Supplementary Material

Wobble↔Watson-Crick tautomeric transitions in the homo-purine DNA mismatches: A key to the intimate mechanisms of the spontaneous transversions

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1. Computational Details.

All calculations of the geometries and harmonic vibrational frequencies of the considered base mispairs and transition states of their conversion have been performed using Gaussian'09 package [1] at the B3LYP DFT/6-311++G(d,p) level of theory [2-4], that has been applied for analogous systems and verified to give accurate geometrical structures, normal mode frequencies, barrier heights and characteristics of intermolecular H-bonds [5-8]. A scaling factor that is equal to 0.9668 has been applied in the present work for the correction of the harmonic frequencies of all studied base pairs [9-11]. We have confirmed the minima and TSs, located by means of Synchronous Transit-guided Quasi-Newton method [12], on the potential energy landscape by the absence or presence, respectively, of the imaginary frequency in the vibrational spectra of the complexes.

In order to consider electronic correlation effects as accurately as possible, we followed geometry optimizations with single point energy calculations using MP2 level of theory [13] and a wide variety of basis sets, in particular, Pople's basis sets of valence triple- ζ quality [14,15], as well as Dunning's cc-type basis sets [16], augmented with polarization and/or diffuse functions: 6-311++G(2df,2pd); 6-311++G(3df,2pd), cc-pVTZ and cc-pVQZ.

Reaction pathways have been established by following intrinsic reaction coordinate (IRC) in the forward and reverse directions from each TS using Hessian-based predictor-corrector integration algorithm [17] with tight convergence criteria. These calculations eventually ensure that the proper reaction pathway, connecting the expected reactants and

products on each side of the TS, has been found. We've have investigated the evolution of the energetic and geometric characteristics of the H-bonds and base pairs along the reaction pathway establishing them at each point of the IRC [18,19].

Electronic interaction energies E_{int} have been calculated at the MP2/6-311++G(2df,pd) level of theory as the difference between the total energy of the base mispair and the energies of the isolated monomers. Gibbs free energy of interaction has been obtained using similar equation. In each case the interaction energy was corrected for the basis set superposition error (BSSE) [20,21] through the counterpoise procedure [22,23].

The Gibbs free energy G for all structures was obtained in the following way:

$$G = E_{\text{el}} + E_{\text{corr}}, \quad (1)$$

where E_{el} – electronic energy, while E_{corr} – thermal correction. We applied the standard TS theory [24] to estimate the activation barriers of the tautomerisation reaction.

The time $\tau_{99.9\%}$ necessary to reach 99.9% of the equilibrium concentration of the reactant and product in the system of reversible first-order forward (k_f) and reverse (k_r) reactions can be estimated by formula [24]:

$$\tau_{99.9\%} = \frac{\ln 10^3}{k_f + k_r}. \quad (2)$$

To estimate the values of the rate constants k_f and k_r :

$$k_{f,r} = \Gamma \cdot \frac{k_B T}{h} e^{-\frac{\Delta \Delta G_{f,r}}{RT}} \quad (3)$$

we applied standard TS theory [24], in which quantum tunneling effect are accounted by Wigner's tunneling correction [25], that has been successfully used for the DPT reactions [26,27]:

$$\Gamma = 1 + \frac{1}{24} \left(\frac{h \nu_i}{k_B T} \right)^2, \quad (4)$$

where k_B – Boltzmann's constant, h – Planck's constant, $\Delta \Delta G_{f,r}$ – Gibbs free energy of activation for the tautomerisation reaction in the forward (f) and reverse (r) directions, ν_i – magnitude of the imaginary frequency associated with the vibrational mode at the TSs.

Bader's quantum theory of Atoms in Molecules (QTAIM) was applied to analyse the electron density distribution [28-31]. The topology of the electron density was analysed using program package AIMAll [32] with all default options. The presence of a bond critical

point (BCP), namely the so-called (3,-1) BCP, and a bond path between hydrogen donor and acceptor, as well as the positive value of the Laplacian at this BCP ($\Delta\rho>0$), were considered as criteria for the H-bond formation [33,34]. Wave functions were obtained at the level of theory used for geometry optimisation.

The energies of the weak CH $\cdots$ N H-bonds [33-35] and attractive N $\cdots$ O van der Waals contact in the base mispairs and TSs of their interconversion *via* the sequential DPT were calculated by the empirical Espinosa-Molins-Lecomte (EML) formula [35,37] based on the electron density distribution at the (3,-1) BCPs of the H-bonds:

$$E_{CH\cdots N/N\cdots O}=0.5\cdot V(r), \quad (5)$$

where $V(r)$ – value of a local potential energy at the (3,-1) BCP.

The energies of all others AH $\cdots$ B conventional H-bonds were evaluated by the empirical Iogansen's formula [38]:

$$E_{AH\cdots B} = 0.33 \cdot \sqrt{\Delta\nu - 40}, \quad (6)$$

where $\Delta\nu$ – magnitude of the frequency shift of the stretching mode of the AH H-bonded group involved in the AH $\cdots$ B H-bond relatively the unbound group. The partial deuteration was applied to minimize the effect of vibrational resonances [8-10].

The atomic numbering scheme for the DNA bases is conventional [39].

Similarly to our recent studies on the related topic [40-43], we have considered the simplest physico-chemical model of the base mispairs in the base-pair recognition pocket of the high-fidelity DNA-polymerase, namely the H-bonded pairs of nucleotide bases in vacuum approximation ($\epsilon=1$). In this case, we have relied on the results obtained in the work [44], in which the adequacy of this model was convincingly proved, at least at the study of the tautomerisation of the H-bonded pairs of nucleotide bases, where insignificance of the influence of the stacking and the sugar-phosphate backbone on the tautomerisation process has been demonstrated. Thereby, their impact can be neglected in the first approximation. In addition, the applied model can help to distinguish the lowest structural level, at which the tautomerisation effects can be observed, and to estimate the changes at the sequential complication of the model.

