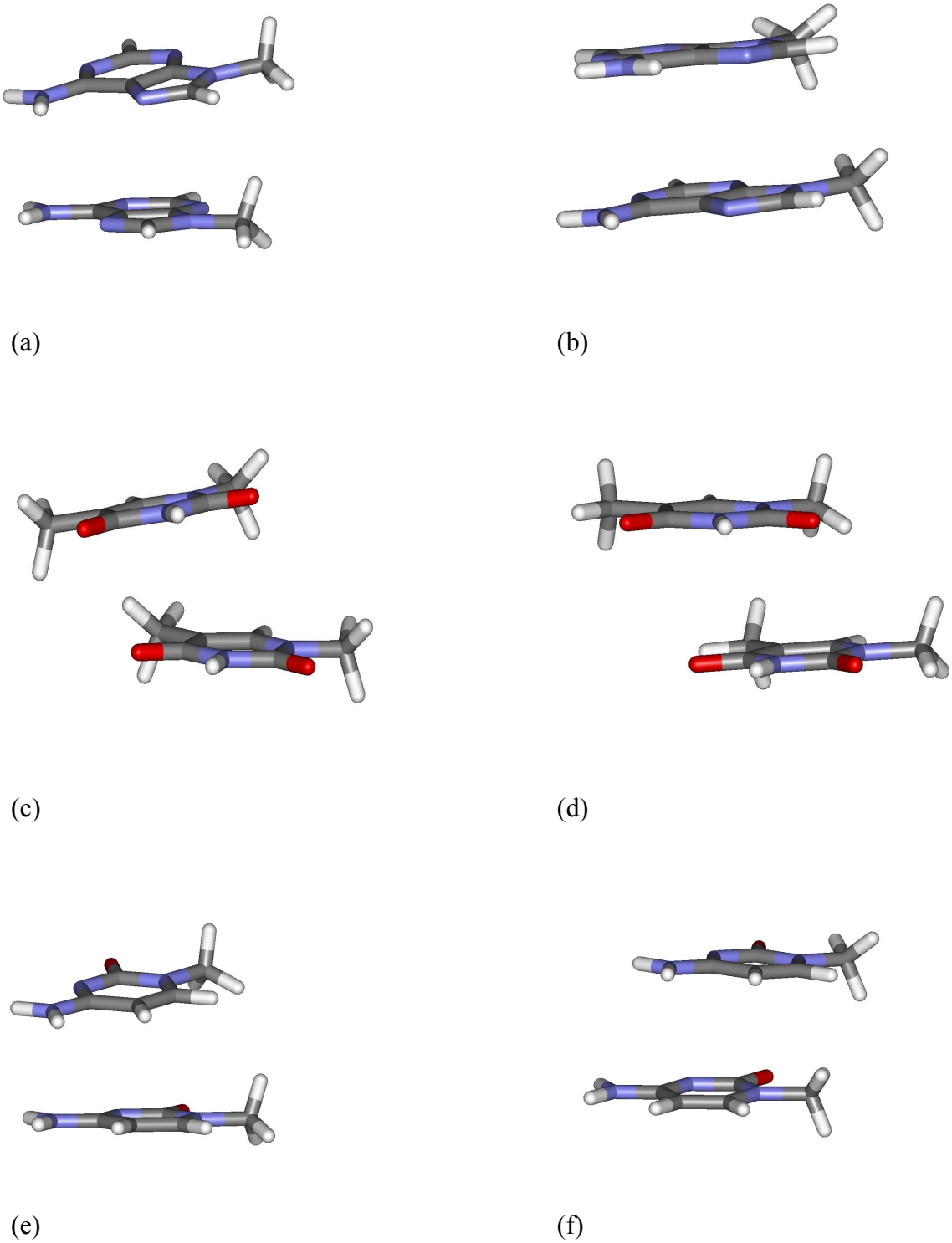
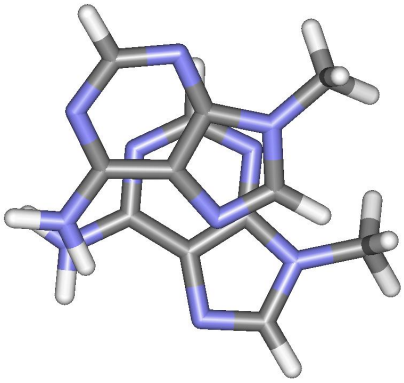
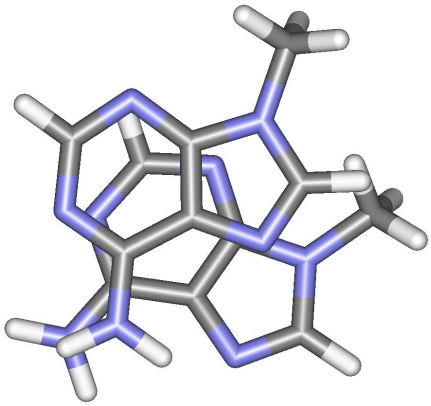


