

## Supplementary Material

# Theoretical Study of the Oxidation Mechanism of Hematoxylin in Aqueous Solution

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## 1. Optimised geometries at B3LYP/6-31G(d) level presented as Gaussian Archives:

1

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1\1\GINC-X17\FOpt\RB3LYP\6-31G(d)\C16H14O6\MXN501\09-Mar-2011\0\#\# opt
  b3lyp/6-31g(d) freq maxdisk=134217728\Title Card Required\0,1\C,0.2
441606806,-0.243120467,-0.005006532\C,0.2145446321,-0.3761448229,1.383
7832977\C,1.0797070859,0.3493002409,2.2103641472\C,1.9689403795,1.2371
791847,1.5876690627\C,2.0139182698,1.3809425109,0.201498804\C,1.150619
7247,0.6358427578,-0.6042507748\O,-0.762964292,-1.231922686,1.86455927
48\C,-0.4924487769,-1.7631042188,3.1720667543\C,-0.2580289535,-0.62527
09209,4.1711421433\C,0.9950500909,0.1905826884,3.7147172427\C,0.123386
4511,-1.1842462878,5.557376256\C,1.6268327797,-1.3061761228,5.47735680
92\C,2.1318263766,-0.5497825959,4.413392051\C,3.4988812747,-0.52538043
79,4.1407414055\C,4.3652011613,-1.2580659933,4.950563304\C,3.855204371
5,-2.011248134,6.0250718862\C,2.4889496724,-2.0429468547,6.2909783323\
O,-1.4356905712,0.1599100622,4.28300636\O,5.7055496674,-1.2498306675,4
.6953195999\O,4.8066621129,-2.699884595,6.7489194105\O,1.1873527532,0.
765526728,-1.9616906421\O,-0.6031829992,-0.9496522919,-0.8231934511\H,
3.9115999311,0.0328228826,3.3068432363\H,2.1092921567,-2.6424370805,7.
11737792\H,0.8953278145,1.1891583204,4.1664466643\H,-0.3885551617,-2.1
28470457,5.7841683204\H,-0.1943712623,-0.4571063553,6.3172724093\H,-1.
7350560234,0.3561956667,3.3793909901\H,0.3764648589,-2.4313691601,3.12
46957671\H,-1.3840868476,-2.3322680561,3.4454881606\H,2.7057752194,2.0
693240511,-0.2725031903\H,2.6299540067,1.8408130351,2.2038422606\H,6.1
316186082,-1.8190632375,5.3588523216\H,4.3790193573,-3.180745696,7.472
9353856\H,-1.1204499662,-1.5438448134,-0.2523539146\H,0.5165203276,0.1
652507289,-2.3300532858\Version=EM64L-G03RevE.01\State=1-A\HF=-1069.4
432539\RMSD=3.178e-09\RMSF=1.590e-05\Thermal=0.\Dipole=-0.3804435,-1.2
893464,1.1873469\PG=C01 [X(C16H14O6)]\@
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**1-B-ox**

```
1\1\GINC-X27\FOpt\RB3LYP\6-31G(d)\C16H12O6\MXN501\09-Mar-2011\0\#\# opt
  freq b3lyp/6-31g(d) maxdisk=134217728\Title Card Required\0,1\C,-0.
0762626376,-0.0165655397,0.0147900947\C,-0.0188764527,-0.0358396169,1.
3621021082\C,1.2585709287,0.0010212345,2.1054999336\C,2.4526913378,0.0
823488932,1.4855463111\C,2.5170576221,0.086893853,0.0141478051\C,1.166
1971239,0.0284123002,-0.7723961438\C,0.9484613411,-0.0463773246,3.5956
676784\C,-0.5299291904,0.4501120765,3.6657283196\C,-1.1568708023,-0.04
84676161,2.3510983625\C,1.8694284752,0.7173050537,4.5205537674\C,1.416
6039294,1.8994237684,5.1186032125\O,0.1363993799,2.404107887,4.9489793
774\C,-0.5221442496,1.9803205715,3.7468024496\C,3.1617305515,0.2805886
148,4.8440258842\C,3.981524099,1.0021573725,5.7101145482\C,3.516260926
6,2.1864947756,6.2854912498\C,2.2235079102,2.6317545789,5.9896030986\O
,1.7947880036,3.7895031006,6.5870612204\O,4.3110072064,2.8990145312,7.
1302406438\O,-1.2510512262,-0.0891966148,4.7581346239\O,3.5678872971,0
.1339951116,-0.6011477957\O,1.1785113041,0.0338661596,-1.9911110218\H,
3.3932940349,0.1482651629,2.0240188521\H,-1.0126249233,-0.0226625556,-
0.5370694882\H,0.9260237588,-1.1055412492,3.8954438172\H,-2.0215594877
,0.5414050196,2.0280433973\H,-1.5117436962,-1.0736400609,2.5248806964\
H,-0.955317204,0.3749278715,5.559498474\H,-0.020931705,2.4233445132,2.
8755796461\H,-1.5413686838,2.3672855154,3.8177932793\H,4.9810422251,0.
6603051178,5.956754347\H,3.5272697457,-0.6512409143,4.4212413599\H,0.9
086188539,3.9874907157,6.2385225632\H,3.8110786816,3.6827686419,7.4169
380999\Version=EM64L-G03RevE.01\State=1-A\HF=-1068.2071921\RMSD=6.960
e-09\RMSF=3.783e-06\Thermal=0.\Dipole=-1.6520008,0.4698935,1.763502\PG
=C01 [X(C16H12O6)]\@
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**1-A-ox**

