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Supporting Information for

Influence of Substituents and Environment on NMR Shielding Constants of Supramolecular Complexes based on A-T and A-U Base Pairs

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Figure S2. Calculated dependence of the NMR *C2*-shielding values (ppm) as a function of the hydrogen-bond strength (kcal·mol^{-1}). **a)** *C2-adenine* shielding of A^{X8}-U, **b)** *C2-adenine* shielding of A-U^{Y6}, **c)** *C2-uracil* shielding of A^{X8}-U, and **d)** *C2-uracil* shielding of A-U^{Y6} base pairs. The proton transfer systems were not included in the plot, due to its particular behavior.

Figure S3. Calculated correlation between the *C2-adenine* shielding values (ppm) of isolated adenine (A^{X8}) bases and A^{X8}-T base pairs at the SAOP/TZ2P level and using the COSMO model. The proton transfer systems were not included in the plot, due to its particular behavior.

Figure S4. Calculated correlation between the *C2-adenine* shielding values (ppm) of isolated adenine (A^{X8}) bases and A^{X8}-T base pairs at the B3LYP/TZ2P level. The proton transfer systems were not included in the plot, due to its particular behavior.

Figure S5. Calculated correlation between the C2 adenine shielding values (ppm) of isolated adenine (A^{X8}) bases and A^{X8}-T base pairs at the SAOP/TZ2P level and using the Spin-Orbit ZORA relativistic correction. The proton transfer systems were not included in the plot, due to its particular behavior.

Energy decomposition analysis setup

The hydrogen bonding in the model systems was analyzed in the conceptual framework provided by the Kohn-Sham molecular orbital model, using a quantitative bond energy decomposition analysis (EDA)[1-3] implemented in the ADF2014 package at the BLYP-D3(BJ)/TZ2P and S12g/TZ2P levels (both functionals lead to the same findings). The hydrogen bond energy, ΔE_{Bond}, contains two components [Eq. (1)].

$$\Delta E_{\mathrm{Bond}} = \Delta E_{\mathrm{prep}} + \Delta E_{\mathrm{int}} \qquad (1)$$

In this formula, the preparation energy, ΔE_{prep}, is the amount of energy required to deform the separate bases from their equilibrium structure to the geometry that they acquire in the pair. The interaction energy, ΔE_{int}, corresponds to the actual energy change when the prepared bases are combined to form the base pair.

ΔE_{int} can be divided into four components as shown in Equation (2).

$$\Delta E_{\mathrm{int}} = \Delta V_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{oi}} + \Delta E_{\mathrm{disp}} \qquad (2)$$

The term $\Delta V_{\mathrm{elstat}}$ corresponds to the classical electrostatic interaction energy between the unperturbed charge distributions of the prepared (i.e. deformed) bases and is usually attractive. The second term in Equation (2), $\Delta E_{\mathrm{Pauli}}$, refers to the repulsive interactions between the fragments, which are caused by the fact that two electrons with the same spin cannot occupy the same region in space. $\Delta E_{\mathrm{Pauli}}$ was computed by enforcing the Kohn-Sham determinant of the superimposed fragments to obey the Pauli principle by antisymmetrization and renormalization. The stabilizing orbital interaction term, ΔE_{oi}, was estimated in the final step of the energy partitioning analysis when the Kohn-Sham orbitals relax to their optimal form. This term can be further partitioned into contributions by the orbitals belonging to different irreducible representations of the point group of the interacting system [Eq. (3)]. In systems with a clear σ and π separation, this symmetry partitioning proves to be very informative.

$$\Delta E_{oi} = \Delta E_{oi,\sigma} + \Delta E_{oi,\pi} \qquad (3)$$

The last term ΔE_{disp} in equation (2) refers to the dispersion correction term.

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(3) F. M. Bickelhaupt, E. J. Baerends, *Kohn-Sham Density Functional Theory: Predicting and Understanding Chemistry*, Reviews in Computational Chemistry, Wiley-VCH: New York, Vol. 15, pp. 1-86, **2000**.

Table S1. EDA analysis (in kcal·mol^{-1}) of the A^{X8}-T^{Y6} base pairs (N and O series) using the BLYP-D3(BJ)/TZ2P level.

X8	H	**NH_2**	**NH^-**	**NH_2**	**NH_3^+**	H	H	H
Y6	H	**NH_2**	H	H	H	**NH^-**	**NH_2**	**NH_3^+**
Bond Energy Decomposition[a]								
ΔE_{prep}	1.92	2.37	76.48	3.16	1.85	3.41	2.46	68.41
ΔE_{int}	-18.42	-18.23	-97.88	-18.39	-21.52	-21.33	-18.52	-95.57
ΔE_{Pauli}	40.14	40.60	172.88	40.42	38.85	45.73	40.53	152.24
ΔV_{elstat}	-32.07	-32.18	-88.68	-32.06	-33.47	-35.24	-32.50	-78.34
ΔE_{disp}	-5.39	-5.40	-5.05	-5.40	-5.30	-5.01	-5.39	-5.26
ΔE_{oi}	-21.10	-21.25	-177.02	-21.35	-21.60	-26.82	-21.16	-164.22
ΔE_{σ}	-19.55	-19.73	-164.10	-19.80	-19.42	-23.70	-19.61	-149.10
ΔE_{π}	-1.56	-1.52	-12.92	-1.55	-2.18	-3.12	-1.55	-15.12
% ΔV_{elstat}[b]	54.8	54.7	32.8	54.5	55.4	52.5	55.0	31.6
% ΔE_{disp}[b]	9.2	9.2	1.9	9.2	8.8	7.5	9.1	2.1
% ΔE_{oi}[b]	36.0	36.1	65.4	36.3	35.8	40.0	35.8	66.3
ΔE_{Bond}	-16.50	-15.86	-21.40	-15.23	-19.67	-17.92	-16.06	-27.16
X8	H	**OH**	**O^-**	**OH**	**OH_2^+**	H	H	H
Y6	H	**OH**	H	H	H	**O^-**	**OH**	**OH_2^+**
Bond Energy Decomposition[a]								
ΔE_{prep}	1.92	1.88	75.00	1.90	1.77	3.27	1.95	72.07
ΔE_{int}	-18.42	-18.53	-95.98	-18.37	-21.80	-20.97	-18.59	-101.51
ΔE_{Pauli}	40.14	40.53	172.21	40.05	38.77	45.02	40.61	147.45
ΔV_{elstat}	-32.07	-32.33	-88.38	-31.97	-33.52	-34.83	-32.43	-76.13
ΔE_{disp}	-5.39	-5.43	-5.08	-5.40	-5.30	-5.02	-5.42	-5.17
ΔE_{oi}	-21.10	-21.29	-174.74	-21.05	-21.75	-26.14	-21.34	-167.66
ΔE_{σ}	-19.55	-19.74	-162.01	-19.50	-19.5	-23.18	-19.78	-151.62
ΔE_{π}	-1.56	-1.54	-12.73	-1.54	-2.24	-2.96	-1.56	-16.03
% ΔV_{elstat}[b]	54.8	54.8	33.0	54.7	55.3	52.8	54.8	30.6
% ΔE_{disp}[b]	9.2	9.2	1.9	9.2	8.8	7.6	9.2	2.1
% ΔE_{oi}[b]	36.0	36.1	65.2	36.0	35.9	39.6	36.1	67.3
ΔE_{Bond}	-16.50	-16.65	-20.98	-16.47	-20.03	-17.70	-16.64	-29.44

[a] Computed at BLYP-D_3(BJ)/TZ2P with bases in C_1 symmetry and base pairs in C_s symmetry. [b] The percentage values give the contribution to the total attractive forces (i.e. $\Delta V_{\text{elstat}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}}$).

Table S2. EDA analysis (in kcal·mol^{-1}) of the A^{X8}-T^{Y6} base pairs (N and O series) using the S12g/TZ2P level.

