Supporting Information

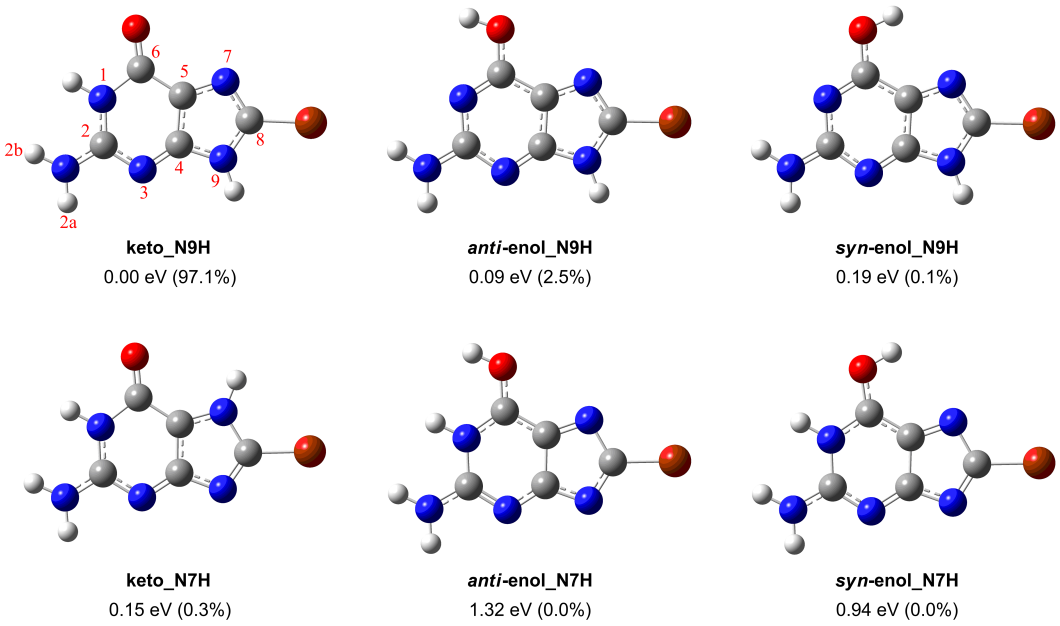
Singlet O_2 Reactions with Radical Cations of 8-Bromoguanine and 8-Bromoguanosine: Guided-Ion Beam Mass Spectrometric Measurements and Theoretical Treatments

Jonathan Benny,[a,b] Toru Saito,*[c] May Myat Moe,[a,b] and Jianbo Liu*[a,b]

[a] Department of Chemistry and Biochemistry, Queens College of the City University of New York, 65-30 Kissena Blvd., Queens, NY 11367, USA; [b] Ph.D. Program in Chemistry, the Graduate Center of the City University of New York, 365 5th Ave., New York, NY 10016, USA; and [c] Department of Biomedical Information Science, Graduate School of Information Science, Hiroshima City University, 3-4-1 Ozuka-Higashi, Asa-Minami-Ku, 731-3194 Hiroshima, Japan

Table of Contents

Scheme S1 Various tautomers of $8BrG^{\bullet+}$ and their relative energies calculated at 298 K using the ωB97XD/6-31+G(d,p) level of theory. Also shown in parentheses are their relative populations.



Cartesian coordinates for tautomers in Scheme S1, optimized at ωB97XD/ 6-31+G(d,p)

keto_N9H

C1	-1.865487	1.467828	-0.000006
C2	-0.627419	0.691453	0.000002
H3	-3.887746	1.083286	-0.000011
C4	-2.959127	-0.762209	0.000008
C5	1.348436	-0.032232	-0.000001
N6	-2.997461	0.595550	-0.000004
N7	0.639635	1.097760	0.000004
N8	0.573004	-1.162832	-0.000006
N9	-1.808615	-1.476934	0.000001
C10	-0.726763	-0.740488	-0.000004
N11	-4.089729	-1.452647	0.000037
H12	-4.028817	-2.462009	0.000003
H13	-5.003747	-1.024330	0.000032
O14	-2.006352	2.659852	-0.000019
H15	0.900043	-2.120840	-0.000011
Br16	3.166726	-0.105923	-0.000002

***anti*-enol_N9H**

C1	-1.930284	1.305338	0.000000
C2	-0.656437	0.632471	-0.000001
C3	-2.945964	-0.758657	0.000009
C4	1.332123	-0.052613	-0.000003
N5	-3.032460	0.599477	0.000005
N6	0.603613	1.067608	-0.000005
N7	0.585115	-1.196392	0.000002
N8	-1.808514	-1.525542	0.000009
C9	-0.729794	-0.799857	0.000004
N10	-4.088401	-1.423002	0.000014
H11	-4.083300	-2.434121	0.000017
H12	-4.965224	-0.919526	0.000014
O13	-1.949683	2.609137	-0.000004
H14	0.934113	-2.146394	0.000005
H15	-2.865029	2.932481	-0.000002
Br16	3.152673	-0.083448	-0.000007

***syn*-enol_N9H**

C1	-1.930004	1.315261	0.000000
C2	-0.670110	0.616297	0.000000
C3	-2.960240	-0.733877	0.000009
C4	1.320676	-0.065587	-0.000003
N5	-3.036398	0.622572	0.000005
N6	0.590863	1.054068	-0.000005
N7	0.571474	-1.206562	0.000002
N8	-1.831915	-1.524018	0.000009
C9	-0.746405	-0.810595	0.000004
N10	-4.110073	-1.383962	0.000014
H11	-4.121241	-2.395245	0.000017
H12	-4.977909	-0.863408	0.000014
O13	-2.004233	2.620877	-0.000004
H14	0.921358	-2.156430	0.000004
H15	-1.127291	3.033612	-0.000007
Br16	3.141937	-0.098549	-0.000007

keto_N7H

C1	-1.897796	1.446084	-0.000001
C2	-0.674846	0.670588	0.000001
H3	-3.913112	1.055600	-0.000012
C4	-2.946683	-0.782756	0.000000
C5	1.339082	-0.177607	-0.000003
N6	-3.015544	0.581608	0.000000
N7	0.615638	1.022158	0.000004
N8	0.593748	-1.241445	-0.000013
N9	-1.791858	-1.481894	-0.000012
C10	-0.690017	-0.763192	-0.000010
N11	-4.067108	-1.488402	-0.000001
H12	-3.983322	-2.497202	0.000040
H13	-4.989841	-1.078704	0.000108
O14	-2.005793	2.648417	-0.000005
H15	0.998016	1.961358	0.000009
Br16	3.166058	-0.135179	0.000003

