Electronic supplementary information for:

An Exploration of the Reactivity of Singlet Oxygen with Biomolecular Constituents

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Computational details:

Using Gaussian 09,[1] the ground state minimum energy geometries of the π-stacked complexes, transition states and adducts were optimised at the MP2/cc-pVDZ level of theory.[2, 3] Optimisations at this level of theory has previously shown to work well on several similar systems studied by our group in the past.[4-7] Intermediate geometries, along the path connecting the optimised structures, were obtained by means of a linear interpolation in internal coordinates (LIIC) using equation 1.

$$R_i(\lambda) = R_0 + \lambda \cdot (R_1 - R_0) \quad (1)$$

where R_i is the x,y,z Cartesian coordinates of the intermediate geometry at a given value of λ between 0 and 1 and R_0 and R_1 are the initial and final x,y,z Cartesian coordinates of the geometries between which the LIIC path is constructed. Using Molpro 2010.1,[8] the subsequent energies of the returned geometries along the LIIC path were obtained by the complete active space second-order perturbation theory (CASPT2) based on a state-averaged complete active space self-consistent field (SA-CASSCF) reference wavefunction.[9] The cc-pVDZ basis was also used for the CASSCF/CASPT2 calculations. State averaged orbitals were compared with state optimised orbitals but the latter were found to be difficult to converge – hence satisfying our use for state averaged orbitals. The active space was also carefully tested in order to gain an appropriate balance between accuracy and reduced computational expense. After careful testing, the active space was seen to be system dependent. For the histidine + O_2 reaction, an active space of 10 electrons in 8 orbitals (10/8) was used. These comprise two histidine centred π orbitals and their π* anti-bonding counterparts, two oxygen centred π_g and two oxygen centred π_u* orbitals. Since guanine contains a far larger π-system than that of histidine, the active space for the guanine + O_2 reaction was increased to 14 electrons in 12 orbitals. This included all orbitals considered in histidine as well as two extra sets of guanine centred π and π* orbitals. An imaginary level shift of 0.5 E_H was used in all CASPT2 calculations in order to aid convergence and to avoid the involvement of intruder states.

Fig. S1: Various H-bonded Guanine-O_2 complexes

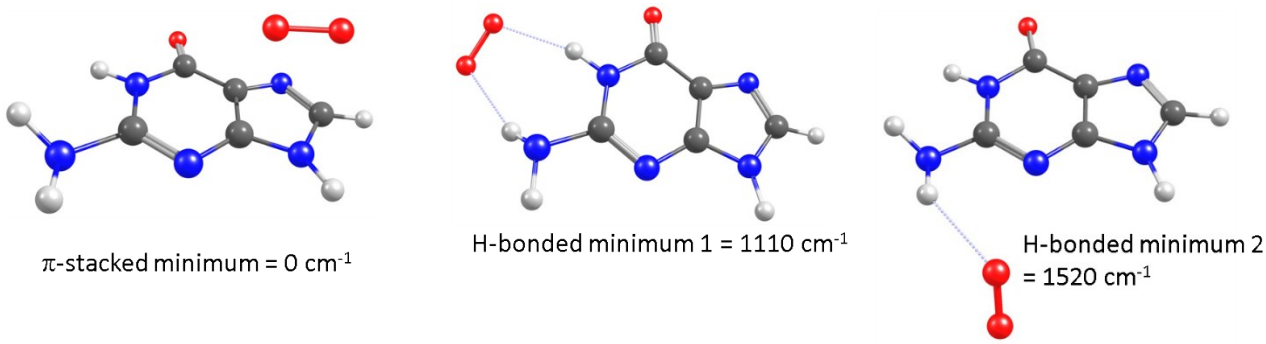


Fig. S2: CASPT2 potential energy profiles accompanying the [4+2] cycloaddition reaction associated with the Cytosine + O_2 reaction.