In this study we have chosen the simplest level of the base pairs that adequately reflects the processes occurring in real systems [45] without deprivation of the structurally functional

properties of the bases in the composition of DNA. In this case, the value of the effective dielectric constant ε ($1 < \varepsilon < 4$), that is characteristic for the anhydrous molecular crystals, satisfactorily models the substantially hydrophobic recognition pocket of the DNA-polymerase machinery as a part of the replisome and can be approximated by vacuum [46].

2. Numerical and Graphical Materials.

Table S1. Electron-topological, structural, vibrational and energetic characteristics of the intermolecular H-bonds in the DNA homo-mispairs containing A and G nucleobases and TSs of their tautomerisation *via* the sequential DPT and structural displacement of the bases relatively to each other, energetic and polar characteristics of the latters obtained at the B3LYP/6-311++G(d,p) level of theory.

Base pair/TS	AH...B H-bond	ρ^a	$\Delta\rho^b$	$100\cdot\epsilon^c$	$d_{A...B}^d$	$d_{H...B}^e$	Δd_{AH}^f	$\angle AH...B^g$	$\Delta\nu^h$	$E_{AH...B}^i$	ΔG^j	μ^k
A·A _{syn↑} (w)	N6H...N7	0.022	0.071	7.85	3.068	2.056	0.013	171.7	235.6	4.62	0.00	3.49
	C8H...N1	0.013	0.039	5.22	3.312	2.388	0.003	142.3	34.1	2.08*		
A·A(w)	N6H...N1	0.023	0.071	7.97	3.077	2.058	0.015	175.8	259.1	4.88	1.04	2.26
	C2H...N1	0.010	0.028	5.61	3.503	2.538	0.0005	147.5	-2.2	1.52*		
A·A _{syn↓} (w)	N6H...N1	0.022	0.068	7.87	3.088	2.081	0.013	169.4	237.7	4.64	1.47	5.21
	C2H...N7	0.010	0.029	5.86	3.487	2.510	-0.0004	149.4	-13.5	1.56*		
A*·A(WC) ^[40]	N6H...N6	0.035	0.091	7.19	2.918	1.885	0.028	176.3	491.5	7.01	5.22	1.75
	N1H...N1	0.034	0.087	6.76	2.943	1.904	0.030	179.0	474.6	6.88		
A*·A _{syn} (TF) ^[41]	N6H...N6	0.032	0.098	7.17	2.937	1.921	0.023	168.9	410.4	6.35	5.82	7.96
	N1H...N7	0.032	0.093	5.99	2.959	1.929	0.022	173.5	389.1	6.17		
TS ^{A⁺·A⁻} _{A·A(w)↔A*·A(WC)}	N6 ⁺ H...N6 ⁻	0.026	0.079	4.53	2.927	2.005	0.019	147.9	298.2	5.30	27.93	9.22
	N1 ⁺ H...N6 ⁻	0.043	0.095	3.74	2.790	1.788	0.045	156.3	697.0	6.41		
	N1 ⁺ H...N1 ⁻	0.017	0.063	120.80	3.009	2.189	0.045	132.7	697.0	2.05		
	C2 ⁺ H...N1 ⁻	0.009	0.029	3.44	3.278	2.668	-0.0008	115.1	-12.7	1.58*		
TS ^{A⁺·A⁻} _{A·A_{syn↓}(w)↔A*·A_{syn}(TF)}	N6 ⁺ H...N6 ⁻	0.037	0.101	2.18	2.814	1.833	0.027	156.7	441.2	6.61	30.86	12.67
	N1 ⁺ H...N6 ⁻	0.028	0.075	4.36	2.934	2.006	0.029	146.7	439.4	4.75		
	N1 ⁺ H...N7 ⁻	0.012	0.043	20.85	3.067	2.368	0.029	123.3	439.4	1.85		
	C2 ⁺ H...N7 ⁻	0.014	0.044	5.09	3.141	2.400	-0.002	124.4	-22.7	2.34*		
TS ^{A⁻·A⁺} _{A·A_{syn↑}(w)↔A*·A_{syn}(TF)}	N6 ⁺ H...N6 ⁻	0.029	0.083	5.57	2.968	1.947	0.025	170.5	414.0	6.38	31.34	5.41
	N7 ⁺ H...N6 ⁻	0.031	0.085	2.72	2.886	1.915	0.038	152.3	586.8	4.41		
	N7 ⁺ H...N1 ⁻	0.025	0.079	19.20	2.875	2.030	0.038	135.6	586.8	3.31		
G·G*(WC) ^[42]	O6H...N6	0.050	0.138	2.48	2.646	1.649	0.036	171.2	687.1	8.39	0.00	8.45
	N1H...N1	0.035	0.091	6.64	2.920	1.893	0.021	172.4	385.6	6.14		
	N2H...N2	0.016	0.048	6.71	3.231	2.244	0.006	163.9	108.6	2.73		
G·G(w)	N1H...O6	0.017	0.060	6.06	3.040	2.134	0.007	146.9	112.6	2.81	4.96	9.90
	N2H...O6	0.020	0.068	9.32	2.926	2.112	0.008	135.5	127.4	3.08		
	N1H...N2	0.016	0.049	9.18	3.146	2.248	0.007	146.1	139.0	3.28		
G*·G*(w)	O6H...N1	0.053	0.103	4.98	2.690	1.712	0.038	163.0	746.9	8.77	5.00	4.94
	N2H...N1	0.022	0.065	7.30	3.111	2.103	0.012	169.9	219.2	4.42		
TS ^{G⁺·G⁻} _{G·G*(WC)↔G*·G*(w)}	O6 ⁺ H...O6 ⁻	0.066	0.168	3.03	2.519	1.519	0.060	163.1	1054.1	10.51	13.94	8.25
	N1 ⁺ H...O6 ⁻	0.036	0.111	5.33	2.720	1.850	0.026	138.9	417.8	4.43		
	N1 ⁺ H...N1 ⁻	0.020	0.068	63.82	3.063	2.119	0.026	150.0	417.8	1.99		
	N2 ⁺ H...N1 ⁻	0.016	0.046	4.91	3.189	2.280	0.011	147.9	78.8	2.05		
TS ^{G⁺·G⁻} _{G·G*(WC)↔G·G(w)}	O6 ⁺ H...N1 ⁻	0.045	0.086	2.58	2.773	1.769	0.056	165.8	965.9	10.04	31.77	14.03
	N1 ⁺ H...N1 ⁻	0.016	0.053	34.09	3.100	2.261	0.017	137.6	272.3	1.96		
	N1 ⁺ H...N2 ⁻	0.024	0.071	4.06	3.025	2.052	0.017	156.6	272.3	3.07		
	N2 ⁺ H...N2 ⁻	0.017	0.050	3.26	3.139	2.242	0.007	146.7	78.7	2.05		

