

SUPPLEMENTARY MATERIAL

Thermochemistry of guanine tautomers re-examined by means of high-level CCSD(T) composite ab initio methods

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(Tables S1 and S2, 8 pages)

Table S1. Tautomerization energies for standard and composite ab initio procedures (relative to tautomer **1**, in kJ mol⁻¹). Structures are shown in Figure 1 of the main text.

	2	3	3'	4	5	4'	6'	6	7	8'	9	10	8
W1-F12	2.37	2.63	4.03	14.31	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
G3	2.80	1.89	2.96	13.06	25.49	43.06	52.86	61.53	79.03	83.98	85.05	100.96	N/A
G3B3	2.75	2.02	3.32	13.25	25.40	43.35	53.07	61.46	77.85	82.71	84.54	101.53	121.82
G3(MP2)	2.69	1.41	2.45	12.79	25.72	42.43	52.22	60.85	78.55	82.96	85.57	100.82	N/A
G3(MP2)B3	2.60	1.49	2.75	12.94	25.54	42.67	52.37	60.70	77.36	81.74	84.93	101.27	120.45
G4	2.52	2.16	3.60	13.46	24.91	43.01	53.21	61.28	77.15	82.70	84.35	100.44	121.54
G4(MP2)	2.35	1.86	3.28	13.43	25.11	42.58	52.71	60.74	76.71	81.95	84.91	100.26	120.30
G4(MP2)-6X	2.41	1.88	3.41	13.39	25.29	42.76	53.09	61.11	77.27	82.60	85.28	100.60	121.17
CBS-APNO	2.38	3.65	5.08	15.03	26.41	45.36	54.41	62.71	79.23	84.56	85.51	99.43	N/A
CBS-QB3	2.82	2.90	4.27	14.07	25.33	44.25	54.20	62.52	78.09	83.98	84.86	101.74	123.48
CCSD(T)/DZ ^a	2.54	2.56	4.65	13.85	26.88	43.36	53.08	60.57	77.84	80.30	86.62	99.77	117.72
MP2/CBS+(T) ^b	2.30	1.85	3.38	13.37	25.37	42.74	52.72	60.74	76.91	81.53	85.60	100.48	119.96
CCSD(T)/CBS ^c	2.26	2.29	3.89	14.04	25.80	43.56	53.22	61.26	77.51	82.03	86.14	100.73	120.48
CCSD(T)/CBS ^d	2.20	2.51	4.06	14.30	25.65	43.78	53.50	61.58	77.37	82.52	86.02	100.70	121.01

^aCCSD(T)/jul-cc-pVDZ. ^bCCSD(T)/jul-cc-pVDZ + MP2/jul-cc-pV{T,Q}Z - MP2/jul-cc-pVDZ. ^cHF/jul-cc-pV{D,T}Z + CCSD/jul-cc-pVTZ + (T)/jul-cc-pVDZ, where the HF energy is extrapolated with an exponent of 5.0.

^dSame as footnote *c* but the HF energy is extrapolated with an optimal exponent of 3.5.

Table S2. B3LYP/jul-cc-pVTZ optimized geometries for the guanine tautomers considered in this work (Cartesian coordinates, Å). Structures are shown in Figure 1 of the main text.

1			
C	-1.687757	-0.530068	-0.001589
N	-0.749055	-1.427397	0.006693
C	0.516596	-0.924603	-0.001769
C	0.818012	0.432615	0.007904
C	-0.183430	1.441271	0.003886
N	-1.457498	0.827397	-0.002828
N	2.191244	0.508759	0.005546
N	1.669712	-1.663073	-0.006900
C	2.639702	-0.774239	-0.003169
O	-0.065982	2.657377	-0.000802
N	-3.006506	-0.917387	-0.064299
H	-3.134460	-1.905469	0.086343
H	-3.690925	-0.336337	0.391329
H	3.691711	-1.008448	-0.006357
H	-2.231855	1.471297	-0.071770
H	2.739368	1.351987	0.007813

2			
C	-1.669881	-0.564690	-0.002199
N	-0.692753	-1.431352	0.003759
C	0.528654	-0.847761	-0.003401
C	0.852514	0.503519	0.005830
C	-0.211600	1.466886	0.006194
N	-1.474332	0.787095	0.000144
N	2.220250	0.677462	0.005045
N	1.728401	-1.500224	-0.008284
C	2.709927	-0.528516	-0.004175
O	-0.193208	2.679517	0.005279
N	-2.966943	-1.006911	-0.061102
H	-3.070920	-1.994489	0.104996
H	-3.687554	-0.430902	0.340171
H	3.756935	-0.782666	-0.007423
H	-2.266236	1.410957	-0.054405
H	1.853399	-2.498146	-0.015995

