model for the dielectric environment in the core of natural DNA.^[9] At an excitation wavelength of 260 nm, about 80 % of the photons are absorbed by G (see Fig. S5 in the SI).^[5c, 8a] Excitation at the red edge of the absorption spectrum at 290 nm promotes the same photochemistry, but the observed product bands in TEAS and TVAS are weaker because of the lower absorption by G at this wavelength. Excitation of C leads to monomer-like deactivation (see Section S12 in the SI). Therefore, the discussion in this paper focuses on the results after 260 nm excitation.

Figures 2a and b show a superposition of the TEAS results for separate G and C solutions and for an equimolar mixture of G and C, all in CHCl₃. The transient absorption map in Fig. 2b is dominated by the G-C WC base pair and exhibits pronounced structure with maxima at 390 nm and 500 nm. Figure 2c compares transient difference spectra between the signals in Fig. 2a and b at selected delay times with the known spectrum of the G[-H] radical.^[10] This radical is one of the key intermediates in the EDPT process (Fig. 1), and its observation demonstrates the involvement of the EDPT pathway in the electronic deactivation of the G-C WC base pair. The partner C[+H] radical absorbs only weakly in this spectral region (cf. Section S11, Fig. S9). The absorption spectrum of the G⁺ radical cation is similar to that of G[-H], but arguments detailed in Section S16 and S17 in the SI exclude this alternative assignment. The lifetime of the EDPT intermediate is 2.9 ± 0.2 ps (Fig. 2d, uncertainties are 2 standard deviations throughout), which supports calculations of a minimum on an excited state potential energy surfaces (PES),^[11] rather than direct deactivation to the electronic ground state (S₀). The prompt absorption rise indicates that EDPT product formation is faster than the experimental time resolution (~40 fs), and hence a lower limit to the quantum yield of $\Phi_{\text{biradical}} \geq 0.6 \pm 0.1$ (see Section S8 in the SI). Prior calculations^[2b] identified crossing from the photo-excited $\pi_G\pi_G^*$ state to a $\pi_G\pi_C^*$ charge transfer (CT) state as the driving force for EDPT to G[-H]·C[+H]. The fast population of the CT state accords with *ab initio* molecular dynamics simulations of the G-C WC base pair.^[12] The oxygen-centered radical shown in Fig. 1 is expected to be the most stable biradical structure^[10a] and provides a favorable starting point for a second hydrogen atom transfer along the N_{4,C}-H··O_{6,G} bond.

To explore the fate of the G[-H]·C[+H] biradical, we performed TVAS experiments after excitation at 260 nm. Figure 3 displays the results, together with calculated IR spectra for the G-C WC base pair (1) and the G⁺·C^{*} tautomer (3) arising from double hydrogen atom transfer (Fig. 1). The transient spectra in Fig. 3a show three distinct negative contributions (bleaches), which match the steady-state IR spectrum of the G-C pair (Fig. 3b1) and reflect population transfer to electronic excited states. The positive features at 1680 cm⁻¹, 1630 cm⁻¹ and 1580 cm⁻¹ decay with increasing delay time. As seen in other systems,^[13] they can be assigned predominantly to vibrationally hot S₀ WC pairs at the $\nu = 1$ level, either of the vibrational mode responsible for the adjacent bleach feature, or of a coupled mode. However, the small positive band at 1720 cm⁻¹ has no corresponding bleach feature to higher wavenumber and shows no decay after its growth within the range of our experiment (1.3 ns); hence, it is attributed to a photoproduct, which also accounts for incomplete WC pair recoveries. As described in detail in Section S6 in the SI, calculations performed at the B3LYP/6-311+G^{**} level of theory for possible photoproducts, including a number of tautomers and the G and C monomers, demonstrate that only the G⁺·C^{*} tautomer

matches the observed spectral characteristics. Figure 3b compares calculated and experimental spectra. The theoretical spectrum of the G-C WC pair (Fig. 3b1) agrees well with the steady-state IR spectrum of G-C. The difference between computed G-C and G⁺·C^{*} spectra is shown in Fig. 3b3 together with a late-time TVAS spectrum. The close resemblance indicates that a fraction of the initially excited G-C pairs indeed forms the G⁺·C^{*} structure. The G⁺·C^{*} quantum yield estimated from incomplete WC band recoveries is ≤10 %. The fate of this product is unknown, and slow back-reaction to the WC structure or formation of other products are possible.^[14] The 1720 cm⁻¹ product band shows a linear UV power dependence, and no build-up of other photoproducts was observed. Hence multi-photon induced photochemistry can be excluded (see Sections S16 and S17 in the SI for an extended discussion).