X8	H	**NH_2**	**NH^-**	**NH_2**	**NH_3^+**	H	H	H
Y6	H	**NH_2**	H	H	H	**NH^-**	**NH_2**	**NH_3^+**
				Bond Energy Decomposition[a]				
ΔE_{prep}	1.74	1.67	78.66	1.82	1.84	3.11	1.78	70.72
ΔE_{int}	-18.04	-17.89	-100.96	-18.02	-21.06	-20.79	-18.18	-97.00
ΔE_{Pauli}	31.37	32.49	164.53	40.42	31.96	38.85	32.63	144.41
ΔV_{elstat}	-28.24	-28.70	-86.73	-28.22	-30.52	-32.35	-29.12	-75.94
ΔE_{disp}	-3.34	-3.36	-3.16	-3.35	-3.32	-3.15	-3.36	-3.27
ΔE_{oi}	-17.83	-18.31	-175.61	-18.04	-19.18	-24.15	-18.32	-162.21
ΔE_{σ}	-16.50	-16.99	-162.95	-16.72	-17.23	-21.29	-16.97	-147.49
ΔE_{π}	-1.32	-1.33	-12.66	-1.32	-1.95	-2.86	-1.35	-14.72
% ΔV_{elstat}[b]	57.2	57.0	32.7	56.9	57.6	54.2	57.3	31.5
% ΔE_{disp}[b]	6.8	6.7	1.2	6.8	6.3	5.3	6.6	1.4
% ΔE_{oi}[b]	36.1	36.4	66.1	36.4	36.2	40.5	36.1	67.2
$\Delta \mathrm{E}_{Bond}$	-16.30	-16.22	-22.30	-16.20	-19.22	-17.68	-16.40	-26.28
X8	H	**OH**	**O^-**	**OH**	**OH_2^+**	H	H	H
Y6	H	**OH**	H	H	H	**O^-**	**OH**	**OH_2^+**
				Bond Energy Decomposition[a]				
ΔE_{prep}	1.74	1.81	77.14	1.81	1.88	3.16	1.84	73.24
ΔE_{int}	-18.04	-18.23	-98.79	-18.06	-21.37	-20.67	-18.25	-101.75
ΔE_{Pauli}	31.37	34.48	165.13	32.60	33.54	39.88	33.30	141.67
ΔV_{elstat}	-28.24	-29.96	-86.89	-28.86	-31.38	-32.90	-29.39	-74.58
ΔE_{disp}	-3.34	-3.39	-3.17	-3.35	-3.33	-3.17	-3.38	-3.24
ΔE_{oi}	-17.83	-19.37	-173.86	-18.45	-20.21	-24.47	-18.78	-165.60
ΔE_{σ}	-16.50	-17.94	-161.34	-17.08	-18.09	-21.67	-17.39	-150.11
ΔE_{π}	-1.32	-1.43	-12.52	-1.37	-2.11	-2.81	-1.39	-15.49
% ΔV_{elstat}[b]	6.8	56.8	32.9	57.0	57.1	54.3	57.0	30.6
% ΔE_{disp}[b]	36.1	6.4	1.2	6.6	6.1	5.2	6.6	1.3
% ΔE_{oi}[b]	36.1	36.7	65.9	36.4	36.8	40.4	36.4	68.0
ΔE_{Bond}	-16.30	-16.42	-21.65	-16.25	-19.49	-17.51	-16.41	-28.51

[a] Computed at S12g/TZ2P with bases in C_1 symmetry and base pairs in C_s symmetry. [b] The percentage values give the contribution to the total attractive forces (i.e. $\Delta V_{elstat} + \Delta E_{oi} + \Delta E_{disp}$).

Table S3. EDA analysis (in kcal·mol^{-1}) of the A^{X8}-U^{Y6} base pairs (N and O series) using the BLYP-D3(BJ)/TZ2P level.

X8	H	**NH_2**	**NH^-**	**NH_2**	**NH_3^+**	H	H	H
Y6	H	**NH_2**	H	H	H	**NH^-**	**NH_2**	**NH_3^+**
				Bond Energy Decomposition[a]				
ΔE_{prep}	1.85	2.45	76.44	3.15	1.63	3.22	2.35	69.58
ΔE_{int}	-18.62	-18.45	-98.59	-18.64	-21.29	-21.49	-18.71	-98.53
ΔE_{Pauli}	40.38	40.75	171.73	40.61	38.70	45.72	40.73	151.40
ΔV_{elstat}	-32.36	-32.43	-88.67	-32.35	-33.40	-35.40	-32.75	-78.16
ΔE_{disp}	-5.34	-5.34	-4.99	-5.36	-5.26	-4.93	-5.33	-5.15
ΔE_{oi}	-21.29	-21.43	-176.65	-21.54	-21.34	-26.88	-21.35	-166.62
ΔE_{σ}	-19.71	-19.89	-163.73	-19.96	-19.20	-23.75	-19.78	-151.14
ΔE_{π}	-1.58	-1.54	-12.92	-1.58	-2.14	-3.13	-1.57	-15.48
% ΔV_{elstat}[b]	54.9	54.8	32.8	54.6	55.6	52.7	55.1	31.2
% ΔE_{disp}[b]	9.0	9.0	1.8	9.0	8.8	7.3	9.0	2.1
% ΔE_{oi}[b]	36.1	36.2	65.4	36.4	35.6	40.0	35.9	66.7
ΔE_{Bond}	-16.77	-16.00	-22.15	-15.49	-19.66	-18.27	-16.36	-28.95
X8	H	**OH**	**O^-**	**OH**	**OH_2^+**	H	H	H
Y6	H	**OH**	H	H	H	**O^-**	**OH**	**OH_2^+**
				Bond Energy Decomposition[a]				
ΔE_{prep}	1.85	2.01	74.95	1.94	1.57	2.96	1.93	73.49
ΔE_{int}	-18.62	-18.81	-96.72	-18.58	-21.55	-20.94	-18.86	-105.56
ΔE_{Pauli}	40.38	40.67	171.06	40.19	38.61	44.76	40.91	146.34
ΔV_{elstat}	-32.36	-32.59	-88.33	-32.23	-33.41	-34.76	-32.76	-75.99
ΔE_{disp}	-5.34	-5.37	-5.02	-5.35	-5.25	-4.94	-5.37	-5.06
ΔE_{oi}	-21.29	-21.52	-174.43	-21.19	-21.49	-26.00	-21.64	-170.86
ΔE_{σ}	-19.71	-19.94	-161.70	-19.63	-19.28	-23.05	-20.05	-154.29
ΔE_{π}	-1.58	-1.57	-12.73	-1.56	-2.21	-2.95	-1.59	-16.57
% ΔV_{elstat}[b]	54.9	54.8	33.0	54.8	55.6	52.9	54.8	30.1
% ΔE_{disp}[b]	9.0	9.0	1.9	9.1	8.7	7.5	9.0	2.2
% ΔE_{oi}[b]	36.1	36.2	65.1	36.1	35.7	39.6	36.2	67.7
ΔE_{Bond}	-16.77	-16.80	-21.77	-16.64	-19.98	-17.98	-16.93	-32.07

[a] Computed at BLYP-D$_3$(BJ)/TZ2P with bases in C_1 symmetry and base pairs in C_s symmetry. [b] The percentage values give the contribution to the total attractive forces (i.e. $\Delta V_{elstat} + \Delta E_{oi} + \Delta E_{disp}$).

Table S4. EDA analysis (in kcal·mol^{-1}) of the A^{X8}-U^{Y6} base pairs (N and O series) using the S12g/TZ2P level.