^aThe electron density at the (3,-1) BCP of the H-bond, a.u.; ^bThe Laplacian of the electron density at the (3,-1) BCP of the H-bond, a.u.; ^cThe ellipticity at the (3,-1) BCP of the H-bond; ^dThe distance between the A (H-bond donor) and B (H-bond acceptor) atoms of the AH...B H-bond, Å; ^eThe distance between the H and B atoms of the AH...B H-bond, Å; ^fThe elongation of the H-bond donating group AH upon the AH...B H-bonding, Å; ^gThe H-bond angle, degree; ^hThe redshift of the stretching vibrational mode $\nu(AH)$ of the AH H-bonded group, cm⁻¹; ⁱEnergy of the H-bonds, calculated by Iogansen's [38] or Espinose-Molins-Lecomte (marked with an asterisk) [36,37] formulas, kcal·mol⁻¹; ^jThe relative Gibbs free energy of the complex obtained at the MP2/cc-pVQZ//B3LYP/6-311++G(d,p) level of theory under normal conditions, kcal·mol⁻¹; ^kThe dipole moment of the complex, D.

Fig. S1. Structures of the stationary points of the (a) $A \cdot A(w) \leftrightarrow A^* \cdot A(WC)$, (b) $A \cdot A_{\text{syn}\downarrow}(w) \leftrightarrow A^* \cdot A_{\text{syn}}(TF)$ and (c) $A \cdot A_{\text{syn}\uparrow}(w) \leftrightarrow A^* \cdot A_{\text{syn}}(TF)$ conversions *via* the sequential DPT obtained at the B3LYP/6-311++G(d,p) level of theory. Dotted lines indicate $AH \cdots B$ H-bonds (their lengths are presented in angstroms); carbon atoms are in light-blue, nitrogen – in dark-blue and hydrogen – in grey; ν_i – value of the imaginary frequency.

(a)

(b)

(c)

Fig. S2. Profiles of the relative electronic energy ΔE of the base mispairs along the IRC of the (a) $A \cdot A(w) \leftrightarrow A^* \cdot A(WC)$, (b) $A \cdot A_{\text{syn}\downarrow}(w) \leftrightarrow A^* \cdot A_{\text{syn}}(TF)$ and (c) $A \cdot A_{\text{syn}\uparrow}(w) \leftrightarrow A^* \cdot A_{\text{syn}}(TF)$ tautomerisations *via* the sequential DPT obtained at the B3LYP/6-311++G(d,p) level of theory.

Table S2. Energetic and kinetic characteristics of the $A \cdot A(w) \leftrightarrow A^* \cdot A(WC)$, $A \cdot A_{\text{syn}\downarrow}(w) \leftrightarrow A^* \cdot A_{\text{syn}}(\text{TF})$ and $A \cdot A_{\text{syn}\uparrow}(w) \leftrightarrow A^* \cdot A_{\text{syn}}(\text{TF})$ tautomerisations *via* the sequential DPT obtained at the different levels of theory for the geometry calculated at the B3LYP/6-311++G(d,p) level of theory (see also Figs. S1 and S2).

