Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.


# Supplementary Material

## DPT tautomerisation of the G·$A_{syn}$ and A*·$G^*_{syn}$ DNA mismatches: A QM/QTAIM combined atomistic investigation

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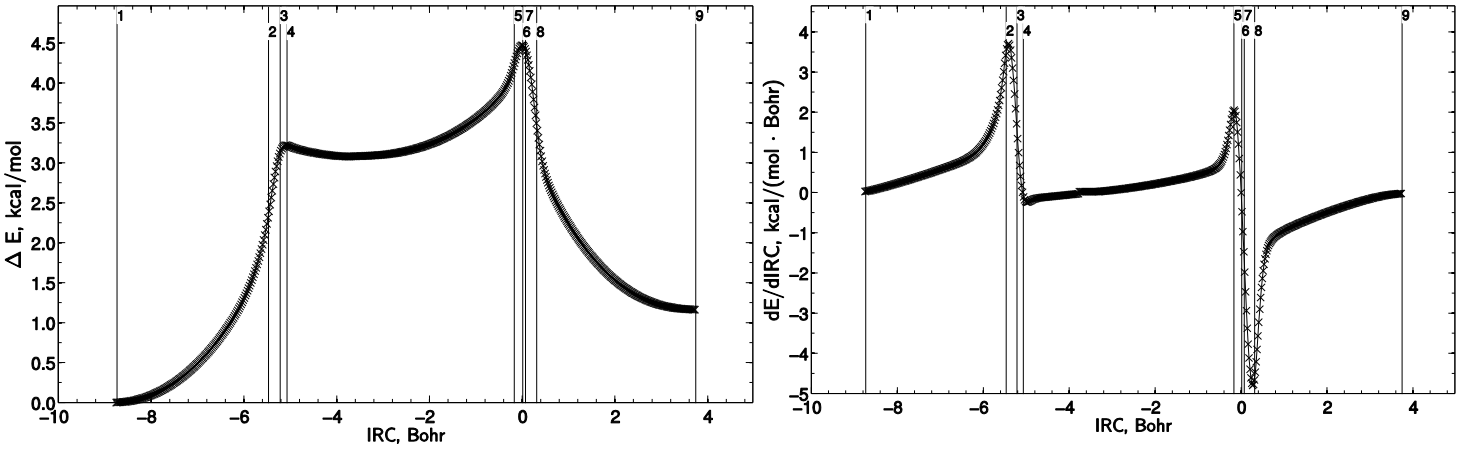



**a** **b**

**Fig. S1** Profiles of: (**a**) the electronic energy E of the base mispair and (**b**) the first derivative of the electronic energy E with respect to the IRC - dE/dIRC - along the IRC of the A*·G*$_{syn}$↔A·G*$_{syn}$ tautomerisation *via* the DPT obtained at the B3LYP/6-311++G(d,p) level of theory *in vacuo*. The position of the TS$_{A*·G*syn↔A·G*syn}$ corresponds to IRC=0.00 Bohr.

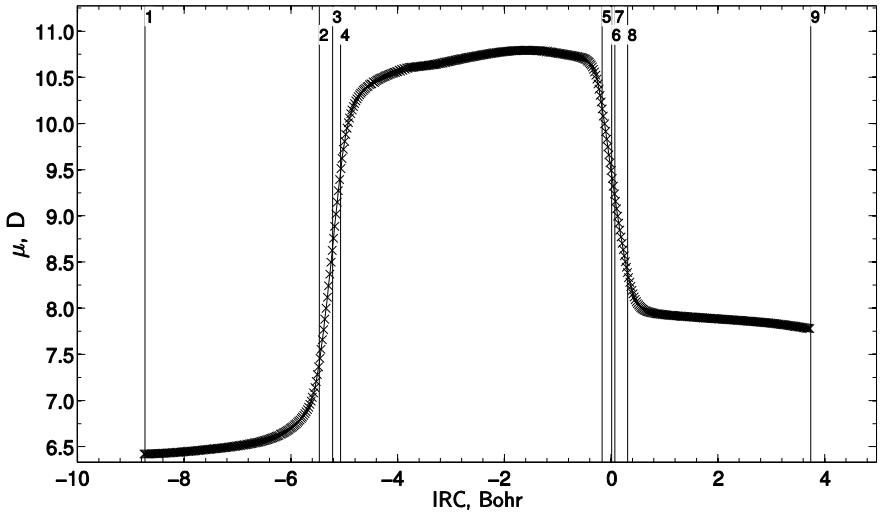



**Fig. S2** Profile of the dipole moment μ of the base mispair along the IRC of the A*·G*$_{syn}$↔A·G*$_{syn}$ tautomerisation *via* the DPT obtained at the B3LYP/6-311++G(d,p) level of theory *in vacuo.*

