Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

ELECTRONIC SUPPLEMENTARY INFORMATION FOR

π-Cooperativity Effect on the Base Stacking Interactions in DNA: Is There a Novel Stabilization Factor Coupled with Base Pairing H-Bonds?

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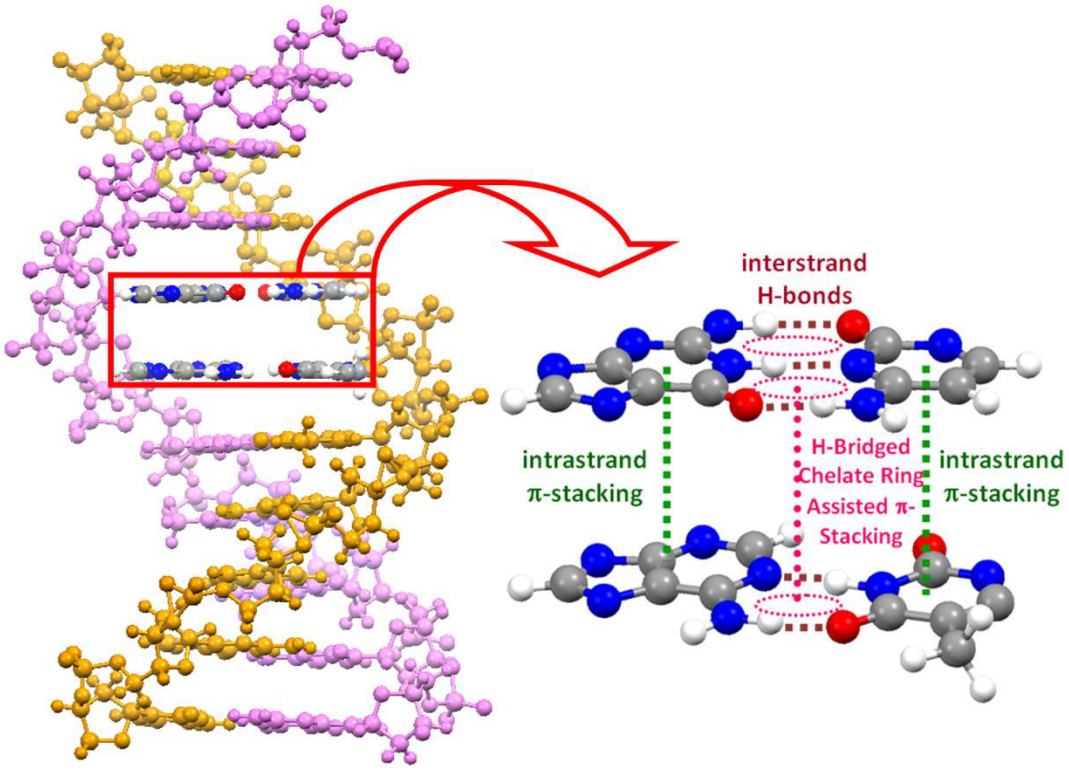
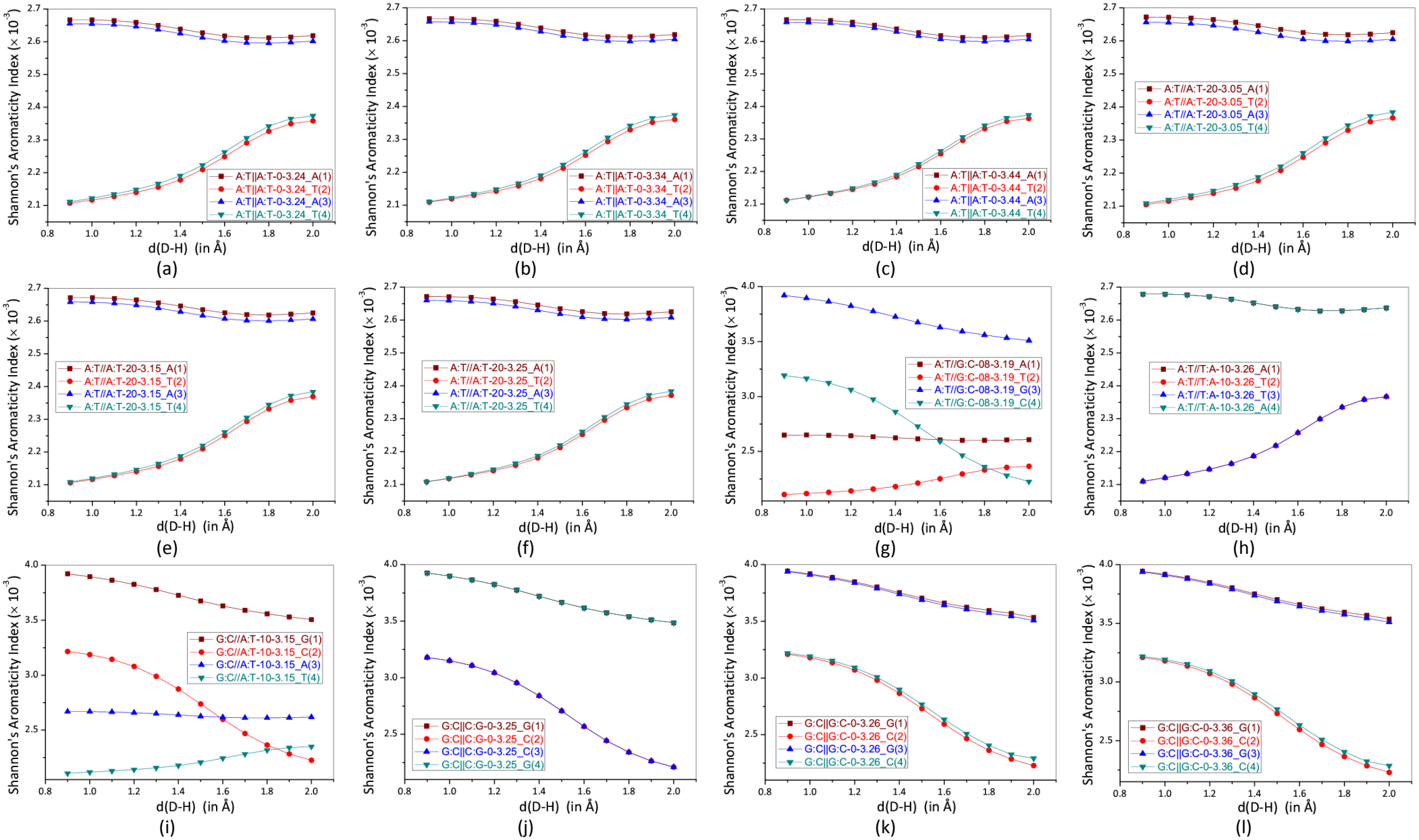
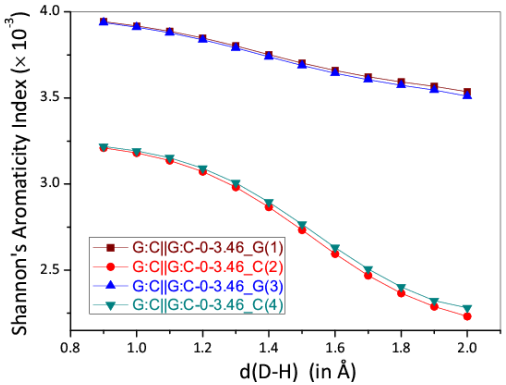


Figure S1. Variations of local aromaticity of nucleobases against H atom movements through RAHBs in the considered dinucleotide steps.