Level of theory	ΔG^a	ΔE^b	$\Delta \Delta G_{\text{TS}}^c$	$\Delta \Delta E_{\text{TS}}^d$	$\Delta \Delta G^e$	$\Delta \Delta E^f$	$\tau_{99.9\%}^g$
$A \cdot A(w) \leftrightarrow A^* \cdot A(WC)$							
MP2/6-311++G(2df,pd)	4.48	1.94	27.06	23.75	22.58	21.81	$3.51 \cdot 10^4$
MP2/6-311++G(3df,2pd)	4.17	1.63	26.67	23.36	22.50	21.73	$3.07 \cdot 10^4$
MP2/cc-pVTZ	4.03	1.50	27.36	24.05	23.32	22.56	$1.23 \cdot 10^5$
MP2/cc-pVQZ	4.18	1.64	26.89	23.59	22.71	21.94	$4.39 \cdot 10^4$
$A \cdot A_{\text{syn}\downarrow}(w) \leftrightarrow A^* \cdot A_{\text{syn}}(\text{TF})$							
MP2/6-311++G(2df,pd)	4.61	3.29	29.65	26.25	25.03	22.96	$2.52 \cdot 10^6$
MP2/6-311++G(3df,2pd)	4.27	2.94	29.01	25.61	24.74	22.66	$1.53 \cdot 10^6$
MP2/cc-pVTZ	4.22	2.90	29.94	26.54	25.72	23.64	$8.04 \cdot 10^6$
MP2/cc-pVQZ	4.35	3.02	29.39	25.99	25.04	22.97	$2.23 \cdot 10^6$
$A \cdot A_{\text{syn}\uparrow}(w) \leftrightarrow A^* \cdot A_{\text{syn}}(\text{TF})$							
MP2/6-311++G(2df,pd)	5.96	4.93	31.43	28.55	25.47	23.62	$5.22 \cdot 10^6$
MP2/6-311++G(3df,2pd)	5.74	4.71	31.11	28.24	25.37	23.52	$4.44 \cdot 10^6$
MP2/cc-pVTZ	5.68	4.65	31.88	29.00	26.20	24.35	$1.80 \cdot 10^7$
MP2/cc-pVQZ	5.82	4.79	31.34	28.47	25.53	23.68	$5.75 \cdot 10^6$

^aThe Gibbs free energy of the product relatively the reactant of the tautomerisation reaction (T=298.15 K), kcal·mol⁻¹

^bThe electronic energy of the product relatively the reactant of the tautomerisation reaction, kcal·mol⁻¹

^cThe Gibbs free energy barrier for the forward reaction of tautomerisation, kcal·mol⁻¹

^dThe electronic energy barrier for the forward reaction of tautomerisation, kcal·mol⁻¹

^eThe Gibbs free energy barrier for the reverse reaction of tautomerisation, kcal·mol⁻¹

^fThe electronic energy barrier for the reverse reaction of tautomerisation, kcal·mol⁻¹

^gThe time necessary to reach 99.9% of the equilibrium concentration between the reactant and the product of the tautomerisation reaction, s

See also summary Table S6 for the Gibbs and electronic energies of the mispairs and TSs relatively the global minimum – the $A \cdot A_{\text{syn}\uparrow}(w)$ base mispair.

Fig. S3. Exchange of the patterns of the intermolecular $AH\cdots B$ H-bonds (their energies $E_{AH\cdots B}$ are estimated by the EML formula at the (3,-1) BCPs) along the IRC of the biologically important $A\cdot A(w)\leftrightarrow A^*\cdot A(WC)$ tautomerisation *via* the sequential DPT obtained at the B3LYP/6-311++G(d,p) level of theory (see Tables S1 and S3). Perpendicular lines in violet denote partition of all range into different regions.

Table S3. Patterns of the intermolecular interactions including $AH\cdots B$ H-bonds and loosened A-H-B covalent bridges that sequentially replace each other along the IRC of the biologically important $A\cdot A(w)\leftrightarrow A^*\cdot A(WC)$ tautomerisation *via* the sequential DPT and ranges of their existence obtained at the B3LYP/6-311++G(d,p) level of theory (see Figs. S1-S3).

Patterns	IRC ranges, Bohr	Intermolecular interactions, forming patterns
I	$[-19.58\div -5.07)$	$N6H\cdots N1$, $C2H\cdots N1$
II	$[-5.07\div -4.62)$	$N6H\cdots N1$, $N6H\cdots HN1$, $C2H\cdots N1$
III	$[-4.62\div -2.63)$	$N6H\cdots N6$, $N6H\cdots N1$, $C2H\cdots N1$
IV	$[-2.63\div -2.07)$	$N6H\cdots N6$, $N6-H-N1$, $C2H\cdots N1$
V	$[-2.07\div -0.40)$	$N6H\cdots N6$, $N1H\cdots N6$, $C2H\cdots N1$
VI	$[-0.40\div 1.37)$	$N6H\cdots N6$, $N1H\cdots N6$, $N1H\cdots N1$, $C2H\cdots N1$
VII	$[1.37\div 4.50)$	$N6H\cdots N6$, $N1H\cdots N6$, $N1H\cdots N1$
VIII	$[4.50\div 7.85)$	$N6H\cdots N6$, $N1H\cdots N1$
IX	$[7.85\div 8.29)$	$N6-H-N6$, $N1H\cdots N1$
X	$[8.29\div 14.40]$	$N6H\cdots N6$, $N1H\cdots N1$

Fig. S4. Structures of the stationary points of the (a) $G \cdot G^*(WC) \leftrightarrow G^* \cdot G^*(w)$ and (b) $G \cdot G^*(WC) \leftrightarrow G \cdot G(w)$ conversions *via* the sequential DPT obtained at the B3LYP/6-311++G(d,p) level of theory. For designations see Fig. S1; oxygen atoms are in red.

Fig. S5. Profiles of the relative electronic energy ΔE of the base mispairs along the IRC of the (a) $\text{G}\cdot\text{G}^*(\text{WC}) \leftrightarrow \text{G}^*\cdot\text{G}^*(\text{w})$ and (b) $\text{G}\cdot\text{G}^*(\text{WC}) \leftrightarrow \text{G}\cdot\text{G}(\text{w})$ tautomerisations *via* the sequential DPT obtained at the B3LYP/6-311++G(d,p) level of theory.

Table S4. Energetic and kinetic characteristics of the $G \cdot G^*(WC) \leftrightarrow G^* \cdot G^*(w)$ and $G \cdot G^*(WC) \leftrightarrow G \cdot G(w)$ tautomerisations *via* the sequential DPT obtained at the different levels of theory for the geometry calculated at the B3LYP/6-311++G(d,p) level of theory (see also Figs. S4 and S5).

