Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry.

Supporting Information

B-DNA Structure and Stability: The Role of Hydrogen Bonding, π-π Stacking Interactions, Twist-Angle, and Solvation

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Appendix S1. Equivalence between equations 2 and 3 of the manuscript.

The cooperativity in the hydrogen bonds and in the stacking interactions is defined as follows:

$$\Delta\Delta E_{\mathrm{coop}}(\mathrm{H}) = \Delta E_{\mathrm{HB}}^{(X/X')\text{-}(Y/Y')} - 2*\Delta E_{\mathrm{HB}}^{X\text{-}Y} - [\Delta \mathrm{E}_{\mathrm{cross}}{}^{X/Y'} + \Delta \mathrm{E}_{\mathrm{cross}}{}^{X'/Y}] \qquad (2)$$

$$\Delta\Delta E_{\mathrm{coop}}(\pi) = \Delta E_{\pi\text{-}\pi}^{(X\text{-}Y)/(X'\text{-}Y')} - \Delta E_{\pi\text{-}\pi}^{X/X'} - \Delta E_{\pi\text{-}\pi}^{Y/Y'} - [\Delta \mathrm{E}_{\mathrm{cross}}{}^{X/Y'} + \Delta \mathrm{E}_{\mathrm{cross}}{}^{X'/Y}] \qquad (3)$$

When each term ΔE in the above equality is written in terms of the ADF total energies, we have:

$$\Delta E_{\mathrm{HB}}^{(X/X')\text{-}(Y/Y')} = E(\mathrm{XY/X'Y'}) - E(\mathrm{X/X'}) - E(\mathrm{Y/Y'})$$

$$\Delta E_{\mathrm{HB}}^{X\text{-}Y} = E(\mathrm{XY}) - E(\mathrm{X}) - E(\mathrm{Y})$$

$$\Delta E_{\pi\text{-}\pi}^{(X\text{-}Y)/(X'\text{-}Y')} = E(\mathrm{XY/X'Y'}) - 2*E(\mathrm{XY})$$

$$\Delta E_{\pi\text{-}\pi}^{X/X'} = E(\mathrm{X/X'}) - 2*E(\mathrm{X})$$

$$\Delta E_{\pi\text{-}\pi}^{Y/Y'} = E(\mathrm{Y/Y'}) - 2*E(\mathrm{Y})$$

From this, it follows that:

$$\Delta\Delta E_{\mathrm{coop}}(\mathrm{H}) = E(\mathrm{XY/X'Y'}) - E(\mathrm{X/X'}) - E(\mathrm{Y/Y'}) - 2*[E(\mathrm{XY}) - E(\mathrm{X}) - E(\mathrm{Y})]$$

$$\Delta\Delta E_{\mathrm{coop}}(\pi) = E(\mathrm{XY/X'Y'}) - 2*E(\mathrm{XY}) - [E(\mathrm{X/X'}) - 2*E(\mathrm{X})] - [E(\mathrm{Y/Y'}) - 2*E(\mathrm{Y})]$$

Now, simple inspection shows that $\Delta\Delta E_{\mathrm{coop}}(\mathrm{H}) = \Delta\Delta E_{\mathrm{coop}}(\pi)$.

Table S1. Stacking energy, $\Delta E_{\pi\text{-}\pi}$,(in kcal/mol), for two identical stacked bases pairs X-Y, at a twist angle of 0° and 36°, calculated both from frozen geometry of the base pairs and from optimized geometry.[a,b]

XY	Stacking (frozen geometry)				Stacking (relaxed geometry)			
	0°		36°		0°		36°	
	gas	wat	gas	wat	gas	wat	gas	wat
ATWC	-3.9	-5.8	-12.2	-9.8	-6.2	-8.1	-16.3	-12.5
GCWC	-3.0	-7.9	-9.8	-9.7	-3.9	-8.3	-23.3	-12.8
GG4[b]	-0.9	-8.1	-10.5	-5.2	-2.7	-9.3	-49.9	-11.4
GGx[b]	1.9	-9.3	-6.5	-8.1	-1.3	-10.6	-42.8	-17.7

[a] Calculated at the BP86-D/TZ2P level of theory in the gas phase and in water (COSMO).

