Electronic Supplementary Information

Photoinduced Electron Transfer in the 5-Bromouracil Labeled DNA.

Contrathermodynamic Mechanism Revisited by Electron Transfer Theories†

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† Electronic supplementary information (ESI) available: ET parameters calculated at BPE0 and CAM-B3LYP, evaluation of experimental charge separation rates, stability of MD simulations in terms of the variability of inter-base pair parameters.
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Table S1. Parameters of electron transfer reactions: V_{DA} – electronic coupling, λ – sum of internal and outer reorganization energy, λ_s – outer (solvent) reorganization energy, λ_i – internal reorganization energy ΔE – electron transfer energy (driving force) for separated donor and acceptor , ΔE_{si} – donor-acceptor self-interaction energy, ΔE_t – sum of ΔE and ΔE_{si}, k_M - ET rate calculated according to the Marcus-Levich-Jortner model, k_{MLJ} - ET rate calculated according to the Marcus theory; ν, λ_s, λ_i, λ, ΔE, ΔE_{si}, ΔE_t in cm^{-1}; k_M, k_{MLJ} in s^{-1}. Temperature = 300 K.

ET process	Computational Model	V_{DA}	λ_s	λ_i	λ	ΔE	ΔE_{si}	ΔE_t	k_{MLJ}	k_M
$BrU^* + G \rightarrow BrU^- + G^+$	PBE0	570	9240	5555	14795	10880	-11167	-287	1.4×10^7	2.4×10^6
	CAM-B3LYP	640	8166	5868	14034	12480	-8706	3774	2.8×10^2	1.4×10^2
$BrU^- + G^+ \rightarrow BrU + G$	PBE0	870	9020	7046	16066	-49060	10736	-38324	6.4×10^6	1.2×10^{-2}
	CAM-B3LYP	1000	8034	8800	16834	-52340	9909	-42431	7.1×10^5	9.6×10^{-7}
$BrU^* + A \rightarrow BrU^- + A^+$	PBE0	540	9370	4692	14062	12670	-9088	3582	3.5×10^2	1.7×10^2
	CAM-B3LYP	720	7950	5047	12997	14616	-8687	5929	2.2×10^{-1}	4.7×10^{-1}
$BrU^- + A^+ \rightarrow BrU + A$	PBE0	890	9130	6182	15312	-50980	8796	-42184	1.0×10^3	4.1×10^{-11}
	CAM-B3LYP	1030	7770	7979	15749	-54610	7682	-46928	1.2×10^0	1.4×10^{-18}
$A^+ + A \rightarrow A + A^+$	PBE0	620	8949	3354	12303	0	0	0	9.3×10^7	3.1×10^7
	CAM-B3LYP	407	8970	4146	13116	0	0	0	1.9×10^7	5.0×10^6

S1. Evaluation of charge separation rate in the GAAAABrU motif using the experimental data.[1]

The number of 320 nm photons absorbed by 5-bromo-2'-deoxyuridine (5BrdU) incorporated into dsDNA per second ($N_{photons}$) can be expressed by the following equation:

$$N_{photons} = \frac{\mathrm{I{\cdot}t}}{(h \cdot c)/_{lambda}} \cdot S \cdot (1 - 10^{-\varepsilon_{320} \cdot con \cdot l}) \cdot \frac{\varepsilon_{BrdU,320}}{\varepsilon_{320}} \qquad (S1)$$

where: *I* – intensity of incident beam (power per surface), *t* - time of irradiation, *h* – Planck's constant, *c* - velocity of light, *lambda* – wavelength of incident light , *S* - surface of the cuvette illuminated by the beam, ε_{320} – absorption coefficient of labeled DNA at 320 nm, $\varepsilon_{BrdU,320}$ – absorption coefficient of BrdU at 320 nm, *con* – concentration of the irradiated solution, and *l* – length of the optical path.

Since SSBs form in the labeled DNA due to electron transfer to the excited BrdU* their rate of formation, v_{SSBs}, is described by: $v_{SSBs} = k_{CS}$*[BrdU*], where k_{CS} stands for the rate constant of charge separation, while [$BrdU^*$] for concentration of the excited BrdU. Thus, the quantum yield of SSBs formation (φ_{SSBs}) can be expressed by:

$$\varphi_{SSBs} = \frac{k_{CS} \cdot [BrdU^*]}{N_{photons}} \qquad (S2)$$

In a stationary state the number of absorbed by BrdU photons (that generate the excited BrdU) must be equal to the total rate of BrdU* decay on all possible ways. Hence:

$$N_{photons} = k_{rel} \cdot [BrdU^*] + k_{CS} \cdot [BrdU^*] \qquad (S3)$$

where k_{rel} indicates sum of rates of radiation and radiation-less relaxation to the BrdU ground state (k_{rel} is a reverse of the average life time of the excited BrdU). Combining eqs. S2 and S3

one obtains the formulae which allows k_{cs} to be calculated if the yield of SSBs formation and k_{rel} are known:

$$k_{cs} = \frac{\varphi_{SSBs} \cdot k_{rel}}{1 - \varphi_{SSBs}} \qquad (S4)$$

Using the values of experimental parameters: I = 5 mW/cm^2, t = 60 min, λ = 320 nm, S = 0.03 cm^2, l = 0.3 cm, ε_{320} = 8.9 x 10^4 M^{-1}cm^{-1}, $\varepsilon_{BrdU,320}$ = 4.6 x 10^1 M^{-1}cm^{-1} as well as assuming k_{rel} = 2.5 x 10^{12} s^{-1} and the limit of detection in the MS assay of oligonucleotides to be equal to 2 pmol [2] we obtained k_{cs} = **1.54 x 10^5** s^{-1}. For $k_{CS} \leq$ the latter value one cannot detect SSBs in the studied system under the conditions of ref. [1].

