Supporting Information

Development of a Double-Well Potential upon Collisional Activation That Facilitates Proton Transfer in the 9-Methyl-8-Oxoguanine–9-Methyladenine Base-Pair Radical Cation

May Myat Moe[ab] and Jianbo Liu*[ab]

[a] Department of Chemistry and Biochemistry, Queens College of the City University of New York, 65-30 Kissena Blvd., Queens, NY 11367, USA; [b] The Ph.D. Program in Chemistry, the Graduate Center of the City University of New York, 365 5th Ave., New York, NY 10016, USA

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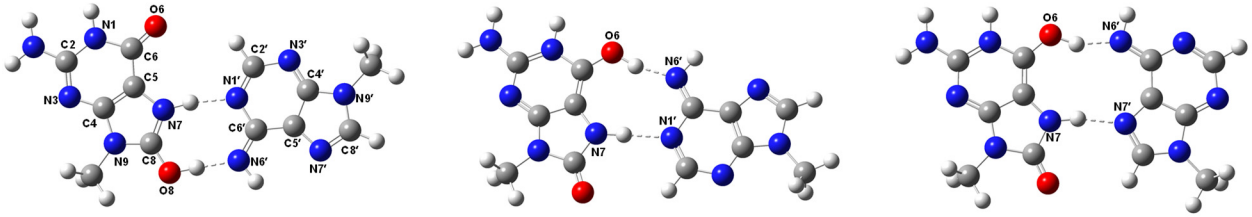

Scheme S1 Various hydrogen-transferred conformers of [9MOG·9MA]$^{\bullet+}$ with atomic numbering. Dashed lines indicate H-bonds. Relative formation enthalpies (ΔH with respect to HG_C$^{\bullet+}$ in Scheme 2) were calculated at 298 K using the ωB97XD/6-311++G(d,p) level of theory, including thermal corrections.

