SUPPORTING INFORMATION

The significant role of the intermolecular CH $\cdots$ O/N hydrogen bonds in governing the biologically important pairs of the DNA and RNA modified bases: a comprehensive theoretical investigation

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Table S1. Selected geometrical (glycosidic) parameters of the biologically important pairs including modified nucleobases containing intermolecular CH $\cdots$ O/N H-bonds, obtained at the DFT and MP2 levels of theory in vacuum (see also Figure 1).

Base pairs	Symmetry	α_1^a		α_2^b		H^c	
		DFT	MP2	DFT	MP2	DFT	MP2
A $\cdot^5$ BrU H	C_s	51.5	52.4	63.3	63.8	7.750	7.674
A $\cdot^5$ BrU rH	C_s	23.5	24.5	33.8	33.0	8.834	8.810
A $\cdot^5$ BrU WC	C_s	55.2	55.4	56.5	56.8	10.003	9.958
A $\cdot^5$ BrU rWC	C_s	31.7	32.0	45.7	45.1	10.403	10.390
P $\cdot$ T rH	C_s	31.9	30.3	27.5	28.2	8.886	8.874
P $\cdot$ T H	C_s	59.0	57.2	70.0	68.8	7.353	7.415
P $\cdot$ T rWC	C_s	31.3	26.9	44.9	50.4	10.466	10.272
P $\cdot$ T WC	C_s	46.8	47.7	47.1	48.1	10.455	10.379
P $\cdot$ T WC _f	C_s	54.6	55.0	55.8	56.3	10.058	9.999
P $\cdot$ U rH	C_s	31.6	30.2	28.0	28.5	8.888	8.876
P $\cdot$ U H	C_s	58.1	56.8	69.8	68.7	7.395	7.438
P $\cdot$ U rWC	C_s	32.1	28.2	44.2	48.9	10.495	10.323
P $\cdot$ U WC	C_s	46.8	47.7	47.5	48.4	10.452	10.376
P $\cdot$ U WC _f	C_s	54.6	55.0	56.1	56.6	10.054	9.996
2AP $\cdot$ T rWC	C_I	26.3	25.7	50.1	50.8	10.305	10.239
2AP $\cdot$ T WC	C_I	49.5	48.9	51.7	51.0	10.244	10.228
2AP $\cdot$ T rH	C_s	30.7	29.2	28.4	29.0	8.884	8.870
2AP $\cdot$ T H	C_s	57.2	55.9	68.6	67.7	7.451	7.483
2AP $\cdot$ C*	C_I	49.7	49.4	52.9	52.5	10.240	10.216
A $\cdot^5$ MC*	C_s	55.6	56.0	57.7	58.3	9.994	9.932
A* $\cdot^5$ MC	C_s	55.4	55.5	58.6	59.3	9.932	9.877
A $\cdot^5$ MC	C_I	74.7	74.3	51.8	52.7	10.007	9.896
A $\cdot$ isoC*	C_s	56.1	56.4	54.4	54.6	10.165	10.112
A $\cdot$ isoC* rWC	C_s	54.1	54.4	53.2	53.7	10.154	10.102
A* $\cdot$ isoC	C_s	55.2	55.2	54.4	55.0	10.128	10.078
A $\cdot$ isoC	C_I	73.8	73.2	47.5	48.0	10.219	10.144
A* $\cdot$ isoC* rWC	C_s	51.3	51.1	52.1	52.8	10.115	10.086
A $\cdot$ 6-azaC*	C_s	55.0	55.5	54.4	55.1	10.046	9.985
A $\cdot$ 6-azaC	C_I	73.1	72.9	46.4	47.3	10.188	10.081
A* $\cdot$ 6-azaC	C_s	53.9	54.1	53.8	54.6	10.103	10.043
8-aza-9-deazaA $\cdot$ C*	C_s	51.1	51.4	57.5	58.0	10.210	10.138
8-aza-9-deazaA* $\cdot$ C	C_s	50.5	50.5	59.0	59.8	10.141	10.079
8-aza-9-deazaA $\cdot$ C	C_I	67.0	69.5	52.2	53.3	10.223	10.095
8-aza-9-deazaA $\cdot$ U	C_I	50.2	50.5	55.6	56.1	10.271	10.201
7-deazaP $\cdot$ U	C_s	50.2	51.2	47.9	48.9	10.404	10.327
7-deazaP $\cdot$ U _f	C_s	54.6	55.0	56.1	56.6	10.054	9.996

A·X	C_s	46.3	46.9	45.0	45.5	12.289	12.241
A·8oxoA _{syn}	C_I	55.9	56.9	45.8	47.1	9.993	9.874
A·8oxoG _{syn}	C_s	54.4	55.2	40.7	41.9	10.216	10.118
8oxoA·T	C_I	56.2	56.5	56.0	56.5	10.038	9.981
3-deazaA·T	C_I	50.9	51.4	55.4	55.8	10.179	10.111
8-azaA·T	C_s	49.6	50.3	54.7	55.4	10.147	10.085

Notes: ^a α_I – the angle subtended at the glycosidic nitrogen of the purine base of the purine·purine or purine·pyrimidine base pairs, degree; ^b α_2 – the angle subtended at the glycosidic nitrogen atom of the other purine or pyrimidine base of the aforementioned pairs, degree; ^c H – the distance between the glycosidic protons, Å.

Table S2. Minimal, maximal and average values of the selected geometrical (glycosidic) parameters of the biologically important pairs including modified nucleobases stabilized by the intermolecular CH···O/N H-bonds, obtained at the DFT and MP2 levels of theory in vacuum (see also Figure 1).

H-bonds	Parameters	α_I^a		α_2^b		H^c	
		DFT	MP2	DFT	MP2	DFT	MP2
CH···O	Min. value	23.5	24.5	27.5	28.2	7.353	7.415
	Max. value	59.0	57.2	70.0	68.8	12.289	12.241
	Avg. value	47.2	47.0	50.9	51.5	9.766	9.712
CH···N	Min. value	49.7	49.4	46.4	47.3	10.007	9.896
	Max. value	74.7	74.3	53.2	53.7	10.240	10.216
	Avg. value	62.8	62.6	50.7	51.2	10.154	10.088

Notes: see Table S1.

Table S3. Selected dihedral angles characterizing the non-planarity of some H-bonded base pairs (in degree).

Base pairs	Dihedral angles	Values of the dihedral angles	
		DFT	MP2
2AP·T _r WC	C6N1N3C2	0.2	7.4
2AP·T WC	C6N1N3C4	0.2	7.3
2AP·C*	C6N1N3C4	0.4	7.6
A· ⁵ MC	N1C2N3C4	13.1	19.7
A·isoC	N1C2N1C2	16.4	17.8
A·6-azaC	N1C2N3C4	13.5	20.3
8-aza-9-deazaA·C	N1C2N3C4	16.6	21.7
8-aza-9-deazaA·U	C2N1N3C2	4.1	7.1
A·8oxoA _{syn}	C6N1C5C6	20.0	20.3
8oxoA·T	C2N1N3C2	5.4	7.9
3-deazaA·T	C2N1N3C2	0.0	7.8

Table S4. Geometrical parameters of the intermolecular CH $\cdots$ O/N H-bonds in the biologically important pairs with the participation of the modified nucleobases, obtained at the DFT and MP2 levels of theory in vacuum (see also Figure 1).