X8	H	**NH_2**	**NH^-**	**NH_2**	**NH_3^+**	H	H	H
Y6	H	**NH_2**	H	H	H	**NH^-**	**NH_2**	**NH_3^+**
Bond Energy Decomposition[a]								
ΔE_{prep}	1.66	2.30	78.79	1.81	3.40	2.94	2.21	71.99
ΔE_{int}	-18.24	-18.10	-101.79	-18.30	-21.26	-20.95	-18.35	-99.97
ΔE_{Pauli}	31.49	32.12	163.37	32.36	35.14	38.72	32.22	143.66
ΔV_{elstat}	-28.47	-28.68	-86.68	-28.82	-32.17	-32.47	-29.06	-75.79
ΔE_{disp}	-3.30	-3.30	-3.11	-3.33	-3.29	-3.09	-3.30	-3.19
ΔE_{oi}	-17.95	-18.23	-175.38	-18.50	-20.93	-24.10	-18.21	-164.65
ΔE_{σ}	-16.61	-16.91	-162.73	-17.15	-18.82	-21.25	-16.87	-149.57
ΔE_{π}	-1.34	-1.32	-12.65	-1.35	-2.12	-2.85	-1.35	-15.08
% ΔV_{elstat}[b]	57.3	57.1	32.7	56.9	57.0	54.4	57.5	31.1
% ΔE_{disp}[b]	6.6	6.6	1.2	6.6	5.8	5.2	6.5	1.3
% ΔE_{oi}[b]	36.1	36.3	66.1	36.5	37.1	40.4	36.0	67.6
ΔE_{Bond}	-16.58	-15.80	-23.03	-16.49	-17.86	-18.01	-16.14	-27.98

X8	H	**OH**	**O^-**	**OH**	**OH_2^+**	H	H	H
Y6	H	**OH**	H	H	H	**O^-**	**OH**	**OH_2^+**
Bond Energy Decomposition[a]								
ΔE_{prep}	1.66	1.85	77.17	1.72	1.57	2.90	1.78	74.85
ΔE_{int}	-18.24	-18.52	-99.61	-18.28	-21.12	-20.68	-18.51	-105.49
ΔE_{Pauli}	31.49	34.39	163.61	32.42	32.49	39.96	33.23	140.83
ΔV_{elstat}	-28.47	-30.11	-86.65	-28.95	-30.83	-33.02	-19.54	-74.49
ΔE_{disp}	-3.30	-3.32	-3.12	-3.31	-3.27	-3.11	-3.31	-3.16
ΔE_{oi}	-17.95	-19.47	-173.44	-18.43	-19.50	-24.51	-18.89	-168.67
ΔE_{σ}	-16.61	-18.01	-160.94	-17.06	-17.46	-21.70	-17.48	-152.68
ΔE_{π}	-1.34	-1.45	-12.50	-1.38	-2.04	-2.81	-1.41	-15.99
% ΔV_{elstat}[b]	6.6	56.9	32.9	57.1	57.5	54.5	46.8	30.2
% ΔE_{disp}[b]	36.1	6.3	1.2	6.5	6.1	5.1	7.9	1.3
% ΔE_{oi}[b]	36.1	36.8	65.9	36.4	36.4	40.4	45.3	68.5
ΔE_{Bond}	-16.58	-16.67	-22.44	-16.56	-19.55	-17.78	-16.73	-30.65

[a] Computed at S12g/TZ2P with bases in C_1 symmetry and base pairs in C_s symmetry. [b] The percentage values give the contribution to the total attractive forces (i.e. $\Delta V_{elstat} + \Delta E_{oi} + \Delta E_{disp}$).

Table S5. EDA analysis (in kcal·mol^{-1}) of the A^{X8}-T^{Y6} base pairs (halogen series) using the BLYP-D3(BJ)/TZ2P level.

X8	**F**	**Cl**	**Br**	H	H	H	**F**	**Cl**	**Br**
Y6	H	H	H	**F**	**Cl**	**Br**	**F**	**Cl**	**Br**
Bond Energy Decomposition[a]									
ΔE_{prep}	1.76	1.73	1.71	2.08	2.07	2.02	1.92	1.79	1.78
ΔE_{int}	-18.26	-18.30	-18.30	-19.02	-18.92	-18.90	-18.76	-18.71	-18.69
$\Delta E_{\mathrm{Pauli}}$	39.05	39.31	39.12	41.01	40.65	40.48	39.87	39.71	39.25
$\Delta V_{\mathrm{elstat}}$	-31.50	-31.67	-31.57	-32.71	-32.42	-32.33	-32.06	-31.91	-31.66
ΔE_{disp}	-5.36	-5.37	-5.37	-5.44	-5.44	-5.45	-5.41	-5.42	-5.42
ΔE_{oi}	-20.44	-20.58	-20.48	-21.88	-21.70	-21.61	-21.16	-21.09	-20.85
ΔE_{σ}	-18.93	-19.04	-18.96	-20.26	-20.08	-20.00	-19.59	-19.50	-19.30
ΔE_{π}	-1.51	-1.53	-1.52	-1.62	-1.62	-1.61	-1.57	-1.58	-1.56
% $\Delta V_{\mathrm{elstat}}$[b]	55.0	55.0	55.0	54.5	54.4	54.4	54.7	54.6	54.7
% ΔE_{disp}[b]	9.4	9.3	9.4	9.1	9.1	9.2	9.2	9.3	9.4
% ΔE_{oi}[b]	35.7	35.7	35.7	36.4	36.4	36.4	36.1	36.1	36.0
ΔE_{Bond}	-16.50	-16.57	-16.59	-16.94	-16.85	-16.88	-16.84	-16.92	-16.91

[a] Computed at BLYP-D$_3$(BJ)/TZ2P with bases in C_1 symmetry and base pairs in C_s symmetry. [b] Percentage ΔE_{oi} of all attractive forces (i.e. $\Delta V_{elstat} + \Delta E_{oi} + \Delta E_{disp}$).

Table S6. EDA analysis (in kcal·mol^{-1}) of the A^{X8}-T^{Y6} base pairs (halogen series) using the S12g/TZ2P level.

X8	**F**	**Cl**	**Br**	H	H	H	**F**	**Cl**	**Br**
Y6	H	H	H	**F**	**Cl**	**Br**	**F**	**Cl**	**Br**
Bond Energy Decomposition[a]									
ΔE_{prep}	1.60	1.52	1.40	1.90	1.82	1.74	1.73	1.46	1.35
ΔE_{int}	-17.88	-17.83	-17.90	-18.61	-18.47	-18.47	-18.35	-18.21	-18.25
$\Delta E_{\mathrm{Pauli}}$	30.01	29.36	29.68	32.85	31.79	32.00	30.94	29.47	30.05
$\Delta V_{\mathrm{elstat}}$	-27.49	-27.17	-27.35	-29.23	-28.56	-28.67	-28.15	-27.28	-27.59
ΔE_{disp}	-3.32	-3.31	-3.32	-3.39	-3.37	-3.38	-3.35	-3.33	-3.36
ΔE_{oi}	-17.06	-16.71	-16.91	-18.85	-18.33	-18.42	-17.78	-17.07	-17.35
ΔE_{σ}	-15.80	-15.42	-15.64	-17.44	-16.95	-17.04	-16.45	-15.77	-16.04
ΔE_{π}	-1.27	-1.29	-1.27	-1.40	-1.38	-1.38	-1.33	-1.30	-1.31
% $\Delta V_{\mathrm{elstat}}$[b]	57.4	57.6	57.5	56.8	56.8	56.8	57.1	57.2	57.1
% ΔE_{disp}[b]	6.9	7.0	7.0	6.6	6.7	6.7	6.8	7.0	7.0
% ΔE_{oi}[b]	35.6	35.4	35.5	36.6	36.5	36.5	36.1	35.8	35.9
ΔE_{Bond}	-16.28	-16.31	-16.50	-16.71	-16.65	-16.73	-16.62	-16.75	-16.90

[a] Computed at S12g/TZ2P with bases in C_1 symmetry and base pairs in C_s symmetry. [b] Percentage ΔE_{oi} of all attractive forces (i.e. $\Delta V_{elstat} + \Delta E_{oi} + \Delta E_{disp}$).