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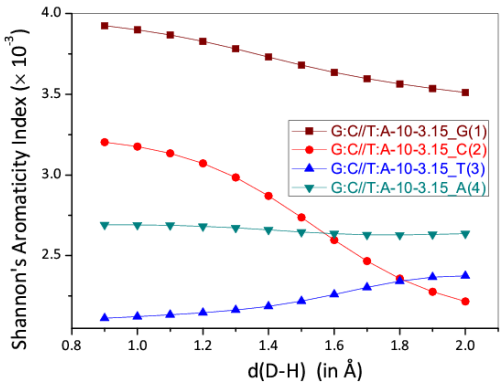

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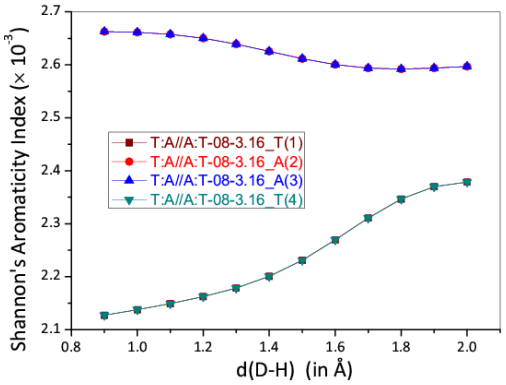

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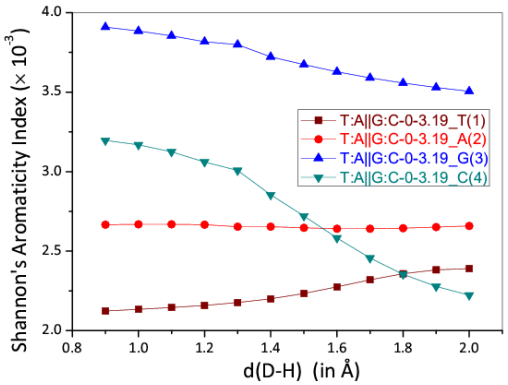

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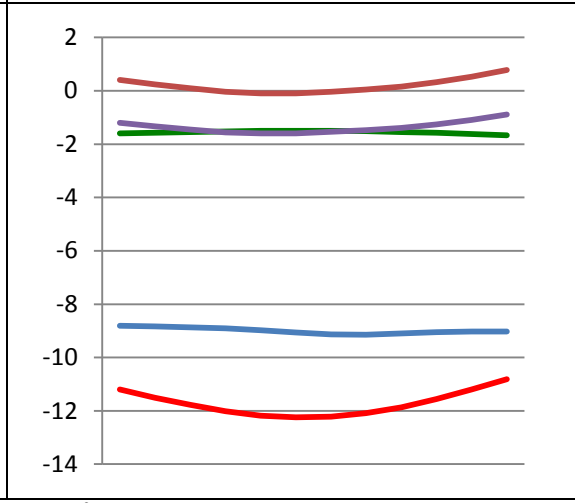
Table S1. A:T||A:T-0-3.24 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	%GD	FRZ*	%FRZ*	POL	%POL	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-1.196	*10.68*	0.404	*-3.60*	-1.599	*14.28*	-8.808	*78.65*	-11.200	1.999	1.474
1.0	-1.333	*11.59*	0.243	*-2.11*	-1.576	*13.70*	-8.838	*76.82*	-11.505	2.026	1.481
1.1	-1.458	*12.38*	0.091	*-0.78*	-1.549	*13.15*	-8.864	*75.25*	-11.780	2.052	1.488
1.2	-1.558	*12.97*	-0.034	*0.28*	-1.524	*12.68*	-8.902	*74.07*	-12.019	2.081	1.496
1.3	-1.602	*13.15*	-0.096	*0.78*	-1.506	*12.37*	-8.976	*73.70*	-12.179	2.112	1.500
1.4	-1.592	*13.00*	-0.095	*0.78*	-1.496	*12.22*	-9.062	*74.00*	-12.246	2.145	1.497
1.5	-1.540	*12.60*	-0.038	*0.31*	-1.502	*12.29*	-9.137	*74.79*	-12.217	2.187	1.493
1.6	-1.472	*12.17*	0.043	*-0.36*	-1.515	*12.53*	-9.149	*75.66*	-12.092	2.233	1.484
1.7	-1.389	*11.70*	0.154	*-1.29*	-1.543	*12.99*	-9.097	*76.60*	-11.875	2.273	1.469
1.8	-1.254	*10.85*	0.323	*-2.80*	-1.578	*13.65*	-9.050	*78.30*	-11.559	2.307	1.456
1.9	-1.089	*9.72*	0.534	*-4.77*	-1.622	*14.48*	-9.020	*80.56*	-11.197	2.331	1.441
2.0	-0.892	*8.25*	0.777	*-7.18*	-1.668	*15.43*	-9.030	*83.50*	-10.814	2.341	1.427



* Positive values of FRZ component are due to predominance of the repulsive exchange interactions appearing at small rise parameters below 3.3 Å with zero twist angle. FRZ term includes two nonseparable contributions: permanent electrostatics interactions and Pauli repulsions as in ref (56).

Table S2. A:T||A:T-0-3.34 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-2.923	*23.79*	-1.515	*12.33*	-1.407	*11.45*	-6.442	*52.43*	-12.287	1.504	1.138
1.0	-3.056	*24.33*	-1.670	*13.29*	-1.386	*11.03*	-6.451	*51.35*	-12.564	1.522	1.146
1.1	-3.193	*24.87*	-1.829	*14.25*	-1.364	*10.62*	-6.453	*50.26*	-12.838	1.541	1.152
1.2	-3.308	*25.28*	-1.965	*15.02*	-1.343	*10.27*	-6.467	*49.43*	-13.082	1.563	1.158
1.3	-3.360	*25.38*	-2.033	*15.35*	-1.328	*10.03*	-6.520	*49.24*	-13.241	1.585	1.162
1.4	-3.354	*25.21*	-2.036	*15.30*	-1.318	*9.90*	-6.597	*49.58*	-13.306	1.613	1.163
1.5	-3.305	*24.89*	-1.985	*14.95*	-1.320	*9.94*	-6.668	*50.22*	-13.279	1.648	1.163
1.6	-3.246	*24.64*	-1.914	*14.53*	-1.332	*10.11*	-6.681	*50.72*	-13.172	1.683	1.159
1.7	-3.165	*24.40*	-1.810	*13.95*	-1.355	*10.45*	-6.641	*51.20*	-12.971	1.710	1.148
1.8	-3.045	*24.00*	-1.660	*13.08*	-1.385	*10.92*	-6.595	*51.99*	-12.686	1.727	1.134
1.9	-2.889	*23.38*	-1.467	*11.87*	-1.422	*11.51*	-6.579	*53.24*	-12.357	1.745	1.124
2.0	-2.698	*22.49*	-1.234	*10.28*	-1.464	*12.20*	-6.602	*55.03*	-11.998	1.764	1.114

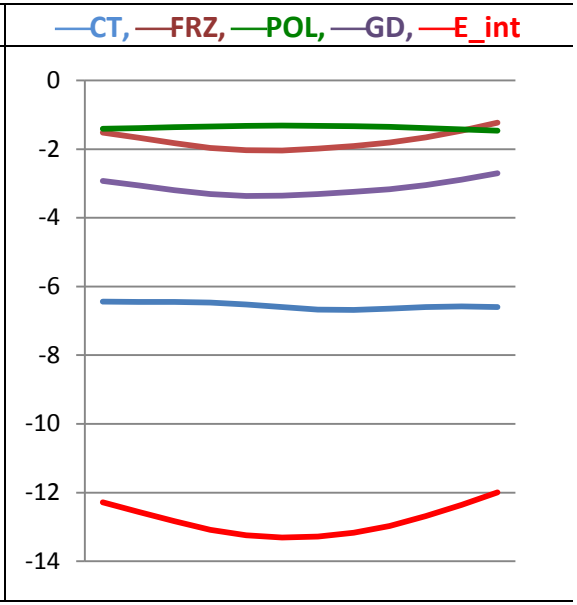


Table S3. A:T||A:T-0-3.44 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-4.302	*33.58*	-3.061	*23.90*	-1.240	*9.68*	-4.208	*32.85*	-12.812	1.125	0.865
1.0	-4.428	*33.89*	-3.205	*24.53*	-1.223	*9.36*	-4.210	*32.22*	-13.066	1.138	0.873
1.1	-4.544	*34.17*	-3.342	*25.13*	-1.202	*9.04*	-4.212	*31.67*	-13.300	1.153	0.881
1.2	-4.633	*34.34*	-3.454	*25.60*	-1.179	*8.74*	-4.225	*31.32*	-13.491	1.177	0.900
1.3	-4.692	*34.43*	-3.522	*25.85*	-1.170	*8.58*	-4.243	*31.14*	-13.627	1.186	0.892
1.4	-4.701	*34.34*	-3.539	*25.86*	-1.162	*8.49*	-4.286	*31.31*	-13.688	1.212	0.896
1.5	-4.667	*34.15*	-3.505	*25.65*	-1.162	*8.50*	-4.333	*31.70*	-13.667	1.239	0.898
1.6	-4.614	*33.99*	-3.443	*25.36*	-1.172	*8.63*	-4.347	*32.02*	-13.576	1.261	0.895
1.7	-4.517	*33.74*	-3.328	*24.86*	-1.189	*8.88*	-4.352	*32.51*	-13.387	1.278	0.887
1.8	-4.383	*33.41*	-3.169	*24.15*	-1.214	*9.26*	-4.354	*33.18*	-13.121	1.294	0.878
1.9	-4.224	*32.99*	-2.979	*23.26*	-1.245	*9.72*	-4.357	*34.02*	-12.805	1.309	0.869
2.0	-4.053	*32.51*	-2.773	*22.25*	-1.280	*10.27*	-4.360	*34.98*	-12.466	1.319	0.857