Base pairs	Symmetry	CH $\cdots$ O/N H-bonds	$d_{C\cdots O/N}^a$		$d_{H\cdots O/N}^b$		$\angle CH\cdots O/N^c$		Δd_{CH}^d		$\Delta d_{H\cdots O/N}^e$	
			DFT	MP2	DFT	MP2	DFT	MP2	DFT	MP2	DFT	MP2
A $\cdot^5$ BrU H	C_s	C8H $\cdots$ O2	3.409	3.347	2.702	2.624	122.6	123.9	-0.00023	0.00010	0.018	0.096
A $\cdot^5$ BrU rH	C_s	C8H $\cdots$ O4	3.376	3.322	2.665	2.597	122.8	124.0	-0.00009	0.00021	0.055	0.123
A $\cdot^5$ BrU WC	C_s	C2H $\cdots$ O2	3.574	3.525	2.734	2.676	133.8	134.8	-0.00042	0.00010	-0.014	0.044
A $\cdot^5$ BrU rWC	C_s	C2H $\cdots$ O2	3.556	3.508	2.715	2.660	133.8	134.8	-0.00041	0.00011	0.005	0.060
P·T rH	C_s	C8H $\cdots$ O4	3.117	3.142	2.281	2.333	132.5	130.4	0.00111	0.00064	0.439	0.387
P·T H	C_s	C8H $\cdots$ O2	3.141	3.164	2.313	2.369	131.8	129.2	0.00083	0.00049	0.407	0.351
P·T rWC	C_s	C6H $\cdots$ O2	3.827	3.499	3.117	2.697	123.6	130.9	-0.00066	0.00031	-0.397	0.023
		C2H $\cdots$ O4	3.555	3.818	2.732	3.081	132.3	125.8	-0.00020	0.00017	-0.012	-0.361
P·T WC	C_s	C6H $\cdots$ O4	3.331	3.351	2.465	2.502	135.6	134.4	-0.00001	0.00027	0.255	0.218
P·T WC _f	C_s	C6H $\cdots$ O4	3.741	3.740	3.011	3.021	124.9	124.3	-0.00054	0.00011	-0.291	-0.301
		C2H $\cdots$ O2	3.626	3.562	2.819	2.744	131.0	132.1	-0.00030	0.00018	-0.099	-0.024
P·U rH	C_s	C8H $\cdots$ O4	3.120	3.140	2.287	2.332	132.2	130.3	0.00111	0.00061	0.433	0.388
P·U H	C_s	C8H $\cdots$ O2	3.165	3.178	2.356	2.392	129.9	128.5	0.00063	0.00041	0.364	0.328
P·U rWC	C_s	C6H $\cdots$ O2	3.888	3.583	3.198	2.809	122.2	128.3	-0.00070	0.00014	-0.478	-0.089
		C2H $\cdots$ O4	3.504	3.719	2.664	2.953	133.7	128.0	-0.00016	0.00019	0.056	-0.233
P·U WC	C_s	C6H $\cdots$ O4	3.329	3.351	2.462	2.501	135.7	134.4	0.00001	0.00025	0.258	0.219
P·U WC _f	C_s	C6H $\cdots$ O4	3.743	3.733	3.013	3.012	124.9	124.4	-0.00057	0.00010	-0.293	-0.292
		C2H $\cdots$ O2	3.624	3.562	2.817	2.745	131.0	132.0	-0.00032	0.00016	-0.097	-0.025
2AP·T rWC	C_I	C6H $\cdots$ O2	3.552	3.485	2.726	2.646	132.4	133.7	-0.00030	0.00028	-0.006	0.074
2AP·T WC	C_I	C6H $\cdots$ O4	3.534	3.464	2.704	2.620	132.7	134.2	-0.00018	0.00040	0.016	0.100
2AP·T rH	C_s	C8H $\cdots$ O4	3.151	3.169	2.336	2.379	130.7	128.9	0.00066	0.00038	0.384	0.341
2AP·T H	C_s	C8H $\cdots$ O2	3.194	3.204	2.401	2.432	128.9	127.4	0.00038	0.00024	0.319	0.288
2AP·C*	C_I	C6H $\cdots$ N4	3.500	3.446	2.658	2.598	133.7	134.4	0.00021	0.00057	0.092	0.152
A $\cdot^5$ MC*	C_s	C2H $\cdots$ O2	3.560	3.497	2.719	2.646	133.9	135.0	-0.00029	0.00014	0.001	0.074
A $\cdot^5$ MC	C_s	C2H $\cdots$ O2	3.514	3.456	2.686	2.623	132.6	133.2	-0.00001	-0.00005	0.034	0.097
A $\cdot^5$ MC	C_I	C2H $\cdots$ N3	3.384	3.330	2.442	2.414	144.0	141.5	0.00038	0.00011	0.308	0.336
A·isoC*	C_s	C2H $\cdots$ O4	3.521	3.469	2.672	2.612	134.6	135.5	-0.00024	0.00013	0.048	0.108
A·isoC* rWC	C_s	C2H $\cdots$ N2	3.596	3.529	2.763	2.689	133.2	134.0	-0.00031	0.00005	-0.013	0.061
A*·isoC	C_s	C2H $\cdots$ O4	3.501	3.452	2.679	2.632	132.0	132.0	0.00008	-0.00010	0.041	0.088
A·isoC	C_I	C2H $\cdots$ N3	3.381	3.322	2.457	2.422	142.0	139.5	0.00008	-0.00009	0.293	0.328
A*·isoC* rWC	C_s	C2H $\cdots$ N2	3.560	3.507	2.801	2.760	126.8	126.0	-0.00041	-0.00062	-0.051	-0.010
A·6-azaC*	C_s	C2H $\cdots$ O2	3.603	3.540	2.760	2.686	134.1	135.3	-0.00023	0.00026	-0.040	0.034
A·6-azaC	C_I	C2H $\cdots$ N3	3.413	3.365	2.473	2.446	144.0	141.8	0.00005	-0.00006	0.277	0.304
A*·6-azaC	C_s	C2H $\cdots$ O2	3.680	3.612	2.870	2.794	131.4	132.2	0.00001	0.00012	-0.150	-0.074
8-aza-9-deazaA·C*	C_s	C2H $\cdots$ O2	3.591	3.523	2.745	2.666	134.4	135.7	0.00000	0.00032	-0.025	0.054
8-aza-9-deazaA*·C	C_s	C2H $\cdots$ O2	3.523	3.458	2.687	2.617	133.3	134.0	-0.00020	-0.00023	0.033	0.103
8-aza-9-deazaA·C	C_I	C2H $\cdots$ N3	3.413	3.351	2.468	2.426	144.5	142.4	0.00044	0.00025	0.282	0.324
8-aza-9-deazaA·U	C_I	C2H $\cdots$ O2	3.662	3.593	2.829	2.749	133.3	134.6	-0.00001	0.00040	-0.109	-0.029
7-dezaP·U	C_s	C6H $\cdots$ O4	3.319	3.345	2.433	2.475	137.6	136.3	-0.00057	-0.00030	0.287	0.245
7-dezaP·U _f	C_s	C6H $\cdots$ O4	3.637	3.635	2.843	2.846	129.9	129.6	0.00317	-0.00001	-0.123	-0.126
		C2H $\cdots$ O2	3.674	3.607	2.917	2.843	126.9	127.6	0.00367	-0.00028	-0.197	-0.123
A·X	C_s	C2H $\cdots$ O2	3.585	3.520	2.753	2.676	133.1	134.3	-0.00037	0.00008	-0.033	0.044
A·8oxoA _{syn}	C_I	C2H $\cdots$ O8	3.656	3.563	2.765	2.650	139.0	141.4	0.00018	0.00084	-0.045	0.070

A·8oxoG _{syn}	C_s	C2H···O8	3.753	3.650	2.855	2.734	139.9	142.0	0.00052	0.00119	-0.135	-0.014
8oxoA·T	C_I	C2H···O2	3.632	3.569	2.801	2.727	133.1	134.4	0.00007	0.00047	-0.081	-0.007
3-deazaA·T	C_I	C2H···O2	3.548	3.491	2.692	2.625	135.2	136.5	-0.00092	-0.00033	0.028	0.095
8-azaA·T	C_s	C2H···O2	3.666	3.599	2.841	2.764	132.7	133.7	0.00006	0.00052	-0.121	-0.044

Notes: ^aThe distance between the C and O/N atoms involved in the CH···O/N H-bond, Å; ^bThe distance between the H and O/N atoms involved in the CH···O/N H-bond, Å; ^cThe CH···O/N H-bond angle, degree; ^dContraction (negative value) or elongation (positive value) of the donating CH group upon the CH···O/N H-bonding, Å; ^eThe difference between the sum of the Bondi's van der Waals radii [1] of the H and O/N atoms (2.720/2.750 Å, respectively) and the $d_{H···O/N}$ distances, accordingly, Å.

Table S5. Electron-topological and energetic characteristics of the intermolecular CH...O/N H-bonds in the investigated base pairs, obtained at the DFT and MP2 levels of theory in vacuum.

Base pair	Symmetry	CH...O/N H-bonds	ρ^a		$\Delta\rho^b$		$100\cdot\epsilon^c$		DI ^d	$E_{CH...O/N}^e$	
			DFT	MP2	DFT	MP2	DFT	MP2		DFT	MP2
A ⁵ BrU H	C_s	C8H...O2	0.006	0.007	0.023	0.027	13.6	11.2	0.026	1.11	1.47
A ⁵ BrU rH	C_s	C8H...O4	0.007	0.008	0.024	0.028	13.4	11.5	0.027	1.23	1.58
A ⁵ BrU WC	C_s	C2H...O2	0.006	0.007	0.020	0.024	7.1	5.4	0.026	1.04	1.31
A ⁵ BrU rWC	C_s	C2H...O2	0.006	0.007	0.021	0.024	7.2	5.6	0.027	1.09	1.36
P·T rH	C_s	C8H...O4	0.014	0.013	0.045	0.043	5.0	6.0	0.046	3.23	3.06
P·T H	C_s	C8H...O2	0.013	0.012	0.042	0.040	4.8	6.1	0.043	2.99	2.79
P·T rWC	C_s	C6H...O2	0.006	0.006	0.020	0.023	7.9	7.5	0.024	0.36	1.21
		C2H...O4	0.002	0.003	0.010	0.011	41.7	37.2	0.011	1.04	0.43
P·T WC	C_s	C6H...O4	0.010	0.010	0.032	0.031	4.2	4.6	0.036	2.10	2.04
P·T WC _f	C_s	C6H...O4	0.003	0.003	0.012	0.013	25.7	28.5	0.013	0.50	0.51
		C2H...O2	0.005	0.006	0.018	0.021	10.1	7.5	0.023	0.81	1.07
P·U rH	C_s	C8H...O4	0.014	0.013	0.044	0.043	4.9	5.8	0.046	3.19	3.07
P·U H	C_s	C8H...O2	0.012	0.012	0.040	0.039	5.7	6.6	0.040	2.70	2.63
P·U rWC	C_s	C6H...O2	0.002	0.005	0.009	0.019	78.6	11.0	0.015	0.29	0.89
		C2H...O4	0.007	0.004	0.023	0.014	5.9	17.9	0.019	1.25	0.60
P·U WC	C_s	C6H...O4	0.010	0.010	0.032	0.031	3.9	4.3	0.036	2.12	2.05
P·U WC _f	C_s	C6H...O4	0.003	0.003	0.012	0.013	24.7	26.3	0.013	0.47	0.52
		C2H...O2	0.005	0.006	0.018	0.021	10.1	7.6	0.022	0.82	1.07
2AP·T rWC	C_I	C6H...O2	0.006	0.007	0.021	0.025	7.3	5.4	0.027	1.06	1.40
2AP·T WC	C_I	C6H...O4	0.006	0.007	0.021	0.026	7.1	5.3	0.029	1.13	1.51
2AP·T rH	C_s	C8H...O4	0.013	0.012	0.041	0.040	5.7	6.7	0.042	2.85	2.75
2AP·T H	C_s	C8H...O2	0.011	0.011	0.037	0.037	6.2	7.2	0.038	2.43	2.40
2AP·C*	C_I	C6H...N4	0.008	0.010	0.024	0.028	0.7	0.3	0.041	1.45	1.79
A ⁵ MC*	C_s	C2H...O2	0.006	0.007	0.021	0.025	6.7	4.9	0.028	1.09	1.41
A ⁵ MC	C_s	C2H...O2	0.006	0.007	0.022	0.026	7.8	5.9	0.029	1.18	1.49
A ⁵ MC	C_I	C2H...N3	0.013	0.013	0.034	0.037	1.7	1.4	0.054	2.34	2.71
A·isoC*	C_s	C2H...O4	0.007	0.008	0.023	0.024	1.6	0.4	0.022	1.24	1.55
A·isoC* rWC	C_s	C2H...N2	0.007	0.008	0.020	0.024	1.6	0.4	0.034	1.12	1.43
A*·isoC	C_s	C2H...O4	0.007	0.007	0.022	0.026	8.1	6.9	0.029	1.21	1.47
A·isoC	C_I	C2H...N3	0.012	0.012	0.033	0.039	0.8	0.6	0.052	2.25	2.64
A*·isoC* rWC	C_s	C2H...N2	0.006	0.007	0.020	0.022	2.9	2.3	0.030	1.04	1.25
A·6-azaC*	C_s	C2H...O2	0.005	0.006	0.019	0.023	7.2	5.1	0.025	0.97	1.26
A·6-azaC	C_I	C2H...N3	0.012	0.012	0.032	0.035	1.7	1.4	0.051	2.17	2.50
A*·6-azaC	C_s	C2H...O2	0.004	0.005	0.016	0.019	12.1	8.5	0.021	0.70	0.92
8-aza-9-deazaA·C*	C_s	C2H...O2	0.006	0.007	0.020	0.024	7.0	5.0	0.027	1.01	1.33
8-aza-9-deazaA*·C	C_s	C2H...O2	0.006	0.007	0.022	0.026	7.4	5.5	0.029	1.18	1.52
8-aza-9-deazaA·C	C_I	C2H...N3	0.012	0.012	0.032	0.038	1.6	1.4	0.053	2.20	2.63
8-aza-9-deazaA·U	C_I	C2H...O2	0.005	0.006	0.017	0.021	9.2	6.5	0.022	0.80	1.06
7-dezaP·U	C_s	C6H...O4	0.011	0.010	0.033	0.033	2.9	3.2	0.039	2.30	2.21
7-dezaP·U _f	C_s	C6H...O4	0.005	0.005	0.017	0.018	10.4	10.1	0.019	0.77	0.82
		C2H...O2	0.005	0.005	0.015	0.018	18.7	14.5	0.018	0.63	0.83
A·X	C_s	C2H...O2	0.005	0.007	0.020	0.023	7.7	5.6	0.026	0.99	1.30
A·8oxoA _{syn}	C_I	C2H...O8	0.005	0.007	0.019	0.024	5.2	3.7	0.029	0.96	1.40
A·8oxoG _{syn}	C_s	C2H...O8	0.005	0.006	0.016	0.021	6.4	3.6	0.025	0.73	1.10
8oxoA·T	C_I	C2H...O2	0.005	0.006	0.018	0.021	8.4	6.1	0.023	0.86	1.12
3-deazaA·T	C_I	C2H...O2	0.006	0.007	0.022	0.025	5.1	3.8	0.029	1.18	1.50
8-azaA·T	C_s	C2H...O2	0.005	0.005	0.017	0.020	10.1	7.3	0.0	0.77	1.01