***anti*_enol_N7H**

C1	-1.824026	1.333888	0.000001
C2	-0.607102	0.647586	0.000002
H3	-3.854179	0.992794	-0.000020
C4	-2.878965	-0.846946	0.000001
C5	1.336501	-0.144514	-0.000001
N6	-2.941998	0.551253	-0.000001
N7	0.643635	1.077587	0.000003
N8	0.631905	-1.264318	-0.000005
N9	-1.748271	-1.531823	-0.000002
C10	-0.638266	-0.811184	-0.000003
N11	-4.034855	-1.504956	-0.000007
H12	-3.985909	-2.515886	0.000017
H13	-4.944770	-1.070314	0.000066
O14	-1.885006	2.633115	-0.000002
H15	-2.769156	3.024941	0.000000
Br16	3.155780	-0.110389	0.000001

***syn*_enol_N7H**

C1	-1.822279	1.330146	-0.000006
C2	-0.611114	0.636982	0.000003
H3	-3.834634	1.053033	-0.000169
C4	-2.893205	-0.826544	0.000005
C5	1.332288	-0.152086	-0.000024
N6	-2.943303	0.566715	0.000004
N7	0.636820	1.071648	0.000041
N8	0.625969	-1.268325	-0.000122
N9	-1.763521	-1.525919	-0.000116
C10	-0.649005	-0.817198	-0.000106
N11	-4.050063	-1.477729	-0.000036
H12	-4.009318	-2.489096	0.000378
H13	-4.955515	-1.032748	0.001227
O14	-2.008332	2.616955	-0.000036
H15	-1.164805	3.099843	-0.000071
Br16	3.152843	-0.118834	0.000037

Cartesian coordinates for structures in Scheme 2, optimized at ωB97XD/ 6-31+G(d,p)

8BrG$^{\bullet+}$

N1	0.573195	-1.162580	-0.000015
C2	1.348323	-0.032188	-0.000005
N3	0.639738	1.097886	0.000000
C4	-0.627390	0.691646	0.000000
C5	-1.865536	1.467869	-0.000003
O6	-2.006673	2.659850	0.000001
N7	-2.997515	0.595443	-0.000004
H8	-3.887800	1.083189	0.000001
C9	-2.959105	-0.762233	-0.000001
N10	-4.089480	-1.452992	0.000012
H11	-5.003638	-1.024957	0.000038
H12	-4.028259	-2.462340	0.000018
N13	-1.808431	-1.476906	-0.000007
C14	-0.726706	-0.740341	-0.000008
Br15	3.166663	-0.105955	0.000004
H16	0.899804	-2.120732	-0.000007

8BrGuo$^{\bullet+}$

O1	3.972929	-0.729973	0.032804
C2	3.978686	0.092080	-1.121129
H3	3.811403	-0.492859	-2.034010
H4	4.934518	0.624046	-1.220321
C5	2.879551	1.128123	-0.997094
H6	3.025818	1.895032	-1.765728
O7	1.593753	0.509171	-1.234102
C8	0.707589	0.943723	-0.251451
H9	0.204830	1.881317	-0.521164
N10	-0.379702	-0.028331	-0.116178
C11	-0.348319	-1.389868	0.066747
N12	-1.560577	-1.953626	0.154889
C13	-2.404394	-0.939255	0.029539
C14	-3.863891	-0.920632	0.044783
O15	-4.630054	-1.835953	0.183491
N16	-4.343818	0.410878	-0.138353
H17	-5.355620	0.484871	-0.131894
C18	-3.573799	1.518633	-0.305753
N19	-4.157509	2.700214	-0.468819
H20	-5.157801	2.829508	-0.474868
H21	-3.562613	3.508581	-0.584715
N22	-2.225674	1.495577	-0.317000
C23	-1.708804	0.301176	-0.149252
C24	2.791824	1.806045	0.388072
H25	3.688172	1.634108	0.988116
C26	1.550380	1.155502	1.016833
H27	1.827612	0.189775	1.446473
O28	2.488751	3.188720	0.285357
H29	4.767345	-1.270270	0.047275
H30	3.290402	3.716902	0.311162
O31	0.908788	1.914801	1.988433
H32	1.087834	2.845257	1.790020
Br33	1.182366	-2.364758	0.170636

Cartesian coordinates for monohydrated structures in Scheme 3, optimized at ωB97XD/6-31+G(d,p)

8BrG$^{\bullet+}$·W12b

C1	1.460578	1.301306	0.000007
C2	0.177243	0.598585	0.000003
H3	3.478405	0.772532	0.000007
C4	2.416980	-0.978554	-0.000001
C5	-1.838394	-0.005965	-0.000002
N6	2.534035	0.374025	0.000004
N7	-1.065775	1.078887	0.000003
N8	-1.133539	-1.180494	-0.000006
N9	1.226592	-1.635237	-0.000005
C10	0.191326	-0.836422	-0.000003
N11	3.516698	-1.712141	-0.000003
H12	3.421064	-2.717693	-0.000007
H13	4.436020	-1.275786	0.000000
O14	1.658010	2.488111	0.000011
H15	-1.516944	-2.116944	-0.000010
O16	5.407931	0.494225	0.000008
H17	5.904598	0.795433	-0.769153
H18	5.904596	0.795428	0.769173
Br19	-3.661364	0.026839	-0.000004