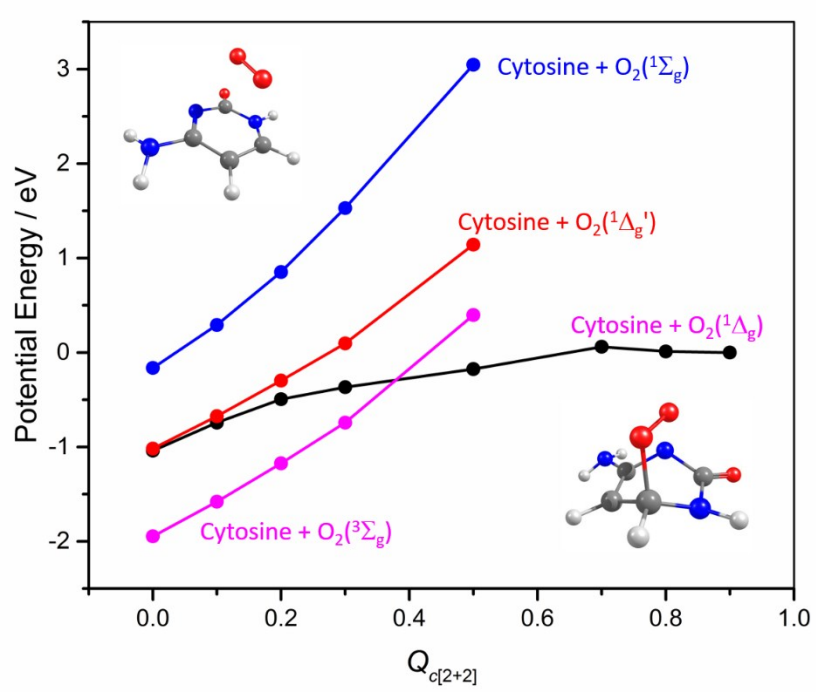
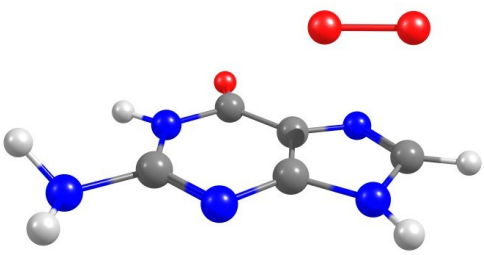


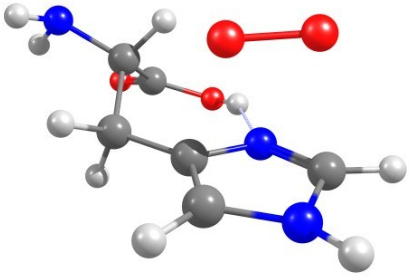
Fig. S3: Molecular depictions and Cartesian coordinates accompanying the depicted structures

Guanine-O_2 (S_0)



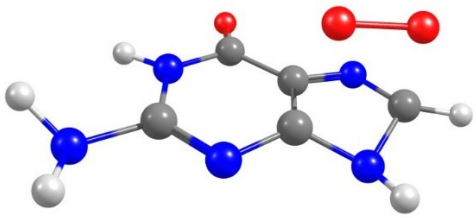
N	1.445790000000	-1.230250000000	-0.907150000000
C	2.345210000000	-0.178300000000	-0.861030000000
H	3.397600000000	-0.317100000000	-1.106970000000
N	1.749900000000	1.009870000000	-0.681900000000
C	0.455710000000	0.677700000000	-0.438300000000
C	-0.672800000000	1.532520000000	-0.085850000000
O	-0.739740000000	2.741560000000	0.039240000000
N	-1.830680000000	0.714440000000	0.105580000000
H	-2.679610000000	1.244960000000	0.297880000000
C	-1.921710000000	-0.648860000000	-0.061350000000
N	-3.186290000000	-1.190430000000	0.079930000000
H	-3.743690000000	-0.782350000000	0.827540000000
H	-3.136570000000	-2.204690000000	0.155360000000
N	-0.919580000000	-1.432920000000	-0.400040000000
C	0.234980000000	-0.724850000000	-0.545760000000
H	1.682410000000	-2.218540000000	-0.894560000000
O	1.036590000000	-0.384600000000	1.663720000000
O	2.330360000000	-0.452760000000	1.459480000000