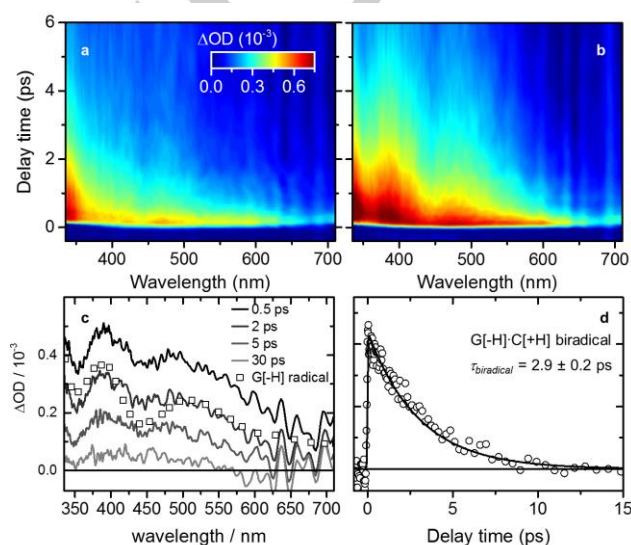
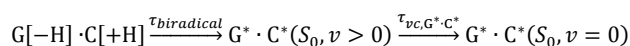


Figure 2. Transient electronic absorption spectra of the G-C Watson-Crick base pair after excitation at 260 nm. (a) Superposition of the transient absorption changes of G and C solutions measured separately, (b) experimental transient absorption changes of an equimolar mixture of G and C in CHCl₃. (c) Transient differences between spectra in (b) and (a) at selected delay times and normalized spectrum of the G[-H] radical.^[10b] (d) Time profile at 400 nm of the difference spectrum (open circles) and fit (line). All spectra were smoothed by replacing each data point of the two-dimensional transient absorption changes with the average of a 3x3 neighborhood.

For a global data analysis of the transient signals, we employed the kinetic model described in Section S7 in the SI. The bleach recoveries (Fig. 3d) and the decays of hot bands (Fig. 3e) are well described by a single exponential function with $\tau_{\text{vc,G-C}} = 7.2 \pm 0.1$ ps associated with the cooling of vibrationally hot S₀ G-C molecules in chloroform. The product band at 1720 cm⁻¹ (Fig. 3c) was modeled with a consecutive reaction scheme,



with $\tau_{\text{biradical}} = 2.9 \pm 0.2$ ps fixed from the TEAS measurements and $\tau_{\text{vc,G}^+\cdot\text{C}^*} = 5 \pm 2$ ps. The lifetime of the G[-H]·C[+H] biradical ($\tau_{\text{biradical}}$) is determined by its decay through a conical intersection returning it to the ground electronic state, whereas $\tau_{\text{vc,G}^+\cdot\text{C}^*}$ represents the vibrational cooling of the G⁺·C^{*} tautomer in its electronic ground state.