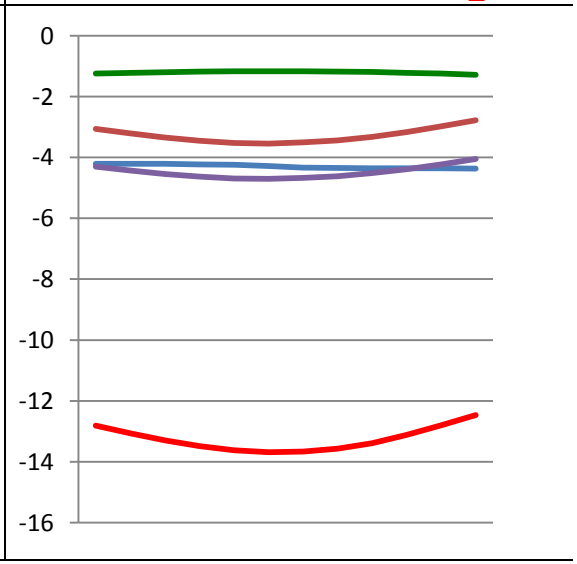


Table S4. A:T||A:T-20-3.05 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-2.744	*19.72*	-0.945	6.79	-1.799	*12.93*	-8.43	*60.56*	-13.913	1.546	1.846
1.0	-2.943	*20.38*	-1.157	8.01	-1.786	*12.37*	-8.55	*59.24*	-14.440	1.613	1.867
1.1	-3.144	*20.95*	-1.366	9.10	-1.778	*11.85*	-8.72	*58.09*	-15.005	1.707	1.897
1.2	-3.325	*21.41*	-1.548	9.97	-1.777	*11.44*	-8.88	*57.19*	-15.535	1.824	1.927
1.3	-3.476	*21.74*	-1.689	10.56	-1.787	*11.18*	-9.04	*56.51*	-15.989	1.951	1.954
1.4	-3.554	*21.81*	-1.746	10.72	-1.808	*11.09*	-9.19	*56.38*	-16.296	2.086	1.971
1.5	-3.584	*21.74*	-1.747	10.59	-1.838	*11.15*	-9.32	*56.52*	-16.489	2.225	1.982
1.6	-3.603	*21.71*	-1.725	10.40	-1.878	*11.32*	-9.39	*56.57*	-16.593	2.350	1.983
1.7	-3.559	*21.52*	-1.629	9.85	-1.930	*11.67*	-9.42	*56.97*	-16.543	2.448	1.975
1.8	-3.452	*21.12*	-1.467	8.97	-1.985	*12.14*	-9.44	*57.77*	-16.349	2.508	1.963
1.9	-3.335	*20.75*	-1.296	8.06	-2.039	*12.69*	-9.40	*58.49*	-16.069	2.510	1.952
2.0	-3.207	*20.40*	-1.119	7.12	-2.087	*13.28*	-9.30	*59.20*	-15.718	2.468	1.941

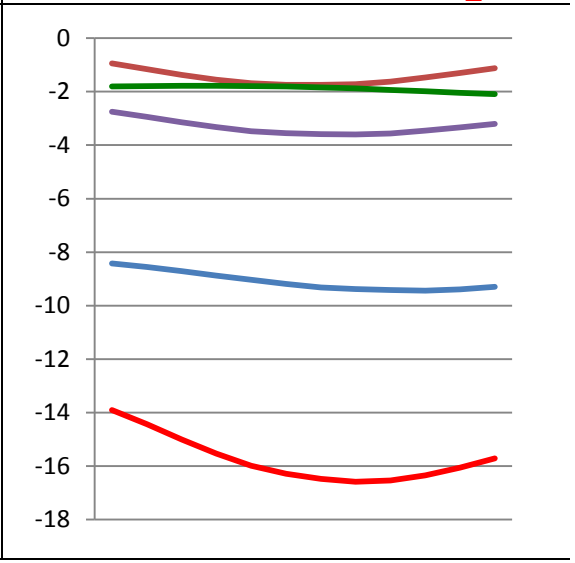


Table S5. A:T||A:T-20-3.15 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-4.420	*29.72*	-2.852	*19.18*	-1.568	*10.55*	-6.032	*40.56*	-14.872	1.158	1.424
1.0	-4.598	*29.93*	-3.038	*19.78*	-1.560	*10.16*	-6.164	*40.13*	-15.361	1.221	1.447
1.1	-4.789	*30.14*	-3.236	*20.37*	-1.553	*9.77*	-6.312	*39.72*	-15.890	1.301	1.468
1.2	-4.974	*30.33*	-3.423	*20.88*	-1.551	*9.46*	-6.450	*39.34*	-16.397	1.399	1.489
1.3	-5.131	*30.49*	-3.572	*21.23*	-1.558	*9.26*	-6.565	*39.02*	-16.827	1.505	1.509
1.4	-5.245	*30.56*	-3.670	*21.39*	-1.574	*9.17*	-6.672	*38.88*	-17.162	1.616	1.521
1.5	-5.309	*30.55*	-3.704	*21.31*	-1.605	*9.24*	-6.762	*38.91*	-17.379	1.736	1.526
1.6	-5.326	*30.50*	-3.683	*21.09*	-1.643	*9.41*	-6.812	*39.00*	-17.465	1.845	1.526
1.7	-5.293	*30.37*	-3.607	*20.70*	-1.686	*9.68*	-6.841	*39.26*	-17.426	1.921	1.517
1.8	-5.200	*30.13*	-3.471	*20.11*	-1.729	*10.02*	-6.860	*39.75*	-17.260	1.974	1.502
1.9	-5.085	*29.90*	-3.316	*19.50*	-1.769	*10.40*	-6.835	*40.19*	-17.006	1.980	1.484
2.0	-4.959	*29.69*	-3.146	*18.84*	-1.813	*10.85*	-6.782	*40.61*	-16.699	1.946	1.471

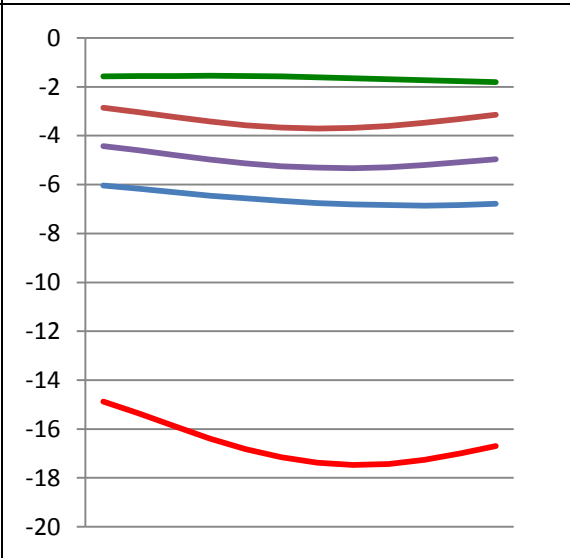


Table S6. A:T||A:T-20-3.25 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-5.182	*35.59*	-3.842	*26.39*	-1.340	*9.20*	-4.196	*28.82*	-14.561	0.850	1.090
1.0	-5.367	*35.68*	-4.035	*26.82*	-1.333	*8.86*	-4.307	*28.63*	-15.042	0.904	1.107
1.1	-5.550	*35.77*	-4.224	*27.22*	-1.326	*8.55*	-4.417	*28.46*	-15.517	0.974	1.125
1.2	-5.739	*35.89*	-4.413	*27.60*	-1.326	*8.29*	-4.512	*28.22*	-15.989	1.052	1.143
1.3	-5.917	*36.02*	-4.583	*27.90*	-1.334	*8.12*	-4.593	*27.96*	-16.427	1.139	1.158
1.4	-6.050	*36.09*	-4.700	*28.03*	-1.351	*8.06*	-4.663	*27.82*	-16.763	1.235	1.168
1.5	-6.127	*36.09*	-4.752	*27.99*	-1.376	*8.10*	-4.721	*27.81*	-16.975	1.335	1.171
1.6	-6.157	*36.07*	-4.751	*27.83*	-1.406	*8.24*	-4.756	*27.86*	-17.070	1.423	1.164
1.7	-6.112	*35.93*	-4.669	*27.44*	-1.444	*8.49*	-4.789	*28.15*	-17.014	1.491	1.150
1.8	-6.031	*35.75*	-4.547	*26.96*	-1.483	*8.79*	-4.807	*28.50*	-16.869	1.540	1.137
1.9	-5.939	*35.61*	-4.419	*26.50*	-1.520	*9.12*	-4.798	*28.77*	-16.675	1.549	1.124
2.0	-5.814	*35.43*	-4.262	*25.97*	-1.552	*9.46*	-4.782	*29.14*	-16.410	1.527	1.107