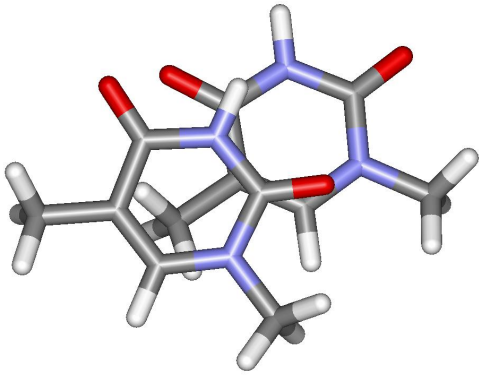
Fig.1 Side view of stacked DNA bases: A-A in A-DNA (a) and in B-DNA (b), T-T in A-DNA (c) and B-DNA (d), C-C in A-DNA (e) and B-DNA (f) conformation . C, O, N, and H atoms are in grey, red, blue, and white colors, respectively.



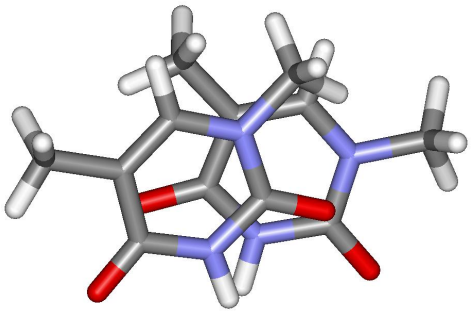
(a)



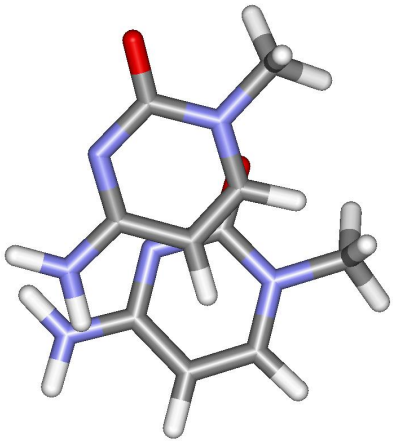
(b)



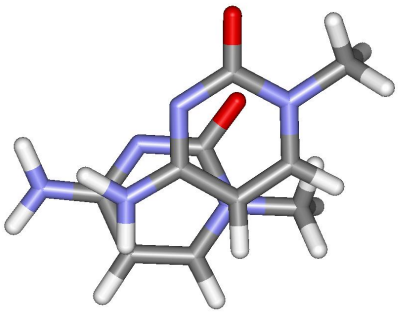
(c)



(d)

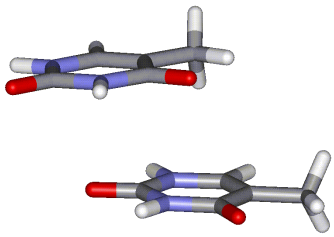


(e)

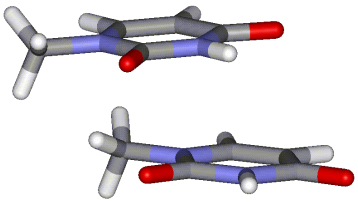


(f)

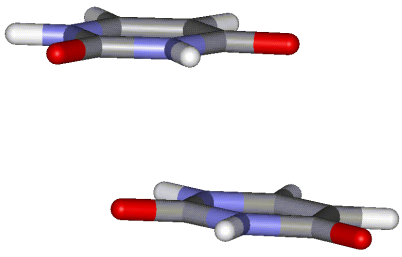
Fig.2 Top view of stacked DNA bases: A-A in A-DNA (a) and in B-DNA (b), T-T in A-DNA (c) and B-DNA (d), C-C in A-DNA (e) and B-DNA (f) conformation . C, O, N, and H atoms are in grey, red, blue, and white colors, respectively.



(a)



(b)



(c)

Fig.3 Structures of non-methylated T (a) methylated uracil (b), and non-methylated uracil (c) in B-DNA conformations. C, O, N, and H atoms are in grey, red, blue, and white colors, respectively.