[b] The stacking interaction is always more attractive at a twist angle of 36° in gas phase (see Table 1 and 2) and in water, but with few exceptions. In particular, for GG4 and GGx in aqueous solution, the lower stacking interaction from 0 to 36° has to be attributed to an artifact of the COSMO calculation, more specifically, to the fact that these calculations are carried out with the frozen geometry of the base pair alone. The relaxation of the stacked base pair at 0° only implies to lower the energy in 1.2 and 1.3 kcal mol^{-1} for GG4 and GGx, respectively, whereas the corresponding relaxation at 36° causes an stabilization of 6.2 and 9.7 kcal mol^{-1}, respectively. ATWC and GCWC are not affected and keep the same trend, as the rest of the systems under analysis. When this point is taken into consideration, we can generalize that in all cases the stacking interaction is more attractive at 36°.

Table S2. Energy decomposition analysis of the stacking energies of stacked mismatched DNA base pairs, in the gas-phase and with twist angles of 0° and 36°.[a] (See also Table 5)

Interaction	System	ΔE_{Pauli}	ΔV_{elstat}	ΔE_{oi}	ΔE_{disp}	ΔE_{int}
XY/X’Y’ stacking	CCx-0°	18.6	6.4	-3.5	-16.9	4.7
	CCx-36°	12.4	0.1	-3.7	-13.9	-5.1
	GCRWC-0°	20.6	8.7	-4.3	-20.6	4.4
	GCRWC-36°	13.0	4.6	-4.3	-15.9	-2.7
	GGx-0°	22.5	8.1	-4.6	-24.2	1.9
	GGx-36°	14.4	2.2	-4.5	-18.6	-6.5
	TT3-0°	30.9	-0.7	-8.1	-21.0	1.2
	TT3-36°	12.2	-2.1	-3.6	-15.6	-9.1
	TT3-0° (Me optimized)	21.0	1.0	-4.2	-20.6	-2.8
	TT3-36° (Me optimized)	12.3	-2.3	-3.6	-15.7	-9.4
X/X’ stacking	CCx-0°	9.4	2.9	-1.6	-7.9	2.8
	CCx-36°	6.2	-1.5	-1.8	-6.2	-3.2
	GCRWC-0°	9.4	3.1	-1.7	-7.9	3.0
	GCRWC-36°	5.2	2.6	-1.6	-5.4	0.8
	GGx-0°	11.3	3.4	-2.2	-11.4	1.1
	GGx-36°	7.4	1.4	-2.1	-8.7	-2.1
	TT3-0°	15.5	0.1	-4.0	-9.9	1.7
	TT3-36°	6.0	-0.5	-1.7	-7.0	-3.2
Y/Y’ stacking	CCx-0°	9.4	3.0	-1.6	-7.9	2.9
	CCx-36°	6.0	1.8	-1.7	-6.1	0.0
	GCRWC-0°	11.4	3.3	-2.1	-11.4	1.1
	GCRWC-36°	7.6	0.3	-2.1	-8.9	-3.1
	GGx-0°	11.3	3.3	-2.1	-11.4	1.1
	GGx-36°	6.7	0.2	-1.9	-8.0	-2.9
	TT3-0°	15.5	0.1	-4.0	-9.9	1.7
	TT3-36°	6.0	-0.5	-1.7	-7.0	-3.2
X/Y’ cross	CCx-0°	0.4	-1.0	-0.3	-0.6	-1.5
	CCx-36°	0.5	-0.5	-0.4	-0.7	-1.1
	GCRWC-0°	0.4	-0.4	-0.4	-0.6	-1.1
	GCRWC-36°	0.5	-0.3	-0.4	-0.7	-1.0
	GGx-0°	0.4	-1.0	-0.4	-0.7	-1.7
	GGx-36°	0.8	-0.4	-0.5	-1.2	-1.3
	TT3-0°	0.4	-0.3	-0.1	-0.6	-0.6
	TT3-36°	0.5	-0.4	-0.2	-0.8	-0.9
Y/X’ cross	CCx-0°	0.4	-1.0	-0.3	-0.6	-1.5
	CCx-36°	0.6	-1.6	-0.4	-0.8	-2.2
	GCRWC-0°	0.4	-0.4	-0.4	-0.6	-1.1
	GCRWC-36°	0.6	-0.6	-0.5	-1.0	-1.4
	GGx-0°	0.4	-1.0	-0.4	-0.7	-1.7
	GGx-36°	0.5	-1.9	-0.5	-0.7	-2.6
	TT3-0°	0.4	-0.3	-0.1	-0.6	-0.6
	TT3-36°	6.0	-0.5	-1.7	-7.0	-3.2

[a] Calculated at the BP86-D/TZ2P level of theory.