Notes: ^aThe electron density at the (3,-1) BCP, a.u.; ^bThe Laplacian of the electron density at the (3,-1) BCP, a.u.; ^cThe ellipticity at the (3,-1) BCP; ^dThe delocalization index at the (3,-1) BCP; ^eThe energy of the CH...O/N H-bonds estimated by the Espinosa–Molins–Lecomte formula [2,3], kcal/mol.

Table S6. Change of the atomic properties of the C, H, O and N atoms involved in the intermolecular CH $\cdots$ O/N H-bonds in the biologically important pairs involving modified nucleobases. Geometries and wave functions were calculated at the MP2/6-31G(d,p) level of theory in vacuum.

Base pair	Symmetry	H-bond	q(H) ^a	$\Delta q(H)$	M(H) ^b	$-\Delta M(H) $	V(H) ^c	$-\Delta V(H)$	-E(H) ^d	$\Delta E(H)$	r(H) ^e	r(O/N) ^f	$\Delta r(H)$	$\Delta r(O/N)$
A $\cdot^5$ BrU H	C_s	C8H $\cdots$ O2	0.092	0.009	0.117	0.022	42.7	4.0	0.615	0.016	2.02	2.96	0.49	0.50
A $\cdot^5$ BrU rH	C_s	C8H $\cdots$ O4	0.106	0.023	0.123	0.016	41.9	4.8	0.608	0.009	2.00	2.93	0.51	0.53
A $\cdot^5$ BrU WC	C_s	C2H $\cdots$ O2	0.079	0.025	0.133	0.014	43.8	4.4	0.624	0.006	2.05	3.01	0.48	0.49
A $\cdot^5$ BrU rWC	C_s	C2H $\cdots$ O4	0.085	0.031	0.136	0.011	43.6	4.6	0.622	0.004	2.04	3.00	0.46	0.50
P $\cdot$ T rH	C_s	C8H $\cdots$ O4	0.143	0.069	0.120	0.023	38.6	7.9	0.584	0.019	1.74	2.68	0.80	0.99
P $\cdot$ T H	C_s	C8H $\cdots$ O2	0.166	0.092	0.129	0.014	38.4	8.1	0.571	0.032	1.78	2.71	0.76	0.83
P $\cdot$ T rWC	C_s	C6H $\cdots$ O2	0.120	0.053	0.135	0.008	42.9	4.7	0.589	0.017	2.07	3.04	0.49	0.50
		C2H $\cdots$ O4	0.090	0.029	0.138	0.007	46.1	0.9	0.607	0.007	2.45	3.40	0.11	0.27
P $\cdot$ T WC	C_s	C6H $\cdots$ O4	0.142	0.075	0.136	0.007	40.7	6.9	0.580	0.026	1.89	2.85	0.63	0.82
P $\cdot$ T WC _f	C_s	C6H $\cdots$ O4	0.073	0.006	0.116	0.027	46.0	1.6	0.602	0.004	2.39	3.34	0.14	0.16
		C2H $\cdots$ O2	0.075	0.014	0.113	0.032	43.9	3.1	0.608	0.006	2.11	3.08	0.45	0.22
P $\cdot$ U rH	C_s	C8H $\cdots$ O4	0.119	0.045	0.108	0.035	39.4	7.1	0.592	0.011	1.74	2.68	0.76	0.97
P $\cdot$ U H	C_s	C8H $\cdots$ O2	0.124	0.050	0.112	0.031	39.9	6.6	0.589	0.014	1.80	2.73	0.72	0.89
P $\cdot$ U rWC	C_s	C6H $\cdots$ O2	0.103	0.036	0.132	0.011	44.6	3.0	0.594	0.012	2.18	3.14	0.34	0.50
		C2H $\cdots$ O4	0.070	0.009	0.122	0.023	45.9	1.1	0.616	0.002	2.31	3.28	0.22	0.39
P $\cdot$ U WC	C_s	C6H $\cdots$ O4	0.134	0.067	0.131	0.012	41.1	6.5	0.581	0.025	1.89	2.85	0.63	0.80
P $\cdot$ U WC _f	C_s	C6H $\cdots$ O4	0.074	0.007	0.116	0.027	46.0	1.6	0.602	0.004	2.38	3.33	0.14	0.32
		C2H $\cdots$ O2	0.074	0.013	0.112	0.033	43.9	3.1	0.609	0.005	2.11	3.08	0.45	0.54
2AP $\cdot$ T rWC	C_I	C6H $\cdots$ O2	0.094	0.061	0.098	0.005	42.2	4.3	0.591	0.028	2.01	3.00	0.54	2.96
2AP $\cdot$ T WC	C_I	C6H $\cdots$ O4	0.103	0.054	0.133	0.004	43.0	5.5	0.607	0.008	2.00	2.97	0.55	0.53
2AP $\cdot$ T rH	C_s	C8H $\cdots$ O4	0.151	0.076	0.129	0.008	38.5	8.8	0.586	0.017	1.79	2.72	0.74	0.78
2AP $\cdot$ T H	C_s	C8H $\cdots$ O2	0.100	0.025	0.111	0.026	40.9	6.4	0.611	0.008	1.84	2.77	0.71	0.53
2AP $\cdot$ C*	C_I	C6H $\cdots$ N4	0.130	0.063	0.141	0.002	41.7	5.3	0.585	0.021	1.91	3.00	0.61	0.64
A $\cdot^5$ MC*	C_s	C2H $\cdots$ O2	0.085	0.031	0.138	0.009	43.3	4.9	0.620	0.002	2.03	2.98	0.50	0.52
A* $\cdot^5$ MC	C_s	C2H $\cdots$ O2	0.095	0.026	0.124	0.019	42.4	4.8	0.617	0.007	2.00	2.96	0.52	0.58
A $\cdot^5$ MC	C_I	C2H $\cdots$ N3	0.127	0.073	0.128	0.019	38.6	9.6	0.604	0.014	1.75	2.82	0.78	0.68
A $\cdot$ isoC*	C_s	C2H $\cdots$ O4	0.076	0.057	0.093	0.008	42.2	4.4	0.607	0.025	1.98	2.96	0.56	0.73
A $\cdot$ isoC* rWC	C_s	C2H $\cdots$ N2	0.132	0.078	0.155	0.008	42.4	5.8	0.586	0.032	2.00	3.09	0.53	0.56