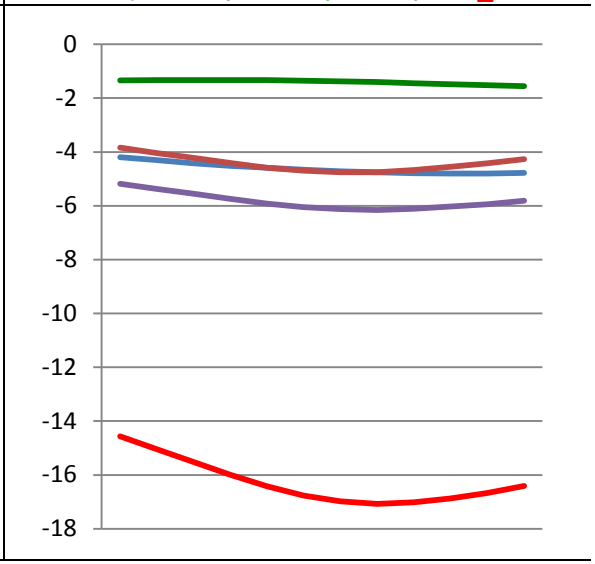


Table S7. A:T//G:C-08-3.19 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-3.739	*28.82*	-2.103	*16.21*	-1.636	*12.61*	-5.496	*42.36*	-12.974	1.142	1.245
1.0	-3.746	*28.76*	-2.119	*16.27*	-1.627	*12.49*	-5.535	*42.49*	-13.026	1.136	1.262
1.1	-3.736	*28.63*	-2.114	*16.20*	-1.622	*12.43*	-5.578	*42.75*	-13.050	1.127	1.279
1.2	-3.739	*28.57*	-2.116	*16.16*	-1.623	*12.40*	-5.611	*42.87*	-13.089	1.116	1.299
1.3	-3.726	*28.46*	-2.099	*16.03*	-1.628	*12.43*	-5.640	*43.08*	-13.093	1.104	1.315
1.4	-3.676	*28.24*	-2.039	*15.66*	-1.637	*12.58*	-5.664	*43.52*	-13.016	1.089	1.328
1.5	-3.597	*28.00*	-1.940	*15.10*	-1.657	*12.90*	-5.654	*44.01*	-12.848	1.070	1.332
1.6	-3.475	*27.63*	-1.795	*14.27*	-1.680	*13.36*	-5.627	*44.74*	-12.577	1.049	1.325
1.7	-3.293	*27.04*	-1.588	*13.04*	-1.705	*14.00*	-5.591	*45.92*	-12.176	1.025	1.309
1.8	-3.081	*26.34*	-1.353	*11.57*	-1.728	*14.77*	-5.536	*47.32*	-11.699	1.001	1.283
1.9	-2.836	*25.46*	-1.086	*9.75*	-1.751	*15.72*	-5.467	*49.08*	-11.140	0.975	1.243
2.0	-2.539	*24.24*	-0.775	*7.40*	-1.764	*16.84*	-5.396	*51.52*	-10.474	0.946	1.195

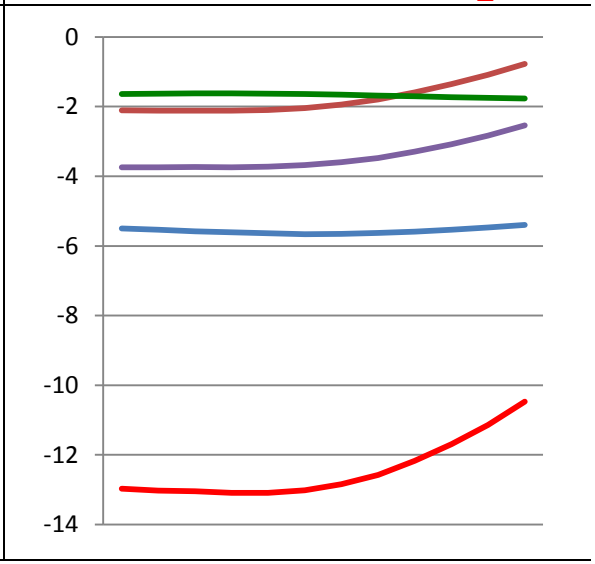


Table S8. A:T//T:A-10-3.26 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-2.788	*22.67*	-1.196	*9.73*	-1.592	*12.94*	-6.725	*54.67*	-12.301	1.471	1.471
1.0	-2.721	*22.30*	-1.146	*9.39*	-1.575	*12.90*	-6.761	*55.40*	-12.203	1.475	1.475
1.1	-2.592	*21.59*	-1.036	*8.63*	-1.556	*12.96*	-6.823	*56.82*	-12.008	1.483	1.483
1.2	-2.427	*20.66*	-0.886	*7.54*	-1.541	*13.11*	-6.894	*58.68*	-11.748	1.499	1.499
1.3	-2.259	*19.71*	-0.728	*6.36*	-1.530	*13.35*	-6.943	*60.58*	-11.460	1.511	1.511
1.4	-2.137	*19.01*	-0.603	*5.36*	-1.534	*13.65*	-6.966	*61.97*	-11.240	1.524	1.524
1.5	-2.071	*18.62*	-0.517	*4.65*	-1.553	*13.97*	-6.978	*62.75*	-11.119	1.545	1.545
1.6	-2.031	*18.36*	-0.432	*3.90*	-1.599	*14.45*	-7.000	*63.28*	-11.061	1.563	1.563
1.7	-2.010	*18.16*	-0.357	*3.23*	-1.653	*14.93*	-7.052	*63.69*	-11.073	1.576	1.575
1.8	-2.046	*18.33*	-0.332	*2.98*	-1.714	*15.35*	-7.070	*63.34*	-11.162	1.582	1.582
1.9	-2.110	*18.72*	-0.329	*2.92*	-1.781	*15.81*	-7.050	*62.56*	-11.271	1.573	1.573
2.0	-2.162	*19.03*	-0.305	*2.69*	-1.857	*16.35*	-7.035	*61.93*	-11.359	1.555	1.555