3			
C	-1.660948	-0.568290	0.003671
N	-0.669766	-1.463404	-0.001973
C	0.528348	-0.888016	-0.009432

C	0.809337	0.484292	-0.005883
C	-0.322194	1.305269	0.010082
N	-1.534498	0.777198	0.015479
N	2.175269	0.709840	-0.013335
N	1.756886	-1.492878	-0.018043
C	2.699461	-0.479715	-0.021230
O	-0.208714	2.638720	0.022847
N	-2.938965	-1.047497	-0.036654
H	-3.071059	-2.021431	0.168737
H	-3.679245	-0.409928	0.193617
H	3.755333	-0.696233	-0.029164
H	-1.107486	2.997705	0.028442
H	1.925662	-2.483930	-0.025958

3'

C	-1.701453	-0.488102	0.010268
N	-0.755748	-1.437504	0.010634
C	0.467480	-0.921443	-0.003110
C	0.796783	0.433693	-0.011541
C	-0.288635	1.316046	0.000000
N	-1.519503	0.852287	0.011280
N	2.167168	0.620420	-0.021607
N	1.679157	-1.566474	-0.007834
C	2.655337	-0.587430	-0.019961
O	-0.128709	2.649048	0.003688
N	-2.998820	-0.905033	-0.021117
H	-3.185128	-1.871074	0.177189
H	-3.709386	-0.224766	0.178065
H	3.703309	-0.838307	-0.026860
H	1.819101	-2.562194	-0.007107
H	0.818917	2.841507	-0.004461

4

C	-1.681442	-0.535465	-0.002109
N	-0.721498	-1.454243	0.004240
C	0.516132	-0.951700	-0.000931
C	0.786757	0.425921	-0.006689
C	-0.296227	1.292372	-0.000174
N	-1.521243	0.813666	0.002538
N	2.163584	0.535919	-0.007315
N	1.699134	-1.657859	0.003328
C	2.637026	-0.743331	-0.001306
O	-0.108670	2.627926	0.005880
N	-2.976211	-0.974238	-0.049908
H	-3.129847	-1.943771	0.163532
H	-3.695853	-0.318979	0.195983

H	3.695806	-0.948221	-0.001158
H	-0.986089	3.036365	0.004688
H	2.705503	1.381690	-0.013019

4'

C	-1.701969	-0.496138	0.002021
N	-0.761953	-1.438589	0.004492
C	0.481380	-0.960856	-0.004565
C	0.782620	0.412903	-0.010688
C	-0.287826	1.305808	0.004308
N	-1.514541	0.845332	0.009838
N	2.169327	0.481585	-0.014460
N	1.647186	-1.698325	-0.005538
C	2.607541	-0.813301	-0.013278
O	-0.165737	2.657194	0.017236
N	-3.004131	-0.906089	-0.040661
H	-3.185683	-1.872322	0.163791
H	-3.710233	-0.229386	0.185357
H	3.661048	-1.044386	-0.018744
H	2.758582	1.294308	-0.034476
H	0.760493	2.916337	0.023696

5

C	-1.743497	-0.359021	0.002032
N	-0.771091	-1.331121	-0.003769
C	0.535641	-0.903523	-0.004532
C	0.803750	0.439657	0.009615
C	-0.229524	1.453962	0.009343
N	-1.521063	0.920097	0.023129
N	2.179188	0.507210	0.004613
N	1.660454	-1.661511	-0.018927
C	2.638147	-0.768317	-0.013572
O	-0.004136	2.654412	0.005998
N	-3.038458	-0.815344	-0.059754
H	-3.254856	-1.700858	0.367316
H	-3.721337	-0.091411	0.095316
H	3.688233	-1.006485	-0.021669
H	2.718100	1.357093	0.011702
H	-0.987377	-2.305484	-0.135014

6

C	-1.687835	-0.461228	-0.002190
N	-0.686003	-1.373314	-0.013670
C	0.615170	-0.928946	-0.003958
C	0.883625	0.462544	0.006157
C	-0.207229	1.312051	0.005315

N	-1.471717	0.835321	0.012724
N	2.247857	0.617512	0.007752
N	1.724699	-1.635845	-0.009961
C	2.675688	-0.633885	-0.002112
O	-0.072725	2.638772	0.004942
N	-2.976490	-0.921062	-0.056708
H	-3.182511	-1.831493	0.318236
H	-3.675505	-0.218276	0.116470
H	3.726518	-0.881390	-0.003738
H	-0.960362	3.023193	0.003029
H	-0.871271	-2.363709	-0.073767