Level of theory	ΔG^a	ΔE^b	$\Delta \Delta G_{TS}^c$	$\Delta \Delta E_{TS}^d$	$\Delta \Delta G^e$	$\Delta \Delta E^f$	$\tau_{99.9\%}^g$
$G \cdot G^*(WC) \leftrightarrow G^* \cdot G^*(w)$							
MP2/6-311++G(2df,pd)	5.00	7.15	14.14	15.37	9.14	8.22	$5.53 \cdot 10^{-6}$
MP2/6-311++G(3df,2pd)	5.08	7.22	14.03	15.27	8.96	8.05	$4.08 \cdot 10^{-6}$
MP2/cc-pVTZ	5.36	7.50	14.43	15.67	9.08	8.16	$4.98 \cdot 10^{-6}$
MP2/cc-pVQZ	5.00	7.14	13.94	15.17	8.94	8.03	$3.98 \cdot 10^{-6}$
$G \cdot G^*(WC) \leftrightarrow G \cdot G(w)$							
MP2/6-311++G(2df,pd)	5.04	6.83	31.72	32.78	26.68	25.95	$4.04 \cdot 10^7$
MP2/6-311++G(3df,2pd)	4.75	6.54	31.67	32.72	26.91	26.18	$6.00 \cdot 10^7$
MP2/cc-pVTZ	5.27	7.06	31.97	33.02	26.70	25.97	$4.15 \cdot 10^7$
MP2/cc-pVQZ	4.96	6.75	31.77	32.83	26.81	26.08	$5.03 \cdot 10^7$

See Table S2 for the designations and also summary Table S6 for the Gibbs and electronic energies of the mispairs and TSs relatively the global minimum – the Watson-Crick-like $G \cdot G^*(WC)$ base mispair.

Fig. S6. Exchange of the patterns of the intermolecular $\text{AH}\cdots\text{B}$ H-bonds and attractive $\text{N}\cdots\text{O}$ van der Waals contact (their energies $E_{\text{AH}\cdots\text{B/N}\cdots\text{O}}$ are estimated by the EML formula at the (3,-1) BCPs) along the IRC of the (a) $\text{G}\cdot\text{G}^*(\text{WC})\leftrightarrow\text{G}^*\cdot\text{G}^*(\text{w})$ and (b) $\text{G}\cdot\text{G}^*(\text{WC})\leftrightarrow\text{G}\cdot\text{G}(\text{w})$ biologically important tautomerisations *via* the sequential DPT obtained at the B3LYP/6-311++G(d,p) level of theory (see Tables S1 and S5). Perpendicular lines in violet denote partition of all range into different regions.

Table S5. Patterns of the intermolecular interactions including AH...B H-bonds, attractive N...O van der Waals contact and loosened A-H-B covalent bridges that sequentially replace each other along the IRC of the $G \cdot G^*(WC) \leftrightarrow G^* \cdot G^*(w)$ and $G \cdot G^*(WC) \leftrightarrow G \cdot G(w)$ biologically important tautomerisations *via* the sequential DPT and ranges of their existence obtained at the B3LYP/6-311++G(d,p) level of theory (see Figs. S4-S6).

Patterns	IRC ranges, Bohr	Intermolecular interactions, forming patterns
$G \cdot G^*(WC) \leftrightarrow G^* \cdot G^*(w)$		
I	[-21.37÷-6.02)	O6H...O6, N1H...N1, N2H...N2
II	[-6.02÷-4.23)	O6H...O6, N1H...N1, N2H...N1, N2H...N2
III	[-4.23÷-4.11)	O6H...O6, N1H...O6, N1H...N1, N2H...N1, N2H...N2
IV	[-4.11÷-3.60)	O6-H-O6, N1H...O6, N1H...N1, N2H...N1, N2H...N2
V	[-3.60÷-1.80)	O6H...O6, N1H...O6, N1H...N1, N2H...N1, N2H...N2
VI	[-1.80÷0.51)	O6H...O6, N1H...O6, N1H...N1, N2H...N1
VII	[0.51÷4.75)	O6H...O6, N1H...O6, N2H...N1
VIII	[4.75÷5.13)	O6H...O6, N1-H-O6, N2H...N1
IX	[5.13÷11.14)	O6H...O6, O6H...N1, N2H...N1
X	[11.14÷12.03]	O6H...N1, N2H...N1
$G \cdot G^*(WC) \leftrightarrow G \cdot G(w)$		
I	[-19.45÷-7.66)	O6H...O6, N1H...N1, N2H...N2
II	[-7.66÷-6.47)	O6H...O6, N1H...N1, N1H...N2, N2H...N2
III	[-6.47÷-6.10)	O6-H-O6, N1H...N1, N1H...N2, N2H...N2
IV	[-6.10÷-4.13)	O6H...O6, N1H...N1, N1H...N2, N2H...N2
V	[-4.13÷-1.42)	O6H...O6, O6H...N1, N1H...N1, N1H...N2, N2H...N2
VI	[-1.42÷3.91)	O6H...N1, N1H...N1, N1H...N2, N2H...N2
VII	[3.91÷4.03)	O6H...N1, N1H...N2, N2H...N2
VIII	[4.03÷4.40)	O6-H-N1, N1H...N2, N2H...N2
IX	[4.40÷9.06)	N1H...O6, N1H...N2, N2H...N2
X	[9.06÷23.82)	N1H...O6, N1H...N2
XI	[23.82÷27.38)	N1H...O6, N2...O6, N1H...N2
XII	[27.38÷38.22]	N1H...O6, N2H...O6, N1H...N2

Table S6. Energetic characteristics of the investigated base mispairs and TSs of their tautomerisation *via* the sequential DPT obtained at the different levels of theory for the geometry calculated at the B3LYP/6-311++G(d,p) level of theory.