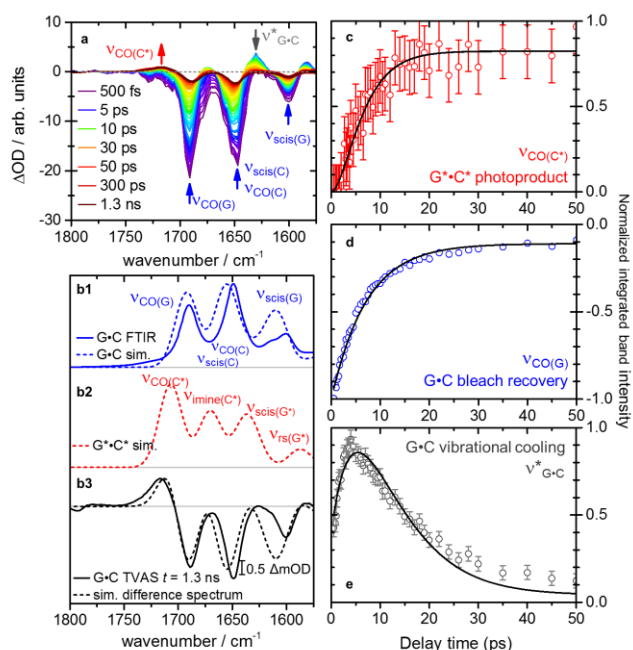


Figure 3. Transient vibrational absorption spectra, calculated vibrational spectra and time profiles of G-C, after excitation at 260 nm. The panels depict transient IR spectra of G-C in CDCl_3 (a), experimental (solid lines) and calculated IR (dashed lines) spectra for the G-C WC structure and the $\text{G}^*\text{-C}^*$ tautomer (b1 and b2), difference spectrum of $\text{G}^*\text{-C}^*$ and G-C (simulated assuming a quantum yield of 7% compared with the experimental transient spectrum at 1.3 ns (b3)), time profiles (open symbols) and fit results (solid lines) to the spectral features centered at 1720 cm^{-1} (c), 1693 cm^{-1} (d) and 1630 cm^{-1} (e). Labels indicate the vibrational character of bands (see Table S2 in the SI). The transient spectra were smoothed using a running average with 1 neighboring pixel. Calculations were performed at the B3LYP/6-311+G** level of theory.

Although the $\text{G}[-\text{H}]\text{-C}[+\text{H}]$ biradical (2) intermediate has a lifetime of 2.9 ps, the CT state is populated within 40 fs. Hence the energy of the absorbed photon dissipates on timescales that may be competitive with formation of excimer states within a DNA single strand, which are precursors for DNA photo-damage products such as cyclobutane dimers or (6-4) adducts of pyrimidine bases.^[15] However, the $\leq 10\%$ $\text{G}^*\text{-C}^*$ (3) quantum yield in solvated, but isolated G-C WC base pairs (1) means that a considerable fraction of photoexcited G-C forms a potentially mutagenic tautomeric photoproduct. The characteristic $\text{G}^*\text{-C}^*$ tautomer band at 1720 cm^{-1} was not observed in a recent TVAS study of natural calf thymus DNA following 266-nm excitation,^[5b] but lifetime shortening to 40 ps of the G-C WC pairs was identified and attributed to inter-strand proton transfer. The details of the interplay between horizontal and vertical interactions in double-stranded DNA, as well as the involvement of H-bonding with water and proteins on the major and minor grooves in natural DNA therefore remain to be established, but collective observations hint at the importance of UV-induced EDPT pathways.

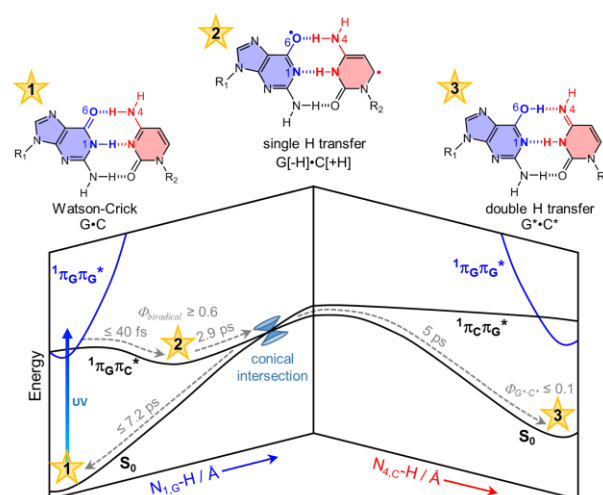


Figure 4. Schematic representation of the potential energy surfaces involved in the deactivation of the G-C Watson-Crick base pair (1) after UV absorption to a locally excited $\pi_{\text{G}}\pi_{\text{G}}^*$ state. EDPT in $\leq 40\text{ fs}$ produces the $\text{G}[-\text{H}]\text{-C}[+\text{H}]$ biradical (2) which is trapped in a local minimum on the excited $\pi_{\text{G}}\pi_{\text{C}}^*$ charge-transfer PES and has a lifetime of 2.9 ps. After crossing the conical intersection, the majority of the molecules return to the S_0 state of the Watson-Crick structure by back-transfer of the electron and the central proton. The subsequent vibrational cooling of the G-C molecules on the S_0 PES is completed in 7.2 ps. A fraction of $\text{G}[-\text{H}]\text{-C}[+\text{H}]$ biradicals instead undergoes EDPT along the $\text{N}_{4,\text{C}}\text{-H}\cdots\text{O}_{6,\text{G}}$ bond, leading to the $\text{G}^*\text{-C}^*$ tautomer (3) which is stable for $> 1\text{ ns}$. Monomer-like deactivation pathways are not shown.

