Cooperative Nature of Hydrogen Bonds in AT and GC Watson-Crick DNA Base Pairs

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Supplementary Information

Part 1.

Supplementary Table S1 Optimized geometries for H-bonds in AT and GC pairs depicted in Fig.1.

Part 2.

Supplementary Figure S1 AT pairs with individual H-bonds: AT1 (containing H-bond A), AT2 (containing H-bond B), AT3 (containing H-bond C), and GC pairs with individual H-bonds: GC1 (containing H-bond D), GC2 (containing H-bond E), GC3 (containing H-bond F).

Part 3.

Supplementary Table S1 Atomic natural charge distribution (*e*) in A, C, T, G monomers, AT, GC conformers containing only one H-bond, and the AT, CG pairs.

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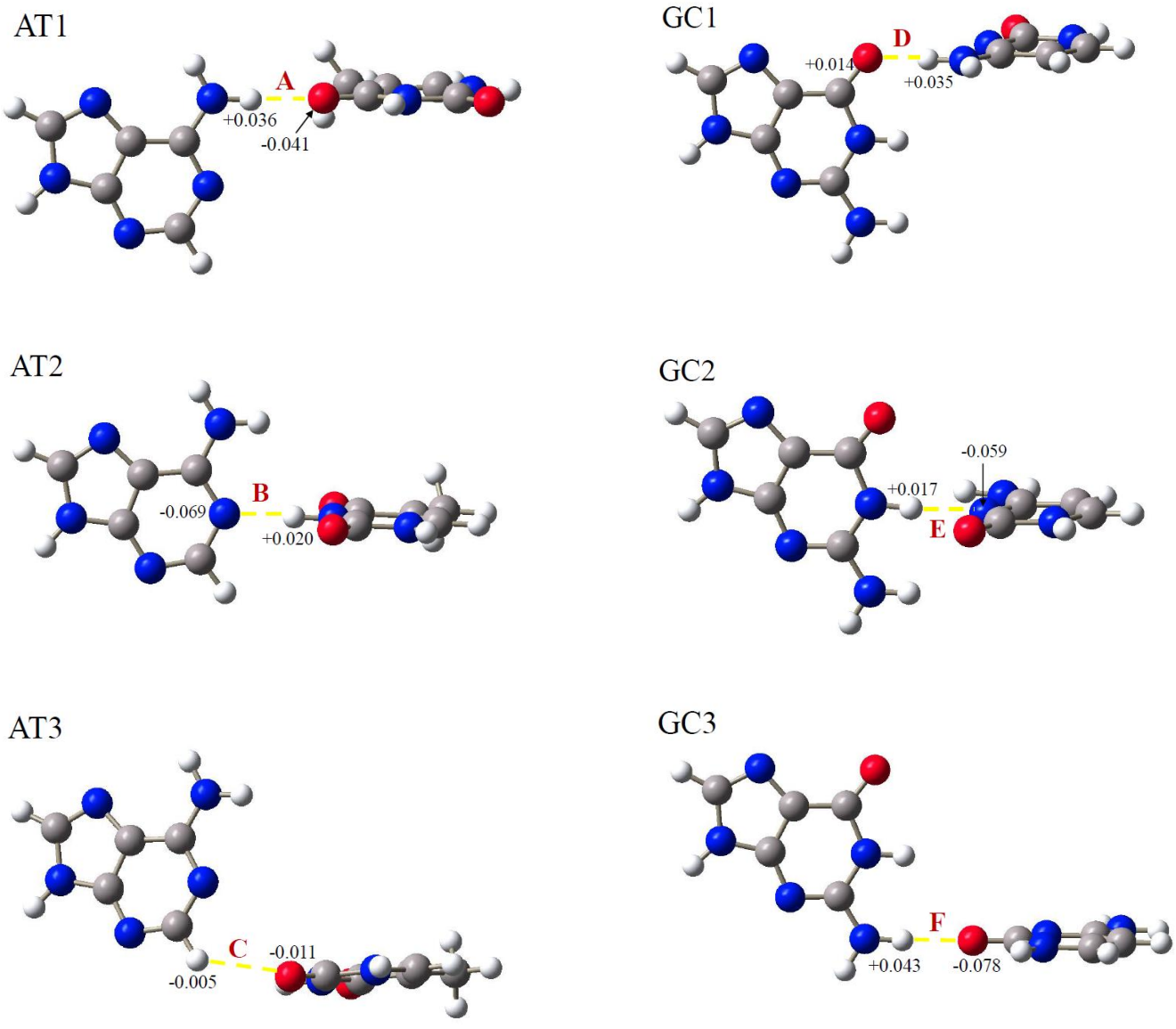
Part 1 Supplementary Table S1 Optimized geometries for H-bonds in AT and GC pairs depicted in Fig.1.