Complex	MP2/6-311++G(2df,2pd)		MP2/6-311++G(3df,2pd)		MP2/cc-pVTZ		MP2/cc-pVQZ	
	ΔG^a	ΔE^b	ΔG^a	ΔE^b	ΔG^a	ΔE^b	ΔG^a	ΔE^b
$A \cdot A_{\text{syn}\uparrow}(w)$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$A \cdot A(w)$	1.04	1.77	1.04	1.77	1.03	1.76	1.04	1.77
$A \cdot A_{\text{syn}\downarrow}(w)$	1.34	1.64	1.47	1.77	1.45	1.75	1.47	1.77
$A^* \cdot A(WC)^{[40]}$	5.52	3.71	5.20	3.40	5.06	3.26	5.22	3.42
$A^* \cdot A_{\text{syn}}(TF)^{[41]}$	5.96	4.93	5.74	4.71	5.68	4.65	5.82	4.79
$TS_{A^* \cdot A(WC) \leftrightarrow A \cdot A^*(WC)}^{[40]}$	12.03	13.54	12.05	13.56	12.05	13.57	12.23	13.75
$TS_{A^+ \cdot A^- \cdot A(w) \leftrightarrow A^* \cdot A(WC)}^{[41]}$	28.10	25.52	27.70	25.13	28.39	25.81	27.93	25.36
$TS_{A^+ \cdot A_{\text{syn}}^- \cdot A(w) \leftrightarrow A^* \cdot A_{\text{syn}}(TF)}^{[41]}$	30.99	27.89	30.48	27.37	31.40	28.29	30.86	27.76
$TS_{A^+ \cdot A_{\text{syn}}^- \cdot A(w) \leftrightarrow A^* \cdot A_{\text{syn}}(TF)}^{[41]}$	31.43	28.55	31.11	28.24	31.88	29.00	31.34	28.47
$G \cdot G^*(WC)^{[42]}$	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
$G \cdot G_{\text{syn}}^*^{[43]}$	1.84	3.06	1.79	3.02	2.41	3.63	1.85	3.08
$G \cdot G(w)$	5.04	6.83	4.75	6.54	5.27	7.06	4.96	6.75
$G^* \cdot G^*(w)$	5.00	7.15	5.08	7.22	5.36	7.50	5.00	7.14
$TS_{G^* \cdot G(WC) \leftrightarrow G \cdot G^*(WC)}^{[42]}$	4.97	7.79	5.46	8.28	5.21	8.03	5.51	8.33
$TS_{G^+ \cdot G^- \cdot G^*(WC) \leftrightarrow G^* \cdot G^*(w)}^{[42]}$	14.14	15.37	14.03	15.27	14.43	15.67	13.94	15.17
$TS_{G^* \cdot G^*(w) \leftrightarrow G^* \cdot N_2 \cdot G(w)}$	17.31	21.11	17.37	21.17	17.97	21.77	17.49	21.29
$G^* \cdot N_2 \cdot G(w)$	18.17	19.81	17.81	19.45	18.57	20.21	17.95	19.59
$TS_{G \cdot G(w) \leftrightarrow G^* \cdot G^* \cdot NH_3^+(w)}$	27.00	29.55	27.57	30.13	27.84	30.40	27.52	30.15
$G^* \cdot G^* \cdot NH_3^+(w)$	27.64	29.60	28.15	30.11	28.47	30.43	28.05	30.01
$TS_{G^+ \cdot G^- \cdot G^*(WC) \leftrightarrow G \cdot G(w)}$	31.72	32.78	31.67	32.72	31.97	33.02	31.77	32.83

^aThe relative Gibbs free energy of the investigated complexes ($\Delta G_{A \cdot A_{\text{syn}\uparrow}(w)/G \cdot G^*(WC)}=0.00$; T=298.15 K), kcal·mol⁻¹

^bThe relative electronic energy of the investigated complexes ($\Delta E_{A \cdot A_{\text{syn}\uparrow}(w)/G \cdot G^*(WC)}=0.00$), kcal·mol⁻¹

Table S7. Interbase interaction energies (in kcal·mol⁻¹) for the investigated DNA base mispairs and TSs of their conversions *via* the sequential DPT obtained at the MP2/6-311++G(3df,2pd)//B3LYP/6-311++G(d,p) level of theory.