8BrG$^{\bullet+}$·W1

C1	1.626794	-1.018590	-0.000029
C2	0.283909	-0.442087	0.000001
H3	3.582465	-0.374289	0.000062
C4	2.371922	1.326104	0.000000
C5	-1.778029	-0.021661	0.000033
N6	2.614040	-0.003379	0.000025
N7	-0.910278	-1.032937	0.000002
N8	-1.182317	1.211584	0.000050
N9	1.128009	1.875324	0.000022
C10	0.168022	0.988248	0.000029
N11	3.392168	2.172444	-0.000042
H12	3.193510	3.163175	-0.000059
H13	4.353556	1.865248	-0.000140
O14	1.932375	-2.185444	-0.000092
H15	-1.648244	2.109912	0.000069
O16	4.882454	-1.516181	-0.000249
H17	5.836579	-1.631661	0.000826
H18	4.481937	-2.393971	-0.000376
Br19	-3.589871	-0.219393	0.000050

8BrG$^{\bullet+}$·W9

C1	2.200142	-1.527381	-0.000017
C2	0.880017	-0.904302	-0.000011
H3	4.160779	-0.903980	-0.000001
C4	3.015566	0.817018	0.000023
C5	-1.160374	-0.412003	-0.000010
N6	3.218578	-0.527140	0.000002
N7	-0.327360	-1.459289	-0.000024
N8	-0.535825	0.800130	0.000011
N9	1.792854	1.390811	0.000028
C10	0.800979	0.531440	0.000012
N11	4.061342	1.634259	0.000039
H12	3.883313	2.629084	0.000054
H13	5.017840	1.313468	0.000037
O14	2.484326	-2.694700	-0.000034
H15	-1.000378	1.729842	0.000024
O16	-1.893970	3.171965	0.000040
H17	-2.224902	3.637935	0.773760
H18	-2.224879	3.637966	-0.773672
Br19	-2.977706	-0.564642	-0.000018

8BrG$^{\bullet+}$·W2a

C1	-0.981761	2.149407	-0.000002
C2	0.012347	1.079049	0.000000
H3	-3.028751	2.304313	-0.000006
C4	-2.621841	0.277514	-0.000006
C5	1.732744	-0.131239	0.000003
N6	-2.296381	1.602072	-0.000005
N7	1.343427	1.142229	0.000002
N8	0.692741	-1.022081	0.000001
N9	-1.688377	-0.711544	-0.000004
C10	-0.456205	-0.276697	-0.000001
N11	-3.887203	-0.086904	-0.000009
H12	-4.142819	-1.087891	-0.000008
H13	-4.636159	0.590463	-0.000013
O14	-0.805106	3.338064	-0.000001
H15	0.759645	-2.031597	0.000001
O16	-4.885806	-2.676402	-0.000003
H17	-5.111721	-3.203100	-0.772163
H18	-5.111827	-3.203046	0.772163
Br19	3.472507	-0.677630	0.000006

8BrG$^{\bullet+}$·W8

O1	5.424236	-0.064245	0.000049
H2	6.063035	-0.782609	0.000117
H3	5.935953	0.749937	0.000029
N4	-3.497115	0.582810	0.000009
C5	-3.450823	-0.775340	0.000008
N6	-2.299098	-1.482966	0.000002
C7	-1.220011	-0.739427	-0.000002
C8	-1.128407	0.693228	-0.000001
C9	-2.370564	1.461651	0.000005
N10	0.134946	1.106014	-0.000007
C11	0.856490	-0.021311	-0.000011
N12	0.080587	-1.153551	-0.000008
H13	-4.389994	1.065185	0.000013
N14	-4.580995	-1.469577	0.000012
H15	-4.516712	-2.478333	0.000010
H16	-5.495633	-1.043536	0.000017
O17	-2.521062	2.653210	0.000006
Br18	2.679357	-0.082989	-0.000019
H19	0.412056	-2.109652	-0.000011

precursor·H_2O

N1	1.048454	-1.254266	-0.011165
C2	1.754745	-0.136441	-0.369021
N3	0.984854	0.906265	-0.673962
C4	-0.258339	0.456911	-0.507329
C5	-1.539886	1.141119	-0.679198
O6	-1.735041	2.277496	-1.023066
N7	-2.613526	0.266200	-0.375033
H8	-3.556827	0.657353	-0.463265
C9	-2.498900	-1.029318	0.015452
N10	-3.600492	-1.717931	0.260974
H11	-4.517829	-1.289386	0.160184
H12	-3.508035	-2.680873	0.551427
N13	-1.310998	-1.670316	0.172320
C14	-0.275308	-0.915968	-0.086915
O15	1.225616	0.943323	2.571477
O16	0.027680	0.818069	2.524853
H17	1.430260	-2.153598	0.251737
Br18	3.576752	-0.126391	-0.443551
O19	-5.484166	0.418209	-0.326435
H20	-6.002776	0.489553	-1.135725
H21	-5.955760	0.936395	0.335419

[5,8-OO-8BrG]$^{\bullet+}$·H_2O

C1	-1.608559	1.234068	-0.193810
C2	-0.262329	0.592548	0.089160
H3	-3.604953	0.678568	-0.251230
C4	-2.523670	-1.048425	0.006659
C5	1.732298	0.012895	0.076825
N6	-2.654967	0.303241	-0.148070
N7	0.870764	0.838744	-0.769743
N8	0.998971	-1.257617	0.033599
N9	-1.337925	-1.701857	0.078715
C10	-0.294018	-0.934784	0.047544
N11	-3.622948	-1.768205	0.068114
H12	-3.532551	-2.770073	0.167883
H13	-4.540925	-1.331140	0.004411
O14	-1.784167	2.397711	-0.401703
O15	0.172918	0.923351	1.409429
O16	1.591395	0.588716	1.361128
Br17	3.557298	-0.122531	-0.319249
H18	1.398995	-2.180237	0.162136
O19	-5.510431	0.399930	-0.274223
H20	-5.990301	0.573682	-1.092201
H21	-6.033031	0.802151	0.429120