6'

C	-1.724185	-0.374766	-0.003681
N	-0.770546	-1.343936	-0.017716
C	0.551462	-0.966884	-0.006935
C	0.866380	0.404604	0.007840
C	-0.173636	1.316198	0.009092
N	-1.454155	0.912473	0.014258
N	2.232124	0.527138	0.010173
N	1.643348	-1.708553	-0.015467
C	2.624592	-0.740650	-0.003864
O	0.019840	2.637022	0.013413
N	-3.032871	-0.770124	-0.057928
H	-3.288190	-1.670874	0.309465
H	-3.694379	-0.030099	0.109005
H	3.667287	-1.019889	-0.006538
H	-1.012110	-2.321836	-0.081716
H	0.975685	2.796528	0.014524

9

C	-1.723148	-0.447116	0.004831
N	-0.770083	-1.425256	-0.001174
C	0.433190	-0.888533	-0.008729
C	0.731899	0.461800	-0.007598
C	-0.329504	1.451473	0.010600
N	-1.572347	0.876276	0.017705
N	2.101922	0.577338	-0.014560
N	1.665612	-1.542182	-0.017429
C	2.659120	-0.628711	-0.021187
O	-0.093200	2.660318	0.023553
N	-3.007096	-0.905508	-0.029384
H	-3.168493	-1.876223	0.167202
H	-3.735428	-0.240310	0.156901
H	3.710625	-0.843263	-0.029248
H	2.590734	1.460269	-0.014171

H 1.792769 -2.541177 -0.022714

7

C -1.735681 -0.387683 0.013670

N -0.726961 -1.344202 0.014834

C 0.549768 -0.839963 -0.010254

C 0.832500 0.501333 0.001024

C -0.261064 1.473744 0.002256

N -1.548078 0.882823 0.039096

N 2.202481 0.681815 0.004218

N 1.740595 -1.502214 -0.011142

C 2.713853 -0.511361 -0.004902

O -0.125921 2.677366 -0.016852

N -3.011109 -0.910466 -0.059307

H -3.193554 -1.752769 0.463741

H -3.719468 -0.201880 0.054017

H 3.762233 -0.758663 -0.012328

H 1.895499 -2.495499 -0.003001

H -0.932088 -2.280822 -0.292276

8

C -1.641055 -0.592515 0.011894

N -0.695080 -1.471376 0.039173

C 0.575064 -0.981334 0.007840

C 0.891088 0.433733 -0.006583

C -0.145334 1.311672 -0.026876

N -1.415791 0.774282 -0.025647

N 2.253343 0.582016 0.009053

N 1.703563 -1.667941 0.028590

C 2.657585 -0.678494 0.023099

O -0.019359 2.646625 -0.081649

N -2.972638 -0.965983 -0.049701

H -3.077749 -1.966228 0.034838

H -3.608485 -0.461411 0.550042

H 3.707539 -0.933789 0.032372

H -0.809901 3.102462 0.229353

H -2.194397 1.370590 -0.259913

8'

C -1.672358 -0.532544 -0.002038

N -0.754417 -1.446780 0.005002

C 0.532037 -1.001940 -0.005197

C 0.880573 0.392436 0.010043

C -0.123625 1.305577 0.003065

N -1.403675 0.825389 -0.008041

N 2.242705 0.525043 0.016209

N	1.652107	-1.713375	-0.008678
C	2.624904	-0.748123	0.002902
O	-0.020880	2.638783	-0.001212
N	-3.010375	-0.868873	-0.069064
H	-3.152810	-1.861957	0.035874
H	-3.649737	-0.318868	0.483837
H	3.669615	-1.023338	0.001640
H	-2.155589	1.490023	-0.108689
H	0.921974	2.861612	-0.003602

10

C	-1.705326	-0.469417	0.003819
N	-0.702752	-1.339729	-0.001180
C	0.613862	-0.877336	-0.006018
C	0.935631	0.489574	0.000000
C	-0.074578	1.482904	0.007940
N	-1.416585	0.831990	0.013850
N	2.300149	0.581548	-0.005297
N	1.692483	-1.638489	-0.013918
C	2.684299	-0.688242	-0.013568
O	-0.078441	2.690976	0.011629
N	-2.997808	-0.898533	-0.049888
H	-3.191429	-1.856506	0.188971
H	-3.720867	-0.248678	0.207486
H	3.724171	-0.976556	-0.019673
H	-2.168177	1.506045	0.000206
H	-0.867903	-2.334514	-0.027978