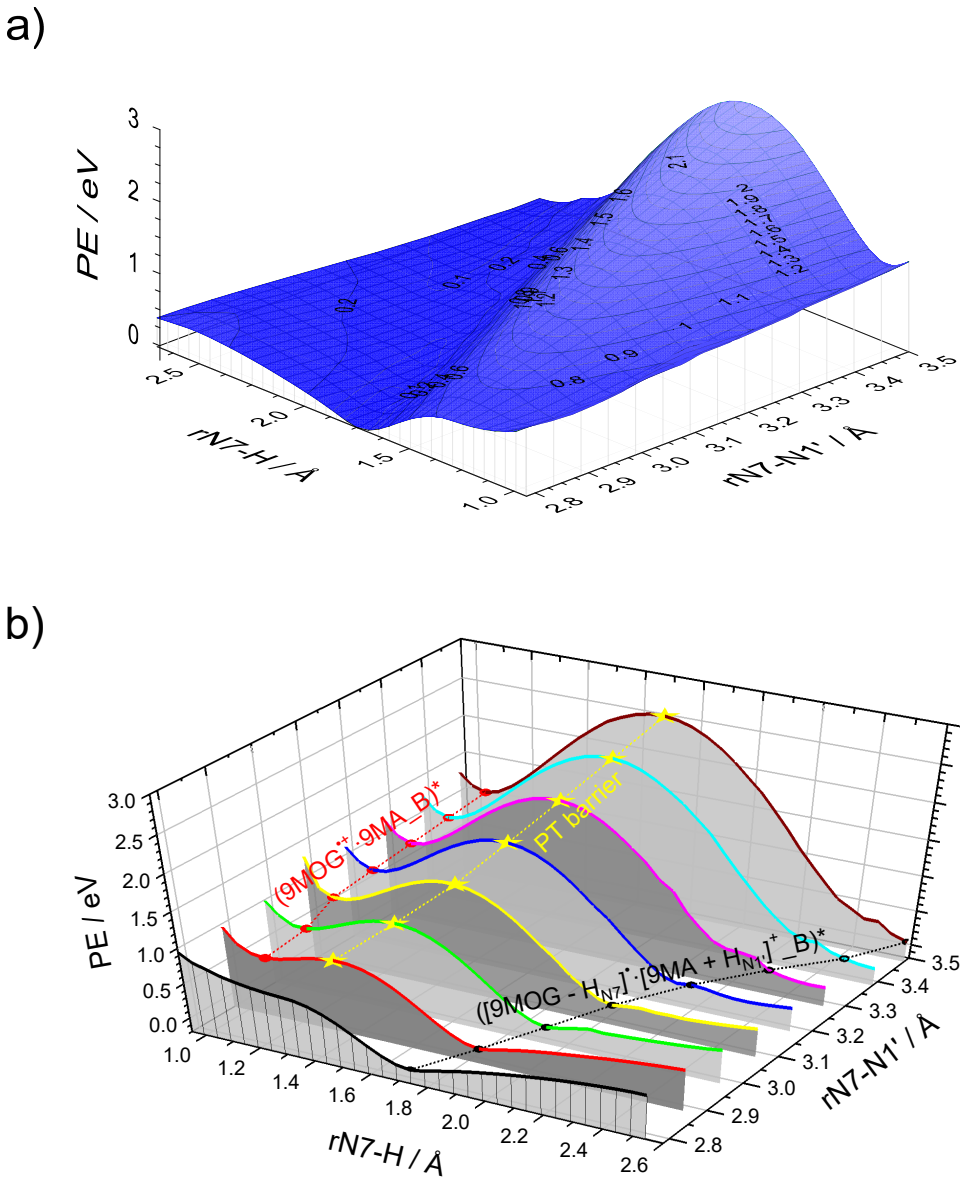

Fig. S1 a) Relaxed 2D PES scan along rN7–N1′ and rN7–H for [9MOG – H_{N7}]•·[9MA + $H_{N1'}$]$^+$_B, calculated at the ωB97XD/6-31+G(d,p) level of theory. Numbers on the contour map are electronic energies with respect to the starting reactant [9MOG – H_{N7}]•·[9MA + $H_{N1'}$]$^+$_B; and b) slice view of the PES cutting at different rN7–N1′ values. The evolution of the 9MOG$^{•+}$·9MA (red dots and trace) ⇌ [9MOG – H_{N7}]•·[9MA + $H_{N1'}$]$^+$ (black dots and trace) equilibrium is highlighted, with the barrier height for PT indicated for each slice.

Cartesian coordinates for structures in Scheme 1, optimized at ωB97XD/ 6-311++G(d,p).

HG_A

C1 2.851423 -1.850512 -0.008644
N2 4.064293 -2.426167 0.019719
C3 4.010269 0.225965 0.014253
N4 3.697034 1.564390 0.003141
N5 1.755724 0.465304 -0.037307
N6 5.226072 -0.324003 0.042752
C7 5.151301 -1.650369 0.042536
H8 6.099079 -2.180566 0.064585
N9 1.766140 -2.636870 -0.031110
H10 0.813115 -2.288414 -0.048751
H11 1.915317 -3.631122 -0.025063
C12 2.793924 -0.441318 -0.012325
C13 4.646748 2.657407 0.043032
H14 5.394073 2.523140 -0.739380
H15 4.113382 3.593646 -0.119128
H16 5.150439 2.687901 1.010532
C17 -2.089488 -1.556490 -0.029748
C18 -2.068519 -0.148892 -0.018813
H19 -3.514786 -3.029437 -0.078167
C20 -4.539935 -1.238419 0.029734
C21 -1.512487 2.027970 -0.031443
N22 -3.426123 -2.025813 -0.004213
N23 -1.022313 0.753880 -0.046653
N24 -2.916909 1.892324 -0.003316
N25 -4.498262 0.066168 0.044030
C26 -3.244260 0.566681 0.005993
N27 -5.752293 -1.876759 -0.001539
H28 -6.533429 -1.265031 0.175239
H29 -5.823078 -2.786295 0.425094
O30 -1.163922 -2.360218 -0.061193
C31 -3.831324 3.010494 0.029486
H32 -4.351767 3.057320 0.988310
H33 -3.239614 3.915030 -0.106898
H34 -4.565188 2.922435 -0.772866
O35 -0.899783 3.079394 -0.040213
H36 -0.009830 0.535279 -0.052115
C37 2.333976 1.638447 -0.025732
H38 1.798635 2.579741 -0.038660

Zero-point correction=	0.293952 (Hartree/Particle)
Thermal correction to Energy=	0.315596
Thermal correction to Enthalpy=	0.316540
Thermal correction to Gibbs Free Energy=	0.240645
Sum of electronic and zero-point Energies=	-1163.425513
Sum of electronic and thermal Energies=	-1163.403869
Sum of electronic and thermal Enthalpies=	-1163.402924
Sum of electronic and thermal Free Energies=	-1163.478819