Table S7. EDA analysis (in kcal·mol^{-1}) of the A^{X8}-U^{Y6} base pairs (halogen series) using the BLYP-D3(BJ)/TZ2P level.

X8	**F**	**Cl**	**Br**	H	H	H	**F**	**Cl**	**Br**
Y6	H	H	H	**F**	**Cl**	**Br**	**F**	**Cl**	**Br**
				Bond Energy Decomposition[a]					
ΔE_{prep}	1.73	1.74	1.79	2.08	2.03	2.01	1.92	1.87	1.82
ΔE_{int}	-18.43	-18.49	-18.52	-19.30	-19.19	-19.18	-19.00	-18.95	-18.94
ΔE_{Pauli}	39.20	39.28	39.28	41.19	40.92	40.67	39.89	39.69	39.29
ΔV_{elstat}	-31.73	-31.80	-31.80	-32.99	-32.75	-32.62	-32.23	-32.07	-31.86
ΔE_{disp}	-5.32	-5.32	-5.32	-5.39	-5.38	-5.38	-5.35	-5.35	-5.35
ΔE_{oi}	-20.58	-20.65	-20.68	-22.12	-21.97	-21.85	-21.31	-21.22	-21.02
ΔE_{σ}	-19.05	-19.11	-19.13	-20.46	-20.31	-20.20	-19.71	-19.61	-19.43
ΔE_{π}	-1.53	-1.55	-1.55	-1.66	-1.66	-1.64	-1.60	-1.61	-1.59
% ΔV_{elstat}[b]	55.1	55.0	55.0	54.5	54.5	54.5	54.7	54.7	54.7
% ΔE_{disp}[b]	9.2	9.2	9.2	8.9	9.0	9.0	9.1	9.1	9.2
% ΔE_{oi}[b]	35.7	35.8	35.8	36.6	36.5	36.5	36.2	36.2	36.1
ΔE_{Bond}	-16.70	-16.75	-16.73	-17.22	-17.16	-17.17	-17.08	-17.08	-17.12

[a] Computed at BLYP-D$_3$(BJ)/TZ2P with bases in C_1 symmetry and base pairs in C_s symmetry. [b] Percentage ΔE_{oi} of all attractive forces (i.e. $\Delta V_{\text{elstat}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}}$).

Table S8. EDA analysis (in kcal·mol^{-1}) of the A^{X8}-U^{Y6} base pairs (halogen series) using the S12g/TZ2P level.

X8	**F**	**Cl**	**Br**	H	H	H	**F**	**Cl**	**Br**
Y6	H	H	H	**F**	**Cl**	**Br**	**F**	**Cl**	**Br**
				Bond Energy Decomposition[a]					
ΔE_{prep}	1.52	1.49	1.43	1.89	1.79	1.70	1.70	1.57	1.37
ΔE_{int}	-18.05	-18.07	-18.11	-18.86	-18.69	-18.72	-18.58	-18.41	-18.48
ΔE_{Pauli}	30.08	29.42	29.74	32.94	31.28	31.68	31.17	29.04	29.76
ΔV_{elstat}	-27.69	-27.36	-27.53	-29.45	-28.47	-28.68	-28.43	-27.22	-27.61
ΔE_{disp}	-3.28	-3.17	-3.27	-3.35	-3.31	-3.33	-3.32	-3.27	-3.30
ΔE_{oi}	-17.16	-16.86	-17.04	-19.00	-18.19	-18.38	-18.00	-16.97	-17.33
ΔE_{σ}	-15.88	-15.59	-15.76	-17.58	-16.80	-16.99	-16.65	-15.66	-16.00
ΔE_{π}	-1.28	-1.27	-1.28	-1.42	-1.38	-1.39	-1.35	-1.31	-1.32
% ΔV_{elstat}[b]	57.5	57.7	57.5	56.9	57.0	56.9	57.1	57.4	57.2
% ΔE_{disp}[b]	6.8	6.7	6.8	6.5	6.6	6.6	6.7	6.9	6.8
% ΔE_{oi}[b]	35.7	35.6	35.6	36.7	36.4	36.5	36.2	35.8	35.9
ΔE_{Bond}	-16.53	-16.58	-16.68	-16.97	-16.90	-17.02	-16.88	-16.84	-17.11

[a] Computed at S12g/TZ2P with bases in C_1 symmetry and base pairs in C_s symmetry. [b] Percentage ΔE_{oi} of all attractive forces (i.e. $\Delta V_{\text{elstat}} + \Delta E_{\text{oi}} + \Delta E_{\text{disp}}$).

Table S9. EDA analysis (in kcal·mol^{-1}) of the A^{X8}-T^{Y6} and A^{X8}-U^{Y6} base pairs using interacting fragments that involves the H3-proton transfer.[a]

	A^{X8}-T^{Y6}				A^{X8}-U^{Y6}			
X8	**NH^-**	**O^-**	H	H	**NH^-**	**O^-**	H	H
Y6	H	H	**NH_3^+**	**OH_2^+**	H	H	**NH_3^+**	**OH_2^+**
ΔE_{prep}	4.70	4.61	4.66	---[c]	4.57	4.43	4.28	---[c]
ΔE_{int}	-55.10	-57.45	-63.96	-56.38	-55.23	-57.56	-62.39	-54.24
ΔE_{Pauli}	49.02	50.40	49.91	44.58	48.71	50.03	47.68	42.26
ΔV_{elstat}	-61.50	-64.40	-69.04	-59.64	-61.53	-64.42	-66.41	-56.80
ΔE_{disp}	-5.61	-5.64	-5.84	-5.74	-5.53	-5.57	-5.72	-5.60
ΔE_{oi}	-37.02	-37.81	-38.99	-35.58	-36.87	-37.61	-37.94	-34.10
ΔE_{σ}	-30.07	-31.09	-33.74	-31.43	-29.91	-30.89	-33.05	-30.29
ΔE_{π}	-6.95	-6.72	-5.26	-4.15	-6.96	-6.72	-4.89	-3.81
% ΔV_{elstat}[b]	59.0	59.7	60.6	59.1	59.2	59.9	60.3	58.9
% ΔE_{disp}[b]	5.4	5.2	5.1	5.7	5.3	5.2	5.2	5.8
% ΔE_{oi}[b]	35.6	35.1	34.3	35.2	35.5	35.0	34.5	35.3
ΔE_{Bond}	-50.40	-52.84	-59.30	---[c]	-50.66	-53.13	-58.11	---[c]

[a] Computed at BLYP-D$_3$(BJ)/TZ2P with bases in C_1 symmetry and base pairs in C_s symmetry. [b] The percentage values give the contribution to the total attractive forces (i.e. $\Delta V_{elstat} + \Delta E_{oi} + \Delta E_{disp}$). [c] The substituted thymine/uracil bases do not converge.

Table S10. VDD atomic charges in the front atoms and the adenine/thymine C2 carbon atoms of the A^{X8}-T^{Y6} base pairs.