A*·isoC	C_s	C2H...O4	0.112	0.068	0.097	0.004	40.8	4.6	0.588	0.031	2.00	2.99	0.53	0.71
A·isoC	C_I	C2H...N3	0.138	0.119	0.098	0.003	37.6	9.0	0.579	0.053	1.74	2.84	0.80	0.80
A*·isoC* rWC	C_s	C2H...N2	0.094	0.025	0.121	0.022	43.3	3.9	0.607	0.003	2.06	3.16	0.46	0.51
A·6-azaC*	C_s	C2H...O2	0.092	0.038	0.135	0.012	43.9	4.3	0.607	0.011	2.06	3.02	0.47	0.48
A·6-azaC	C_I	C2H...N3	0.130	0.076	0.125	0.022	39.2	9.0	0.592	0.026	1.78	2.85	0.65	0.75
A*·6-azaC	C_s	C2H...O2	0.079	0.010	0.116	0.027	44.6	2.6	0.613	0.003	2.16	3.13	0.36	0.41
8-aza-9-deazaA·C*	C_s	C2H...O4	0.094	0.400	0.132	0.013	43.4	4.7	0.607	0.011	2.04	3.00	0.50	0.57
8-aza-9-deazaA*·C	C_s	C2H...O2	0.100	0.033	0.123	0.019	42.7	4.6	0.603	0.008	2.00	2.96	0.56	0.76
8-aza-9-deazaA·C	C_I	C2H...N3	0.130	0.114	0.095	0.004	37.8	8.8	0.582	0.051	1.74	2.85	0.83	0.79
8-aza-9-deazaA·U	C_I	C2H...O2	0.095	0.041	0.139	0.006	44.0	4.1	0.605	0.013	2.12	3.08	0.42	0.49
7-dezaP·U	C_s	C6H...O4	0.115	0.092	0.134	0.001	41.9	7.5	0.591	0.036	1.86	2.82	0.65	0.87
7-dezaP·U _f	C_s	C6H...O4	0.059	0.036	0.117	0.018	46.0	3.4	0.609	0.018	2.21	3.18	0.31	0.51
		C2H...O2	0.063	0.019	0.115	0.027	45.0	3.0	0.613	0.009	2.22	3.17	0.32	0.52
A·X	C_s	C2H...O2	0.059	0.005	0.112	0.035	44.1	4.1	0.617	0.001	2.06	3.01	0.47	0.64
A·8oxoA _{syn}	C_I	C2H...O8	0.114	0.060	0.146	0.001	42.2	6.0	0.608	0.010	2.01	3.00	0.52	0.50
A·8oxoG _{syn}	C_s	C2H...O8	0.107	0.053	0.147	0.001	43.6	4.6	0.610	0.008	2.08	3.09	0.45	0.41
8oxoA·T	C_I	C2H...O2	0.084	0.021	0.136	0.011	43.9	3.2	0.623	0.010	2.10	3.07	0.18	0.23
3-deazaA·T	C_I	C2H...O2	0.083	0.057	0.143	0.005	44.0	5.8	0.617	0.009	2.00	2.96	0.37	0.34
8-azaA·T	C_s	C2H...O2	0.068	0.025	0.119	0.015	44.8	3.2	0.626	0.001	2.13	3.10	0.13	0.20

Notes: ^aThe charge of the hydrogen atom; ^bThe dipolar polarization of the hydrogen atom; ^cThe volume of the hydrogen atom; ^dThe energy of the hydrogen atom; ^eThe radius of the hydrogen atom upon the H-bonding; ^fThe radius of the O/N acceptor atoms upon the H-bonding. All changes of values are indicated with respect to free monomers (bases). All units are given in atomic units (a.u.).

Table S7. Vibrational characteristics of the intermolecular CH $\cdots$ O/N H-bonds in the investigated pairs containing modified nucleobases, obtained at the DFT and MP2 levels of theory in vacuum.

Base pairs	Symmetry	CH $\cdots$ O/N H-bonds	$-\Delta\nu(\text{CH})^a$		$I_\nu/I_{\nu 0}^b$		$\Delta\gamma(\text{CH})^c$		$I_\gamma/I_{\gamma 0}^d$	
			DFT	MP2	DFT	MP2	DFT	MP2	DFT	MP2
A $\cdot$ ⁵ BrU H	C_s	C8H $\cdots$ O2	12.1	7.3	4.5	9.9	25.2	24.1	2.5	1.1
A $\cdot$ ⁵ BrU rH	C_s	C8H $\cdots$ O4	10.3	6.7	6.6	13.0	32.0	29.5	2.7	1.1
A $\cdot$ ⁵ BrU WC	C_s	C2H $\cdots$ O2	14.0	8.0	0.1	0.1	23.6	24.6	1.1	1.1
A $\cdot$ ⁵ BrU rWC	C_s	C2H $\cdots$ O2	14.5	8.4	0.1	0.1	26.6	27.4	1.1	1.1
P $\cdot$ T rH	C_s	C8H $\cdots$ O4	-1.6	3.0	90.4	79.3	62.5	52.4	1.0	0.9
P $\cdot$ T H	C_s	C8H $\cdots$ O2	1.6	5.0	60.4	50.3	56.0	46.4	1.0	0.9
P $\cdot$ T rWC	C_s	C6H $\cdots$ O2	14.9	7.5	0.2	0.4	15.6	26.1	1.1	1.1
		C2H $\cdots$ O4	13.1	5.7	0.1	0.1	31.4	14.6	1.3	1.3
P $\cdot$ T WC	C_s	C6H $\cdots$ O4	10.9	7.5	1.2	1.2	40.3	35.7	1.0	1.1
P $\cdot$ T WC _f	C_s	C6H $\cdots$ O4	14.6	6.8	0.1	0.1	19.0	35.7	1.0	1.1
		C2H $\cdots$ O2	12.8	7.7	0.1	0.1	26.0	24.5	1.3	1.4
P $\cdot$ U rH	C_s	C8H $\cdots$ O4	-1.1	3.5	78.0	75.4	62.2	52.4	1.0	0.9
P $\cdot$ U H	C_s	C8H $\cdots$ O2	4.6	5.8	37.4	40.3	52.1	44.3	1.0	0.9
P $\cdot$ U rWC	C_s	C6H $\cdots$ O2	14.7	7.8	0.2	1.2	13.0	21.9	1.1	1.1
		C2H $\cdots$ O4	13.1	6.4	0.1	0.1	34.1	18.7	1.4	1.4
P $\cdot$ U WC	C_s	C6H $\cdots$ O4	11.0	7.8	1.3	1.2	39.2	35.5	1.0	1.1
P $\cdot$ U WC _f	C_s	C6H $\cdots$ O4	15.3	7.1	0.1	0.1	19.0	17.4	1.1	1.1
		C2H $\cdots$ O2	13.2	7.8	0.1	0.1	26.2	23.8	1.3	1.4
2AP $\cdot$ T rWC	C_I	C6H $\cdots$ O2	12.5	5.9	0.1	0.2	25.3	28.7	0.9	0.9
2AP $\cdot$ T WC	C_I	C6H $\cdots$ O4	11.2	4.8	0.1	0.3	28.8	32.6	0.9	0.9
2AP $\cdot$ T rH	C_s	C8H $\cdots$ O4	4.9	6.3	46.4	47.3	62.1	50.1	10.7	0.8
2AP $\cdot$ T H	C_s	C8H $\cdots$ O2	8.1	7.9	26.3	30.3	52.6	43.3	1.8	0.9
2AP $\cdot$ C*	C_I	C6H $\cdots$ N4	6.6	2.1	0.5	0.9	35.7	37.5	0.9	0.9
A $\cdot$ ⁵ MC*	C_s	C2H $\cdots$ O2	12.8	8.0	0.2	0.1	28.1	29.8	1.2	1.2
A* $\cdot$ ⁵ MC	C_s	C2H $\cdots$ O2	11.6	11.7	0.1	0.1	53.6	52.7	1.0	1.8
A $\cdot$ ⁵ MC	C_I	C2H $\cdots$ N3	7.2	10.3	1.2	1.1	60.2	61.8	1.2	1.3
A $\cdot$ isoC*	C_s	C2H $\cdots$ O4	13.2	8.6	0.1	0.1	32.5	33.2	1.2	1.2
A $\cdot$ isoC* rWC	C_s	C2H $\cdots$ N2	13.1	8.9	0.1	0.1	30.5	30.1	1.1	1.4
A* $\cdot$ isoC	C_s	C2H $\cdots$ O4	11.2	12.4	0.2	0.1	56.6	25.4	1.0	0.7
A $\cdot$ isoC	C_I	C2H $\cdots$ N3	12.1	13.6	1.1	1.1	58.8	61.1	1.2	1.7
A* $\cdot$ isoC* rWC	C_s	C2H $\cdots$ N2	16.8	17.9	0.3	0.2	52.2	18.6	1.1	0.8
A $\cdot$ 6-azaC*	C_s	C2H $\cdots$ O2	11.7	6.3	0.1	0.1	25.8	26.8	1.1	1.2
A $\cdot$ 6-azaC	C_I	C2H $\cdots$ N3	11.3	11.6	0.8	0.7	52.7	52.7	1.6	1.3
A* $\cdot$ 6-azaC	C_s	C2H $\cdots$ O2	10.3	8.6	0.03	0.06	45.5	17.1	1.1	0.7
8-aza-9-deazaA $\cdot$ C*	C_s	C2H $\cdots$ O2	8.2	5.0	0.2	0.2	26.8	26.9	0.9	1.1
8-aza-9-deazaA* $\cdot$ C	C_s	C2H $\cdots$ O2	13.5	13.4	0.04	0.3	51.4	49.8	0.6	1.0
8-aza-9-deazaA $\cdot$ C	C_I	C2H $\cdots$ N3	6.7	8.2	1.0	1.1	56.8	57.8	1.0	1.0
8-aza-9-deazaA $\cdot$ U	C_I	C2H $\cdots$ O2	7.8	3.6	0.2	0.2	23.2	22.8	0.9	1.1
7-deazaP $\cdot$ U	C_s	C6H $\cdots$ O4	18.7	15.2	0.6	0.3	42.0	37.1	1.1	1.2
7-deazaP $\cdot$ U _f	C_s	C6H $\cdots$ O4	18.3	10.2	0.1	0.1	24.0	24.2	4.6	1.5
		C2H $\cdots$ O2	17.8	12.5	0.2	0.1	20.0	27.1	6.3	1.4
A $\cdot$ X	C_s	C2H $\cdots$ O2	13.2	8.0	0.2	0.1	24.2	25.3	1.1	1.2
A $\cdot$ 8oxoA _{syn}	C_I	C2H $\cdots$ O8	7.6	-0.03	0.1	0.1	23.9	27.6	1.2	2.1

A·8oxoG _{syn}	C_s	C2H...O8	2.9	-4.2	0.1	0.1	29.6	35.7	0.9	1.4
8oxoA·T	C_I	C2H...O2	7.6	3.3	0.1	0.01	26.0	27.9	1.0	1.1
3-deazaA·T	C_I	C2H...O2	19.8	13.1	0.2	0.2	28.9	26.6	1.6	0.9
8-azaA·T	C_s	C2H...O2	7.6	2.5	0.2	0.2	23.5	24.9	1.2	1.2

Notes: ^aThe red shift (positive value) or the blue shift (negative value) $\Delta\nu(\text{CH})=\nu_0(\text{CH})-\nu(\text{CH})$ of the stretching vibrational mode of the H-bonded CH group, cm^{-1} ; ^bThe ratio of the intensity of the $\nu(\text{CH})$ stretching vibrational mode of the H-bonded CH group in the base pair I_ν to the corresponding mode of the non-bonded CH group in the monomer $I_{\nu 0}$; ^cThe shift $\Delta\gamma(\text{CH})=\gamma(\text{CH})-\gamma_0(\text{CH})$ of the out-of-plane vibrational mode of the H-bonded CH group, cm^{-1} ; ^dThe ratio of the intensity of the $\nu(\text{CH})$ out-of-plane vibrational mode of the H-bonded CH group in the base pair I_γ to the corresponding mode of the non-bonded CH group in the monomer $I_{\gamma 0}$.