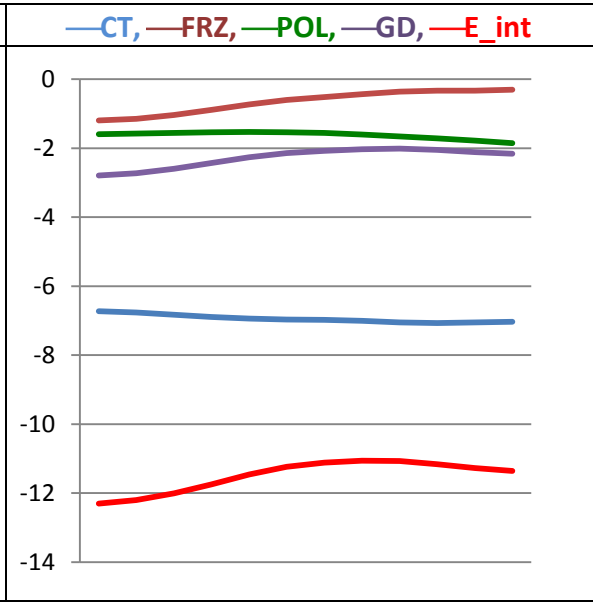


Table S9. G:C//A:T-10-3.15 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-2.198	*19.58*	-0.477	*4.25*	-1.721	*15.33*	-6.829	*60.84*	-11.224	1.359	0.854
1.0	-2.439	*20.70*	-0.738	*6.27*	-1.701	*14.43*	-6.905	*58.60*	-11.783	1.396	0.874
1.1	-2.689	*21.74*	-1.014	*8.20*	-1.675	*13.54*	-6.988	*56.51*	-12.365	1.437	0.899
1.2	-2.949	*22.76*	-1.296	*10.00*	-1.653	*12.76*	-7.061	*54.49*	-12.959	1.473	0.927
1.3	-3.192	*23.60*	-1.560	*11.54*	-1.632	*12.07*	-7.139	*52.79*	-13.523	1.505	0.959
1.4	-3.439	*24.37*	-1.822	*12.91*	-1.617	*11.46*	-7.232	*51.26*	-14.109	1.538	0.998
1.5	-3.685	*25.08*	-2.079	*14.16*	-1.606	*10.93*	-7.320	*49.83*	-14.690	1.564	1.038
1.6	-3.918	*25.73*	-2.316	*15.21*	-1.603	*10.52*	-7.393	*48.54*	-15.229	1.574	1.075
1.7	-4.111	*26.24*	-2.507	*16.00*	-1.604	*10.24*	-7.445	*47.52*	-15.667	1.566	1.109
1.8	-4.253	*26.62*	-2.646	*16.56*	-1.608	*10.06*	-7.474	*46.77*	-15.981	1.550	1.144
1.9	-4.330	*26.81*	-2.715	*16.81*	-1.616	*10.00*	-7.489	*46.37*	-16.150	1.526	1.175
2.0	-4.362	*26.91*	-2.734	*16.87*	-1.628	*10.05*	-7.484	*46.17*	-16.208	1.500	1.200

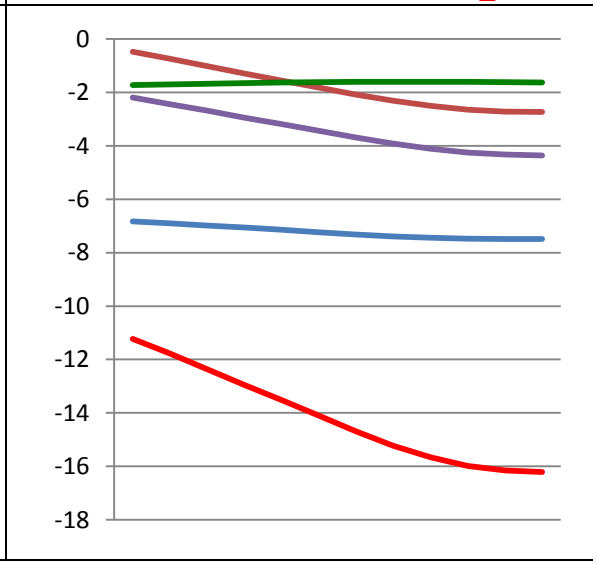


Table S10. G:C//C:G-0-3.25 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-3.774	*24.64*	-1.654	*10.79*	-2.121	*13.84*	-7.772	*50.73*	-15.321	1.009	1.009
1.0	-3.743	*24.41*	-1.644	*10.72*	-2.100	*13.69*	-7.850	*51.18*	-15.337	1.013	1.013
1.1	-3.703	*24.17*	-1.624	*10.60*	-2.080	*13.57*	-7.915	*51.66*	-15.322	1.015	1.015
1.2	-3.641	*23.86*	-1.582	*10.37*	-2.059	*13.49*	-7.976	*52.28*	-15.258	1.019	1.019
1.3	-3.582	*23.61*	-1.538	*10.14*	-2.044	*13.47*	-8.010	*52.78*	-15.174	1.024	1.024
1.4	-3.561	*23.53*	-1.521	*10.05*	-2.041	*13.48*	-8.010	*52.93*	-15.133	1.028	1.028
1.5	-3.576	*23.59*	-1.526	*10.07*	-2.050	*13.52*	-8.009	*52.83*	-15.162	1.034	1.034
1.6	-3.586	*23.54*	-1.534	*10.07*	-2.052	*13.47*	-8.062	*52.92*	-15.233	1.040	1.040
1.7	-3.628	*23.61*	-1.575	*10.25*	-2.053	*13.36*	-8.108	*52.77*	-15.363	1.044	1.044
1.8	-3.668	*23.71*	-1.610	*10.41*	-2.057	*13.30*	-8.134	*52.58*	-15.469	1.041	1.041
1.9	-3.690	*23.78*	-1.626	*10.48*	-2.064	*13.30*	-8.137	*52.44*	-15.517	1.041	1.041
2.0	-3.735	*24.01*	-1.655	*10.64*	-2.080	*13.37*	-8.085	*51.97*	-15.556	1.047	1.047

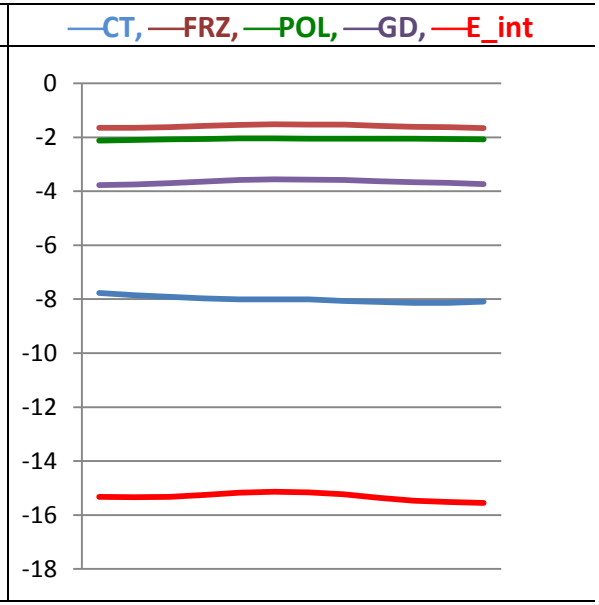
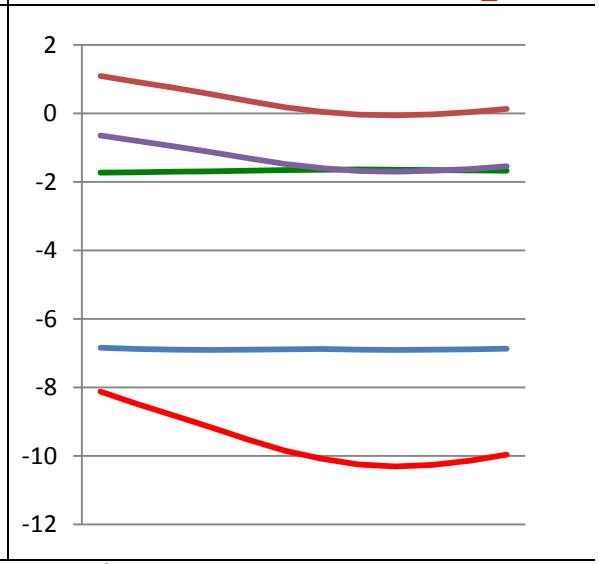


Table S11. G:C//G:C-0-3.26 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ*	*%FRZ**	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-0.642	*7.90*	1.089	*-13.40*	-1.731	*21.30*	-6.843	*84.20*	-8.127	1.077	1.073
1.0	-0.803	*9.46*	0.916	*-10.80*	-1.719	*20.26*	-6.881	*81.08*	-8.486	1.082	1.077
1.1	-0.964	*10.92*	0.743	*-8.41*	-1.707	*19.33*	-6.900	*78.16*	-8.828	1.078	1.081
1.2	-1.132	*12.35*	0.557	*-6.08*	-1.690	*18.42*	-6.907	*75.31*	-9.172	1.069	1.089
1.3	-1.313	*13.79*	0.361	*-3.79*	-1.674	*17.57*	-6.899	*72.43*	-9.525	1.054	1.100
1.4	-1.479	*15.02*	0.181	*-1.84*	-1.660	*16.85*	-6.892	*69.97*	-9.850	1.032	1.116
1.5	-1.602	*15.88*	0.047	*-0.46*	-1.649	*16.35*	-6.883	*68.23*	-10.088	1.004	1.129
1.6	-1.680	*16.38*	-0.040	*0.39*	-1.641	*16.00*	-6.895	*67.23*	-10.256	0.971	1.141
1.7	-1.702	*16.51*	-0.058	*0.56*	-1.645	*15.95*	-6.910	*66.99*	-10.314	0.943	1.154
1.8	-1.679	*16.36*	-0.026	*0.25*	-1.652	*16.10*	-6.903	*67.28*	-10.260	0.921	1.167
1.9	-1.626	*16.04*	0.035	*-0.34*	-1.661	*16.38*	-6.888	*67.92*	-10.141	0.901	1.177
2.0	-1.544	*15.50*	0.127	*-1.28*	-1.672	*16.78*	-6.876	*69.00*	-9.964	0.884	1.183



* Positive values of FRZ component are due to predominance of the repulsive exchange interactions appearing at small rise parameters below 3.3 Å with zero twist angle. FRZ term includes two nonseparable contributions: permanent electrostatics interactions and Pauli repulsions as in ref (56).