HG_B

C1 -2.334159 -1.560187 -0.030821
C2 -2.300689 -0.153864 -0.035628
H3 -3.760616 -3.026155 0.085362
C4 -4.781032 -1.229948 0.039186
C5 -1.736024 2.022678 -0.034352
N6 -3.671831 -2.022634 0.010732
N7 -1.248986 0.745140 -0.063399
N8 -3.142919 1.889620 0.004038
N9 -4.731338 0.074030 0.031633
C10 -3.474292 0.567503 0.006986
N11 -5.994446 -1.861712 0.129650
H12 -6.778931 -1.242711 -0.001533
H13 -6.093183 -2.764973 -0.304809
O14 -1.415764 -2.375779 -0.050017
C15 2.174909 -0.949906 -0.037756
N16 1.525605 0.226992 -0.054859
C17 4.166792 0.348538 0.009832
C18 -4.051411 3.011790 0.052237
H19 -4.767730 2.957062 -0.769018
H20 -4.592911 3.029655 1.000175
H21 -3.449676 3.915306 -0.040764
O22 -1.127061 3.072659 -0.040421
H23 -0.236805 0.512434 -0.070801
N24 5.516958 0.119599 0.049704
N25 4.539347 -1.901670 0.023230
C26 5.666322 -1.245611 0.052989
H27 6.648393 -1.697136 0.082744
N28 3.537026 1.529797 -0.006409
C29 2.223978 1.374896 -0.038042
H30 1.618582 2.278117 -0.051456
N31 1.486333 -2.096386 -0.052684
H32 1.996417 -2.962334 -0.030412
H33 0.467480 -2.113807 -0.060479
C34 3.583273 -0.909669 -0.004651
C35 6.551555 1.132785 0.054347
H36 6.330799 1.877957 0.818831
H37 7.508153 0.658996 0.274415
H38 6.607059 1.629085 -0.916154

Zero-point correction=	0.293882 (Hartree/Particle)
Thermal correction to Energy=	0.315556
Thermal correction to Enthalpy=	0.316500
Thermal correction to Gibbs Free Energy=	0.240000
Sum of electronic and zero-point Energies=	-1163.424943
Sum of electronic and thermal Energies=	-1163.403270
Sum of electronic and thermal Enthalpies=	-1163.402325
Sum of electronic and thermal Free Energies=	-1163.478825

HG_C

C1 -2.482292 -1.752641 -0.020363
C2 -2.357489 -0.342136 -0.022291
H3 -4.027594 -3.101486 0.074635
C4 -4.908557 -1.234508 0.017393
C5 -1.643959 1.781218 -0.012826
N6 -3.860639 -2.107740 0.002105
N7 -1.245243 0.481177 -0.033434
N8 -3.043921 1.759880 0.007425
N9 -4.765738 0.062363 0.011869
C10 -3.472877 0.458542 0.004817
N11 -6.166041 -1.777330 0.090568

H12	-6.902044	-1.104121	-0.053309
H13	-6.321726	-2.671499	-0.346033
O14	-1.626318	-2.618185	-0.028436
C15	2.388056	0.981791	-0.018564
N16	1.516022	-0.042694	-0.029604
C17	4.080210	-0.689380	-0.002072
C18	-3.870042	2.945367	0.042546
H19	-4.586318	2.931424	-0.780099
H20	-4.410991	3.010024	0.988608
H21	-3.205947	3.803173	-0.057306
O22	-0.946022	2.789122	-0.012848
H23	-0.241423	0.206921	-0.038227
N24	5.449872	-0.735142	0.005540
N25	4.895697	1.440882	0.006663
C26	5.869020	0.572738	0.015128
H27	6.922201	0.817931	0.022764
N28	3.226074	-1.720309	-0.012461
C29	1.969988	-1.306971	-0.026764
H30	1.196859	-2.070625	-0.036397
N31	1.941364	2.242865	-0.021641
H32	2.615539	2.988530	-0.008212
H33	0.944290	2.462372	-0.022523
C34	3.760082	0.660361	-0.003951
C35	6.262807	-1.932759	0.059647
H36	5.740388	-2.732652	-0.464154
H37	7.219416	-1.744117	-0.428218
H38	6.434269	-2.240778	1.093331