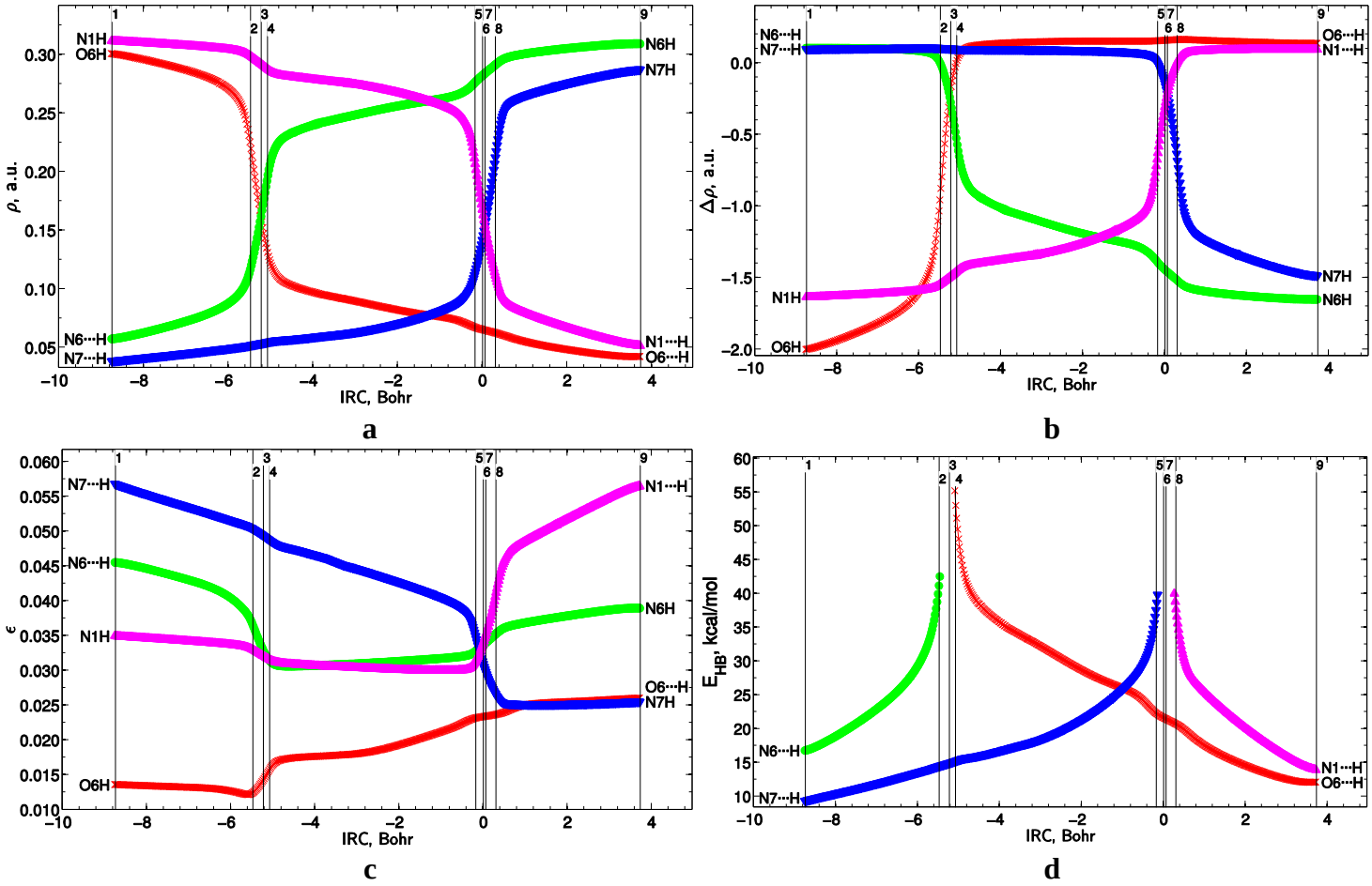



**Fig. S3** Profiles of: (**a**) the electron density ρ; (**b**) the Laplacian of the electron density Δρ; (**c**) the ellipticity ε and (**d**) the energy of the H-bond $E_{HB}$, estimated by the EML formula [1,2], at the (3,-1) BCPs of the covalent and hydrogen bonds along the IRC of the A*·G*$_{syn}$↔A·G*$_{syn}$ tautomerisation *via* the DPT obtained at the B3LYP/6-311++G(d,p) level of theory *in vacuo*.