Complex	$-\Delta E_{\text{int}}^{\text{a}}$	$\Sigma E_{\text{HB}}^{\text{b}}$	$\Sigma E_{\text{HB}}/ \Delta E_{\text{int}} , \%$	$-\Delta G_{\text{int}}^{\text{c}}$
$\text{A} \cdot \text{A}_{\text{syn}\uparrow}(\text{w})$	8.70	6.70	77.0	-4.92
$\text{A} \cdot \text{A}(\text{w})$	6.91	6.41	92.8	0.99
$\text{A} \cdot \text{A}_{\text{syn}\downarrow}(\text{w})$	7.06	6.20	87.8	-6.27
$\text{A}^* \cdot \text{A}(\text{WC})^{[40]}$	17.89	13.89	77.6	4.32
$\text{A}^* \cdot \text{A}_{\text{syn}}(\text{TF})^{[41]}$	16.73	12.52	74.8	3.83
$\text{TS}_{\text{A} \cdot \text{A}(\text{w}) \leftrightarrow \text{A}^* \cdot \text{A}(\text{WC})}^{\text{A}^+ \cdot \text{A}^-}$	118.21	15.34	13.0	104.59
$\text{TS}_{\text{A} \cdot \text{A}_{\text{syn}\downarrow}(\text{w}) \leftrightarrow \text{A}^* \cdot \text{A}_{\text{syn}}(\text{TF})}^{\text{A}^+ \cdot \text{A}_{\text{syn}}^-}$	115.24	15.55	13.5	101.07
$\text{TS}_{\text{A} \cdot \text{A}_{\text{syn}\uparrow}(\text{w}) \leftrightarrow \text{A}^* \cdot \text{A}_{\text{syn}}(\text{TF})}^{\text{A}^- \cdot \text{A}_{\text{syn}}^+}$	122.98	18.71	15.2	108.35
$\text{G} \cdot \text{G}^*(\text{WC})^{[42]}$	23.40	17.26	73.8	9.65
$\text{G} \cdot \text{G}_{\text{syn}}^*(\text{WC})^{[43]}$	19.82	13.78	69.5	7.28
$\text{G} \cdot \text{G}(\text{w})$	13.52	9.18	67.9	1.46
$\text{G}^* \cdot \text{G}^*(\text{w})$	14.82	13.19	89.0	3.29
$\text{TS}_{\text{G} \cdot \text{G}^*(\text{WC}) \leftrightarrow \text{G}^* \cdot \text{G}(\text{w})}^{\text{G}^+ \cdot \text{G}^-}$	135.17	18.98	14.0	120.13
$\text{TS}_{\text{G} \cdot \text{G}_{\text{syn}}^*(\text{WC}) \leftrightarrow \text{G}^* \cdot \text{G}(\text{w})}^{\text{G}^+ \cdot \text{G}^-}$	121.07	17.12	14.1	105.85

^aThe BSSE-corrected electronic interaction energy

^bThe total energy of the intermolecular H-bonds (see Table S1)

^cThe BSSE-corrected Gibbs free energy of interaction (T=298.15 K)

Fig. S7. Profiles of the $R(H_9-H_{9'})$ distances between the H_9 and $H_{9'}$ glycosidic hydrogens and the $\alpha_1 = \angle N1H_9H_{9'}$ (angle for the base on the left within the base pair) or $\alpha_2 = \angle N1H_9'H_9$ (angle for the base on the right within the base pair) glycosidic angles along the IRC of the (a) $A \cdot A(w) \leftrightarrow A^* \cdot A(WC)$, (b) $A \cdot A_{syn\downarrow}(w) \leftrightarrow A^* \cdot A_{syn}(TF)$ and (c) $A \cdot A_{syn\uparrow}(w) \leftrightarrow A^* \cdot A_{syn}(TF)$ tautomerisations *via* the sequential DPT obtained at the B3LYP/6-311++G(d,p) level of theory (see Figs. S1 and S2). Continuity of the depicted dependencies and range of their changes unequivocally indicates the non-dissociative nature of the tautomerisation processes.

Fig. S8. Interconversion of the pseudo-twofold symmetrical $A\cdot A(w)$ mismatches *via* the tautomeric transition. Presented isoenergetic structures are linked with each other by the pseudo-dyadic axis of symmetry.

Fig. S9. Profiles of the $R(H_9-H_{9'})$ distances between the H_9 and $H_{9'}$ glycosidic hydrogens and the α_1 ($\angle N9H_9(G)H_{9'}(G^*)$) or α_2 ($\angle N9H_9(G^*)H_9(G)$) glycosidic angles of the G and G^* bases, respectively, along the IRC of the (a) $G \cdot G^*(WC) \leftrightarrow G^* \cdot G^*(w)$ and (b) $G \cdot G^*(WC) \leftrightarrow G \cdot G(w)$ biologically important tautomerisations *via* the sequential DPT obtained at the B3LYP/6-311++G(d,p) level of theory (see Figs. S4 and S5). Continuity of the depicted dependencies and range of their changes unequivocally indicates the non-dissociative nature of the tautomerisation processes.

Fig. S10. Interconversion of the pseudo-twofold symmetrical $G^* \cdot G^*(w)$ mismatches *via* the tautomeric transition. Presented isoenergetic structures are linked with each other by the pseudo-dyadic axis of symmetry.

Fig. S11. Interconversion of the pseudo-twofold symmetrical $G \cdot G(w)$ mismatches *via* the tautomeric transition. Presented isoenergetic structures are linked with each other by the pseudodyadic symmetrical axis.

Fig. S12. Transition states of the conformational interconversions of the mirror-symmetric enantiomers of the **(a)** $\text{G}\cdot\text{G}^*(\text{WC})$, **(b)** $\text{TS}_{\text{TS}}^{\text{G}^+\cdot\text{G}^-}_{\text{G}\cdot\text{G}^*(\text{WC})\leftrightarrow\text{G}^*\cdot\text{G}^*(\text{w})}$, **(c)** $\text{TS}_{\text{TS}}^{\text{G}^+\cdot\text{G}^-}_{\text{G}\cdot\text{G}^*(\text{WC})\leftrightarrow\text{G}\cdot\text{G}(\text{w})}$ and **(d)** $\text{G}\cdot\text{G}(\text{w})$ biologically important complexes. For designations see Figs. S1 and S4.

Fig. S13. Profiles of the relative electronic energy ΔE of the conformational interconversion of the mirror-symmetric enantiomers of the (a) Watson-Crick-like $G \cdot G^*(WC)$ and (b) wobble $G \cdot G(w)$ base mispairs along the IRC obtained at the B3LYP/6-311++G(d,p) level of theory.