Table S12. G:C//G:C-0-3.36 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-1.936	*22.31*	-0.387	*4.46*	-1.549	*17.85*	-4.807	*55.38*	-8.679	0.834	0.833
1.0	-2.090	*23.19*	-0.552	*6.13*	-1.538	*17.07*	-4.830	*53.61*	-9.009	0.838	0.837
1.1	-2.245	*24.07*	-0.720	*7.72*	-1.525	*16.35*	-4.839	*51.87*	-9.329	0.835	0.841
1.2	-2.413	*25.01*	-0.901	*9.34*	-1.513	*15.68*	-4.821	*49.97*	-9.648	0.828	0.846
1.3	-2.595	*26.01*	-1.097	*10.99*	-1.498	*15.02*	-4.787	*47.98*	-9.977	0.816	0.852
1.4	-2.755	*26.81*	-1.267	*12.33*	-1.488	*14.48*	-4.766	*46.38*	-10.277	0.802	0.862
1.5	-2.869	*27.32*	-1.391	*13.25*	-1.478	*14.07*	-4.763	*45.36*	-10.500	0.785	0.875
1.6	-2.940	*27.58*	-1.468	*13.77*	-1.472	*13.81*	-4.780	*44.84*	-10.661	0.761	0.887
1.7	-2.955	*27.59*	-1.481	*13.82*	-1.474	*13.76*	-4.802	*44.83*	-10.712	0.736	0.896
1.8	-2.922	*27.40*	-1.443	*13.53*	-1.479	*13.87*	-4.822	*45.20*	-10.666	0.716	0.905
1.9	-2.874	*27.17*	-1.391	*13.14*	-1.484	*14.02*	-4.831	*45.66*	-10.580	0.698	0.907
2.0	-2.793	*26.78*	-1.305	*12.51*	-1.488	*14.27*	-4.845	*46.45*	-10.431	0.683	0.908

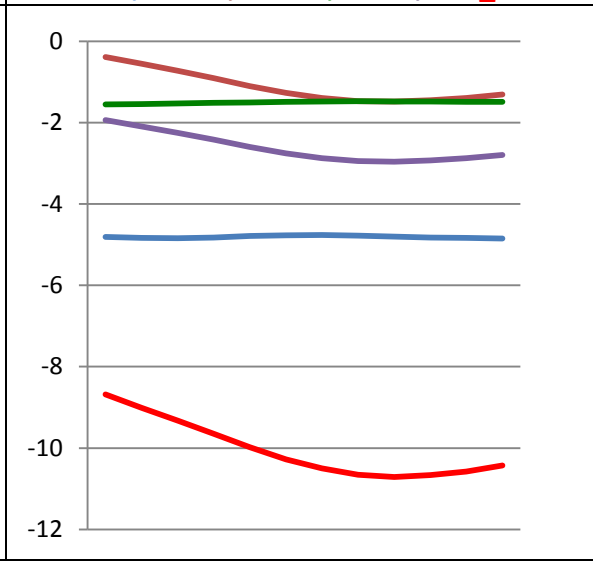


Table S13. G:C//G:C-0-3.46 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-2.895	*32.55*	-1.541	*17.33*	-1.354	*15.23*	-3.103	*34.89*	-8.894	0.629	0.629
1.0	-3.021	*32.92*	-1.679	*18.29*	-1.342	*14.63*	-3.136	*34.17*	-9.178	0.633	0.633
1.1	-3.139	*33.26*	-1.808	*19.16*	-1.331	*14.10*	-3.159	*33.48*	-9.436	0.630	0.634
1.2	-3.258	*33.60*	-1.940	*20.01*	-1.318	*13.59*	-3.181	*32.80*	-9.698	0.625	0.637
1.3	-3.391	*33.96*	-2.085	*20.89*	-1.306	*13.08*	-3.202	*32.07*	-9.984	0.619	0.642
1.4	-3.515	*34.30*	-2.223	*21.70*	-1.292	*12.61*	-3.216	*31.39*	-10.246	0.604	0.643
1.5	-3.610	*34.59*	-2.328	*22.31*	-1.282	*12.29*	-3.215	*30.81*	-10.435	0.589	0.646
1.6	-3.682	*34.81*	-2.406	*22.75*	-1.276	*12.06*	-3.214	*30.38*	-10.578	0.574	0.652
1.7	-3.704	*34.87*	-2.429	*22.87*	-1.275	*12.01*	-3.214	*30.26*	-10.621	0.558	0.657
1.8	-3.682	*34.80*	-2.406	*22.73*	-1.276	*12.06*	-3.217	*30.40*	-10.581	0.541	0.663
1.9	-3.644	*34.67*	-2.365	*22.50*	-1.279	*12.17*	-3.222	*30.66*	-10.510	0.526	0.670
2.0	-3.573	*34.39*	-2.291	*22.06*	-1.281	*12.34*	-3.242	*31.21*	-10.387	0.514	0.673

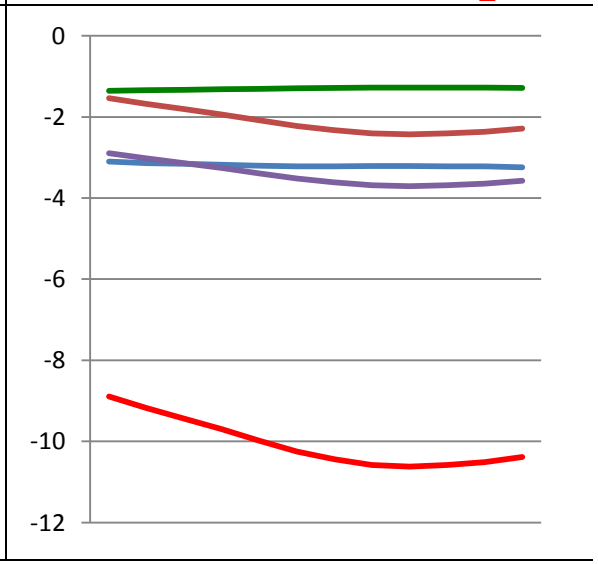
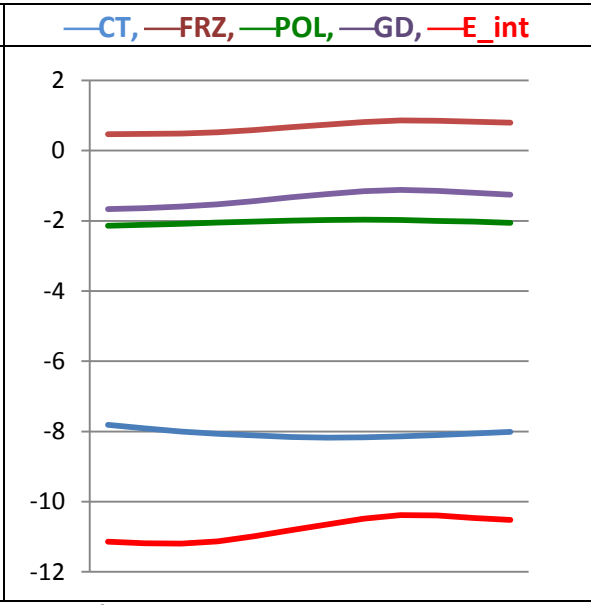


Table S14. G:C//T:A-10-3.15 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ*	*%FRZ**	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-1.663	*14.93*	0.473	*-4.25*	-2.136	*19.18*	-7.814	*70.14*	-11.141	1.190	1.389
1.0	-1.636	*14.63*	0.474	*-4.24*	-2.110	*18.86*	-7.914	*70.75*	-11.186	1.192	1.397
1.1	-1.597	*14.26*	0.487	*-4.35*	-2.084	*18.61*	-8.003	*71.48*	-11.196	1.197	1.412
1.2	-1.531	*13.76*	0.521	*-4.68*	-2.052	*18.44*	-8.066	*72.48*	-11.128	1.204	1.431
1.3	-1.433	*13.05*	0.585	*-5.33*	-2.018	*18.38*	-8.115	*73.91*	-10.980	1.214	1.445
1.4	-1.327	*12.27*	0.666	*-6.16*	-1.993	*18.44*	-8.157	*75.45*	-10.811	1.225	1.452
1.5	-1.235	*11.60*	0.741	*-6.96*	-1.976	*18.56*	-8.175	*76.80*	-10.645	1.232	1.452
1.6	-1.158	*11.05*	0.812	*-7.75*	-1.970	*18.80*	-8.164	*77.90*	-10.480	1.238	1.442
1.7	-1.120	*10.79*	0.857	*-8.26*	-1.977	*19.04*	-8.141	*78.42*	-10.380	1.250	1.419
1.8	-1.146	*11.03*	0.852	*-8.20*	-1.998	*19.23*	-8.102	*77.95*	-10.394	1.262	1.387
1.9	-1.201	*11.48*	0.823	*-7.87*	-2.024	*19.35*	-8.058	*77.03*	-10.460	1.267	1.357
2.0	-1.256	*11.93*	0.798	*-7.58*	-2.053	*19.51*	-8.011	*76.13*	-10.523	1.279	1.325



* Positive values of FRZ component are due to predominance of the repulsive exchange interactions appearing at small rise parameters below 3.3 Å with zero twist angle. FRZ term includes two nonseparable contributions: permanent electrostatics interactions and Pauli repulsions as in ref (56).