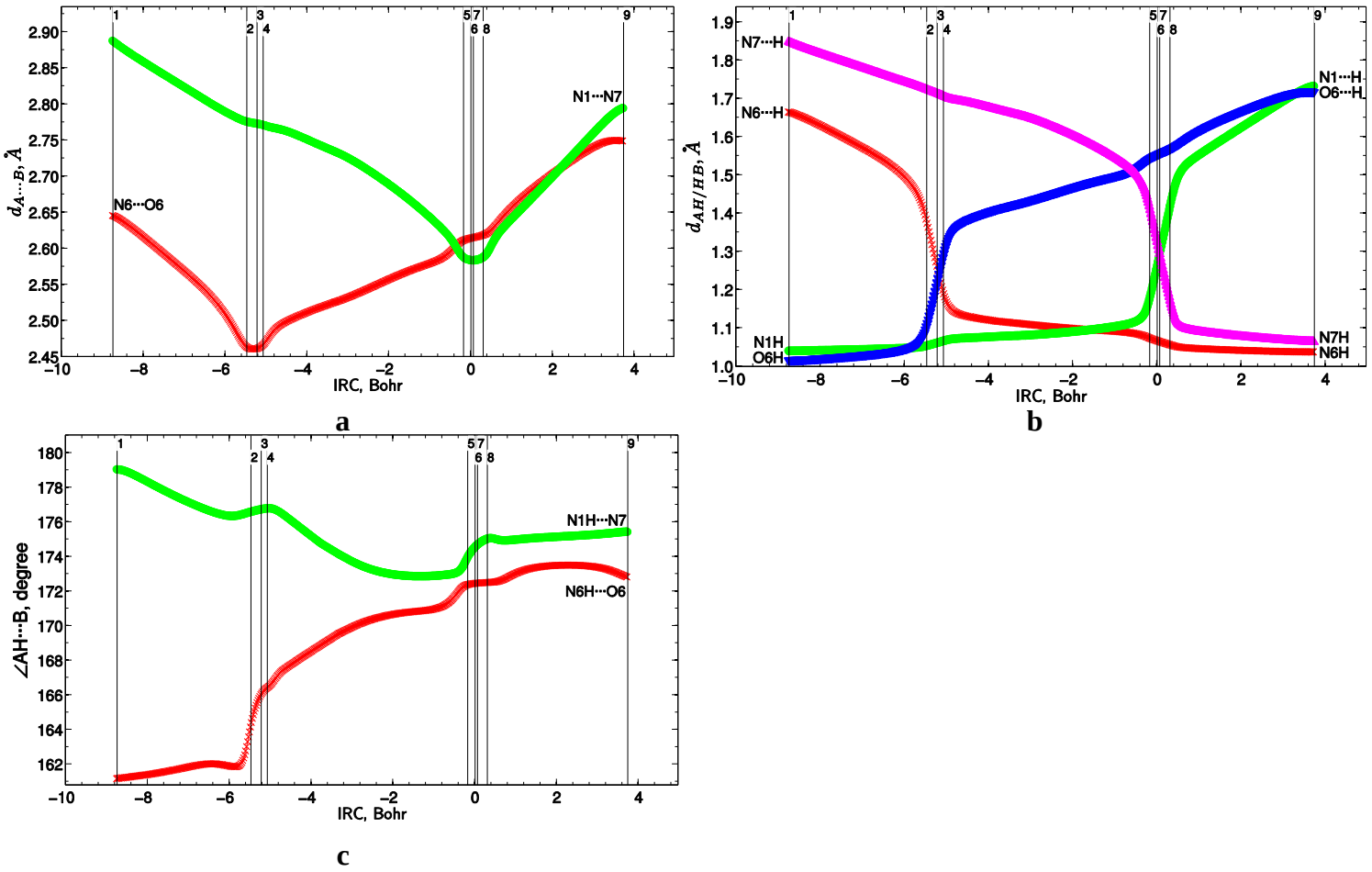



**Fig. S4** Profiles of: (**a**) the distance $d_{A\cdots B}$ between the electronegative A and B atoms; (**b**) the distance $d_{AH/HB}$ between the hydrogen and electronegative A or B atoms and (**c**) the angle ∠AH···B of the AH···B H-bonds along the IRC of the A*·G*$_{syn}$↔A·G*$_{syn}$ tautomerisation *via* the DPT obtained at the B3LYP/6-311++G(d,p) level of theory *in vacuo*.