Histidine-O_2 (S_0)



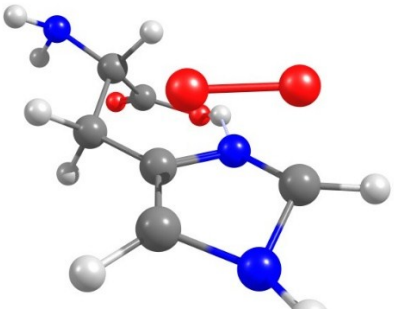
N	-2.536900000000	-1.773330000000	0.224440000000
H	-3.358720000000	-1.539650000000	-0.328160000000
C	-1.602070000000	-0.663190000000	0.194370000000
H	-0.983960000000	-0.688590000000	1.100890000000
C	-0.619640000000	-0.673180000000	-1.029250000000
C	-2.435990000000	0.638300000000	0.195000000000
H	-0.425590000000	-1.717390000000	-1.300210000000
H	-1.106440000000	-0.215550000000	-1.902430000000
C	0.699910000000	-0.016580000000	-0.763730000000
O	-3.611300000000	0.641470000000	-0.099190000000
N	0.832020000000	1.082860000000	0.024550000000
C	1.972610000000	-0.404000000000	-1.226020000000
C	2.130270000000	1.332130000000	0.107900000000
N	2.840510000000	0.525510000000	-0.745310000000
H	2.277930000000	-1.208390000000	-1.876390000000
H	2.582560000000	2.146570000000	0.654210000000
H	3.846950000000	0.429600000000	-0.738350000000
H	-2.118270000000	-2.629730000000	-0.126470000000
O	-1.791940000000	1.768620000000	0.505820000000
H	-0.815940000000	1.613030000000	0.585150000000
O	1.862910000000	-1.408090000000	0.854800000000
O	2.450520000000	-0.541510000000	1.555620000000

Guanine-O_2 (TS)



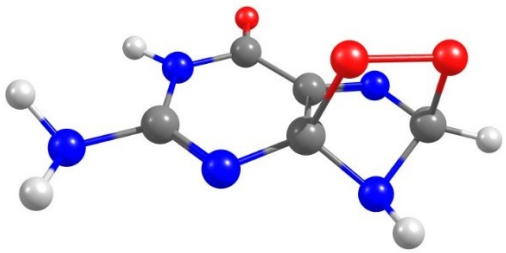
N	-0.355790000000	0.514580000000	-0.180700000000
C	0.517290000000	1.542300000000	0.269240000000
H	1.578060000000	1.487830000000	0.014960000000
N	-0.141570000000	2.778210000000	0.255420000000
C	-1.400460000000	2.386660000000	0.442830000000
C	-2.593240000000	3.194350000000	0.751200000000
O	-2.698500000000	4.403850000000	0.841410000000
N	-3.714710000000	2.341650000000	0.911070000000
H	-4.596940000000	2.834280000000	1.040680000000
C	-3.735900000000	0.966340000000	0.719790000000
N	-4.988510000000	0.396710000000	0.777820000000
H	-5.628370000000	0.806070000000	1.453860000000
H	-4.932850000000	-0.616860000000	0.850950000000
N	-2.700110000000	0.214010000000	0.443170000000
C	-1.531440000000	0.937700000000	0.413280000000
H	-0.071750000000	-0.444690000000	0.023750000000
O	-0.875560000000	1.046530000000	2.159280000000
O	0.458150000000	1.224370000000	1.925210000000

Histidine-O_2 (TS)