Table S1. Excitation energies (in eV) and their splitting (ΔE) of model ethylene-dimer system in stacked conformation[a]

	SAC-CI[b] cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ
1^1B_2 ($\pi\rightarrow\pi^*$)	8.547 (8.608)	7.466 (7.520)	8.042	7.264 (7.334)
2^1B_2 ($\pi\rightarrow\pi^*$)	8.937 (8.988)	7.747 (7.808)	8.470	7.556 (7.604)
ΔE	0.390 (0.380)	0.281 (0.288)	0.428	0.292 (0.270)
	RI-CC2 cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ
1^1B_2 ($\pi\rightarrow\pi^*$)	8.515	7..748	8.074	7.547
2^1B_2 ($\pi\rightarrow\pi^*$)	8.911	7.773	8.516	7.815
ΔE	0.396	0.245	0.442	0.267
	CASPT2[c] cc-pVDZ	cc-pVTZ	MR-AQCC[d] cc-pVTZ	
1^1B_2 ($\pi\rightarrow\pi^*$)	8.152(8.103)	7.729(7.782)	8.275	
2^1B_2 ($\pi\rightarrow\pi^*$)	8.488(8.455)	8.142(8.167)	8.699	
ΔE	0.336(0.341)	0.413(0.384)	0.424	

[a] C_{2v} symmetry was used. Molecules were oriented in stacked conformation at the distance 3.4 Å. [b]Calculations with singles and doubles linked excitation operators. Calculations which include excitation operators through sextuples are given in parantheses. [c]Results obtained with the active space which includes 12 electrons (orbitals of a_1 and b_2 symmetry) and π^* (b_2 symmetry) virtual orbitals The results of calculations with 4 electrons in π orbitals (a_1 symmetry) in active space are given in parantheses. Inner shell orbitals were kept frozen. [d]The same active space as used for CASPT2 calculations.

Comapared to energy splitting obtained with cc-pVD(T)Z basis set, those obtained with augmented basis sets are systematically underestimated. The corresponding states have significant contribution of Rydberg-type states

Table S2. Excitation energies (in eV) end their splitting (ΔE) of model ethylene- acetylene system in stacked conformation[a]

	SAC-CI[b] cc-pVDZ	aug-cc-pVDZ	cc-pVTZ	aug-cc-pVTZ	RI-CC2 cc-pVDZ
$1^1A_2(\pi\rightarrow\pi^*)$	7.450(7.504)	6.892(6.901)	6.992	6.628(6.670)	7.559
$1^1B_2(\pi\rightarrow\pi^*)$	7.740(7.842)	7.023(7.073)	7.256	6.772(6.894)	7.807
$2^1A_2(\pi\rightarrow\pi^*)$	7.830(7.891)	7.192(7.217)	7.371	6.970(7.037)	7.946
$\Delta E(1A_2,1B_2)$	0.290(0.338)	0.132(0.172)	0.265	0.144(0.224)	0.248
$\Delta E(2A_2,1B_2)$	0.090(0.048)	0.169(0.144)	0.115	0.144(0.143)	0.139
	MR-AQCC[c] cc-pVDZ		cc-pVTZ		
$1^1A_2(\pi\rightarrow\pi^*)$	7.440		7.249		
$1^1B_2(\pi\rightarrow\pi^*)$	7.785		7.578		
$2^1A_2(\pi\rightarrow\pi^*)$	7.853				
$\Delta E(1A_2,1B_2)$	0.345		0.329		
$\Delta E(2A_2,1B_2)$	0.070				

[a]C_{2v} symmetry was used. Molecules were oriented in stack conformation at the distance 3.4 Å. [b]Calculations with singles and doubles linked excitation operators. Calculations which include excitation operators through sextuples are given in parantheses. [c]Active space includes occupied π (a_1 and b_1 symmetry) and virtual π^* (b_2 and a_2 symmetry) orbitals. Inner shell orbitals were kept frozen.

Different values of calculated energy splittings using cc-pVD(T)Z basis sets and corresponding augmented basis set result from significant contribution of Rydberg type character in the excited states of the latter.