Table S8. Grunenberg's compliance constants C_{ij} (in Å/mDyn) for the CH $\cdots$ O/N H-bonds in the biologically important pairs involving modified nucleobases, obtained at the DFT and MP2 levels of theory in vacuum.

Base pairs	Symmetry	CH $\cdots$ O/N H-bonds	C_{ij}	
			DFT	MP2
A $\cdot^5$ BrU H	C_s	C8H $\cdots$ O2	15.894	13.901
A $\cdot^5$ BrU rH	C_s	C8H $\cdots$ O4	14.893	13.535
A $\cdot^5$ BrU WC	C_s	C2H $\cdots$ O2	16.106	14.718
A $\cdot^5$ BrU rWC	C_s	C2H $\cdots$ O2	14.512	14.565
P $\cdot$ T rH	C_s	C8H $\cdots$ O4	15.096	18.048
P $\cdot$ T H	C_s	C8H $\cdots$ O2	17.728	23.367
P $\cdot$ T rWC	C_s	C6H $\cdots$ O2	413.612	287.719
		C2H $\cdots$ O4	306.648	223.596
P $\cdot$ T WC	C_s	C6H $\cdots$ O4	42.077	41.251
P $\cdot$ T WC _f	C_s	C6H $\cdots$ O4	274.837	453.501
		C2H $\cdots$ O2	226.973	340.929
P $\cdot$ U rH	C_s	C8H $\cdots$ O4	14.745	17.776
P $\cdot$ U H	C_s	C8H $\cdots$ O2	22.715	27.038
P $\cdot$ U rWC	C_s	C6H $\cdots$ O2	178.011	426.360
		C2H $\cdots$ O4	119.717	453.129
P $\cdot$ U WC	C_s	C6H $\cdots$ O4	33.631	39.780
P $\cdot$ U WC _f	C_s	C6H $\cdots$ O4	420.647	352.310
		C2H $\cdots$ O2	331.678	265.370
2AP $\cdot$ T rWC	C_I	C6H $\cdots$ O2	17.142	16.435
2AP $\cdot$ T WC	C_I	C6H $\cdots$ O2	17.142	16.435
2AP $\cdot$ T rH	C_s	C8H $\cdots$ O4	18.788	22.875
2AP $\cdot$ T H	C_s	C8H $\cdots$ O2	27.356	35.625
2AP $\cdot$ C*	C_I	C6H $\cdots$ N4	15.828	13.605
A $\cdot^5$ MC*	C_s	C2H $\cdots$ O2	16.020	14.353
A* $\cdot^5$ MC	C_s	C2H $\cdots$ O2	11.978	10.923
A $\cdot^5$ MC	C_I	C2H $\cdots$ N3	14.085	11.701
A $\cdot$ isoC*	C_s	C2H $\cdots$ O4	15.118	13.898
A $\cdot$ isoC* rWC	C_s	C2H $\cdots$ N2	14.011	12.997
A* $\cdot$ isoC	C_s	C2H $\cdots$ O4	11.156	10.127
A $\cdot$ isoC	C_I	C2H $\cdots$ N3	14.426	11.996
A* $\cdot$ isoC* rWC	C_s	C2H $\cdots$ N2	10.799	10.127
A $\cdot$ 6-azaC*	C_s	C2H $\cdots$ O2	15.459	14.900
A $\cdot$ 6-azaC	C_I	C2H $\cdots$ N3	15.172	13.298
A* $\cdot$ 6-azaC	C_s	C2H $\cdots$ O2	14.341	13.693
8-aza-9-deazaA $\cdot$ C*	C_s	C2H $\cdots$ O2	15.799	14.906
8-aza-9-deazaA* $\cdot$ C	C_s	C2H $\cdots$ O2	12.319	11.076
8-aza-9-deazaA $\cdot$ C	C_I	C2H $\cdots$ N3	14.971	12.562
8-aza-9-deazaA $\cdot$ U	C_I	C2H $\cdots$ O2	17.439	16.771
7-deazaP $\cdot$ U	C_s	C6H $\cdots$ O4	26.657	30.355
7-deazaP $\cdot$ U _f	C_s	C6H $\cdots$ O4	358.124	317.811
		C2H $\cdots$ O2	305.181	299.013
A $\cdot$ X	C_s	C2H $\cdots$ O2	16.245	15.060

$A \cdot 8oxoA_{syn}$	C_I	$C2H \cdots O8$	31.567	21.056
$A \cdot 8oxoG_{syn}$	C_s	$C2H \cdots O8$	16.055	14.656
$8oxoA \cdot T$	C_I	$C2H \cdots O2$	17.553	17.138
$3-deazaA \cdot T$	C_I	$C2H \cdots O2$	15.685	14.537
$8-azaA \cdot T$	C_s	$C2H \cdots O2$	17.947	16.996

Table S9. Summary of the NBO analysis of the donor-acceptor interactions corresponding to the CH...O/N H-bonds in the biologically important pairs containing modified nucleobases, obtained at the DFT level of theory in vacuum.

Base pairs	Symmetry	CH...O/N H-bonds	Donor-acceptor NBOs	E ^{(2)a}	Occupancy of LP ^b	Energy of LP ^c	Occupancy of BD* ^d	Energy of BD* ^e	q _C ^f	q _H ^g	q _{O/N} ^h
A ⁵ BrU H	C _s	C8H...O2	LP(1) _{O2} – BD* _{C8H}	0.70	1.864	-0.238	0.019	0.494	0.227	0.252	-0.637
			LP(2) _{O2} – BD* _{C8H}		1.865	0.236					
A ⁵ BrU rH	C _s	C8H...O4	LP(1) _{O4} – BD* _{C8H}	0.79	1.976	-0.685	0.019	0.475	0.229	0.255	-0.595
			LP(2) _{O4} – BD* _{C8H}		1.860	-0.255					
A ⁵ BrU WC	C _s	C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.76	1.975	-0.687	0.026	0.499	0.263	0.237	-0.625
			LP(2) _{O2} – BD* _{C2H}		1.841	-0.253					
A ⁵ BrU rWC	C _s	C2H...O4	LP(1) _{O4} – BD* _{C2H}	0.82	1.976	-0.677	0.026	0.501	0.264	0.240	-0.583
			LP(2) _{O4} – BD* _{C2H}		1.857	-0.248					
P·T rH	C _s	C8H...O4	LP(1) _{O4} – BD* _{C8H}	3.34	1.870	-0.246	0.025	0.480	0.245	0.266	-0.640
			LP(2) _{O4} – BD* _{C8H}		1.894	-0.385					
P·T H	C _s	C8H...O2	LP(1) _{O2} – BD* _{C8H}	2.99	1.972	-0.684	0.024	0.478	0.245	0.265	-0.668
			LP(2) _{O2} – BD* _{C8H}		1.849	-0.250					
P·T rWC	C _s	C6H...O2	LP(1) _{O2} – BD* _{C6H}	0.13	1.962	-0.660	0.021	0.477	0.077	0.257	-0.643
			LP(2) _{O2} – BD* _{C6H}		1.845	-0.235					
		C2H...O4	LP(1) _{O4} – BD* _{C2H}	0.80	1.976	-0.663	0.026	0.494	0.249	0.245	-0.622
			LP(2) _{O4} – BD* _{C2H}		1.868	-0.232					
P·T WC	C _s	C6H...O4	LP(1) _{O4} – BD* _{C6H}	2.05	1.975	-0.665	0.025	0.492	0.077	0.268	-0.627
			LP(2) _{O4} – BD* _{C6H}		1.868	-0.235					
P·T WC _f	C _s	C6H...O4	LP(1) _{O4} – BD* _{C6H}	0.27	1.977	-0.662	0.021	0.479	0.078	0.259	-0.618
			LP(2) _{O4} – BD* _{C6H}		1.867	-0.231					
		C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.57	1.975	-0.671	0.025	0.491	0.249	0.244	-0.648