VDD atomic charges Q_A (a.u.)									
X8	Y6	N6	H6	O4	N1	H3	N3	*C2-adenine*	*C2-thymine*
H	H	-0.171	0.135	-0.291	-0.187	0.153	-0.121	0.092	0.208
NH_2	NH_2	-0.177	0.127	-0.308	-0.187	0.151	-0.131	0.083	0.208
OH	OH	-0.176	0.130	-0.302	-0.184	0.152	-0.127	0.087	0.209
NH^-	H	-0.184	0.116	-0.336	-0.080	0.147	-0.237	0.060	0.189
NH_2	H	-0.176	0.128	-0.291	-0.187	0.153	-0.121	0.084	0.207
NH_3^+	H	-0.158	0.150	-0.285	-0.171	0.153	-0.118	0.115	0.211
O^-	H	-0.184	0.118	-0.335	-0.083	0.147	-0.235	0.065	0.189
OH	H	-0.175	0.131	-0.290	-0.185	0.153	-0.121	0.088	0.207
OH_2^+	H	-0.157	0.151	-0.284	-0.169	0.153	-0.119	0.117	0.211
H	NH^-	-0.176	0.123	-0.366	-0.189	0.132	-0.137	0.090	0.194
H	NH_2	-0.172	0.133	-0.308	-0.188	0.150	-0.129	0.093	0.209
H	NH_3^+	-0.157	0.148	-0.284	-0.073	0.160	-0.223	0.110	0.205
H	O^-	-0.176	0.124	-0.358	-0.189	0.133	-0.136	0.090	0.192
H	OH	-0.172	0.133	-0.301	-0.188	0.152	-0.127	0.093	0.210
H	OH_2^+	-0.155	0.150	-0.268	-0.072	0.164	-0.222	0.109	0.210
F	H	-0.172	0.135	-0.289	-0.184	0.153	-0.122	0.092	0.208
Cl	H	-0.171	0.139	-0.288	-0.185	0.152	-0.121	0.096	0.211
Br	H	-0.171	0.138	-0.288	-0.185	0.150	-0.123	0.092	0.210
H	F	-0.171	0.134	-0.287	-0.188	0.155	-0.126	0.093	0.212
H	Cl	-0.170	0.135	-0.285	-0.187	0.154	-0.125	0.092	0.208
H	Br	-0.171	0.134	-0.284	-0.185	0.154	-0.124	0.090	0.208
F	F	-0.171	0.134	-0.285	-0.182	0.155	-0.125	0.091	0.212
Cl	Cl	-0.171	0.137	-0.283	-0.184	0.154	-0.126	0.093	0.210
Br	Br	-0.171	0.139	-0.283	-0.184	0.155	-0.122	0.096	0.210

Table S11. VDD atomic charges in the front atoms and the adenine/uracil C2 carbon atoms of the A^{X8}-U^{Y6} base pairs.

VDD atomic charges Q_A (a.u.)									
X8	Y6	N6	H6	O4	N1	H3	N3	*C2-adenine*	*C2-uracil*
H	H	-0.171	0.136	-0.297	-0.186	0.151	-0.122	0.091	0.213
NH_2	NH_2	-0.176	0.130	-0.315	-0.186	0.149	-0.128	0.082	0.210
OH	OH	-0.174	0.133	-0.305	-0.184	0.151	-0.125	0.089	0.213
NH^-	H	-0.185	0.117	-0.349	-0.078	0.147	-0.235	0.059	0.192
NH_2	H	-0.177	0.133	-0.297	-0.185	0.152	-0.120	0.085	0.212
NH_3^+	H	-0.157	0.150	-0.293	-0.169	0.154	-0.118	0.113	0.214
O^-	H	-0.184	0.120	-0.347	-0.081	0.148	-0.234	0.064	0.192
OH	H	-0.175	0.136	-0.298	-0.184	0.152	-0.119	0.090	0.212
OH_2^+	H	-0.156	0.151	-0.292	-0.166	0.154	-0.118	0.116	0.214
H	NH^-	-0.175	0.122	-0.377	-0.192	0.131	-0.136	0.092	0.197
H	NH_2	-0.171	0.133	-0.314	-0.188	0.148	-0.128	0.091	0.211
H	NH_3^+	-0.155	0.148	-0.289	-0.073	0.162	-0.220	0.107	0.207
H	O^-	-0.175	0.124	-0.370	-0.192	0.132	-0.135	0.093	0.196
H	OH	-0.171	0.135	-0.305	-0.187	0.151	-0.128	0.091	0.216
H	OH_2^+	-0.153	0.151	-0.274	-0.070	0.165	-0.218	0.108	0.213
F	H	-0.171	0.139	-0.296	-0.183	0.153	-0.119	0.095	0.212
Cl	H	-0.172	0.137	-0.296	-0.185	0.155	-0.121	0.092	0.214
Br	H	-0.171	0.136	-0.298	-0.187	0.153	-0.119	0.092	0.212
H	F	-0.171	0.137	-0.292	-0.185	0.152	-0.126	0.092	0.219
H	Cl	-0.171	0.137	-0.292	-0.186	0.152	-0.126	0.091	0.216
H	Br	-0.170	0.138	-0.292	-0.186	0.151	-0.125	0.091	0.216
F	F	-0.171	0.139	-0.291	-0.183	0.154	-0.123	0.094	0.217
Cl	Cl	-0.171	0.140	-0.291	-0.184	0.153	-0.122	0.095	0.214
Br	Br	-0.172	0.140	-0.292	-0.185	0.153	-0.123	0.094	0.216

Table S12. NMR *C2-adenine* shielding values (ppm) computed with SAOP, KT2, and S12g functionals in combination with the TZ2P all-electron basis for the A^{X8}-T^{Y6} and A^{X8}-U^{Y6} base pairs.

		A^{X8}-T^{Y6}				A^{X8}-U^{Y6}			
X8	Y6	SAOP	KT2	S12g	ΔE_{Bond}	SAOP	KT2	S12g	ΔE_{Bond}
H	H	30.66	44.24	33.69	-16.50	30.77	44.35	33.81	-16.77
NH_2	NH_2	33.64	46.98	36.70	-15.86	33.73	47.06	36.80	-16.00
OH	OH	31.97	45.60	35.14	-16.65	32.06	45.69	35.24	-16.80
NH^-	H	52.04	65.60	57.50	-21.40	52.10	65.65	57.55	-22.15
NH_2	H	33.66	47.02	36.76	-15.23	33.77	47.13	36.87	-15.49
NH_3^+	H	24.88	37.49	26.30	-19.67	24.82	37.58	26.39	-19.66
O^-	H	50.13	64.11	55.73	-20.98	50.20	64.17	55.78	-21.77
OH	H	31.91	45.56	35.09	-16.47	32.01	45.66	35.21	-16.64
OH_2^+	H	24.31	36.87	25.59	-20.03	24.25	36.94	25.66	-19.98
H	NH^-	29.38	42.12	31.48	-17.92	29.40	42.16	31.50	-18.27
H	NH_2	30.66	44.21	33.66	-16.06	30.75	44.30	33.75	-16.36
H	NH_3^+	39.04	52.73	43.03	-27.16	39.25	52.91	43.23	-28.95
H	O^-	29.40	42.18	31.53	-17.70	29.35	42.15	31.50	-17.98
H	OH	30.72	44.28	33.74	-16.64	30.83	44.38	33.85	-16.93
H	OH_2^+	39.31	52.90	43.25	-29.44	39.60	53.15	43.53	-32.07
F	H	30.39	44.18	33.59	-16.50	30.49	44.28	33.70	-16.70
Cl	H	30.48	44.06	33.31	-16.57	30.57	44.15	33.41	-16.75
Br	H	30.81	44.34	33.58	-16.59	30.91	44.43	33.68	-16.73
H	F	30.91	44.46	33.93	-16.94	31.00	44.55	34.04	-17.22
H	Cl	30.88	44.46	33.94	-16.85	30.99	44.57	34.05	-17.16
H	Br	30.83	44.41	33.88	-16.88	30.94	44.51	34.00	-17.17
F	F	30.62	44.38	33.82	-16.84	30.70	44.46	33.91	-17.08
Cl	Cl	30.69	44.28	33.55	-16.92	30.78	44.36	33.65	-17.08
Br	Br	30.98	44.49	33.76	-16.91	31.07	44.58	33.86	-17.12

Table S13. NMR *C2-thymine/uracil* shielding values (ppm) computed with SAOP, KT2, and S12g functionals in combination with the TZ2P all-electron basis for the A^{X8}-T^{Y6} and A^{X8}-U^{Y6} base pairs.