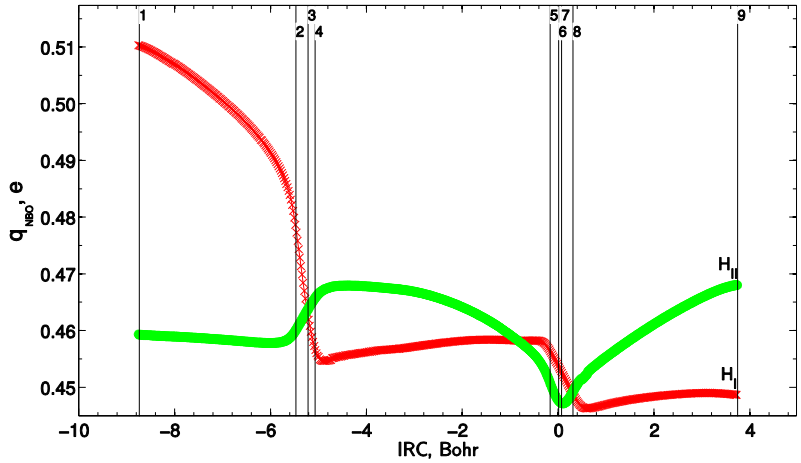
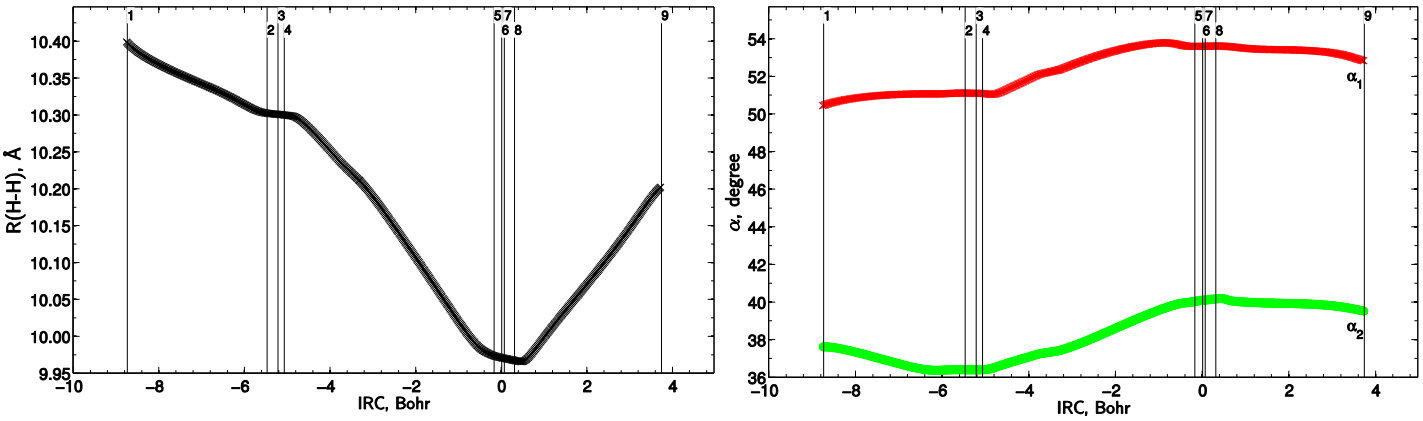



**Fig. S5** Profiles of the NBO charges of the hydrogen atoms involved in the $O6H_I\cdots N6/N6H_I\cdots O6$ and $N1H_{II}\cdots N7/N7H_{II}\cdots N1$ H-bonds along the IRC of the $A^*\cdot G^*_{syn}\leftrightarrow A\cdot G^*_{syn}$ tautomerisation *via* the DPT obtained at the B3LYP/6-311++G(d,p) level of theory *in vacuo*.




**a** **b**

**Fig. S6** Profiles of: (**a**) the distance R(H-H) between the glycosidic hydrogens and (**b**) the $\alpha_1$ ($\angle$N9H(A)H($G_{syn}$)) and $\alpha_2$ ($\angle$N9H($G_{syn}$)H(A)) glycosidic angles along the IRC of the $A^*\cdot G^*_{syn}\leftrightarrow A\cdot G^*_{syn}$ tautomerisation *via* the DPT obtained at the B3LYP/6-311++G(d,p) level of theory *in vacuo*.

**References.**

1. Espinosa E., Molins E., Lecomte C. Hydrogen bond strengths revealed by topological analyses of experimentally observed electron densities, *Chem. Phys. Lett.*, 1998, **285**, 170–173.

2. Mata I., Alkorta I., Espinosa E., Molins E. Relationships between interaction energy, intermolecular distance and electron density properties in hydrogen bonded complexes under external electric fields, *Chem. Phys. Lett.*, 2011, **507**, 185–189.