Zero-point correction=	0.293943 (Hartree/Particle)
Thermal correction to Energy=	0.315548
Thermal correction to Enthalpy=	0.316492
Thermal correction to Gibbs Free Energy=	0.240321
Sum of electronic and zero-point Energies=	-1163.424897
Sum of electronic and thermal Energies=	-1163.403292
Sum of electronic and thermal Enthalpies=	-1163.402348
Sum of electronic and thermal Free Energies=	-1163.478519

Cartesian coordinates for structures in Scheme 2, optimized at ωB97XD/ 6-311++G(d,p).

HG_A$^{\bullet+}$

C1 2.785519 -1.872447 -0.007136
N2 3.994378 -2.444620 0.001464
C3 3.971011 0.197933 0.005648
N4 3.687431 1.556969 0.003063
N5 1.769282 0.510604 -0.013336
N6 5.172657 -0.357654 0.014448
C7 5.091437 -1.686358 0.011048
H8 6.033433 -2.224365 0.017137
N9 1.701092 -2.655220 -0.017021
H10 0.746055 -2.319533 -0.018798
H11 1.854795 -3.650761 -0.016216
C12 2.753764 -0.459712 -0.005300
C13 4.689798 2.616238 0.028436
H14 5.400622 2.451044 -0.779679
H15 4.192327 3.575601 -0.101778
H16 5.216869 2.593870 0.981591
C17 -2.175855 -1.593324 -0.006006
C18 -2.054157 -0.160834 -0.009011
H19 -3.676846 -2.987345 0.008509
C20 -4.599252 -1.131672 0.013546
C21 -1.408594 1.911285 -0.016397
N22 -3.529625 -1.986120 0.005210
N23 -0.965622 0.591586 -0.018834
N24 -2.830150 1.912835 -0.006765
N25 -4.487878 0.191480 0.012096
C26 -3.240322 0.634128 0.000489
N27 -5.824085 -1.661583 0.024478
H28 -6.607503 -1.028225 0.031338
H29 -5.999001 -2.651777 0.025932
O30 -1.286900 -2.418656 -0.011580
C31 -3.660287 3.105194 0.008452
H32 -4.149704 3.212955 0.976997
H33 -3.009697 3.959544 -0.170026
H34 -4.412416 3.039031 -0.777173
O35 -0.714773 2.900499 -0.023101
H36 0.724636 0.402061 -0.020360
C37 2.358471 1.695217 -0.007469
H38 1.818270 2.631318 -0.011462

Zero-point correction=	0.294073 (Hartree/Particle)
Thermal correction to Energy=	0.315562
Thermal correction to Enthalpy=	0.316506
Thermal correction to Gibbs Free Energy=	0.241228
Sum of electronic and zero-point Energies=	-1163.183718
Sum of electronic and thermal Energies=	-1163.162229
Sum of electronic and thermal Enthalpies=	-1163.161285
Sum of electronic and thermal Free Energies=	-1163.236563

HG_B$^{\bullet+}$

C1 2.383537 -1.586309 0.002339
C2 2.288430 -0.154646 -0.001045
H3 3.850710 -3.013446 0.009815
C4 4.813036 -1.176371 0.008298
C5 1.679381 1.928813 -0.004323
N6 3.724835 -2.009404 0.007612
N7 1.211852 0.615591 -0.004238
N8 3.105669 1.900821 -0.000492
N9 4.729207 0.147046 0.003337
C10 3.490041 0.616939 -0.000296
N11 6.026250 -1.734097 0.013858
H12 6.823448 -1.118276 0.013604
H13 6.179016 -2.727800 0.018560
O14 1.475365 -2.396257 0.001216
C15 -2.148726 -0.961900 -0.008280
N16 -1.548627 0.256438 -0.004832
C17 -4.150357 0.344989 -0.002183
C18 3.956085 3.078524 -0.010879
H19 4.706026 2.997066 0.775440
H20 4.448277 3.181379 -0.978613
H21 3.319770 3.943312 0.169201
O22 1.011832 2.931614 -0.004240
H23 -0.504591 0.322302 -0.004668
N24 -5.488036 0.102176 -0.007118
N25 -4.485737 -1.908634 -0.012213
C26 -5.622216 -1.265989 -0.009676
H27 -6.598040 -1.730677 -0.013941
N28 -3.530164 1.542646 0.000096
C29 -2.237450 1.437475 -0.002216
H30 -1.609582 2.322837 -0.001890
N31 -1.436625 -2.078114 -0.011424
H32 -1.937498 -2.953090 -0.013527
H33 -0.416801 -2.098018 -0.008494
C34 -3.550808 -0.909375 -0.007279
C35 -6.548751 1.098939 0.040256
H36 -6.218431 1.988399 -0.493593
H37 -7.437177 0.694318 -0.442215
H38 -6.776278 1.361037 1.074117