***anti*-[4-OO-8BrG]$^{\bullet+}$·H_2O**

C1	-1.389581	1.322520	0.534751
C2	-0.077640	0.613076	0.374199
H3	-3.349721	0.975999	-0.021015
C4	-2.202337	-0.613347	-0.726433
C5	1.913504	0.065229	-0.077511
N6	-2.402507	0.585607	-0.047819
N7	1.092230	1.140156	0.248129
N8	1.277264	-1.071552	-0.219387
N9	-1.061082	-1.277669	-0.769838
C10	-0.118934	-0.865375	0.131505
N11	-3.255407	-1.073306	-1.390871
H12	-3.173847	-1.969072	-1.847925
H13	-4.142489	-0.580474	-1.377331
O14	-1.530734	2.382242	1.083599
O15	-1.451461	-1.810290	1.793657
O16	-0.218954	-1.579504	1.489877
Br17	3.691630	0.285243	-0.343867
H18	1.688363	-1.969621	-0.452126
O19	-5.192398	0.979526	-0.550722
H20	-5.519183	1.718259	-1.075926
H21	-5.865343	0.810340	0.117807

***syn*-[4-OO-8BrG]$^{\bullet+}$·H_2O**

C1	-1.520609	1.255806	0.532994
C2	-0.190784	0.586016	0.353237
H3	-3.483786	0.827660	0.047572
C4	-2.301952	-0.739186	-0.654868
C5	1.796224	0.079782	-0.167939
N6	-2.528017	0.458138	0.021059
N7	0.945407	1.144856	0.135429
N8	1.196301	-1.078922	-0.239588
N9	-1.150738	-1.379778	-0.689661
C10	-0.192757	-0.911903	0.185591
N11	-3.352184	-1.232347	-1.303268
H12	-3.253095	-2.127833	-1.757298
H13	-4.246005	-0.751945	-1.300325
O14	-1.682263	2.330439	1.045042
O15	0.533758	-1.213141	2.368607
O16	-0.351297	-1.603977	1.491814
Br17	3.551223	0.353566	-0.514934
H18	1.632025	-1.971915	-0.445344
O19	-5.325049	0.797978	-0.485971
H20	-5.658086	1.529423	-1.017497
H21	-6.001172	0.622696	0.177764

***anti*-[5-OO-8BrG]$^{\bullet+}$·H_2O**

C1	-1.295186	1.203568	-0.360586
C2	-0.117686	0.546769	0.355242
H3	-3.282956	0.699849	-0.738269
C4	-2.300770	-1.024688	-0.210229
C5	1.913388	-0.010466	-0.045465
N6	-2.369461	0.307538	-0.487492
N7	1.198230	1.033446	0.124253
N8	1.210124	-1.239132	-0.047873
N9	-1.122119	-1.700956	-0.079929
C10	-0.092327	-0.938906	0.065897
N11	-3.413130	-1.719889	-0.176146
H12	-3.351945	-2.718471	-0.030193
H13	-4.315978	-1.264389	-0.302212
O14	-1.358116	2.345469	-0.705434
O15	-0.348998	0.728697	1.824542
O16	-1.436498	0.165720	2.249413
Br17	3.725232	-0.030988	-0.327734
H18	1.603402	-2.149322	-0.252749
O19	-5.207603	0.458539	-0.810630

H20	-5.661979	0.551407	-1.655760
H21	-5.733964	0.953397	-0.172100

***syn*-[5-OO-8BrG]$^{\bullet+}$·H_2O**

C1	-1.404650	1.205367	-0.351842
C2	-0.197144	0.561988	0.323870
H3	-3.416502	0.702671	-0.594088
C4	-2.406522	-1.025776	-0.135353
C5	1.817950	-0.009551	-0.122789
N6	-2.493962	0.313535	-0.371872
N7	1.112697	1.038745	0.047200
N8	1.103615	-1.237259	-0.112687
N9	-1.225229	-1.697404	-0.047562
C10	-0.186491	-0.932473	0.043690
N11	-3.517116	-1.725811	-0.073432
H12	-3.446958	-2.727302	0.045897
H13	-4.424983	-1.273771	-0.170912
O14	-1.483346	2.332096	-0.736804
O15	-0.529125	0.746443	1.761847
O16	0.364694	0.204075	2.534242
Br17	3.621677	-0.046262	-0.449047
H18	1.491680	-2.153562	-0.300001
O19	-5.338986	0.458431	-0.620292
H20	-5.813513	0.564976	-1.452710
H21	-5.853214	0.937839	0.039547

***anti*-[8-OO-8BrG]$^{\bullet+}$·H_2O**

C1	-1.717499	1.255443	0.405442
C2	-0.392357	0.575290	0.348562
H3	-3.703944	0.735867	0.076328
C4	-2.589198	-0.955873	-0.266098
C5	1.691519	-0.040670	0.411939
N6	-2.748857	0.360369	0.066524
N7	0.758095	1.047392	0.618701
N8	0.913384	-1.204629	0.045135
N9	-1.397510	-1.602531	-0.314255
C10	-0.367470	-0.863675	-0.019070
N11	-3.668977	-1.651427	-0.554022
H12	-3.557324	-2.625713	-0.799429
H13	-4.592278	-1.221748	-0.531065
O14	-1.923484	2.397971	0.697660
O15	2.359272	-0.231670	1.665087
O16	3.034907	-1.352490	1.663748
Br17	2.944246	0.427105	-0.954974
H18	1.315102	-2.113184	-0.152364
O19	-5.600347	0.473504	-0.175386
H20	-6.037177	0.952589	-0.888883
H21	-6.178674	0.557670	0.591398

***syn*-[8-OO-8BrG]$^{\bullet+}$·H_2O**

C1	-1.626719	1.304877	0.106772
C2	-0.320112	0.588489	0.142691
H3	-3.631022	0.793664	-0.112700
C4	-2.562511	-0.956655	-0.224302
C5	1.743284	-0.079051	0.330404
N6	-2.685124	0.396753	-0.083557
N7	0.845070	1.061575	0.329761
N8	0.940344	-1.246153	0.050457
N9	-1.386018	-1.633835	-0.202993
C10	-0.336183	-0.887848	-0.023799
N11	-3.663083	-1.659472	-0.388165
H12	-3.578274	-2.661561	-0.490074
H13	-4.576116	-1.208183	-0.408401
O14	-1.800855	2.483210	0.225609
O15	2.369420	-0.187822	1.637960
O16	1.471703	-0.387434	2.566325
Br17	3.165411	0.163006	-0.899045
H18	1.304800	-2.188659	-0.009166
O19	-5.537736	0.545054	-0.287067
H20	-5.979030	0.925906	-1.054997
H21	-6.094889	0.758621	0.470186