			LP(2) _{O2} – BD* _{C2H}		1.846	-0.236					
P·U rH	C _s	C8H...O4	LP(1) _{O4} – BD* _{C8H}	3.29	1.973	-0.675	0.025	0.480	0.062	0.245	-0.625
			LP(2) _{O4} – BD* _{C8H}		1.868	-0.246					
P·U H	C _s	C8H...O2	LP(1) _{O2} – BD* _{C8H}	2.53	1.973	-0.687	0.023	0.475	0.245	0.264	-0.662
			LP(2) _{O2} – BD* _{C8H}		1.849	-0.253					
P·U rWC	C _s	C6H...O2	LP(1) _{O2} – BD* _{C6H}	0.09	1.956	-0.658	0.021	0.475	0.077	0.255	-0.638
			LP(2) _{O2} – BD* _{C6H}		1.844	-0.234					
		C2H...O4	LP(1) _{O4} – BD* _{C2H}	1.03	1.976	-0.663	0.026	0.496	0.249	0.248	-0.615
			LP(2) _{O4} – BD* _{C2H}		1.866	-0.232					
P·U WC	C _s	C6H...O4	LP(1) _{O4} – BD* _{C6H}	2.08	1.975	-0.665	0.025	0.492	0.077	0.268	-0.619
			LP(2) _{O4} – BD* _{C6H}		1.866	-0.235					
P·U WC _f	C _s	C6H...O4	LP(1) _{O4} – BD* _{C6H}	0.27	1.977	-0.661	0.021	0.479	0.078	0.259	-0.610
			LP(2) _{O4} – BD* _{C6H}		1.865	-0.230					
		C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.57	1.975	-0.674	0.025	0.490	0.249	0.244	-0.644
			LP(2) _{O2} – BD* _{C2H}		1.845	-0.240					
2AP·T rWC	C _I	C6H...O2	LP(1) _{O2} – BD* _{C6H}	0.80	1.975	-0.677	0.022	0.493	0.091	0.255	-0.638
			LP(2) _{O2} – BD* _{C6H}		1.844	-0.243					
2AP·T WC	C _I	C6H...O4	LP(1) _{O4} – BD* _{C6H}	0.89	1.976	-0.668	0.023	0.495	0.091	0.258	-0.610
			LP(2) _{O4} – BD* _{C6H}		1.866	-0.238					
2AP·T rH	C _s	C8H...O4	LP(1) _{O4} – BD* _{C8H}	2.73	1.974	-0.670	0.024	0.490	0.230	0.261	-0.638
			LP(2) _{O4} – BD* _{C8H}		1.870	-0.240					
2AP·T H	C _s	C8H...O2	LP(1) _{O2} – BD* _{C8H}	2.15	1.973	-0.678	0.022	0.487	0.229	0.260	-0.665
			LP(2) _{O2} – BD* _{C8H}		1.849	-0.243					
2AP·C*	C _I	C6H...N4	LP(1) _{N4} – BD* _{C6H}	1.61	1.930	-0.361	0.024	0.504	0.092	0.262	-0.731
A ^{·5} MC*	C _s	C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.82	1.975	-0.670	0.026	0.511	0.263	0.237	-0.641
			LP(2) _{O2} – BD* _{C2H}		1.845	-0.235					
A* ^{·5} MC	C _s	C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.95	1.975	-0.658	0.024	0.497	0.285	0.250	-0.658

			LP(2) _{O2} – BD* _{C2H}		1.853	-0.225						
A ⁵ MC	<i>C_I</i>	C2H...N3	LP(1) _{N3} – BD* _{C2H}	3.13	1.889	-0.306	0.030	0.528	0.263	0.259	-0.618	
A·isoC*	<i>C_s</i>	C2H...O4	LP(1) _{O4} – BD* _{C2H}	1.45	1.974	-0.677	0.015	0.493	0.491	0.265	-0.639	
			LP(2) _{O4} – BD* _{C2H}		1.843	-0.243						
A·isoC* rWC	<i>C_s</i>	C2H...N2	LP(1) _{N2} – BD* _{C2H}	1.07	1.913	-0.362	0.026	0.512	0.264	0.240	-0.770	
A*·isoC	<i>C_s</i>	C2H...O4	LP(1) _{O4} – BD* _{C2H}	0.97	1.976	-0.650	0.024	0.497	0.285	0.251	-0.621	
			LP(2) _{O4} – BD* _{C2H}		1.875	-0.220						
A·isoC	<i>C_I</i>	C2H...N3	LP(1) _{N3} – BD* _{C2H}	2.87	1.883	-0.312	0.029	0.526	0.264	0.259	-0.610	
A*·isoC* rWC	<i>C_s</i>	C2H...N2	LP(1) _{N2} – BD* _{C2H}	0.91	1.918	-0.354	0.024	0.490	0.289	0.253	-0.787	
A·6-azaC*	<i>C_s</i>	C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.70	1.976	-0.682	0.026	0.501	0.264	0.237	-0.626	
			LP(2) _{O2} – BD* _{C2H}		1.839	-0.248						
A·6-azaC	<i>C_I</i>	C2H...N3	LP(1) _{N3} – BD* _{C2H}	2.84	1.893	-0.332	0.029	0.517	0.262	0.256	-0.595	
A*·6-azaC	<i>C_s</i>	C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.48	1.976	-0.671	0.023	0.484	0.285	0.247	-0.637	
			LP(2) _{O2} – BD* _{C2H}		1.846	-0.238						
8-aza-9-deazaA·C*	<i>C_s</i>	C2H...O2	LP(1) _{O4} – BD* _{C2H}	0.75	1.975	-0.677	0.026	0.508	0.248	0.235	-0.632	
			LP(2) _{O4} – BD* _{C2H}		1.844	-0.243						
8-aza-9-deazaA*·C	<i>C_s</i>	C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.94	1.974	-0.665	0.025	0.497	0.269	0.248	-0.649	
			LP(2) _{O2} – BD* _{C2H}		1.852	-0.232						
8-aza-9-deazaA·C	<i>C_I</i>	C2H...N3	LP(1) _{N3} – BD* _{C2H}	2.88	1.889	-0.312	0.029	0.524	0.246	0.258	-0.620	
8-aza-9-deazaA·U	<i>C_I</i>	C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.54	1.975	-0.684	0.026	0.500	0.248	0.235	-0.626	
			LP(2) _{O2} – BD* _{C2H}		1.842	-0.251						
7-deazaP·U	<i>C_s</i>	C6H...O4	LP(1) _{O4} – BD* _{C6H}	2.34	1.974	-0.663	0.026	0.496	0.083	0.260	-0.622	
			LP(2) _{O4} – BD* _{C6H}		1.867	-0.233						
7-deazaP·U _f	<i>C_s</i>	C6H...O4	LP(1) _{O4} – BD* _{C6H}	0.54	1.976	-0.660	0.022	0.484	0.084	0.253	-0.616	
			LP(2) _{O4} – BD* _{C6H}		1.867	-0.229						
		C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.37	1.976	-0.670	0.025	0.495	0.246	0.239	-0.643	

			LP(2) _{O2} – BD* _{C2H}		1.846	-0.236					
A·X	C _s	C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.71	1.975	-0.680	0.026	0.504	0.263	0.236	-0.632
			LP(2) _{O2} – BD* _{C2H}		1.841	-0.247					
A·8oxoA _{syn}	C _I	C2H...O8	LP(1) _{O8} – BD* _{C2H}	0.71	1.975	-0.667	0.026	0.495	0.262	0.240	-0.634
			LP(2) _{O8} – BD* _{C2H}		1.829	-0.235					
A·8oxoG _{syn}	C _s	C2H...O8	LP(1) _{O8} – BD* _{C2H}	0.53	1.975	-0.655	0.026	0.506	0.262	0.237	-0.646
			LP(2) _{O8} – BD* _{C2H}		1.827	-0.221					
8oxoA·T	C _I	C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.60	1.975	-0.682	0.026	0.495	0.260	0.239	-0.633
			LP(2) _{O2} – BD* _{C2H}		1.843	-0.248					
3-deazaA·T	C _I	C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.93	1.975	-0.672	0.020	0.512	0.034	0.247	-0.641
			LP(2) _{O2} – BD* _{C2H}		1.845	-0.238					
8-azaA·T	C _s	C2H...O2	LP(1) _{O2} – BD* _{C2H}	0.52	1.975	-0.684	0.026	0.490	0.276	0.241	-0.634
			LP(2) _{O2} – BD* _{C2H}		1.843	-0.250					

Notes: ^aThe interaction energy of the listed orbital pairs, kcal/mol; ^bOccupancy of the orbital corresponding to a lone electron pair (LP), e; ^cEnergy of the LP orbital, a.u.; ^dOccupancy of the BD* antibonding orbital, e; ^eEnergy of the BD* antibonding orbital, a.u.; ^{f,g,h}The NBO partial charges of the donor (C), hydrogen (H) and acceptor (O/N) atoms involved in the CH...O/N H-bonds, respectively, e.

Table S10. Energetic characteristics for the studied pairs involving modified nucleobases, obtained at the DFT and MP2 levels of theory in vacuum.