Zero-point correction=	0.294611 (Hartree/Particle)
Thermal correction to Energy=	0.316031
Thermal correction to Enthalpy=	0.316975
Thermal correction to Gibbs Free Energy=	0.241717
Sum of electronic and zero-point Energies=	-1163.191574
Sum of electronic and thermal Energies=	-1163.170154
Sum of electronic and thermal Enthalpies=	-1163.169210
Sum of electronic and thermal Free Energies=	-1163.244468

HG_C$^{\bullet+}$

C1 -2.374266 -1.730238 0.001414
C2 -2.293752 -0.290769 0.001440
H3 -3.848589 -3.157991 0.001522
C4 -4.813508 -1.326385 0.000139
C5 -1.703783 1.791335 -0.001879
N6 -3.725172 -2.153585 0.000832
N7 -1.225117 0.490189 0.000675
N8 -3.118935 1.763644 -0.004198
N9 -4.735232 0.000855 0.000474
C10 -3.499326 0.472534 0.000349

N11 -6.026855 -1.882730 -0.000489
H12 -6.823890 -1.266726 -0.000152
H13 -6.179332 -2.876582 -0.001003
O14 -1.466624 -2.527275 0.001669
C15 2.339641 1.010611 0.002140
N16 1.508077 -0.065153 -0.000629
C17 4.040672 -0.669462 -0.001689
C18 -3.977131 2.936255 0.004169
H19 -4.730580 2.844029 -0.777513
H20 -4.464897 3.041140 0.973850
H21 -3.348924 3.804847 -0.185153
O22 -1.031806 2.802398 -0.004685
H23 0.475476 0.096750 -0.000075
N24 5.399974 -0.698571 -0.006863
N25 4.818934 1.471718 0.001478
C26 5.804439 0.615693 -0.002773
H27 6.853560 0.875938 -0.005854
N28 3.193335 -1.719189 -0.005562
C29 1.947471 -1.359236 -0.005008
H30 1.157700 -2.103153 -0.007907
N31 1.862951 2.245372 0.004561
H32 2.527813 3.003425 0.006017
H33 0.864837 2.463659 0.002119
C34 3.703293 0.679214 0.002224
C35 6.243710 -1.885753 0.009284
H36 5.617886 -2.748727 -0.211562
H37 7.017627 -1.795752 -0.752317
H38 6.700282 -2.012492 0.991322

Zero-point correction=	0.294850 (Hartree/Particle)
Thermal correction to Energy=	0.316146
Thermal correction to Enthalpy=	0.317090
Thermal correction to Gibbs Free Energy=	0.242374
Sum of electronic and zero-point Energies=	-1163.192151
Sum of electronic and thermal Energies=	-1163.170855
Sum of electronic and thermal Enthalpies=	-1163.169911
Sum of electronic and thermal Free Energies=	-1163.244627