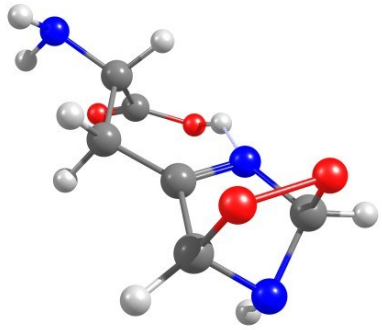
N	-0.898190000000	-0.045590000000	1.617040000000
H	-1.599440000000	-0.171190000000	2.351890000000
C	0.089020000000	-1.104780000000	1.770340000000
H	0.657810000000	-1.213860000000	0.828650000000
C	1.122690000000	-0.853210000000	2.901310000000
C	-0.682450000000	-2.407840000000	2.055210000000
H	1.387450000000	0.219820000000	2.892230000000
H	0.667350000000	-1.059580000000	3.889130000000
C	2.402300000000	-1.611930000000	2.740700000000
O	-1.804470000000	-2.391960000000	2.522210000000
N	2.543080000000	-2.692960000000	1.972260000000
C	3.706940000000	-1.212540000000	3.235420000000
C	3.912810000000	-2.870370000000	1.885620000000
N	4.518830000000	-2.292400000000	3.018030000000
H	3.960070000000	-0.419150000000	3.939400000000
H	4.344220000000	-3.759750000000	1.422350000000
H	5.527320000000	-2.142050000000	2.988880000000
H	-0.454500000000	0.861880000000	1.769490000000
O	-0.042760000000	-3.557490000000	1.790730000000
H	0.897780000000	-3.350930000000	1.576600000000
O	3.900320000000	-0.452440000000	1.472590000000
O	4.318920000000	-1.543890000000	0.796770000000

Endoperoxy-guanine cycloadduct (S_0)



N	1.481282000000	-1.139978000000	-1.001506000000
C	2.354064000000	-0.149182000000	-0.392338000000
H	3.406172000000	-0.144510000000	-0.696457000000
N	1.652731000000	1.148632000000	-0.533598000000
C	0.426278000000	0.747987000000	-0.358040000000
C	-0.792018000000	1.551951000000	-0.075493000000
O	-0.887107000000	2.761440000000	0.013690000000
N	-1.891080000000	0.693221000000	0.107739000000
H	-2.783906000000	1.170871000000	0.217300000000
C	-1.885063000000	-0.701216000000	-0.039289000000
N	-3.147504000000	-1.262103000000	-0.044695000000
H	-3.813172000000	-0.832840000000	0.593645000000
H	-3.095377000000	-2.271694000000	0.077372000000
N	-0.841473000000	-1.456767000000	-0.213569000000
C	0.368064000000	-0.742046000000	-0.169145000000
H	1.784348000000	-2.081856000000	-0.726225000000
O	0.902869000000	-0.829003000000	1.235426000000
O	2.318489000000	-0.434531000000	1.037333000000

Endoperoxy-histidine cycloadduct (S_0)



N	-2.906793000000	1.604741000000	-0.557469000000
H	-3.488553000000	1.496462000000	0.277864000000
C	-1.833564000000	0.624396000000	-0.468623000000
H	-1.394531000000	0.469033000000	-1.470946000000
C	-0.683349000000	1.033047000000	0.483675000000
C	-2.456972000000	-0.696216000000	0.017942000000
H	-0.400572000000	2.081630000000	0.263889000000
H	-1.032939000000	1.023261000000	1.534709000000
C	0.571486000000	0.230893000000	0.351892000000
O	-3.475596000000	-0.714684000000	0.679189000000
N	0.740646000000	-0.779359000000	-0.453539000000
C	1.946071000000	0.601173000000	0.924357000000
C	2.219931000000	-0.991054000000	-0.379574000000
N	2.639959000000	-0.686416000000	0.988475000000
H	2.039695000000	1.262700000000	1.794740000000
H	2.566614000000	-1.938419000000	-0.806975000000
H	2.133004000000	-1.306688000000	1.630833000000
H	-2.514422000000	2.547882000000	-0.532442000000
O	-1.798340000000	-1.823658000000	-0.301429000000
H	-0.929998000000	-1.573094000000	-0.691257000000
O	2.608777000000	1.234822000000	-0.187428000000
O	2.805585000000	0.072399000000	-1.117919000000

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