Table S8. Energetic, vibrational, kinetic and geometric characteristics of the conformational interconversions of the mirror-symmetric enantiomers of the biologically important base mispairs and TSs of their tautomerisation *via* the sequential DPT calculated at the MP2/cc-pVQZ//B3LYP/6-311++G(d,p) level of theory (see also Figs. S12 and S13).

Transition state of the interconversion	$\Delta\Delta G_{TS}^a$	$\Delta\Delta E_{TS}^b$	$\tau_{99.9\%}^c$	ν_i^d	β^e
$TS_{G \cdot G^*(WC)}$	5.44	6.15	$5.43 \cdot 10^{-9}$	238.7i	$\angle C6N1(G)N1C6(G^*) = \pm 36.4$
$TS_{TS}^{G^+ \cdot G^-}_{G \cdot G^*(WC) \leftrightarrow G^* \cdot G(w)}$	9.24	7.45	$3.33 \cdot 10^{-6}$	209.3i	$\angle C6N1(G^+)N1C6(G^-) = \pm 30.0$
$TS_{TS}^{G^+ \cdot G^-}_{G \cdot G^*(WC) \leftrightarrow G \cdot G(w)}$	3.41	3.62	$1.78 \cdot 10^{-10}$	103.3i	$\angle C2N1(G^+)C2N3(G^-) = \pm 49.8$
$TS_{G \cdot G(w)}$	8.94	8.91	$2.01 \cdot 10^{-6}$	191.6i	$\angle C6N1(G)N1C6(G) = \pm 96.1$

^aThe Gibbs free energy barrier of the conformational interconversion under normal conditions, kcal·mol⁻¹

^bThe electronic energy barrier of the conformational interconversion, kcal·mol⁻¹

^cThe time necessary to reach 99.9% of the equilibrium concentration between the mirror-symmetric enantiomers, s

^dImaginary frequency in the transition state of the conformational interconversion, cm⁻¹

^eDihedral angle that characterize the non-planarity of the complex, °; signs “±” correspond to the mirror-symmetric enantiomers

Fig. S14. Structures of the stationary points of the (a) $G^* \cdot G^*(w) \leftrightarrow G^*_{N2} \cdot G(w)$ and (b) $G \cdot G(w) \leftrightarrow G^* \cdot G^*_{NH3^+}(w)$ conversions *via* the DPT along the intermolecular H-bonds obtained at the B3LYP/6-311++G(d,p) level of theory. For designations see Figs. S1 and S4.

Fig. S15. Profiles of the relative electronic energy ΔE of the (a) $G^* \cdot G^*(w) \leftrightarrow G^* \cdot N_2 \cdot G(w)$ and (b) $G \cdot G(w) \leftrightarrow G^* \cdot G^* \cdot NH_3^+(w)$ tautomerisations *via* the sequential DPT along the intermolecular H-bonds along the IRC obtained at the B3LYP/6-311++G(d,p) level of theory.

Table S9. Energetic and kinetic characteristics of the $G^* \cdot G^*(w) \leftrightarrow G^* \cdot N_2 \cdot G(w)$ and $G \cdot G(w) \leftrightarrow G^* \cdot G^* \cdot NH_3^+(w)$ tautomerisations *via* the sequential DPT along the intermolecular H-bonds obtained at the different levels of theory for the geometry calculated at the B3LYP/6-311++G(d,p) level of theory (see also Figs. S14 and S15).

Level of theory	ΔG^a	ΔE^b	$\Delta \Delta G_{TS}^c$	$\Delta \Delta E_{TS}^d$	$\Delta \Delta G^e$	$\Delta \Delta E^f$	$\tau_{99.9\%}^g$
$G^* \cdot G^*(w) \leftrightarrow G^* \cdot N_2 \cdot G(w)$							
MP2/6-311++G(2df,pd)	13.17	12.66	12.31	13.96	-0.86	1.30	$1.21 \cdot 10^{-13}$
MP2/6-311++G(3df,2pd)	12.73	12.23	12.30	13.94	-0.44	1.72	$2.46 \cdot 10^{-13}$
MP2/cc-pVTZ	13.21	12.70	12.62	14.26	-0.60	1.56	$1.88 \cdot 10^{-13}$
MP2/cc-pVQZ	12.95	12.44	12.49	14.14	-0.46	1.70	$2.37 \cdot 10^{-13}$
$G \cdot G(w) \leftrightarrow G^* \cdot G^* \cdot NH_3^+(w)$							
MP2/6-311++G(2df,pd)	22.60	22.77	21.95	22.73	-0.64	-0.04	$3.67 \cdot 10^{-13}$
MP2/6-311++G(3df,2pd)	23.39	23.57	22.81	23.59	-0.58	0.02	$4.07 \cdot 10^{-13}$
MP2/cc-pVTZ	23.20	23.37	22.57	23.34	-0.63	-0.03	$3.74 \cdot 10^{-13}$
MP2/cc-pVQZ	23.42	23.27	22.91	23.26	-0.51	-0.01	$4.58 \cdot 10^{-13}$

See Table S2 for the designations and summary Table S6 for the Gibbs and electronic energies of the mispairs and TSs relatively the global minimum – the $G \cdot G^*(WC)$ Watson-Crick base mispair.

Short-lived $G^* \cdot N_2 \cdot G(w)$ ($\tau = 3.44 \cdot 10^{-14}$ s) and $G^* \cdot G^* \cdot NH_3^+(w)$ ($\tau = 6.63 \cdot 10^{-14}$ s) complexes are dynamically unstable structures: any of their 6 intermolecular low-frequency vibrations (13.8, 32.4, 60.2, 65.5, 75.0, 123.0 cm^{-1} and 19.6, 30.9, 45.2, 86.2, 90.9, 99.0 cm^{-1} , respectively) can develop during their lifetimes.

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