S2. Stability of the MD simulations

The stability of the MD simulations was assessed by computing the inter-base pairs parameters along the last 80 ns of each trajectory. These parameters fluctuate around the typical values for B-DNA (see Ref. 32 of the main text), but do not drift with time (Figure S1), demonstrating that our trajectories are stable within the investigated time window.

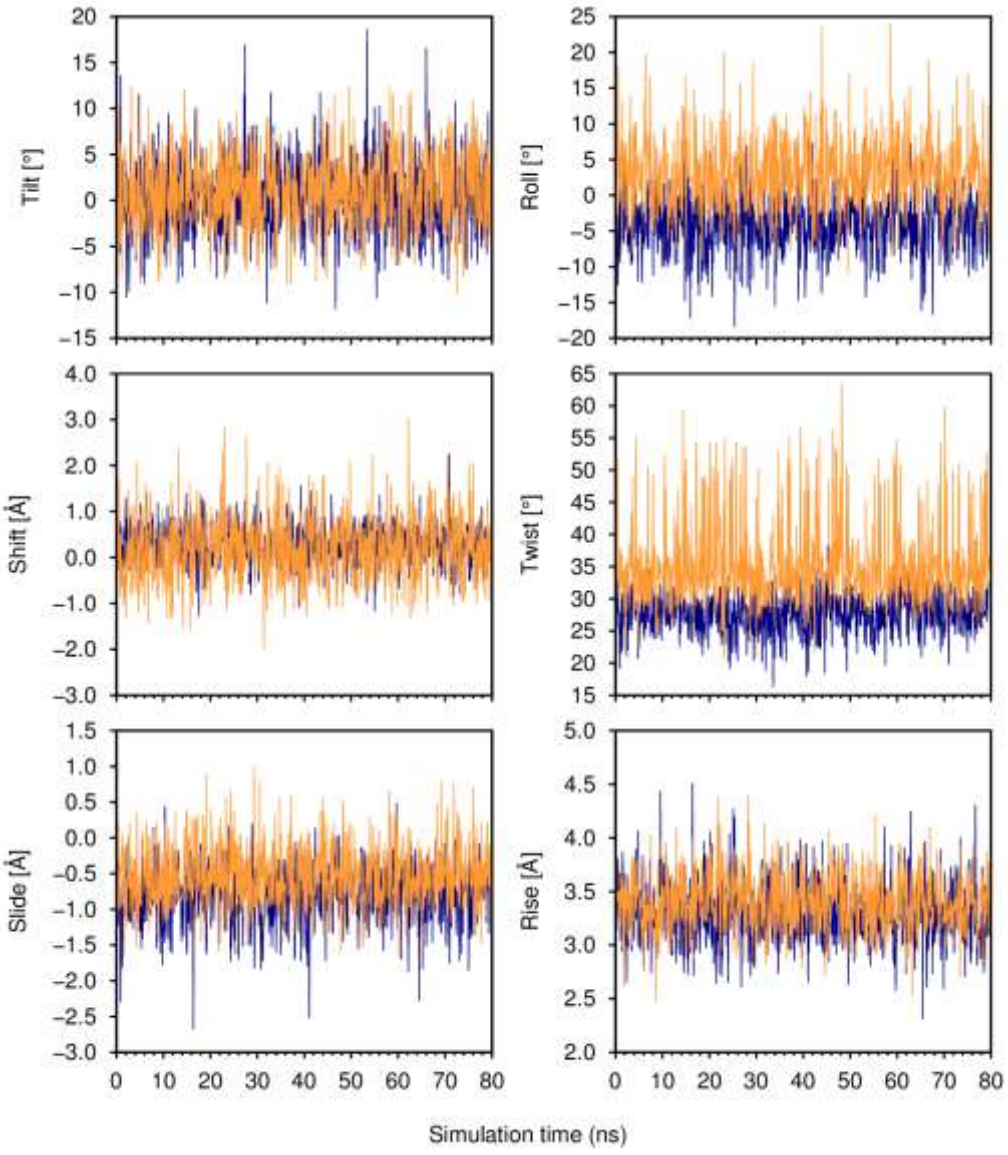

Figure S1. Inter-base pair parameters for the A/BrU or G/BrU base steps along the last 80 ns of each trajectory. Orange lines refer to the GBrU sequence, whereas blue lines to the ABrU one.

References

1 P. Wityk, M. Zdrowowicz, J. Wiczk, J. Rak, *J. Pharm. Biomed. Anal.* **2017**, *142*, 262-269.

2 K. J. Fountain, M. Gilar, J. C. Gebler, *Rapid Commun. Mass Spectrom.* **2004**, *18*, 1295–1302.