Stacking

C1 2.028732 -0.469962 -1.575845
C2 0.955622 0.450376 -1.289189
H3 3.804254 -1.007730 -0.709354
C4 3.031122 0.525924 0.442895
C5 -0.934067 1.665098 -1.200161
N6 3.045025 -0.346757 -0.601088
N7 -0.211957 0.674304 -1.901582
N8 -0.088819 2.067252 -0.152120
N9 2.042430 1.401199 0.671057
C10 1.040871 1.331518 -0.172261
N11 4.059925 0.535699 1.281307
H12 4.032327 1.188944 2.048683
H13 4.859392 -0.067695 1.182301
O14 2.105076 -1.236663 -2.497090
C15 0.193060 -1.544203 1.278312
N16 0.495379 -2.380951 0.281826
C17 -1.867449 -1.165987 0.169301
C18 -0.456800 3.049889 0.859729
H19 -0.580958 2.547509 1.819105
H20 0.318607 3.812356 0.921996
H21 -1.397299 3.501669 0.549952
O22 -2.029572 2.064783 -1.451061
N23 -2.998295 -0.422815 0.370048
N24 -1.616996 0.063704 2.076899
C25 -2.779713 0.287735 1.520852
H26 -3.530591 0.963711 1.906211
N27 -1.592531 -2.000512 -0.836550
C28 -0.400527 -2.566351 -0.700773
H29 -0.099948 -3.258310 -1.480593
N30 1.112030 -1.351046 2.266734
H31 0.772817 -0.918339 3.113148
H32 1.768297 -2.106964 2.393488
C33 -1.029582 -0.858132 1.239631
C34 -4.164194 -0.371938 -0.498920
H35 -5.048991 -0.161106 0.100437
H36 -4.038721 0.403802 -1.255860
H37 -4.278906 -1.341082 -0.982110
H38 -0.610087 0.133933 -2.659343

Zero-point correction=	0.294910 (Hartree/Particle)
Thermal correction to Energy=	0.316128
Thermal correction to Enthalpy=	0.317073
Thermal correction to Gibbs Free Energy=	0.244283
Sum of electronic and zero-point Energies=	-1163.165557
Sum of electronic and thermal Energies=	-1163.144339
Sum of electronic and thermal Enthalpies=	-1163.143395
Sum of electronic and thermal Free Energies=	-1163.216184

Cartesian coordinates for structures in Scheme S1, optimized at ωB97XD/ 6-311++G(d,p).

HG_D$^{\bullet+}$

C1 -2.557852 -1.786631 0.007723
C2 -2.370328 -0.376329 0.013504
H3 -4.165631 -3.056049 -0.027654
C4 -4.955540 -1.140225 -0.016206
C5 -1.580346 1.671790 0.013933
N6 -3.946518 -2.068897 -0.006720
N7 -1.215791 0.393157 0.021334
N8 -2.931445 1.764444 -0.000922
N9 -4.742827 0.157597 -0.010047
C10 -3.441175 0.475274 0.000911
N11 -6.221362 -1.598149 -0.048273
H12 -6.962259 -0.919320 -0.003282
H13 -6.451318 -2.570615 0.051519
O14 -1.728935 -2.669921 0.011737
C15 2.300671 0.899924 0.004645
N16 1.496737 -0.223288 0.021161
C17 4.126509 -0.694008 -0.000065
C18 -3.709851 2.996070 0.001104
H19 -4.490288 2.919975 -0.754188
H20 -4.162279 3.148819 0.980823
H21 -3.043819 3.823819 -0.232995
O22 -0.812451 2.705274 0.017393
H23 -0.224057 0.061678 0.025530
N24 5.499789 -0.637931 -0.017063
N25 4.765646 1.497039 -0.026033
C26 5.812548 0.683164 -0.030512
H27 6.840803 1.018394 -0.045683
N28 3.351948 -1.745612 0.015303
C29 2.027468 -1.420950 0.024896
H30 1.335460 -2.257567 0.036455
N31 1.734813 2.076407 0.000418
H32 2.431286 2.821031 -0.012634
H33 0.185932 2.450774 0.012072
C34 3.710794 0.663976 -0.007077
C35 6.405181 -1.779752 0.001095
H36 6.129162 -2.471791 -0.793361
H37 7.420582 -1.422115 -0.161019
H38 6.342090 -2.287036 0.963573

Zero-point correction=	0.292274 (Hartree/Particle)
Thermal correction to Energy=	0.313743
Thermal correction to Enthalpy=	0.314688
Thermal correction to Gibbs Free Energy=	0.239028
Sum of electronic and zero-point Energies=	-1163.150491
Sum of electronic and thermal Energies=	-1163.129022
Sum of electronic and thermal Enthalpies=	-1163.128078
Sum of electronic and thermal Free Energies=	-1163.203737