Table S15. T:A//A:T-08-3.16 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-2.493	*21.37*	-1.109	*9.50*	-1.384	*11.87*	-6.681	*57.26*	-11.666	1.480	1.480
1.0	-2.680	*22.09*	-1.322	*10.90*	-1.358	*11.19*	-6.772	*55.82*	-12.132	1.503	1.503
1.1	-2.879	*22.80*	-1.553	*12.30*	-1.326	*10.50*	-6.867	*54.39*	-12.625	1.533	1.533
1.2	-3.101	*23.61*	-1.803	*13.73*	-1.298	*9.88*	-6.934	*52.79*	-13.135	1.570	1.570
1.3	-3.345	*24.46*	-2.068	*15.12*	-1.278	*9.34*	-6.984	*51.07*	-13.675	1.613	1.613
1.4	-3.603	*25.29*	-2.331	*16.36*	-1.272	*8.93*	-7.042	*49.42*	-14.248	1.666	1.666
1.5	-3.857	*26.04*	-2.571	*17.36*	-1.286	*8.68*	-7.100	*47.93*	-14.813	1.722	1.722
1.6	-4.081	*26.63*	-2.775	*18.11*	-1.305	*8.52*	-7.163	*46.74*	-15.325	1.771	1.771
1.7	-4.246	*26.98*	-2.908	*18.48*	-1.338	*8.50*	-7.247	*46.05*	-15.738	1.815	1.815
1.8	-4.369	*27.18*	-2.990	*18.60*	-1.379	*8.57*	-7.339	*45.65*	-16.076	1.858	1.858
1.9	-4.491	*27.37*	-3.065	*18.68*	-1.427	*8.70*	-7.424	*45.25*	-16.407	1.895	1.895
2.0	-4.656	*27.77*	-3.179	*18.96*	-1.477	*8.81*	-7.454	*44.46*	-16.766	1.923	1.923

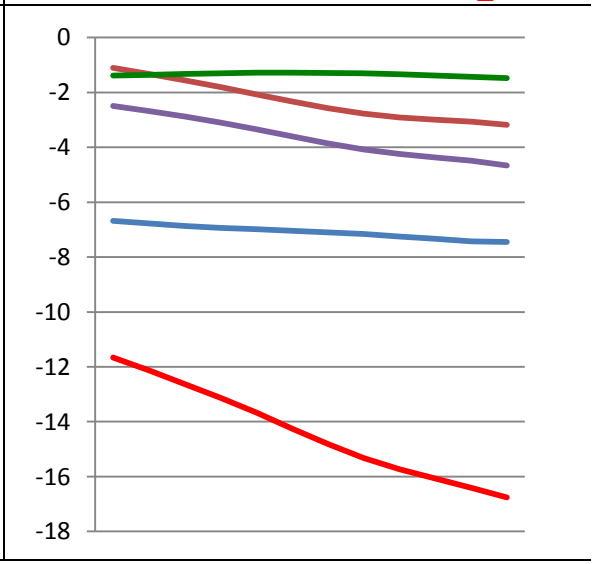


Table S16. T:A//G:C-0-3.19 Energy terms in *kcal/mol* and the transferred charges in *e* units. Percentages of the relevant energy components were italicalized.

d(D-H)	GD	*%GD*	FRZ	*%FRZ*	POL	*%POL*	CT	*%CT*	$E_{interaction}$	Upward CT	Downward CT
0.9	-4.676	*28.91*	-2.981	*18.42*	-1.696	*10.48*	-6.82	*42.18*	-16.177	1.366	1.037
1.0	-4.613	*28.59*	-2.934	*18.18*	-1.679	*10.41*	-6.91	*42.82*	-16.135	1.383	1.032
1.1	-4.513	*28.19*	-2.852	*17.82*	-1.661	*10.37*	-6.98	*43.62*	-16.008	1.399	1.030
1.2	-4.378	*27.68*	-2.743	*17.35*	-1.635	*10.34*	-7.06	*44.63*	-15.814	1.420	1.028
1.3	-4.256	*27.24*	-2.643	*16.92*	-1.613	*10.33*	-7.11	*45.51*	-15.623	1.444	1.027
1.4	-4.168	*26.92*	-2.566	*16.57*	-1.603	*10.35*	-7.15	*46.16*	-15.484	1.469	1.033
1.5	-4.121	*26.73*	-2.518	*16.34*	-1.603	*10.40*	-7.17	*46.53*	-15.414	1.494	1.041
1.6	-4.114	*26.67*	-2.508	*16.26*	-1.606	*10.41*	-7.20	*46.65*	-15.424	1.515	1.046
1.7	-4.150	*26.72*	-2.524	*16.25*	-1.626	*10.47*	-7.23	*46.57*	-15.533	1.533	1.048
1.8	-4.242	*26.99*	-2.585	*16.45*	-1.657	*10.54*	-7.23	*46.02*	-15.720	1.546	1.047
1.9	-4.367	*27.40*	-2.676	*16.79*	-1.691	*10.61*	-7.20	*45.20*	-15.938	1.551	1.043
2.0	-4.486	*27.80*	-2.761	*17.11*	-1.725	*10.69*	-7.16	*44.40*	-16.137	1.547	1.038

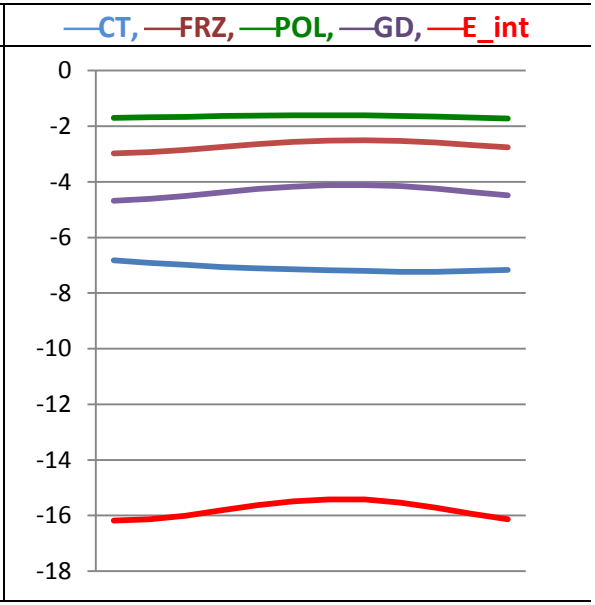


Table S17. Comparison of the base stacking energies of the dinucleotide steps at M06-2X/cc-pVTZ level with their corresponding values in high-quality literature data (kcal/mol).