Cartesian coordinates for the structures in Scheme 4, optimized at ωB97XD/6-31+G(d,p)

8BrG$^{\bullet+}$

N1	0.573195	-1.162580	-0.000015
C2	1.348323	-0.032188	-0.000005
N3	0.639738	1.097886	0.000000
C4	-0.627390	0.691646	0.000000
C5	-1.865536	1.467869	-0.000003
O6	-2.006673	2.659850	0.000001
N7	-2.997515	0.595443	-0.000004
H8	-3.887800	1.083189	0.000001
C9	-2.959105	-0.762233	-0.000001
N10	-4.089480	-1.452992	0.000012
H11	-5.003638	-1.024957	0.000038
H12	-4.028259	-2.462340	0.000018
N13	-1.808431	-1.476906	-0.000007
C14	-0.726706	-0.740341	-0.000008
Br15	3.166663	-0.105955	0.000004
H16	0.899804	-2.120732	-0.000007

$^1O_2$

O1	0.000000	0.000000	0.602292
O2	0.000000	0.000000	-0.602292

precursor complex

N1	0.553397	-1.229597	0.208972
C2	1.330069	-0.226024	-0.309375
N3	0.624076	0.779016	-0.828244
C4	-0.643363	0.421057	-0.639483
C5	-1.879374	1.118759	-0.985273
O6	-2.017578	2.180514	-1.527941
N7	-3.012337	0.349152	-0.578965
H8	-3.901807	0.788555	-0.793715
C9	-2.976554	-0.860543	0.038214
N10	-4.108991	-1.468387	0.359995
H11	-5.021693	-1.079931	0.173658
H12	-4.050256	-2.368436	0.816992
N13	-1.828253	-1.504535	0.354773
C14	-0.745622	-0.852857	0.015268
O15	0.719865	1.429883	2.340162
O16	-0.477878	1.322255	2.260053
H17	0.878923	-2.084518	0.642219
Br18	3.148382	-0.308537	-0.307119

TS58

C1	-1.935336	1.380877	-0.306718
C2	-0.642736	0.655751	-0.035521
H3	-3.942674	0.972166	-0.363601
C4	-2.997235	-0.849210	-0.100525
C5	1.285469	-0.033495	-0.049411
N6	-3.047949	0.506367	-0.245844
N7	0.545121	0.921193	-0.693014
N8	0.513529	-1.259293	-0.026100
N9	-1.848749	-1.562074	-0.038286
C10	-0.758922	-0.860272	-0.053386
N11	-4.124131	-1.530708	-0.036078
H12	-4.064703	-2.537055	0.053152
H13	-5.038576	-1.103104	-0.068924
O14	-2.060622	2.547772	-0.516908
O15	-0.292768	0.846190	1.477723
O16	0.990582	0.467313	1.511510
Br17	3.117628	-0.209279	-0.2582210
H18	0.859249	-2.187747	0.187137

[5,8-OO-8BrG]$^{\bullet+}$

C1	-1.973362	1.367514	-0.288490
C2	-0.668951	0.667659	0.040058
H3	-3.968219	0.932432	-0.403197
C4	-3.008013	-0.873522	-0.074421
C5	1.295171	-0.007462	0.086307
N6	-3.071136	0.480779	-0.253029
N7	0.495390	0.847987	-0.792490
N8	0.497562	-1.242436	0.040625
N9	-1.857357	-1.571810	0.033491
C10	-0.773900	-0.855816	0.016047
N11	-4.131795	-1.560958	-0.021558
H12	-4.067466	-2.564272	0.094865
H13	-5.048186	-1.141237	-0.085358
O14	-2.099595	2.529394	-0.523803
O15	-0.254170	0.993469	1.367136
O16	1.146853	0.589267	1.359822
Br17	3.118202	-0.240167	-0.261255
H18	0.847762	-2.183296	0.186093

TS8c

C1	-1.970783	1.481569	-0.209637
C2	-0.711799	0.700709	-0.197151
H3	-3.985270	1.087773	-0.204242
C4	-3.046735	-0.757661	-0.231323
C5	1.263035	-0.045893	-0.020438
N6	-3.090782	0.607742	-0.212511
N7	0.508497	1.114092	-0.207995
N8	0.461385	-1.179506	-0.247534
N9	-1.906398	-1.481147	-0.241815
C10	-0.815713	-0.765837	-0.213588
N11	-4.182524	-1.433072	-0.239644
H12	-4.131358	-2.443257	-0.249816
H13	-5.092710	-0.996415	-0.236189
O14	-2.097689	2.670281	-0.213386
O15	1.289055	0.001660	1.766646
O16	0.140302	-0.096796	2.218134
Br17	3.055322	-0.090992	-0.457603
H18	0.780450	-2.138622	-0.185495

***syn*-[8-OO-8BrG]$^{\bullet+}$**

C1	-1.967646	1.489085	-0.109300
C2	-0.715879	0.697330	0.038863
H3	-3.970567	1.115890	-0.353153
C4	-3.049364	-0.737723	-0.267051
C5	1.292149	-0.081272	0.357493
N6	-3.085174	0.628428	-0.255847

N7 0.472330 1.110064 0.221937
N8 0.414698 -1.215830 0.163844
N9 -1.922330 -1.473714 -0.139880
C10 -0.827509 -0.782878 0.009874
N11 -4.179686 -1.403604 -0.406016
H12 -4.135238 -2.414637 -0.409705
H13 -5.081828 -0.960810 -0.505551
O14 -2.079492 2.678028 -0.106001
O15 1.873200 -0.106373 1.687986
O16 0.939052 -0.159191 2.600845
Br17 2.752032 -0.053785 -0.847538
H18 0.715055 -2.182367 0.202057