		C2-thymine shielding of A^{X8}-T^{Y6}				*C2-uracil* shielding of A^{X8}-U^{Y6}			
X8	Y6	SAOP	KT2	S12g	ΔE_{Bond}	SAOP	KT2	S12g	ΔE_{Bond}
H	H	34.00	44.41	36.46	-16.50	34.07	44.61	36.49	-16.77
NH_2	NH_2	36.06	46.83	38.73	-15.86	35.08	45.78	37.60	-16.00
OH	OH	36.76	47.65	39.42	-16.65	35.75	46.53	38.24	-16.80
NH^-	H	28.42	38.75	30.35	-21.40	29.08	39.62	31.08	-22.15
NH_2	H	33.94	44.34	36.38	-15.23	34.00	44.53	36.41	-15.49
NH_3^+	H	34.69	45.19	37.25	-19.67	34.62	45.26	37.16	-19.66
O^-	H	28.42	38.76	30.36	-20.98	29.07	39.61	31.08	-21.77
OH	H	34.01	44.42	36.46	-16.47	34.07	44.60	36.49	-16.64
OH_2^+	H	34.75	45.26	37.33	-20.03	34.69	45.34	37.24	-19.98
H	NH^-	32.89	43.42	35.43	-17.92	31.82	42.26	34.21	-18.27
H	NH_2	36.11	46.89	38.80	-16.06	35.13	45.86	37.67	-16.36
H	NH_3^+	35.20	46.46	37.85	-27.16	34.62	45.60	37.02	-28.95
H	O^-	32.60	43.20	35.07	-17.70	31.50	42.02	33.82	-17.98
H	OH	36.75	47.64	39.42	-16.64	35.74	46.53	38.23	-16.93
H	OH_2^+	36.63	47.65	39.15	-29.44	36.83	47.82	39.12	-32.07
F	H	34.07	44.50	36.54	-16.50	34.12	44.67	36.56	-16.70
Cl	H	34.09	44.51	36.56	-16.57	34.15	44.69	36.58	-16.75
Br	H	34.08	44.50	36.55	-16.59	34.16	44.69	36.58	-16.73
H	F	37.09	47.82	39.56	-16.94	36.36	47.07	38.71	-17.22
H	Cl	36.52	47.22	39.13	-16.85	35.82	46.55	38.36	-17.16
H	Br	36.34	46.98	38.93	-16.88	35.73	46.41	38.25	-17.17
F	F	37.17	47.90	39.64	-16.84	36.42	47.15	33.91	-17.08
Cl	Cl	36.61	47.32	39.24	-16.92	35.91	46.65	38.47	-17.08
Br	Br	36.43	47.07	39.04	-16.91	35.82	46.51	38.35	-17.12

Table S14. NMR *C2-adenine* shielding (σ) values (ppm) computed with SAOP/TZ2P level for the isolated adenine (A^{X8}) bases and A^{X8}-U base pairs.[a]

	Adenine (A^{X8})		A^{X8}-U			VDD charges[d]	
X8	*C2* (σ)	Δσ	*C2* (σ)	Δσ	ΔΔ(σ)[c]	Q_A	ΔQ_A
H	29.39	0.00	30.77	0.00	0.00	0.091	0.000
NH^-	43.59	14.20	52.10[b]	21.33	7.13[b]	0.059	-0.032
NH_2	32.59	3.20	33.77	3.00	0.20	0.085	-0.006
NH_3^+	23.68	-5.71	24.82	-5.94	0.24	0.113	0.022
O^-	41.53	12.15	50.20[b]	19.43	7.28[b]	0.064	-0.027
OH	30.80	1.42	32.01	1.24	0.18	0.090	-0.001
OH_2^+	23.05	-6.34	24.25	-6.52	0.18	0.116	0.025
F	29.31	-0.07	30.49	-0.28	0.20	0.095	0.004
Cl	29.32	-0.07	30.57	-0.20	0.13	0.092	0.001
Br	29.67	0.28	30.91	0.15	0.00	0.092	0.001

[a] Geometries optimized at the BLYP-D3(BJ)/TZ2P level.

[b] Proton transfer occurs in the N1···H3-N3 hydrogen-bond from uracil to adenine.

[c] Absolute ΔΔ(σ) calculated as Δσ (A^{X8}-U) - Δσ (A^{X8}).

[d] VDD atomic charges Q_A (a.u.) in the *C2-adenine* atom of the A^{X8}-U base pairs.

Table S15. NMR *C2-uracil* shielding (σ) values (ppm) computed with SAOP/TZ2P level for the isolated uracil (U^{Y6}) bases and A-U^{Y6} base pairs.[a]

	Uracil (U^{Y6})		A-U^{Y6}			VDD charges[d]	
X8	*C2* (σ)	Δσ	*C2* (σ)	Δσ	ΔΔ(σ)[c]	Q_A	ΔQ_A
H	34.64	0.00	34.07	0.00	0.00	0.213	0.000
NH^-	31.92	-2.73	31.82	-2.25	0.47	0.197	-0.016
NH_2	35.83	1.19	35.13	1.06	0.13	0.211	0.002
NH_3^+	40.46	5.81	34.62[b]	0.55	5.26[b]	0.207	-0.006
O^-	31.80	-2.85	31.50	-2.58	0.27	0.196	-0.017
OH	36.68	2.03	35.74	1.67	0.36	0.216	0.003
OH_2^+	42.88	8.24	36.83[b]	2.76	5.48[b]	0.213	0.000
F	37.55	2.91	36.36	2.29	0.62	0.219	0.006
Cl	36.77	2.13	35.82	1.75	0.38	0.216	0.003
Br	36.72	2.08	35.73	1.66	0.42	0.216	0.003

[a] Geometries optimized at the BLYP-D3(BJ)/TZ2P level.

[b] Proton transfer occurs in the N1···H3-N3 hydrogen-bond from uracil to adenine.

[c] Absolute ΔΔ(σ) calculated as Δσ (A-U^{Y6}) - Δσ (U^{Y6}).

[d] VDD atomic charges Q_A (a.u.) in the *C2-uracil* atom of the A-U^{Y6} base pairs.

Table S16. VDD atomic charges Q_A (a.u.) in the C2 carbon atom of the isolated A^{X8}, T^{Y6} and U^{Y6} bases.

	Adenine (A^{X8})		Thymine (T^{Y6})		Uracil (U^{Y6})	
X8	Q_A	ΔQ_A	Q_A	ΔQ_A	Q_A	ΔQ_A
H	0.090	0.000	0.207	0.000	0.210	0.000
NH^-	0.042	-0.048	0.192	-0.015	0.193	-0.017
NH_2	0.082	-0.008	0.206	-0.001	0.211	0.001
NH_3^+	0.115	0.025	0.220	0.013	0.225	0.015
O^-	0.047	-0.043	0.191	-0.016	0.194	-0.016
OH	0.087	-0.003	0.209	0.002	0.213	0.003
OH_2^+	0.119	0.029	0.225	0.018	0.230	0.020
F	0.091	0.001	0.213	0.006	0.216	0.006
Cl	0.092	0.002	0.208	0.001	0.215	0.005
Br	0.091	0.001	0.208	0.001	0.216	0.006

Table S17. NMR *C2-adenine* shielding (σ) values (ppm) for the isolated adenine (A^{X8})[a] and the A^{X8}//A^{X8}-T[b] bases computed with SAOP/TZ2P level.