	Parameter	Bond length	Bond angles
AT pair	N6-H11 ··O6 (H-bond A)	1.9143	173.4
	N1 ··H8-N3 (H-bond B)	1.7754	179.8
	C2-H10 ··O2 (H-bond C)	2.7552	133.3
GC pair	O6 ·H8-N4 (H-bond D)	1.7450	178.8
	N1-H10 ··N3 (H-bond E)	1.8871	177.3
	N2-H11 ··O2 (H-bond F)	1.8876	178.1

Bond length in Å and bond angles in degrees.

Part 2. Supplementary Figure 1 AT pairs with individual H-bonds: AT1 (containing H-bond A), AT2 (containing H-bond B), AT3 (containing H-bond C), and GC pairs with individual H-bonds: GC1 (containing H-bond D), GC2 (containing H-bond E), GC3 (containing H-bond F). The corresponding H-bond labels are given in Figure 1. The geometries of these structures were optimized with the constraints that (i) the planes of the bases remain perpendicular to each other, (ii) the X-H ⋯Y angles and the lengths of H-bonds remain fixed. H-bonds are illustrated by yellow dashed lines, and the atomic charges changes (positive charge: *e*) on forming the individual H-bonds are also given.



Part 3. Supplementary Table S2 Atomic natural charge distribution (*e*) in A, C, T, G monomers, AT, GC conformers containing only one H-bond, and the AT, CG pairs. The corresponding atomic labels are given in Figure 1. Atoms directly involved in H-bonds and their atomic charges are marked in bold.

(a) 2Charge distribution (*e*) of AT pair.

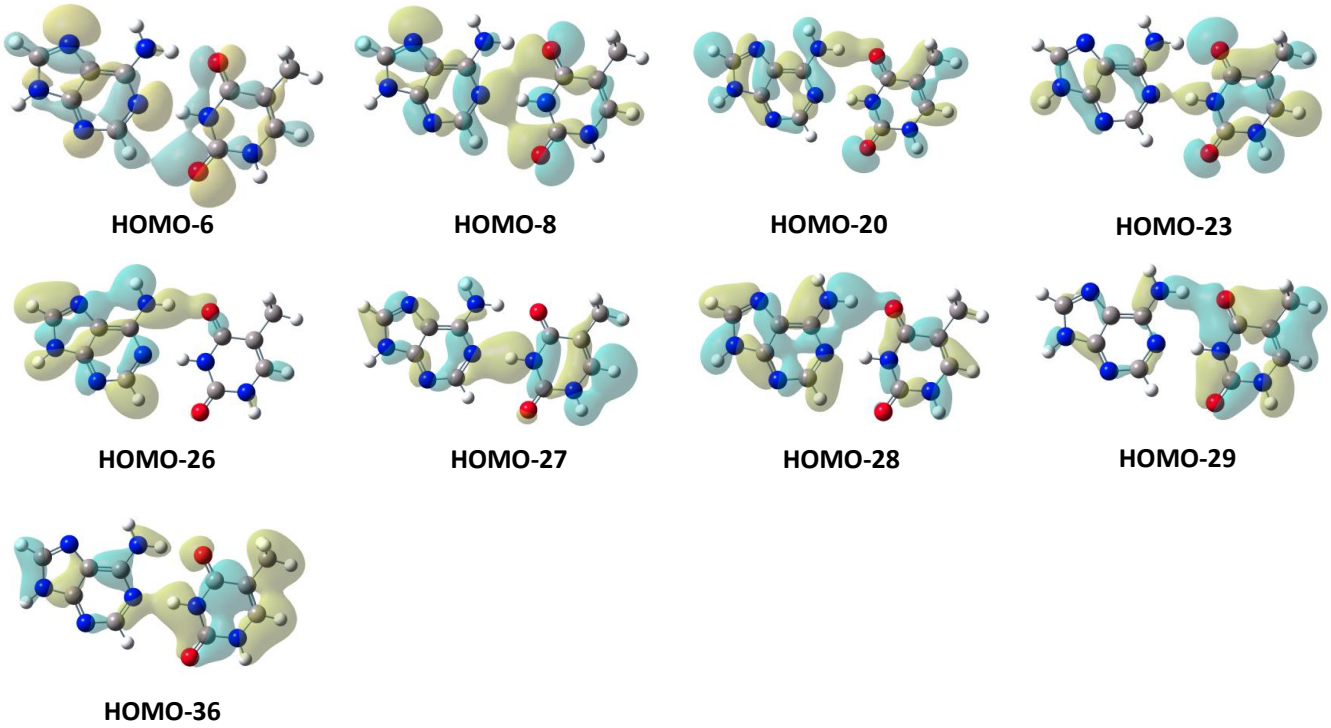
	A and T monomers	AT with H-bond **A**	AT with H-bond **B**	AT with H-bond **C**	AT pair with three H-bonds
N1	**-0.527**	-0.554	**-0.596**	-0.553	**-0.622**
C2	0.289	0.289	0.316	0.286	0.306
N3	-0.539	-0.546	-0.525	-0.536	-0.535
C4	0.403	0.358	0.366	0.362	0.337
C5	-0.019	-0.007	-0.001	-0.005	0.087
C6	0.419	0.427	0.446	0.422	0.411
N6	-0.794	-0.764	-0.748	-0.763	-0.759
N7	-0.499	-0.494	-0.488	-0.493	-0.511
C8	0.232	0.233	0.243	0.239	0.236
N9	-0.603	-0.560	-0.554	-0.558	-0.558
H10	**0.190**	0.169	0.179	**0.185**	**0.194**
H11	**0.400**	**0.436**	0.403	0.399	**0.439**
H12	0.404	0.394	0.407	0.403	0.401
H13	0.213	0.190	0.195	0.193	0.193
H14	0.431	0.415	0.419	0.417	0.417
Adenine	0	**-0.014**	**+0.062**	**-0.002**	**+0.036**
N1	-0.620	-0.602	-0.609	-0.602	-0.602
C2	0.811	0.804	0.804	0.806	0.807
O2	**--0.611**	-0.619	-0.638	**-0.622**	**-0.635**
N3	0.640	-0.630	-0.683	-0.634	-0.664
C4	0.628	0.669	0.647	0.649	0.661
C5	-0.207	-0.166	-0.166	-0.166	-0.166
C6	0.106	0.075	0.064	0.067	0.074
C	-0.567	-0.585	-0.583	-0.584	-0.583
O6	**-0.601**	**-0.642**	-0.612	-0.602	**-0.658**
H7	0.423	0.419	0.412	0.416	0.415
H8	**0.435**	0.425	**0.455**	0.422	**0.465**
H9	0.208	0.221	0.220	0.223	0.222
H10	0.199	0.204	0.199	0.201	0.201
H11	0.232	0.230	0.221	0.223	0.222
H12	0.204	0.209	0.203	0.206	0.206
Thymine	0	**0.014**	**-0.062**	**+0.002**	**-0.036**

