Supporting Information

The nature of the transition mismatches with Watson-Crick architecture: the $G^* \cdot T$ or $G \cdot T^*$ DNA base mispair or both? A QM/QTAIM perspective for the biological problem

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Figure S1. Profiles of the electronic energy ΔE along the IRC of the $G^* \cdot T \leftrightarrow G \cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S2. Profiles of the first derivative of the electronic energy with respect to the IRC - $dE/dIRC$ - along the IRC of the $G^* \cdot T \leftrightarrow G \cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S3. Profiles of the dipole moment μ along the IRC of the $G^* \cdot T \leftrightarrow G \cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S4. Profiles of the electron density ρ at the (3,-1) BCPs of the covalent and hydrogen bonds along the IRC of the $G^*\cdot T \leftrightarrow G\cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S5. Profiles of the Laplacian of the electron density $\Delta\rho$ at the (3,-1) BCPs of the covalent and hydrogen bonds along the IRC of the $G^*\cdot T \leftrightarrow G\cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S6. Profiles of the ellipticity ϵ at the (3,-1) BCPs of the covalent and hydrogen bonds along the IRC of the $G^*\cdot T \leftrightarrow G\cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S7. Profiles of the energy of the H-bonds E_{HB} , estimated by the EML formula [1, 2], at the (3,-1) BCPs of the $AH \cdots B$ H-bonds along the IRC of the $G^* \cdot T \leftrightarrow G \cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S8. Profiles of the NBO charges q_{NBO} of the hydrogen atoms involved in the $N3H_I \cdots N1$, $O6H_{II} \cdots O4$ and $N2H_{III} \cdots O2$ H-bonds along the IRC of the $G^* \cdot T \leftrightarrow G \cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S9. Profiles of the distance $d_{A \cdots B}$ between the electronegative A and B atoms involved in the $AH \cdots B$ H-bonds along the IRC of the $G^* \cdot T \leftrightarrow G \cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S10. Profiles of the distance $d_{AH/HB}$ between the hydrogen and electronegative A or B atoms involved in the $AH \cdots B$ H-bonds along the IRC of the $G^* \cdot T \leftrightarrow G \cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S11. Profiles of the angle $\angle AH \cdots B$ of the $AH \cdots B$ H-bonds along the IRC of the $G^* \cdot T \leftrightarrow G \cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S12. Profiles of the distance $R(H_9-H_1)$ between the H9 and H1 glycosidic protons along the IRC of the $G^* \cdot T \leftrightarrow G \cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S13. Profiles of the α_1 ($\angle N9HH$) and α_2 ($\angle N1HH$) glycosidic angles along the IRC of the $G^* \cdot T \leftrightarrow G \cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

Figure S14. Profile of the $\angle C6N1(G)N3C4(T)$ dihedral angle along the IRC of the $G^* \cdot T \leftrightarrow G \cdot T^*$ tautomerisation *via* the DPT obtained at the DFT level of theory (a) *in vacuo* and (b) in the continuum with a low dielectric constant ($\epsilon=4$).

References:

1. Espinosa, E., Molins, E., & Lecomte, C. (1998). Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities. *Chemical Physics Letters*, 285, 170–173.
2. Mata, I., Alkorta, I., Espinosa, E., & Molins, E. (2011). Relationships between interaction energy, intermolecular distance and electron density properties in hydrogen bonded complexes under external electric fields. *Chemical Physics Letters*, 507, 185–189.