Base pairs	Symmetry	CH...O/N H-bonds	$-\Delta E_{\text{int}}^a$		$E_{\text{CH...O/N}}^b$		$E_{\text{CH...O/N}}/ \Delta E_{\text{int}} , \%$	
			DFT	MP2	DFT	MP2	DFT	MP2
A ⁵ BrU H	C_s	C8H...O2	15.11	15.01	1.11	1.47	7.3	9.8
A ⁵ BrU rH	C_s	C8H...O4	14.95	14.91	1.23	1.58	8.2	10.6
A ⁵ BrU WC	C_s	C2H...O2	14.73	14.42	1.04	1.31	7.1	9.1
A ⁵ BrU rWC	C_s	C2H...O2	14.23	13.99	1.09	1.36	7.7	9.7
P·T rH	C_s	C8H...O4	9.19	9.80	3.23	3.06	35.1	31.2
P·T H	C_s	C8H...O2	8.90	9.60	2.99	2.79	33.6	29.1
P·T rWC	C_s	C6H...O2	7.85	8.38	1.04	1.21	13.2	14.4
		C2H...O4			0.36	0.43	4.6	5.1
P·T WC	C_s	C6H...O4	8.05	8.52	2.10	2.04	26.1	23.9
P·T WC _f	C_s	C6H...O4	7.82	7.74	0.50	0.51	6.4	6.6
		C2H...O2			0.81	1.07	10.4	13.8
P·U rH	C_s	C8H...O4	9.40	9.90	3.19	3.07	33.9	31.0
P·U H	C_s	C8H...O2	8.86	9.53	2.70	2.63	30.5	27.6
P·U rWC	C_s	C6H...O2	7.99	8.40	0.29	0.60	3.6	10.6
		C2H...O4			1.25	0.89	15.6	7.1
P·U WC	C_s	C6H...O4	8.20	8.58	2.12	2.98	25.9	34.7
P·U WC _f	C_s	C6H...O4	7.93	8.35	0.47	0.52	5.9	6.2
		C2H...O2			0.82	1.07	10.3	12.8
2AP·T rWC	C_I	C6H...O2	13.57	12.74	1.06	1.40	7.8	11.0
2AP·T WC	C_I	C6H...O4	13.22	12.54	1.13	1.51	8.5	12.0
2AP·T rH	C_s	C8H...O4	9.28	9.69	2.85	2.75	30.7	28.4
2AP·T H	C_s	C8H...O2	8.99	9.69	2.43	2.40	27.0	24.8
2AP·C*	C_I	C6H...N4	12.91	12.46	1.45	1.79	11.2	14.4
A ⁵ MC*	C_s	C2H...O2	14.47	14.03	1.09	1.41	7.5	10.0
A* ⁵ MC	C_s	C2H...O2	23.35	22.55	1.18	1.49	5.1	6.6
A ⁵ MC	C_I	C2H...N3	6.04	6.70	2.34	2.71	38.7	40.4
A·isoC*	C_s	C2H...O4	14.05	13.92	1.24	1.55	8.8	11.2
A·isoC* rWC	C_s	C2H...N2	13.58	13.67	1.12	1.43	8.2	10.4
A*·isoC	C_s	C2H...O4	25.33	23.05	1.21	1.47	4.8	6.4
A·isoC	C_I	C2H...N3	6.57	7.02	2.25	2.64	34.2	37.7
A*·isoC* rWC	C_s	C2H...N2	34.34	29.34	1.04	1.25	3.0	4.3
A·6-azaC*	C_s	C2H...O2	15.14	14.68	0.97	1.26	6.4	8.6
A·6-azaC	C_I	C2H...N3	7.02	7.57	2.17	2.50	30.9	33.0
A*·6-azaC	C_s	C2H...O2	22.98	21.79	0.70	0.92	3.0	4.2
8-aza-9-deazaA·C*	C_s	C2H...O2	15.13	14.17	1.01	1.33	6.7	9.4
8-aza-9-deazaA*·C	C_s	C2H...O2	21.15	20.74	1.18	1.52	5.6	7.3
8-aza-9-deazaA·C	C_I	C2H...N3	4.95	5.66	2.20	2.63	44.4	46.5
8-aza-9-deazaA·U	C_I	C2H...O2	14.37	13.50	0.80	1.06	5.6	7.9
7-dezaP·U	C_s	C6H...O4	8.97	9.24	2.30	2.21	25.6	23.9
7-dezaP·U _f	C_s	C6H...O4	8.66	8.91	0.77	0.82	8.9	9.2
		C2H...O2			0.63	0.83	7.3	9.3
A·X	C_s	C2H...O2	14.06	13.63	0.99	1.30	7.0	9.5
A·8oxoA _{syn}	C_I	C2H...O8	11.91	13.14	0.96	1.40	8.1	10.7
A·8oxoG _{syn}	C_s	C2H...O8	14.71	13.14	0.73	1.10	5.0	8.4
8oxoA·T	C_I	C2H...O2	12.94	14.33	0.86	1.12	6.6	7.8

3-deazaA·T	C_I	C2H···O2	14.39	13.77	1.18	1.50	8.2	10.9
8-azaA·T	C_s	C2H···O2	14.12	13.86	0.77	1.57	5.5	11.3

Notes: ^aThe BSSE corrected electronic interaction energy, kcal/mol; ^bThe energy of the CH···O/N H-bonds estimated by the Espinosa–Molins–Lecomte formula [2,3], kcal/mol.

Table S11. Energy decomposition analysis of the interaction energies (ΔE_{int}) between two moieties in the pairs involving natural and modified DNA and RNA bases optimized at the B3LYP-D3/TZP level of theory into four main physical components performed at the same level of theory. Geometries of the base pairs were optimized in ADF program at the same level of theory.

Base pairs	Symmetry	$-\Delta E_{\text{oi}}^{\text{a}}$	$\Delta E_{\text{Pauli}}^{\text{b}}$	$-\Delta V_{\text{elstat}}^{\text{c}}$	$-\Delta E_{\text{disp}}^{\text{d}}$	$-\Delta E_{\text{int}}^{\text{e}}$
A·T H	C_s	17.96	34.40	30.96	4.43	18.95
A·T rH	C_s	17.18	33.03	30.13	4.35	18.63
A·T WC	C_s	19.42	37.32	31.86	4.46	18.43
A·T rWC	C_s	18.75	36.44	31.28	4.45	18.04
A*·T* L	C_s	57.09	83.47	62.85	4.72	41.18
A·T*	C_s	19.67	35.03	27.83	3.90	16.38
A·U H	C_s	18.02	34.23	30.93	4.34	19.06
A·U rH	C_s	17.61	33.91	30.52	4.35	18.57
A·U WC	C_s	19.86	37.97	32.38	4.44	18.71
A·U rWC	C_s	18.66	36.16	31.01	4.42	17.93
A·U HH ₁	C_I	6.21	11.65	12.88	2.78	10.21
A·U HH ₂	C_I	3.53	7.28	8.46	2.58	7.29
A·U*	C_s	19.80	35.33	28.12	3.84	16.43
A*·U* L	C_s	52.66	77.09	59.49	4.59	39.65
A·A _{syn 1}	C_I	7.66	16.02	15.66	3.00	10.30
A·A _{syn 2}	C_I	6.79	14.87	13.59	3.37	8.88
A·A _{syn 3}	C_I	6.20	13.27	12.60	2.98	8.51
A·A ₄	C_I	7.49	16.28	14.20	3.13	8.54
A·G ₁	C_I	6.46	13.62	13.22	2.98	9.03
A·G ₂	C_I	6.89	14.63	13.96	3.22	9.45
G·G	C_I	15.41	27.46	29.84	4.52	22.30
G·U ₁	C_I	11.25	19.84	22.43	3.89	17.73
G·U ₂	C_s	10.16	19.31	17.05	3.35	11.25
G·U ₃	C_I	6.88	13.11	13.58	3.02	10.36
G·C HH	C_I	5.56	9.83	13.07	2.86	11.66
G·C ⁺ H	C_s	35.86	46.82	55.65	4.70	49.39
G·C ⁺	C_s	33.80	42.57	53.60	4.60	49.43
U·U ₁	C_s	9.27	17.52	16.48	3.03	11.27
U·U ₂	C_s	8.76	16.66	15.55	3.01	10.66
U·U ₃	C_{2h}	3.75	7.39	9.36	2.62	8.33

C·C	C_I	6.40	13.20	14.11	5.22	12.53
A·C*	C_s	20.16	39.89	33.92	4.59	18.78
A*·C	C_s	26.43	45.91	41.94	4.76	27.22
A·C	C_s	8.40	17.16	14.84	3.32	9.40
H*·U	C_s	26.00	46.70	37.57	4.26	21.13
H·U*	C_s	34.68	54.77	46.32	4.37	30.59
H·C	C_s	20.99	34.41	35.28	4.42	26.27
A· ⁵ BrU H	C_s	18.06	33.13	30.36	4.45	19.74
A· ⁵ BrU rH	C_s	17.18	31.50	29.37	4.27	19.32
A· ⁵ BrU WC	C_s	19.07	35.12	30.91	4.48	19.33
A· ⁵ BrU rWC	C_s	17.93	33.29	29.75	4.34	18.72
P·T rH	C_s	10.35	20.92	19.72	3.32	12.47
P·T H	C_s	9.59	19.34	18.88	3.25	12.39
P·T rWC	C_s	11.49	23.47	20.37	3.50	11.89
P·T WC	C_s	11.16	22.69	19.95	3.47	11.88
P·T WC _f	C_s	9.81	19.49	18.04	3.25	11.61
P·U rH	C_s	10.14	20.12	19.58	3.24	12.85
P·U H	C_s	9.68	19.44	18.89	3.24	12.36
P·U rWC	C_s	11.26	22.77	20.02	3.44	11.95
P·U WC	C_s	11.91	24.29	19.9	4.21	11.72
P·U WC _f	C_s	9.88	19.53	18.17	3.22	11.74
2AP·T rWC	C_I	15.76	29.58	27.55	4.35	18.08
2AP·T WC	C_I	18.30	35.60	30.61	4.54	17.85
2AP·T rH	C_s	11.59	23.03	20.81	3.42	12.79
2AP·T H	C_s	10.13	20.39	19.36	3.30	12.39
2AP·C*	C_I	17.71	35.40	30.71	4.57	17.60
A· ⁵ MC*	C_s	19.67	38.74	33.2	4.58	18.72
A*· ⁵ MC	C_s	25.49	44.23	41.37	4.76	27.40
A· ⁵ MC	C_I	8.37	17.14	14.86	3.35	9.44
A·isoC*	C_s	19.30	37.64	32.31	4.52	18.49
A·isoC* rWC	C_s	16.83	32.79	29.74	4.39	18.17
A*·isoC	C_s	49.30	74.29	58.72	4.86	38.59
A·isoC	C_I	7.40	14.20	13.51	3.20	9.90
A*·isoC* rWC	C_s	45.12	69.32	55.25	4.22	35.27
A·6-azaC*	C_s	20.63	39.42	33.57	4.47	19.25
A·6-azaC	C_I	8.81	17.22	15.46	3.22	10.26

A*·6-azaC	C_s	25.55	43.33	40.2	4.47	26.90
8-aza-9-deazaA·C*	C_s	19.75	38.47	33.28	4.58	19.14
8-aza-9-deazaA*·C	C_s	23.05	40.17	37.51	4.68	25.07
8-aza-9-deazaA·C	C_I	6.18	12.18	11.03	3.09	8.13
8-aza-9-deazaA·U	C_I	19.74	37.22	32.18	4.47	19.17
7-dezaP·U	C_s	12.00	23.47	20.96	3.45	12.93
7-dezaP·U _f	C_s	11.51	22.46	20.22	3.33	12.60
A·X	C_s	19.28	36.56	31.53	4.43	18.68
A·8oxoA _{syn}	C_I	14.20	27.66	24.53	4.81	15.88
A·8oxoG _{syn}	C_s	18.17	33.30	29.95	4.36	19.18
8oxoA·T	C_I	18.22	35.12	30.72	4.45	18.27
3-deazaA·T	C_I	21.07	39.84	33.46	4.61	19.30
8-azaA·T	C_s	19.19	36.72	31.85	4.39	18.73

Notes: ^aThe energy of the orbital interaction, kcal/mol; ^bThe energy of the Pauli repulsion, kcal/mol; ^cThe electrostatic part of the interaction energy, kcal/mol; ^dThe dispersion component of the interaction energy, kcal/mol.