A-A (A-DNA)

C	6.958000	-5.037000	2.040000
N	3.084000	-0.815000	0.130000
C	4.301000	-1.290000	0.430000
C	4.530000	-2.594000	0.910000
N	3.676000	-3.650000	1.190000
C	4.470000	-4.580000	1.610000
N	5.785000	-4.219000	1.620000
C	5.825000	-2.930000	1.170000
N	6.922000	-2.156000	1.020000
C	6.579000	-0.971000	0.560000
N	5.377000	-0.499000	0.260000
H	6.679000	-6.088000	1.967000
H	7.204000	-4.770000	3.068000
H	7.786000	-4.808000	1.370000
H	2.979000	0.149000	-0.218000
H	2.254000	-1.414000	0.247000
H	4.120000	-5.563000	1.927000
H	7.404000	-0.276000	0.403000
C	8.576000	-0.480000	4.600000
N	3.036000	0.980000	2.690000
C	4.316000	1.238000	2.990000
C	5.213000	0.264000	3.470000
N	5.065000	-1.086000	3.750000
C	6.236000	-1.439000	4.170000
N	7.147000	-0.425000	4.180000
C	6.485000	0.681000	3.730000
N	6.990000	1.925000	3.580000
C	6.061000	2.737000	3.120000
N	4.794000	2.485000	2.820000
H	8.910000	-1.515000	4.527000
H	8.640000	-0.122000	5.628000
H	9.150000	0.161000	3.930000
H	2.426000	1.734000	2.342000
H	2.661000	0.028000	2.807000
H	6.472000	-2.455000	4.487000
H	6.380000	3.767000	2.963000

A-A (B-DNA)

C	5.841000	0.470000	6.290000
N	4.615000	-0.371000	6.340000
C	4.519000	-1.735000	6.260000
N	3.298000	-2.174000	6.330000
C	2.540000	-1.026000	6.480000
C	1.152000	-0.813000	6.610000
N	0.255000	-1.812000	6.620000
N	0.730000	0.454000	6.730000
C	1.628000	1.435000	6.720000
N	2.936000	1.369000	6.600000
C	3.329000	0.087000	6.480000
H	5.526000	1.392000	6.779000
H	6.673000	0.008000	6.821000
H	6.164000	0.659000	5.266000
H	5.410000	-2.343000	6.198000
H	-0.728000	-1.603000	6.720000
H	0.565000	-2.773000	6.530000
H	1.303000	2.460000	6.821000
C	4.449000	3.814000	9.670000

N	3.952000	2.412000	9.720000
C	4.675000	1.253000	9.640000
N	3.946000	0.179000	9.710000
C	2.659000	0.663000	9.860000
C	1.410000	0.020000	9.990000
N	1.271000	-1.316000	10.000000
N	0.324000	0.797000	10.110000
C	0.473000	2.118000	10.100000
N	1.571000	2.834000	9.980000
C	2.642000	2.027000	9.860000
H	3.652000	4.374000	10.159000
H	5.394000	3.930000	10.201000
H	4.599000	4.157000	8.646000
H	5.753000	1.286000	9.578000
H	0.353000	-1.724000	10.100000
H	2.087000	-1.912000	9.910000
H	-0.392000	2.756000	10.201000

T-T (A-DNA)

C	3.134000	7.998000	0.520000
O	1.226000	3.064000	2.090000
C	1.598000	4.186000	1.730000
N	2.935000	4.520000	1.740000
C	3.486000	5.733000	1.360000
O	4.686000	5.933000	1.410000
N	2.589000	6.676000	0.940000
C	1.239000	6.432000	0.890000
C	0.738000	5.248000	1.260000
C	-0.728000	4.927000	1.230000
H	2.332000	8.732000	0.593000
H	3.485000	7.906000	-0.508000
H	3.955000	8.252000	1.190000
H	3.591000	3.795000	2.063000
H	0.565000	7.215000	0.543000
H	-1.304000	5.852000	1.226000
H	-0.956000	4.354000	0.331000
H	-0.990000	4.340000	2.111000
C	6.958000	5.037000	-2.040000
O	2.687000	1.916000	-0.470000
C	3.606000	2.659000	-0.830000
N	4.912000	2.218000	-0.820000
C	6.031000	2.941000	-1.200000
O	7.148000	2.461000	-1.150000
N	5.785000	4.219000	-1.620000
C	4.517000	4.743000	-1.670000
C	3.456000	4.018000	-1.300000
C	2.049000	4.539000	-1.330000
H	6.679000	6.088000	-1.967000
H	7.204000	4.770000	-3.068000
H	7.786000	4.808000	-1.370000
H	5.072000	1.253000	-0.497000
H	4.373000	5.766000	-2.017000
H	2.065000	5.629000	-1.334000
H	1.547000	4.180000	-2.229000
H	1.512000	4.187000	-0.449000

T-T (B-DNA)