(b) Charge distribution (*e*) of GC pair.

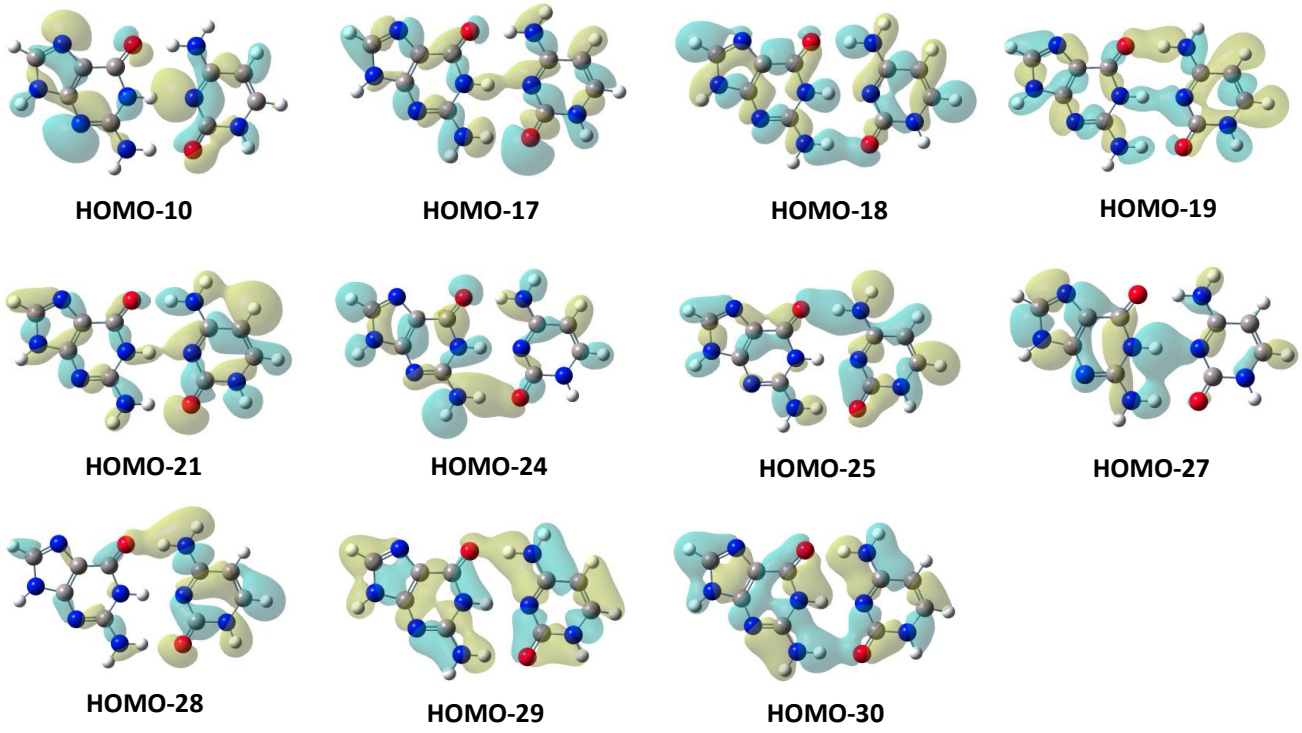
	G and C monomers	GC with H-bond **D**	GC with H-bond **E**	GC with H-bond **F**	GC pair with three H-bonds
N1	-0.599	-0.611	-0.664	-0.625	-0.645
C2	0.651	0.632	0.634	0.636	0.640
N2	-0.804	-0.783	-0.794	-0.791	-0.790
N3	-0.584	-0.587	-0.605	-0.606	-0.601
C4	0.411	0.365	0.357	0.361	0.372
C5	-0.043	-0.045	-0.053	-0.059	-0.057
C6	0.575	0.648	0.644	0.641	0.654
O6	**-0.651**	**-0.637**	-0.610	-0.619	**-0.682**
N7	-0.439	-0.440	-0.449	-0.449	-0.450
C8	0.208	0.221	0.206	0.206	0.212
H14	0.215	0.194	0.188	0.188	0.189
N9	-0.604	-0.555	-0.559	-0.560	-0.561
H13	0.431	0.415	0.410	0.411	0.412
H10	**0.427**	0.414	**0.444**	0.415	**0.448**
H11	**0.391**	0.400	0.399	**0.434**	**0.436**
H12	0.416	0.414	0.404	0.400	0.399
Guanine	0	**+0.045**	**-0.048**	**-0.017**	**-0.024**
N1	-0.598	-0.598	-0.591	-0.588	-0.592
C2	0.776	0.765	0.788	0.797	0.795
O2	**-0.630**	-0.653	-0.613	**-0.708**	**-0.688**
N3	**-0.595**	-0.599	**-0.654**	-0.587	**-0.657**
C4	0.443	0.441	0.465	0.449	0.468
N4	-0.761	-0.773	-0.749	-0.748	-0.737
C5	-0.372	-0.369	-0.368	-0.359	-0.351
C6	0.105	0.095	0.115	0.108	0.101
H7	0.412	0.411	0.417	0.416	0.416
H8	**0.406**	**0.441**	0.402	0.409	**0.449**
H9	0.388	0.376	0.494	0.392	0.385
H10	0.220	0.215	0.225	0.225	0.225
H11	0.206	0.203	0.211	0.212	0.210
Cytosine	0	**-0.045**	**+0.048**	**+0.017**	**+0.024**