	Adenine (A^{X8})[a]		Adenine A^{X8}//A^{X8}-T[b]		
X8	*C2* (σ)	Δσ	*C2* (σ)	Δσ	ΔΔ(σ)[c]
H	29.39	0.00	29.70	0.00	0
NH^-	43.59	14.20	45.17	15.47	1.26
NH_2	32.59	3.20	32.82	3.11	0.09
NH_3^+	23.68	-5.71	24.04	-5.67	0.04
O^-	41.53	12.15	43.10	13.39	1.25
OH	30.80	1.42	31.09	1.39	0.03
OH_2^+	23.05	-6.34	23.48	-6.23	0.11
F	29.31	-0.07	29.61	-0.09	0.02
Cl	29.32	-0.07	29.60	-0.10	0.03
Br	29.67	0.28	29.94	0.23	0.05

[a] Geometries optimized at the BLYP-D3(BJ)/TZ2P level.

[b] A^{X8} bases at the A^{X8}-T geometry.

[c] Absolute ΔΔ(σ) calculated as Δσ (A^{X8}//A^{X8}-T) - Δσ (A^{X8}).

Table S18. NMR *C2-adenine* shielding (σ) values (ppm) computed at the SAOP/TZ2P level and using the COSMO model for the isolated adenine (A^{X8}) bases and A^{X8}-T base pairs.[a]

	Adenine (A^{X8})		A^{X8}-T		
X8	*C2* (σ)	Δσ	*C2* (σ)	Δσ	ΔΔ(σ)[c]
H	28.82	0.00	30.71	0.00	0.00
NH^-	46.70	17.88	45.56[b]	14.85	3.03[b]
NH_2	32.43	3.61	34.26	3.55	0.06
NH_3^+	26.94	-1.88	28.58	-2.13	0.25
O^-	44.86	16.04	43.48[b]	12.77	3.27[b]
OH	30.27	1.45	31.98	1.27	0.17
OH_2^+	26.12	-2.70	27.83	-2.88	0.18
F	28.52	-0.30	30.31	-0.41	0.10
Cl	28.77	-0.05	30.59	-0.12	0.07
Br	29.00	0.18	30.88	0.17	0.02

[a] Geometries optimized at the BLYP-D3(BJ)/TZ2P level and using the COSMO model.

[b] Proton transfer occurs in the N1···H3-N3 hydrogen-bond from thymine to adenine.

[c] Absolute ΔΔ(σ) calculated as Δσ (A^{X8}-T) - Δσ (A^{X8}).

Table S19. NMR *C2-adenine* shielding (σ) values (ppm) computed at the B3LYP/TZ2P level for the isolated adenine (A^{X8}) bases and A^{X8}-T base pairs.[a]

	Adenine (A^{X8})		A^{X8}-T		
X8	*C2* (σ)	Δσ	*C2* (σ)	Δσ	ΔΔ(σ)[c]
H	21.55	0.00	22.44	0.00	0.00
NH^-	37.62	16.07	45.71[b]	23.27	7.20[b]
NH_2	24.99	3.44	25.61	3.17	0.27
NH_3^+	14.59	-6.96	15.06	-7.38	0.42
O^-	36.22	14.67	44.28[b]	21.84	7.17[b]
OH	23.49	1.94	24.07	1.63	0.31
OH_2^+	14.14	-7.41	14.45	-7.99	0.58
F	22.23	0.68	22.55	0.11	0.57
Cl	21.96	0.41	21.96	-0.48	0.89
Br	22.10	0.55	22.64	0.20	0.35

[a] Geometries optimized at the B3LYP-D3(BJ)/TZ2P level.

[b] Proton transfer occurs in the N1···H3-N3 hydrogen-bond from thymine to adenine.

[c] Absolute ΔΔ(σ) calculated as Δσ (A^{X8}-T) - Δσ (A^{X8}).

Table S20. NMR *C2-adenine* shielding (σ) values (ppm) computed at the SAOP/TZ2P level and using the Spin-Orbit ZORA relativistic correction for the isolated adenine (A^{X8}) bases and A^{X8}-T base pairs.[a]

	Adenine (A^{X8})		A^{X8}-T		
X8	*C2* (σ)	Δσ	*C2* (σ)	Δσ	ΔΔ(σ)[c]
H	29.51	0.00	30.55	0.00	0.00
NH^-	43.58	14.07	51.84[b]	21.29	7.22[b]
NH_2	32.69	3.20	33.57	3.02	0.16
NH_3^+	23.79	-5.72	24.78	-5.77	0.05
O^-	41.73	12.22	50.09[b]	19.54	7.32[b]
OH	30.92	1.41	31.76	1.21	0.20
OH_2^+	23.21	-6.30	24.19	-6.36	0.06
F	29.44	-0.07	30.29	-0.26	0.19
Cl	29.52	0.01	30.46	-0.09	0.10
Br	29.70	0.19	30.64	0.09	0.10

[a] Geometries optimized at the BLYP-D3(BJ)/TZ2P level and using the SO-ZORA correction.

[b] Proton transfer occurs in the N1···H3-N3 hydrogen-bond from thymine to adenine.

[c] Absolute ΔΔ(σ) calculated as Δσ (A^{X8}-T) - Δσ (A^{X8}).

Figure S1. Calculated correlation between the *C2-thymine* shielding values (ppm) of isolated thymine (T^{Y6}) bases and A-T^{Y6} base pairs. The proton transfer systems were not included in the plot, due to its particular behavior.

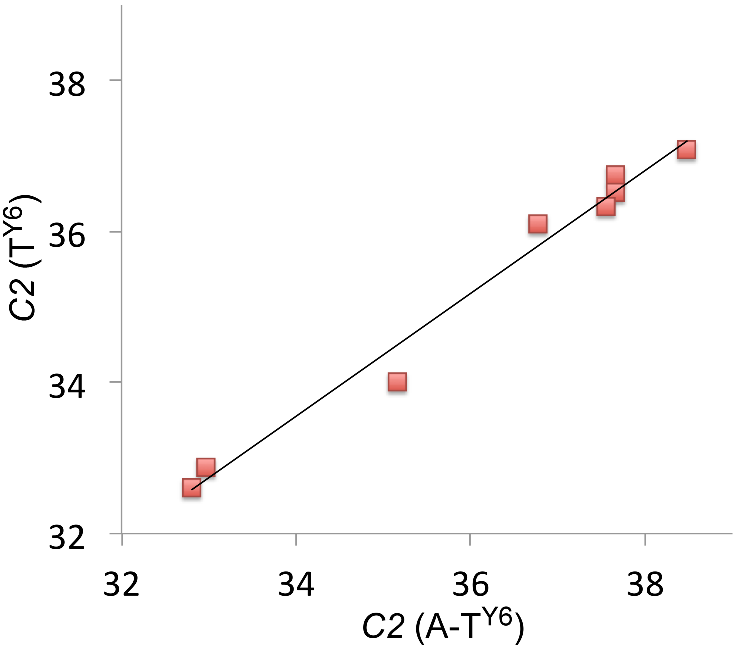

Figure S2. Calculated dependence of the NMR *C2*-shielding values (ppm) as a function of the hydrogen-bond strength (kcal·mol^{-1}). **a)** *C2-adenine* shielding of A^{X8}-U, **b)** *C2-adenine* shielding of A-U^{Y6}, **c)** *C2-uracil* shielding of A^{X8}-U, and **d)** *C2-uracil* shielding of A-U^{Y6} base pairs. The proton transfer systems were not included in the plot, due to its particular behavior.