TS8d
C1 -1.973228 1.404923 -0.305165
C2 -0.691698 0.656384 -0.152344
H3 -3.980999 0.993366 -0.268219
C4 -3.017671 -0.834586 -0.114989
C5 1.295150 -0.038420 0.119421
N6 -3.080471 0.527493 -0.212681
N7 0.514464 1.026590 -0.574102
N8 0.492560 -1.228901 -0.090360
N9 -1.867561 -1.542374 -0.071770
C10 -0.779196 -0.832479 -0.099222
N11 -4.142163 -1.521395 -0.057945
H12 -4.078081 -2.528629 0.016124
H13 -5.058515 -1.097308 -0.077940
O14 -2.102654 2.580635 -0.466372
O15 -0.173902 0.613894 1.659621
O16 1.185235 0.393605 1.484976
Br17 3.103254 -0.196245 -0.309771
H18 0.816342 -2.168740 0.107993

TS8a
N1 0.294836 -1.207559 -0.075151
C2 1.135881 -0.074017 0.013097
N3 0.362965 1.086694 -0.142279
C4 -0.860248 0.683268 -0.125103
C5 -2.110819 1.474129 -0.140266
O6 -2.229508 2.663546 -0.182331
N7 -3.238784 0.611087 -0.092789
H8 -4.128832 1.099311 -0.092871
C9 -3.205652 -0.753442 -0.036016
N10 -4.346943 -1.419180 0.010218
H11 -5.253571 -0.975367 0.003625
H12 -4.303644 -2.428795 0.053159
N13 -2.071185 -1.484436 -0.022243
C14 -0.972290 -0.778547 -0.067917
O15 1.374149 0.018283 1.788719
O16 2.551567 0.148059 2.131243
H17 0.602412 -2.169136 0.002703
Br18 2.816758 -0.130849 -0.727849

***anti*-[8-OO-8BrG]$^{\bullet+}$**
C1 -2.081519 1.438720 0.317071
C2 -0.801879 0.678592 0.307818
H3 -4.067763 1.054059 -0.022312
C4 -3.079319 -0.745426 -0.305657
C5 1.240282 -0.056479 0.423963
N6 -3.165418 0.588411 -0.016698
N7 0.370077 1.090549 0.583226
N8 0.395577 -1.184210 0.078363
N9 -1.928306 -1.453257 -0.311055
C10 -0.857613 -0.768417 -0.017086
N11 -4.184106 -1.406266 -0.594817
H12 -4.103691 -2.393114 -0.804381
H13 -5.100089 -0.981703 -0.620141
O14 -2.235856 2.596350 0.567136
O15 1.875220 -0.251909 1.691633
O16 2.485755 -1.409349 1.728729
Br17 2.531180 0.292368 -0.939918
H18 0.744804 -2.121392 -0.085831

TS8b
C1 -1.943555 1.369060 -0.557050
C2 -0.718063 0.658744 -0.100382
H3 -3.953203 0.977396 -0.692055
C4 -3.088001 -0.734424 0.091844
C5 1.274960 -0.009625 0.449461
N6 -3.084190 0.541105 -0.399622
N7 0.478697 1.087193 -0.059125
N8 0.355008 -1.096036 0.748132
N9 -1.985351 -1.396743 0.507290
C10 -0.870917 -0.725809 0.412644
N11 -4.235516 -1.379835 0.179072
H12 -4.220868 -2.323126 0.545391
H13 -5.121974 -0.985622 -0.101425
O14 -2.020360 2.477505 -0.994674
O15 1.974631 0.311066 1.660488
O16 1.888054 1.572149 2.004864
Br17 2.551289 -0.519850 -0.881245
H18 0.635262 -1.997125 1.116902

TS4c
C1 -1.841896 1.557425 0.105733
C2 -0.575531 0.761840 0.062184
H3 -3.828961 1.212635 -0.189457
C4 -2.843754 -0.593035 -0.595362
C5 1.378742 0.001494 -0.201133
N6 -2.929273 0.745412 -0.211423
N7 0.631409 1.179087 -0.080657
N8 0.646859 -1.088046 -0.247882
N9 -1.750596 -1.317766 -0.529707
C10 -0.702042 -0.724872 0.118051
N11 -3.965609 -1.143929 -1.057336
H12 -3.944388 -2.122962 -1.303609
H13 -4.812784 -0.624153 -1.222920
O14 -1.923345 2.724118 0.369457
O15 0.193574 -0.720030 2.340345
O16 -0.821921 -1.082633 1.640830
Br17 3.173803 0.044655 -0.395366
H18 0.993916 -2.040521 -0.299064

***syn*-[4-OO-8BrG]$^{\bullet+}$**

C1	-1.834085	1.546888	0.125392
C2	-0.564029	0.751645	0.149328
H3	-3.797664	1.192671	-0.315674
C4	-2.738523	-0.575092	-0.726025
C5	1.390991	-0.005019	-0.142082
N6	-2.889373	0.742537	-0.293295
N7	0.624226	1.164834	-0.103119
N8	0.690576	-1.102804	-0.025330
N9	-1.650168	-1.291506	-0.564722
C10	-0.695073	-0.745362	0.273373
N11	-3.788649	-1.114019	-1.343753
H12	-3.729172	-2.083389	-1.620319
H13	-4.609690	-0.589201	-1.600360
O14	-1.934320	2.702126	0.428427
O15	-0.114224	-0.675138	2.511868
O16	-0.985500	-1.156063	1.665521
Br17	3.174126	0.055204	-0.429992
H18	1.052477	-2.051254	-0.028847