HG_E$^{\bullet+}$

C1 2.244302 -1.498647 0.007940
C2 2.236418 -0.131085 0.012070
H3 3.510503 -3.092378 -0.012922
C4 4.665978 -1.363905 -0.020093
C5 1.832129 2.084798 0.022234
N6 3.501402 -2.079679 -0.008946
N7 1.252563 0.838479 0.029152
N8 3.237699 1.857862 0.008308
N9 4.684848 -0.042199 -0.017028
C10 3.482887 0.532813 -0.000662
N11 5.828339 -2.037794 -0.035647
H12 6.679732 -1.498293 -0.043244
H13 5.890227 -3.041780 -0.036827
O14 1.268869 -2.359242 0.016536
C15 -2.079789 -0.792871 0.014665
N16 -1.544091 0.477796 0.005015
C17 -4.217043 0.354154 -0.008409
C18 4.220922 2.926684 -0.011378
H19 4.932841 2.791556 0.804112
H20 4.751917 2.933666 -0.965082
H21 3.679982 3.864235 0.115731
O22 1.291484 3.166993 0.027907
H23 0.226804 0.699087 0.023659
N24 -5.545492 -0.004374 -0.009038
N25 -4.354706 -1.927857 0.016338
C26 -5.558063 -1.363665 0.004599
H27 -6.487829 -1.917758 0.007385
N28 -3.694327 1.555640 -0.018000
C29 -2.328167 1.530939 -0.009371
H30 -1.838876 2.500799 -0.015215
N31 -1.268003 -1.820665 0.027397
H32 -1.792673 -2.697296 0.034168
H33 0.301466 -1.993020 0.022692
C34 -3.509184 -0.878107 0.008484
C35 -6.680057 0.909658 -0.041981
H36 -6.728989 1.406555 -1.011983
H37 -7.593797 0.340634 0.127068
H38 -6.563763 1.656911 0.743479

Zero-point correction=	0.291907 (Hartree/Particle)
Thermal correction to Energy=	0.313498
Thermal correction to Enthalpy=	0.314443
Thermal correction to Gibbs Free Energy=	0.237813
Sum of electronic and zero-point Energies=	-1163.148420
Sum of electronic and thermal Energies=	-1163.126829
Sum of electronic and thermal Enthalpies=	-1163.125884
Sum of electronic and thermal Free Energies=	-1163.202514

HG_F$^{\bullet+}$

C1 2.571797 -1.802080 -0.012189
N2 3.731395 -2.543142 0.001385
C3 4.032150 0.119565 0.011868
N4 3.895591 1.493038 0.009516
N5 1.825348 0.635679 -0.021169
N6 5.130689 -0.587733 0.025556
C7 4.887244 -1.933907 0.018574
H8 5.772587 -2.560632 0.028624
N9 1.404913 -2.400117 -0.027325

H10 -0.209797 -2.160677 -0.032996
H11 1.565245 -3.409972 -0.027834
C12 2.712310 -0.383154 -0.008082
C13 4.985679 2.459251 0.044345
H14 5.691319 2.235596 -0.754646
H15 4.572179 3.456156 -0.098241
H16 5.496805 2.404825 1.005299
C17 -2.100044 -1.488261 -0.016060
C18 -1.996513 -0.128289 -0.019016
H19 -3.471453 -2.989123 0.011303
C20 -4.503673 -1.188940 0.025134
C21 -1.446340 2.053225 -0.028566
N22 -3.392967 -1.980749 0.006672
N23 -0.953340 0.773114 -0.041768
N24 -2.862314 1.921619 -0.006491
N25 -4.429937 0.127868 0.023979
C26 -3.195425 0.617753 0.002056
N27 -5.707293 -1.780433 0.047088
H28 -6.518841 -1.185280 0.058703
H29 -5.835733 -2.776753 0.042979
O30 -1.196588 -2.421106 -0.031495
C31 -3.773435 3.052266 0.018739
H32 -4.279928 3.109327 0.982774
H33 -3.178215 3.950707 -0.135763
H34 -4.510622 2.951600 -0.777376
O35 -0.834500 3.090094 -0.035224
H36 0.066542 0.600295 -0.040471
C37 2.566440 1.734769 -0.009330
H38 2.152896 2.734842 -0.015544

Zero-point correction=	0.291644 (Hartree/Particle)
Thermal correction to Energy=	0.313195
Thermal correction to Enthalpy=	0.314139
Thermal correction to Gibbs Free Energy=	0.237846
Sum of electronic and zero-point Energies=	-1163.146502
Sum of electronic and thermal Energies=	-1163.124950
Sum of electronic and thermal Enthalpies=	-1163.124006
Sum of electronic and thermal Free Energies=	-1163.200299