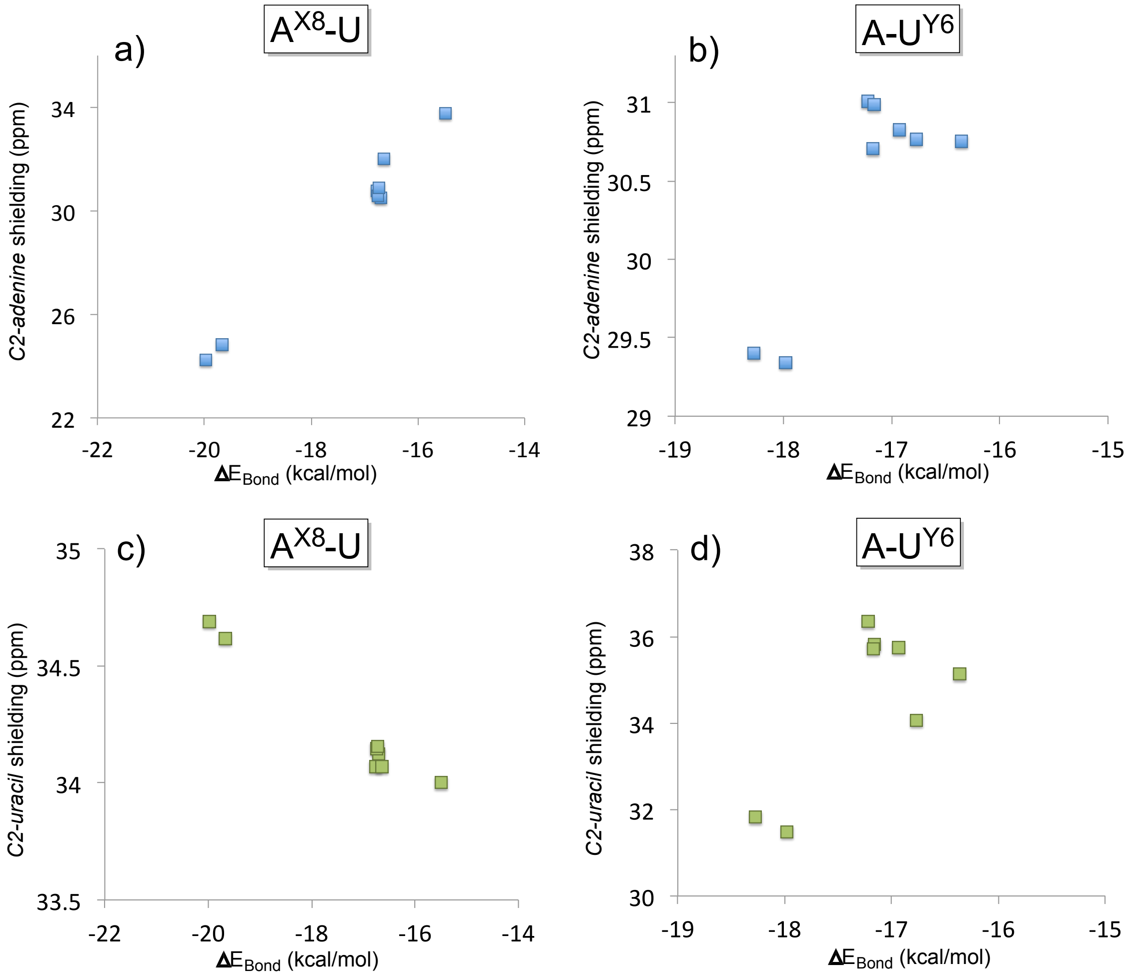

Figure S3. Calculated correlation between the *C2-adenine* shielding values (ppm) of isolated adenine (A^{X8}) bases and A^{X8}-T base pairs at the SAOP/TZ2P level and using the COSMO model. The proton transfer systems were not included in the plot, due to its particular behavior.

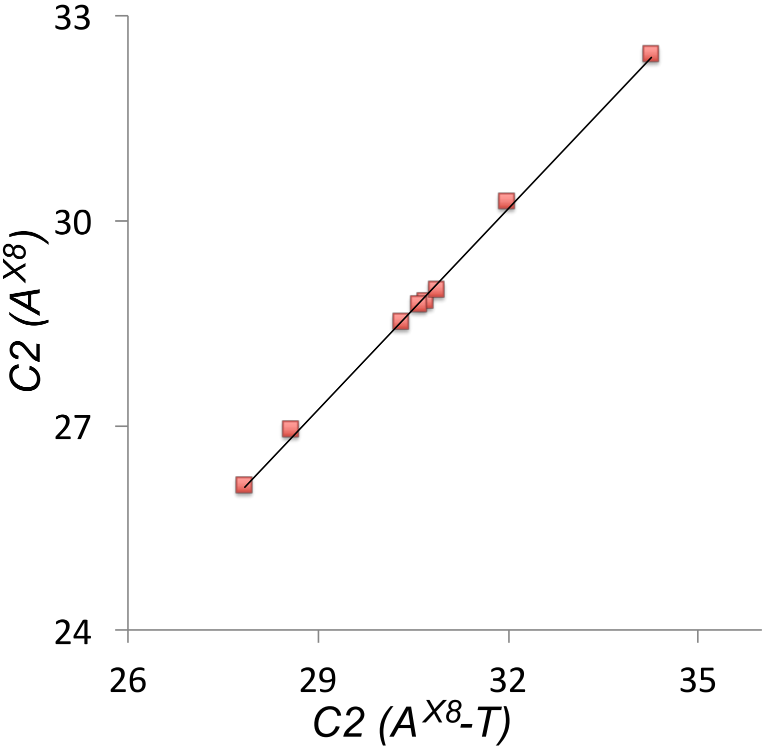

Figure S4. Calculated correlation between the *C2-adenine* shielding values (ppm) of isolated adenine (A^{X8}) bases and A^{X8}-T base pairs at the B3LYP/TZ2P level. The proton transfer systems were not included in the plot, due to its particular behavior.

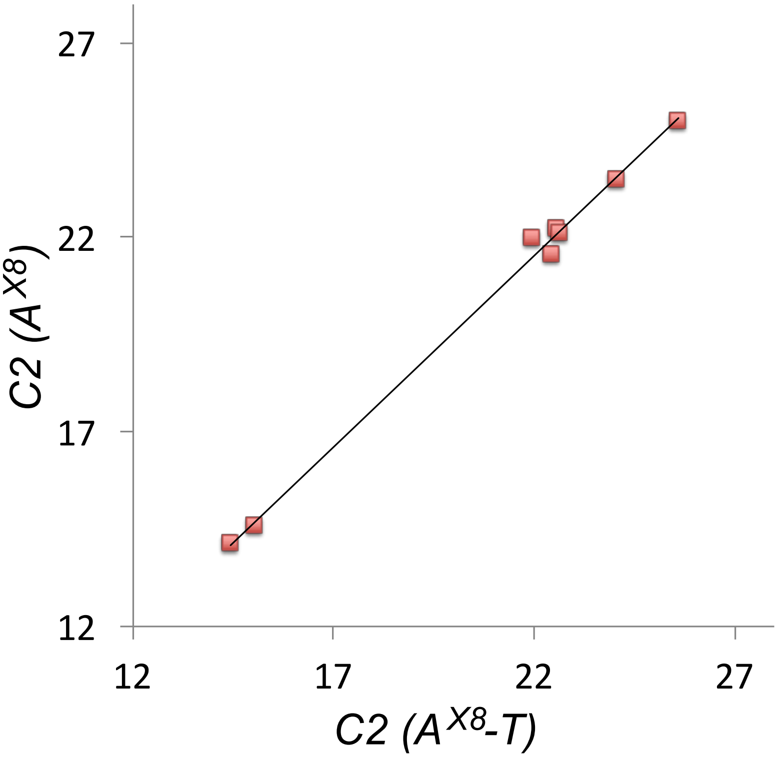

Figure S5. Calculated correlation between the *C2-adenine* shielding values (ppm) of isolated adenine (A^{X8}) bases and A^{X8}-T base pairs at the SAOP/TZ2P level and using the Spin-Orbit ZORA relativistic correction. The proton transfer systems were not included in the plot, due to its particular behavior.