TS4d

C1	-1.773985	1.422184	-0.414680
C2	-0.538319	0.779109	0.162516
H3	-3.634404	0.866483	-1.023212
C4	-2.655190	-0.899643	-0.497277
C5	1.405431	-0.029077	-0.011752
N6	-2.777868	0.475036	-0.646506
N7	0.704915	1.091634	-0.216477
N8	0.717226	-1.094560	0.439758
N9	-1.598484	-1.513403	0.005771
C10	-0.658899	-0.704184	0.543833
N11	-3.681189	-1.635358	-0.911682
H12	-3.625525	-2.636125	-0.784415
H13	-4.494962	-1.252673	-1.367608
O14	-1.903743	2.588623	-0.646466
O15	-0.819232	0.945726	1.939332
O16	-0.899929	-0.363455	2.035134
Br17	3.184586	-0.141967	-0.380303
H18	1.051203	-2.049774	0.469946

TS4a

C1	-1.658116	1.639118	0.161307
C2	-0.419796	0.799159	0.127915
H3	-3.637105	1.390481	-0.262464
C4	-2.682306	-0.403641	-0.773554
C5	1.520150	-0.004697	-0.094665
N6	-2.750449	0.899242	-0.286276
N7	0.810965	1.181879	0.065100
N8	0.758205	-1.071897	-0.195509
N9	-1.599177	-1.155510	-0.739079
C10	-0.603884	-0.672004	0.045060
N11	-3.786676	-0.884640	-1.336774
H12	-3.777533	-1.844694	-1.649944
H13	-4.630286	-0.346405	-1.456086
O14	-1.715414	2.781969	0.519191
O15	-2.033847	-1.316760	1.842361
O16	-0.800560	-1.133639	1.593530
Br17	3.325823	-0.021491	-0.209150
H18	1.073314	-2.030890	-0.300531

***anti*-[4-OO-8BrG]$^{\bullet+}$**

C1	-1.672870	1.622402	0.183220
C2	-0.432398	0.780565	0.201235
H3	-3.623703	1.376188	-0.366164
C4	-2.613861	-0.401238	-0.845557
C5	1.512347	-0.012629	-0.049023
N6	-2.729563	0.898466	-0.355033
N7	0.785523	1.172387	0.058298
N8	0.771220	-1.093547	-0.050791
N9	-1.546413	-1.159128	-0.712836
C10	-0.611887	-0.709771	0.186233
N11	-3.663183	-0.872157	-1.514471
H12	-3.629757	-1.829449	-1.834121
H13	-4.475005	-0.317555	-1.735372
O14	-1.746689	2.752727	0.576058
O15	-2.112167	-1.231958	1.878711
O16	-0.848749	-1.201868	1.607260
Br17	3.310773	-0.000776	-0.242208
H18	1.101161	-2.051352	-0.116116

TS4b

C1	-1.771495	1.500513	-0.242429
C2	-0.507303	0.746816	0.041045
H3	-3.697927	1.025735	-0.742945
C4	-2.593216	-0.760665	-0.719817
C5	1.460310	-0.041510	-0.046318
N6	-2.789769	0.609364	-0.571124
N7	0.686634	1.094084	-0.286469
N8	0.769123	-1.089201	0.321173
N9	-1.512260	-1.407237	-0.338959
C10	-0.637560	-0.697243	0.467655
N11	-3.582993	-1.438518	-1.297705
H12	-3.492013	-2.441775	-1.368350
H13	-4.385303	-0.996022	-1.717584
O14	-1.893472	2.690747	-0.199134
O15	-1.421090	0.256165	2.396447
O16	-0.931744	-0.852522	1.893079
Br17	3.248875	-0.034173	-0.320217
H18	1.135516	-2.013898	0.524096

TS5c

C1	-1.828822	1.311245	-0.583348
C2	-0.601608	0.627991	-0.085557
H3	-3.836616	0.888369	-0.712363
C4	-2.908479	-0.882164	-0.180431
C5	1.378699	-0.073190	-0.181451
N6	-2.952937	0.447619	-0.476155
N7	0.695231	1.010042	-0.344521
N8	0.601170	-1.239899	-0.011200
N9	-1.759133	-1.580234	-0.008976
C10	-0.682318	-0.853350	-0.051374
N11	-4.036397	-1.560732	-0.083992

H12 -3.977664 -2.552528 0.107520
H13 -4.949709 -1.140073 -0.176349
O14 -1.934991 2.435685 -0.970249
O15 -0.820868 0.883108 1.642288
O16 0.245730 0.695352 2.252367
Br17 3.197515 -0.212671 -0.277717
H18 0.951619 -2.186186 0.072931

***syn*-[5-OO-8BrG]$^{\bullet+}$**
C1 -1.726591 1.300047 -0.617460
C2 -0.601448 0.658003 0.186503
H3 -3.708592 0.890494 -1.003143
C4 -2.866953 -0.859320 -0.280426
C5 1.402717 -0.046198 -0.085866
N6 -2.868423 0.458968 -0.630743
N7 0.745150 1.045456 -0.041730
N8 0.618309 -1.233408 -0.030327
N9 -1.731931 -1.568969 -0.066080
C10 -0.655899 -0.852271 0.022162
N11 -4.007470 -1.515802 -0.220600
H12 -3.975899 -2.506894 -0.017182
H13 -4.908652 -1.077093 -0.346293
O14 -1.727537 2.383396 -1.111346
O15 -1.012857 0.970979 1.581554
O16 -0.197961 0.448302 2.448560
Br17 3.215240 -0.201491 -0.293998
H18 0.966171 -2.181019 -0.116726

TS5a
C1 -1.649131 1.381628 -0.549990
C2 -0.477898 0.634878 -0.018417
H3 -3.640409 0.985699 -0.890751
C4 -2.753005 -0.824869 -0.425080
C5 1.522039 -0.036932 -0.093635
N6 -2.774964 0.520589 -0.635528
N7 0.832587 1.058310 -0.064968
N8 0.758607 -1.210675 -0.155119
N9 -1.608080 -1.544917 -0.276083
C10 -0.533772 -0.824376 -0.189759
N11 -3.882384 -1.505065 -0.437418
H12 -3.832724 -2.509284 -0.324318
H13 -4.791337 -1.071624 -0.512654
O14 -1.716824 2.541654 -0.828984
O15 -0.882276 0.693775 1.754394
O16 -1.890993 0.066404 2.105703
Br17 3.346896 -0.139211 -0.104654
H18 1.114086 -2.156775 -0.213208