Part 4. Supplementary Figure S2 MOs involved in intrermolecular interaction in AT and GC pairs. Isovalue: 0.02 a.u.

(a) MOs in AT pairs.



(b) MOs in GC pairs.



Part 5 Supplementary Table S3: Energies for H-Bonds in Base Pairs with the Basis Set Superposition Error (BSSE) correction.

	Parameter	Interaction Energy -BSSE corrected
AT pair	AT pair	-17.65
	AT1 (H-bond A)	-5.21
	AT2 (H-bond B)	-7.33
	AT3 (H-bond C)	-1.17
	Cooperativity	-3.94
GC pair	GC pair	-29.69
	GC1 (H-bond D)	-5.14
	GC2 (H-bond E)	-10.56
	GC3 (H-bond F)	-11.91
	Cooperativity	-2.08

The interaction energy (kcal/mol) followed by the energies of each H-bond individually and the cooperativity (total interaction less the sum of the individual bonds).

Here, we performed the interaction calculation with the BSSE correction. For the latest DFT calculation, it adds the dispersion correction into the functional. This factor results in a stronger attraction*, for which the interaction energy of AT pair is -17.65 kcal/mol and of GC is -29.69 kcal/mol.

*a) A. Asensio, N. Kobko, and J. J. Dannenberg, J. Phys. Chem. A, 2003, **107**, 6441;
b) J. Sponer, P. Jurecka, and P. Hobza, *J. Am. Chem. Soc.* 2004, **126**, 10142.

Part 6. Supplementary Figure S3: Calculated harmonic and anharmonic infrared spectra of (a) AT pair and (b) GC pair in the region 0-4000 cm^{-1}.