The mechanism that emerges from the above analysis is summarized in Fig. 4. After excitation of G-C (1), ultrafast internal conversion from the $\pi_{\text{G}}\pi_{\text{G}}^*$ to a CT $\pi_{\text{G}}\pi_{\text{C}}^*$ state and subsequent proton transfer take place. This EDPT process forms the $\text{G}[-\text{H}]\text{-C}[+\text{H}]$ biradical (2) with $\Phi_{\text{biradical}} \geq 0.6 \pm 0.1$ (for excitation at 260 nm), which is trapped in a minimum on the CT state for $\sim 3\text{ ps}$. At a conical intersection which connects the CT and S_0 states, an electron transfers back from $\text{C}[+\text{H}]$ to $\text{G}[-\text{H}]$, followed by a proton transfer. This proton transfer occurs predominantly along the central $\text{N}_{1,\text{G}}\text{-H}\cdots\text{N}_{\text{C}}$ hydrogen bond, restoring the initial WC structure. However, up to 10% of the overall excited-state population undergoes a proton transfer along the $\text{N}_{4,\text{C}}\text{-H}\cdots\text{O}_{6,\text{G}}$ hydrogen bond to form the long-lived ($\tau > 1\text{ ns}$) $\text{G}^*\text{-C}^*$ tautomer (3). Alternatively, the initially excited $\pi_{\text{G}}\pi_{\text{G}}^*$ state can be depopulated via monomer-like deactivation pathways with a quantum yield $\leq 0.4 \pm 0.1$. These findings provide the most compelling experimental evidence to date for the involvement of EDPT driven relaxation in a WC base pair and are consistent with the most recent comprehensive computational study by Sauri *et al.*, on G-C base pairs.^[12a] The authors concluded that the EDPT process is a likely deactivation mechanism that could compete with monomer-like deactivation pathways, and that it could be responsible for the formation of the $\text{G}^*\text{-C}^*$ tautomer. The simulations predicted a timescale for the first H-atom transfer of 50 fs, which agrees well with our experimental determination of $< 40\text{ fs}$. A clear understanding of the interplay between inter-strand and intra-strand dynamics remains to be established, but the fast ($< 40\text{ fs}$) population of CT states leading to inter-strand EDPT deactivation and tautomerization is shown here to be fast enough to compete effectively with monomer relaxation and excimer photochemical pathways. Although the present measurements do not confirm the participation of purely inter-strand EDPT in more complex DNA duplexes, our work encourages greater consideration of this mechanism in future analysis of UV-induced photodynamics in double-stranded and higher-order DNA architectures.

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All experimental data are archived in the University of Bristol's Research Data Storage Facility (DOI 10.5523/bris.rql1plzevlth1oxdiuegc1reu). The supplementary materials contain summaries of the experimental details, data analysis procedures and outcomes.

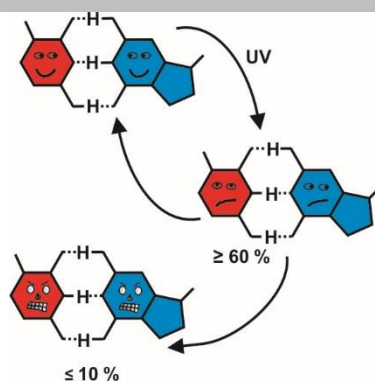
Keywords: Photochemistry • DNA • Ultrafast Spectroscopy • Proton Transfer • Biophysics

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Entry for the Table of Contents

COMMUNICATION

Ultrafast energy dissipation processes after absorption of UV light render DNA intrinsically photostable. We report direct observation of one of the most debated mechanisms in individual guanine-cytosine Watson-Crick base pairs. A sequence of hydrogen transfers across the hydrogen bonds in the dimer lead to an efficient relaxation of the base pair back to the original structure, but up to 10 % of the excited molecules instead form a potentially mutagenic tautomer.



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Page No. – Page No.

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