***anti*-[5-OO-8BrG]$^{\bullet+}$**
C1 -1.602281 1.279354 -0.658300
C2 -0.519153 0.636682 0.202296
H3 -3.543408 0.848122 -1.195656
C4 -2.738396 -0.883285 -0.388362
C5 1.504687 -0.041087 -0.001250
N6 -2.719198 0.420894 -0.785137
N7 0.831570 1.043530 0.036073
N8 0.737768 -1.234259 0.031838
N9 -1.608027 -1.590105 -0.122306
C10 -0.548579 -0.866981 0.030789
N11 -3.877673 -1.539780 -0.359528
H12 -3.855108 -2.524004 -0.124050
H13 -4.774176 -1.100967 -0.515490
O14 -1.584854 2.378159 -1.119647
O15 -0.853759 0.948219 1.629730
O16 -1.997198 0.470638 2.008201
Br17 3.326641 -0.167819 -0.141718
H18 1.098010 -2.175685 -0.068546

TS5b
C1 -1.628940 1.371065 -0.538125
C2 -0.549336 0.656131 0.270062
H3 -3.611527 1.025175 -0.994410
C4 -2.792961 -0.797871 -0.451234
C5 1.466300 -0.024947 -0.028574
N6 -2.784224 0.550272 -0.646798
N7 0.810585 1.057590 0.128091
N8 0.680578 -1.206951 -0.105963
N9 -1.658231 -1.525736 -0.297880
C10 -0.598874 -0.830521 -0.046922
N11 -3.931183 -1.457788 -0.494970
H12 -3.901049 -2.465102 -0.399298
H13 -4.830688 -1.008546 -0.593501
O14 -1.602138 2.488046 -0.948750
O15 -0.956589 0.926298 1.671886
O16 -1.290037 -0.139213 2.340231
Br17 3.283116 -0.165181 -0.214596
H18 1.024494 -2.136090 -0.317462

Approximately spin-projected structures and energies, optimized at ωB97XD/6-31+G(d,p)

8BrG$^{\bullet+}$

N1 0.573195 -1.162580 -0.000015
C2 1.348323 -0.032188 -0.000005
N3 0.639738 1.097886 0.000000
C4 -0.627390 0.691646 0.000000
C5 -1.865536 1.467869 -0.000003
O6 -2.006673 2.659850 0.000001
N7 -2.997515 0.595443 -0.000004
H8 -3.887800 1.083189 0.000001
C9 -2.959105 -0.762233 -0.000001
N10 -4.089480 -1.452992 0.000012
H11 -5.003638 -1.024957 0.000038
H12 -4.028259 -2.462340 0.000018
N13 -1.808431 -1.476906 -0.000007
C14 -0.726706 -0.740341 -0.000008
Br15 3.166663 -0.105955 0.000004
H16 0.899804 -2.120732 -0.000007

E(UwB97XD) = -3113.27869334 <S**2>= 0.7664
Zero-point correction= 0.108533 (Hartree/Particle)
Thermal correction to Energy= 0.117957
Thermal correction to Enthalpy= 0.118901
Thermal correction to Gibbs Free Energy= 0.071920
Sum of electronic and zero-point Energies= -3113.170160
Sum of electronic and thermal Energies= -3113.160737
Sum of electronic and thermal Enthalpies= -3113.159793
Sum of electronic and thermal Free Energies= -3113.206773

$^1O_2$

O1 0.000000 0.000000 0.602292
O2 0.000000 0.000000 -0.602292

closed-shell solution
E(UwB97XD) = -150.215776806 <S**2>= 0.0000
Zero-point correction= 0.003902 (Hartree/Particle)
Thermal correction to Energy= 0.006265
Thermal correction to Enthalpy= 0.007209
Thermal correction to Gibbs Free Energy= -0.015024
Sum of electronic and zero-point Energies= -150.211874
Sum of electronic and thermal Energies= -150.209512
Sum of electronic and thermal Enthalpies= -150.208568
Sum of electronic and thermal Free Energies= -150.230800

open-shell (broken-symmetry) solution
E(UwB97XD) = -150.258561602 <S**2>= 1.0039
Zero-point correction= 0.003921 (Hartree/Particle)
Thermal correction to Energy= 0.006284
Thermal correction to Enthalpy= 0.007228
Thermal correction to Gibbs Free Energy= -0.015005
Sum of electronic and zero-point Energies= -150.254640
Sum of electronic and thermal Energies= -150.252278
Sum of electronic and thermal Enthalpies= -150.251334
Sum of electronic and thermal Free Energies= -150.273566

precursor complex
8BrG$^{\bullet+}$ (S=1/2), $^1O_2$ (S=0)

N1 0.554703 -1.219327 0.220112
C2 1.330463 -0.216981 -0.302480
N3 0.623591 0.785514 -0.824963
C4 -0.643462 0.427435 -0.633873
C5 -1.880205 1.120844 -0.985890
O6 -2.019624 2.178996 -1.535174
N7 -3.012028 0.351315 -0.576571
H8 -3.901985 0.787702 -0.795069
C9 -2.975047 -0.857162 0.043042
N10 -4.107515 -1.465505 0.363069
H11 -5.020495 -1.080615 0.170946
H12 -4.050279 -2.363900 0.823250
N13 -1.826443 -1.497838 0.364193
C14 -0.744493 -0.845035 0.024740
O15 0.716287 1.373634 2.313370
O16 -0.482313 1.300511 2.219629
H17 0.880973 -2.072674 0.655817
Br18 3.148876 -0.301088 -0.303957

Zero-point correction= 0.113127 (Hartree/Particle)
Thermal correction to Energy= 0.126572
Thermal correction to Enthalpy= 0.127516
Thermal correction to Gibbs Free Energy= 0.069499
Sum of electronic and zero-point Energies= -3263.429978
Sum of electronic and thermal Energies= -3263.416534
Sum of electronic and thermal Enthalpies= -3263.415589
Sum of electronic and thermal Free Energies= -3263.473606