Dinucleotide Step	Ref. (9)	This work	Difference
A:T ||A:T-0-3.24	-13.12	-11.50	1.62
A:T ||A:T-0-3.34	-13.10	-12.56	0.54
A:T ||A:T-0-3.44	-12.57	-13.06	-0.49
A:T //A:T-20-3.05	-14.74	-14.44	0.30
A:T //A:T-20-3.15	-14.73	-15.36	-0.63
A:T //A:T-20-3.25	-14.07	-15.04	-0.97
A:T//G:C-08-3.19	-12.50	-13.03	-0.53
A:T//T:A-10-3.26	-13.30	-12.20	1.10
G:C//A:T-10-3.15	-12.90	-11.78	1.12
G:C||C:G-0-3.25	-15.80	-15.34	0.46
G:C||G:C-0-3.26	-11.20	-8.49	2.71
G:C||G:C-0-3.36	-13.66	-9.01	4.65
G:C||G:C-0-3.46	-12.87	-9.18	3.69
G:C//T:A-10-3.15	-13.40	-11.19	2.21
T:A//A:T-08-3.16	-12.80	-12.13	0.67
T:A||G:C-0-3.19	-15.10	-16.14	1.04

Table S18. Total Dipole Moment values (in debye) of dinucleotide steps in every step during DPT reactions.

d(D-H)	A:T||A:T-0-3.24	A:T||A:T-0-3.34	A:T||A:T-0-3.44	A:T||A:T-20-3.05	A:T||A:T-20-3.15	A:T||A:T-20-3.25	A:T//G:C-08-3.19	A:T//T:A-10-3.26
0.9	3.3519	3.3539	3.3590	3.4759	3.4437	3.4197	7.2685	0.0454
1.0	3.0826	3.0856	3.0920	3.1840	3.1538	3.1290	7.0815	0.0999
1.1	2.6756	2.6794	2.6892	2.7375	2.7121	2.6889	6.8224	0.1711
1.2	2.1659	2.1712	2.1728	2.1938	2.1709	2.1518	6.4944	0.2531
1.3	1.6666	1.6741	1.6856	1.6881	1.6711	1.6584	6.1512	0.3208
1.4	1.2342	1.2416	1.2535	1.3823	1.3752	1.3734	5.8565	0.3634
1.5	0.9218	0.9301	0.9435	1.3357	1.3372	1.3472	5.6503	0.3739
1.6	0.7902	0.7991	0.8127	1.4622	1.4713	1.4831	5.546	0.3473
1.7	0.8794	0.8857	0.8984	1.6562	1.6694	1.6775	5.5988	0.2717
1.8	1.1847	1.1923	1.2021	1.9199	1.9300	1.9363	5.7847	0.1547
1.9	1.6751	1.6821	1.6909	2.3021	2.3046	2.3096	6.0546	0.0104
2.0	2.2802	2.2864	2.2946	2.8187	2.8205	2.8230	6.3823	0.1503
d(D-H)	**G:C//A:T-10-3.15**	**G:C||C:G-0-3.25**	**G:C||G:C-0-3.26**	**G:C||G:C-0-3.36**	**G:C||G:C-0-3.46**	**G:C//T:A-10-3.15**	**T:A//A:T-8-3.16**	**T:A||G:C-0-3.19**
0.9	6.5625	4.8159	10.3850	10.4071	10.4239	3.9680	1.8089	4.4017
1.0	6.4008	4.7708	10.2772	10.3002	10.3200	4.0197	1.7294	4.4307
1.1	6.1849	4.7343	10.1681	10.1939	10.2125	4.1305	1.5945	4.5015
1.2	5.9159	4.7064	10.0349	10.0607	10.0812	4.2858	1.4046	4.5981
1.3	5.6437	4.6840	9.8852	9.9120	9.9314	4.4444	1.1979	4.6729
1.4	5.4336	4.6679	9.7762	9.8024	9.823	4.6024	1.003	4.7432
1.5	5.3117	4.6542	9.7284	9.7542	9.7754	4.7392	0.8433	4.7956
1.6	5.2623	4.6363	9.6939	9.7197	9.7402	4.8007	0.7526	4.7712
1.7	5.3337	4.6220	9.7164	9.7424	9.7632	4.7823	0.7588	4.6669
1.8	5.5131	4.6119	9.7762	9.8015	9.8229	4.6958	0.8483	4.4907
1.9	5.7541	4.6084	9.8252	9.8481	9.8653	4.5295	1.0025	4.2421
2.0	6.0387	4.6252	9.8667	9.8884	9.9045	4.3296	1.1896	3.9649

Table S19. Total energy values (in a.u) of dinucleotide steps in every step during DPT reactions. The cases of which d(D-H) is equal to 1.6 Å can be nearly accepted as transition state of the rare WC pair formations in dinucleotide steps. ΔE(C→R) stands for potential barrier high for transition from canonical and rare base pairs in kcal/mol.

d(D-H)	A:T||A:T-0-3.24	A:T||A:T-0-3.34	A:T||A:T-0-3.44	A:T||A:T-20-3.05	A:T||A:T-20-3.15	A:T||A:T-20-3.25	A:T//G:C-08-3.19	A:T//T:A-10-3.26
0.9	-1842.878643	-1842.881370	-1842.883512	-1842.876341	-1842.879005	-1842.880230	-1858.941486	-1842.880142
1.0	-1842.936207	-1842.938927	-1842.941048	-1842.934035	-1842.936656	-1842.937880	-1858.999117	-1842.937439
1.1	-1842.924758	-1842.927496	-1842.929563	-1842.922590	-1842.925183	-1842.926380	-1858.987972	-1842.925536
1.2	-1842.881613	-1842.884371	-1842.886364	-1842.878997	-1842.881584	-1842.882761	-1858.945668	-1842.881687
1.3	-1842.829353	-1842.832127	-1842.834138	-1842.825661	-1842.828263	-1842.829470	-1858.895192	-1842.828746
1.4	-1842.782712	-1842.785495	-1842.787562	-1842.777174	-1842.779857	-1842.781145	-1858.851011	-1842.781474
1.5	-1842.750645	-1842.753434	-1842.755536	-1842.742704	-1842.745456	-1842.746810	-1858.821840	-1842.748652
1.6	-1842.737283	-1842.740085	-1842.742188	-1842.726646	-1842.729401	-1842.730768	-1858.811868	-1842.734608
1.7	-1842.743177	-1842.745980	-1842.748024	-1842.729634	-1842.732385	-1842.733695	-1858.820938	-1842.739747
1.8	-1842.763996	-1842.766823	-1842.768824	-1842.748327	-1842.751101	-1842.752433	-1858.843813	-1842.760376
1.9	-1842.789423	-1842.792267	-1842.794273	-1842.773665	-1842.776446	-1842.777844	-1858.868720	-1842.786274
2.0	-1842.801675	-1842.804531	-1842.806597	-1842.789719	-1842.792515	-1842.793931	-1858.874572	-1842.800073
ΔE(C→R)	124.827	124.775	124.787	130.139	130.055	129.965	117.501	127.278
d(D-H)	**G:C//A:T-10-3.15**	**G:C||C:G-0-3.25**	**G:C||G:C-0-3.26**	**G:C||G:C-0-3.36**	**G:C||G:C-0-3.46**	**G:C//T:A-10-3.15**	**T:A//A:T-8-3.16**	**T:A||G:C-0-3.19**
0.9	-1858.938555	-1875.002881	-1874.998035	-1875.000004	-1875.001427	-1858.937472	-1842.880128	-1858.944244
1.0	-1858.996616	-1875.060850	-1875.056262	-1875.058218	-1875.059600	-1858.995156	-1842.937664	-1859.001678
1.1	-1858.985851	-1875.050298	-1875.046010	-1875.047964	-1875.049332	-1858.984009	-1842.926164	-1858.990344
1.2	-1858.943873	-1875.009159	-1875.005247	-1875.007204	-1875.008595	-1858.941528	-1842.883006	-1858.947935
1.3	-1858.893717	-1874.960899	-1874.957470	-1874.959417	-1874.960699	-1858.890732	-1842.830931	-1858.897618
1.4	-1858.849900	-1874.919962	-1874.916837	-1874.918753	-1874.919896	-1858.846288	-1842.784475	-1858.853775
1.5	-1858.821054	-1874.894669	-1874.891764	-1874.893659	-1874.894694	-1858.816889	-1842.752447	-1858.825013
1.6	-1858.811401	-1874.889095	-1874.886374	-1874.888272	-1874.889247	-1858.806740	-1842.739019	-1858.815610
1.7	-1858.820900	-1874.902577	-1874.899792	-1874.901705	-1874.902727	-1858.815887	-1842.744754	-1858.825353
1.8	-1858.844375	-1874.928177	-1874.925246	-1874.927151	-1874.928254	-1858.839228	-1842.765669	-1858.848731
1.9	-1858.870095	-1874.951882	-1874.948718	-1874.950633	-1874.951821	-1858.864972	-1842.791599	-1858.873579
2.0	-1858.877395	-1874.948225	-1874.944882	-1874.946797	-1874.947933	-1858.872285	-1842.805258	-1858.878266
ΔE(C→R)	116.224	107.778	106.606	106.643	106.898	118.233	124.652	116.759