Table S12. The matrix of the linear correlation coefficients χ between all physico-chemical parameters that describe the CH $\cdots$ O H-bonds in the investigated pairs involving modified nucleobases. The values above and below the diagonal are obtained at the DFT and MP2 methods, respectively.

DFT															
MP2	χ	$d_{C\cdots O}$	$d_{H\cdots O}$	$\angle CH\cdots O$	Δd_{CH}	ρ	$\Delta\rho$	$E_{CH\cdots O}$	Δv	I_v/I_{v0}	$\Delta\gamma$	C_{ij}	$\Delta d_{H\cdots O}$	DI	$E^{(2)}$
	$d_{C\cdots O}$	1.000	0.974	-0.006	-0.657	-0.916	-0.936	-0.960	-0.488	-0.760	-0.800	0.356	-0.974	-	-0.933
	$d_{H\cdots O}$	0.963	1.000	-0.233	-0.665	-0.903	-0.915	-0.956	-0.488	-0.713	-0.801	0.436	-1.000	-	-0.938
	$\angle CH\cdots O$	0.318	0.049	1.000	0.118	0.059	0.024	0.099	0.062	-0.111	0.096	-0.392	0.233	-	0.141
	Δd_{CH}	-0.058	-0.110	0.201	1.000	0.684	0.691	0.720	0.962	0.817	0.716	-0.312	0.665	-	0.710
	ρ	-0.957	-0.966	-0.149	0.162	1.000	0.993	0.961	0.551	0.811	0.768	-0.285	0.903	-	0.957
	$\Delta\rho$	-0.979	-0.977	-0.191	0.150	0.985	1.000	0.969	0.555	0.830	0.778	-0.296	0.915	-	0.958
	$E_{CH\cdots O}$	-0.963	-0.966	-0.169	0.155	0.992	0.994	1.000	0.569	0.843	0.811	-0.292	0.956	-	0.992
	Δv	0.109	0.076	0.165	0.966	-0.015	-0.028	-0.024	1.000	0.770	0.525	-0.264	0.488	-	0.562
	I_v/I_{v0}	-0.789	-0.717	-0.398	0.353	0.809	0.831	0.841	0.239	1.000	0.702	-0.147	0.713	-	0.840
	$\Delta\gamma$	-0.786	-0.820	-0.031	0.152	0.811	0.831	0.835	-0.037	0.689	1.000	-0.325	0.801	-	0.802
	C_{ij}	0.386	0.509	-0.363	-0.065	-0.399	-0.416	-0.396	-0.015	-0.146	-0.370	1.000	-0.436	-	-0.272
	$\Delta d_{H\cdots O}$	-0.963	-1.000	-0.049	0.110	0.966	0.977	0.966	-0.076	0.717	0.820	-0.509	1.000	-	0.938
	DI	-0.920	-0.956	-0.046	0.167	0.963	0.970	0.972	-0.018	0.771	0.828	-0.446	0.956	1.000	-
	$\Delta r(H)+\Delta r(O)$	-0.541	-0.570	-0.013	0.032	0.558	0.555	0.549	-0.075	0.375	0.467	-0.263	0.570	0.546	-

Notes: see Tables S4-S9 in the present study.

Table S13. The matrix of the linear correlation coefficients χ between all physico-chemical parameters that describe the CH $\cdots$ O H-bonds in the investigated pairs containing canonical and modified nucleobases. The values above and below the diagonal are obtained at the DFT and MP2 methods, respectively.

DFT														
MP2	χ	$d_{C\cdots O}$	$d_{H\cdots O}$	$\angle CH\cdots O$	Δd_{CH}	ρ	$\Delta\rho$	$E_{CH\cdots O}$	Δv	I_v/I_{v0}	$\Delta\gamma$	C_{ij}	$\Delta d_{H\cdots O}$	$E^{(2)}$
	$d_{C\cdots O}$	1.000	0.923	-0.259	-0.489	-0.851	-0.909	-0.872	-0.410	-0.539	-0.760	0.298	-0.923	-0.722
	$d_{H\cdots O}$	0.892	1.000	-0.597	-0.687	-0.945	-0.952	-0.966	-0.623	-0.712	-0.800	0.321	-1.000	-0.893
	$\angle CH\cdots O$	-0.164	-0.578	1.000	0.770	0.624	0.517	0.632	0.780	0.722	0.469	-0.162	0.597	0.781
	Δd_{CH}	-0.314	-0.585	0.764	1.000	0.756	0.681	0.768	0.993	0.960	0.663	-0.178	0.687	0.886
	ρ	-0.832	-0.973	0.637	0.673	1.000	0.986	0.985	0.706	0.788	0.805	-0.214	0.945	0.944
	$\Delta\rho$	-0.916	-0.983	0.507	0.570	0.979	1.000	0.976	0.621	0.726	0.808	-0.236	0.952	0.896
	$E_{CH\cdots O}$	-0.834	-0.971	0.635	0.675	0.996	0.982	1.000	0.715	0.801	0.820	-0.219	0.966	0.955
	Δv	-0.272	-0.558	0.788	0.991	0.654	0.542	0.658	1.000	0.955	0.589	-0.144	0.623	0.859
	I_v/I_{v0}	-0.618	-0.785	0.657	0.622	0.829	0.798	0.840	0.606	1.000	0.671	-0.140	0.712	0.903
	$\Delta\gamma$	-0.669	-0.808	0.606	0.641	0.835	0.816	0.852	0.616	0.839	1.000	-0.278	0.800	0.775
	C_{ij}	0.314	0.346	-0.159	-0.097	-0.259	-0.296	-0.262	-0.090	-0.166	-0.285	1.000	-0.321	-0.187
	$\Delta d_{H\cdots O}$	-0.892	-1.000	0.578	0.585	0.973	0.983	0.971	0.558	0.785	0.808	-0.346	1.000	0.893
	$\Delta r(H)+\Delta r(O)$	-0.669	-0.752	0.436	0.446	0.742	0.746	0.735	0.422	0.561	0.610	-0.215	0.752	-

Notes: see Tables S4-S9 in the present study and Tables S4-S9 in our previous study [4].

Table S14. The matrix of the linear correlation coefficients χ between all physico-chemical parameters that describe the CH $\cdots$ N H-bonds in the investigated pairs of the canonical and modified nucleobases. The values above and below the diagonal are obtained at the DFT and MP2 methods, respectively.

DFT														
MP2	χ	$d_{C\cdots N}$	$d_{H\cdots N}$	$\angle CH\cdots N$	Δd_{CH}	ρ	$\Delta\rho$	$E_{CH\cdots N}$	Δv	I_v/I_{v0}	$\Delta\gamma$	C_{ij}	$\Delta d_{H\cdots N}$	$E^{(2)}$
	$d_{C\cdots N}$	1.000	0.746	0.061	-0.240	-0.772	-0.865	-0.692	-0.174	-0.204	-0.764	0.447	-0.746	-0.448
	$d_{H\cdots N}$	0.371	1.000	-0.603	-0.622	-0.980	-0.968	-0.940	-0.594	-0.559	-0.752	0.318	-1.000	-0.797
	$\angle CH\cdots N$	0.249	-0.773	1.000	0.736	0.540	0.423	0.595	0.773	0.726	0.258	0.010	0.603	0.697
	Δd_{CH}	-0.010	-0.650	0.771	1.000	0.596	0.531	0.618	0.995	0.955	0.630	-0.383	0.622	0.609
	ρ	-0.464	-0.970	0.717	0.706	1.000	0.979	0.921	0.566	0.525	0.804	-0.428	0.980	0.789
	$\Delta\rho$	-0.682	-0.915	0.487	0.470	0.921	1.000	0.896	0.490	0.470	0.833	-0.412	0.968	0.726
	$E_{CH\cdots N}$	-0.471	-0.983	0.717	0.680	0.989	0.946	1.000	0.588	0.568	0.723	-0.372	0.940	0.860
	Δv	-0.013	-0.615	0.759	0.990	0.682	0.445	0.655	1.000	0.961	0.569	-0.328	0.594	0.606
	I_v/I_{v0}	-0.302	-0.623	0.539	0.880	0.728	0.577	0.710	0.885	1.000	0.519	-0.331	0.559	0.629
	$\Delta\gamma$	-0.361	-0.887	0.620	0.636	0.879	0.831	0.885	0.553	0.612	1.000	-0.654	0.752	0.533
	C_{ij}	-0.217	0.399	-0.525	-0.547	-0.388	-0.229	-0.383	-0.462	-0.416	-0.589	1.000	-0.318	-0.441
	$\Delta d_{H\cdots N}$	-0.371	-1.000	0.773	0.650	0.970	0.915	0.983	0.615	0.623	0.887	-0.427	1.000	0.797
	$\Delta r(H)+\Delta r(N)$	-0.281	-0.963	0.766	0.602	0.902	0.867	0.926	0.566	0.570	0.833	-0.498	0.963	-

Notes: see Tables S4-S9 in the present study and Tables S4-S9 in our previous study [4].

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