C	4.330000	3.887000	44.048000
N	3.833000	2.485000	44.098000
C	4.704000	1.429000	43.998000
C	4.260000	0.157000	44.048000
C	5.167000	-1.031000	43.938000
C	2.854000	-0.130000	44.198000
O	2.364000	-1.264000	44.248000
N	2.057000	0.988000	44.288000
C	2.474000	2.303000	44.248000
O	1.690000	3.232000	44.338000
H	3.525000	4.450000	44.521000
H	5.266000	4.007000	44.594000
H	4.496000	4.224000	43.025000
H	5.766000	1.605000	43.909000
H	5.896000	-1.008000	44.748000
H	4.578000	-1.946000	44.006000
H	5.687000	-1.004000	42.980000
H	1.057000	0.887000	44.398000
C	1.239000	5.773000	47.428000
N	1.660000	4.347000	47.478000
C	2.986000	4.005000	47.378000
C	3.374000	2.715000	47.428000
C	4.806000	2.287000	47.318000
C	2.405000	1.657000	47.578000
O	2.676000	0.451000	47.628000
N	1.104000	2.092000	47.668000
C	0.668000	3.401000	47.628000
O	-0.512000	3.692000	47.718000
H	0.257000	5.756000	47.901000
H	1.927000	6.420000	47.973000
H	1.176000	6.143000	46.405000
H	3.742000	4.771000	47.289000
H	5.383000	2.734000	48.128000
H	4.867000	1.201000	47.386000
H	5.211000	2.614000	46.360000
H	0.354000	1.423000	47.778000

C-C (A-DNA)

C	3.134000	7.998000	0.520000
N	1.279000	3.042000	2.100000
C	1.697000	4.244000	1.720000
N	3.017000	4.491000	1.760000
C	3.486000	5.710000	1.370000
O	4.696000	5.989000	1.390000
N	2.589000	6.676000	0.940000
C	1.250000	6.429000	0.900000
C	0.753000	5.226000	1.270000
H	2.332000	8.732000	0.593000
H	3.485000	7.906000	-0.508000
H	3.955000	8.252000	1.190000
H	0.274000	2.817000	2.082000
H	1.960000	2.335000	2.412000
H	0.569000	7.212000	0.565000
H	-0.315000	5.013000	1.228000
C	6.958000	5.037000	-2.040000
N	2.720000	1.869000	-0.460000
C	3.721000	2.654000	-0.840000
N	4.965000	2.149000	-0.800000
C	6.018000	2.922000	-1.190000

O	7.187000	2.503000	-1.170000
N	5.785000	4.219000	-1.620000
C	4.525000	4.735000	-1.660000
C	3.457000	3.991000	-1.290000
H	6.679000	6.088000	-1.967000
H	7.204000	4.770000	-3.068000
H	7.786000	4.808000	-1.370000
H	1.753000	2.223000	-0.478000
H	2.911000	0.906000	-0.148000
H	4.375000	5.761000	-1.995000
H	2.443000	4.389000	-1.332000

C-C (B-DNA)

C	-5.841000	-0.470000	23.190000
N	-4.615000	0.371000	23.240000
C	-4.683000	1.723000	23.140000
C	-3.563000	2.495000	23.190000
C	-2.317000	1.810000	23.340000
N	-1.184000	2.493000	23.390000
N	-2.260000	0.476000	23.440000
C	-3.389000	-0.273000	23.390000
O	-3.368000	-1.507000	23.480000
H	-5.519000	-1.420000	23.617000
H	-6.652000	-0.035000	23.774000
H	-6.197000	-0.602000	22.168000
H	-5.644000	2.201000	23.018000
H	-3.641000	3.580000	23.122000
H	-0.305000	2.007000	23.500000
H	-1.198000	3.501000	23.320000
C	-4.449000	-3.814000	26.570000
N	-3.952000	-2.412000	26.620000
C	-4.801000	-1.359000	26.520000
C	-4.349000	-0.076000	26.570000
C	-2.938000	0.103000	26.720000
N	-2.423000	1.321000	26.770000
N	-2.109000	-0.943000	26.820000
C	-2.582000	-2.213000	26.770000
O	-1.839000	-3.199000	26.860000
H	-3.630000	-4.393000	26.997000
H	-5.361000	-3.939000	27.154000
H	-4.659000	-4.130000	25.548000
H	-5.859000	-1.537000	26.398000
H	-5.051000	0.755000	26.503000
H	-1.427000	1.444000	26.880000
H	-3.027000	2.128000	26.700000