```
1\1\GINC-X17\FOpt\RB3LYP\6-31G(d)\C16H12O6\MXN501\09-Mar-2011\0\#\# opt
  freq b3lyp/6-31g(d) maxdisk=134217728\Title Card Required\0,1\C,0.0
049174168,-0.0344954023,0.0030742604\C,0.0076896076,-0.00924215,1.3987
```

938013\C,1.2170578447,0.0262062239,2.1025889777\C,2.4368381744,0.04348  
00479,1.4255530849\C,2.4396965378,0.0183781202,0.0318855871\C,1.221285  
599,-0.0239079213,-0.6733876438\C,0.9384002228,0.0074805759,3.60221996  
98\C,-0.5554061911,0.4556217907,3.6783468327\C,-1.1706420646,-0.013285  
6083,2.3436932002\C,1.8298330179,0.8303702938,4.5047706913\C,1.3485794  
714,1.939075094,5.1312683941\O,0.0937943814,2.4306966485,4.9701692084\  
C,-0.5893891288,1.9815584743,3.7869457655\C,3.1894591922,0.3737017535,  
4.7853731823\C,4.0490236125,0.9905568814,5.6278560842\C,3.6347764173,2  
.194890352,6.3499723875\C,2.1779317218,2.7037425656,6.1044318962\O,1.7  
602623947,3.679801082,6.6930503962\O,4.3480725781,2.8038581675,7.12854  
74407\O,-1.2628954505,-0.1256499647,4.7619550076\O,3.6227763105,0.0420  
528138,-0.643808196\O,1.352796046,-0.0386359626,-2.0444410865\H,3.3913  
6715,0.0902044659,1.9395071214\H,-0.9289703324,-0.0554852033,-0.556605  
773\H,0.9724115835,-1.033934046,3.9603334485\H,-2.0024863957,0.6251547  
674,2.0200212013\H,-1.5798164062,-1.0218178699,2.4924132051\H,-1.02750  
15961,0.3653739739,5.5669653193\H,-0.1214317983,2.4448855041,2.9097891  
866\H,-1.615005121,2.3410184708,3.8929334938\H,5.0525959838,0.61910576  
63,5.8084891183\H,3.5047194179,-0.536297884,4.2790143024\H,3.417992508  
1,0.0292118468,-1.5946496117\H,0.4770948344,-0.0635759443,-2.458135583  
\Version=EM64L-G03RevE.01\State=1-A\HF=-1068.2010719\RMSD=6.556e-09\R  
MSF=7.970e-06\Thermal=0.\Dipole=-1.2179207,-1.4296685,-2.5174074\PG=C0  
1 [X(C16H12O6)]\@

### **Catechol**

1\1\GINC-X144\FOpt\RB3LYP\6-31G(d)\C6H6O2\MXN501\10-Feb-2010\0\#\b3lyp  
/6-31G\* Opt freq=Noraman Symm=Loose maxdisk=134217728\title\0,1\C,0.  
0863862831,0.,0.0906262289\C,0.1067917274,0.,1.4963626094\C,1.31485116  
84,0.,2.1844295142\C,2.520227712,0.,1.473305117\C,2.5032699373,0.,0.07  
95854107\C,1.288098152,0.,-0.6118983682\O,-1.1363350846,0.,2.094043297  
3\O,-1.101866252,0.,-0.5811459058\H,3.4617219618,0.,2.0143055942\H,3.4  
353399377,0.,-0.4779746495\H,1.2531263352,0.,-1.6969406416\H,1.3153457  
132,0.,3.2732167575\H,-1.8109365783,0.,0.084349285\H,-1.0332554186,0.,  
3.0572083689\Version=EM64L-G03RevE.01\State=1-A'\HF=-382.6816055\RMSD  
=6.892e-09\RMSF=1.188e-04\Thermal=0.\Dipole=-0.0247049,0.,0.9916944\PG  
=CS [SG(C6H6O2)]\@

### **catechol-ox**

1\1\GINC-X146\FOpt\RB3LYP\6-31G(d)\C6H4O2\MXN501\10-Feb-2010\0\#\b3lyp  
/6-31G\* Opt freq=Noraman Symm=Loose maxdisk=134217728\title\0,1\C,-0.  
.1087371727,0.,-0.0234883788\C,-0.0356106586,0.,1.449103721\C,1.159968  
3816,0.,2.076172465\C,2.4271455911,0.,1.3445659424\C,2.4818753821,0.,-  
0.0043703426\C,1.2431351276,0.,-0.8039937298\H,1.2064511552,0.,3.16243  
98539\H,3.3446403386,0.,1.9279533578\H,3.4195385217,0.,-0.552186432\O,  
1.2415618831,0.,-2.022263838\O,-1.1629720025,0.,-0.6339654039\H,-0.97  
88639741,0.,1.9872373605\Version=EM64L-G03RevE.01\State=1-A1\HF=-381.  
4404832\RMSD=6.053e-09\RMSF=4.741e-05\Thermal=0.\Dipole=1.0498794,0.,1  
.818441\PG=C02V [SGV(C6H4O2)]\@

## **2**

1\1\GINC-X87\FOpt\RB3LYP\6-31G(d)\C16H13O6(1-)\MXN501\27-May-2011\0\#\  
opt b3lyp/6-31g(d) freq maxdisk=536870912\Title Card Required\ -1,1\  
C,-0.0058461458,-0.0163633824,-0.0048283071\C,-0.0060158142,-0.0160907  
268,1.390485691\C,1.2021966328,-0.0175397057,2.1009532638\C,2.42188715  
54,-0.0031818723,1.4270798042\C,2.4283562906,-0.0105511037,0.032246097  
5\C,1.2150693615,-0.0203473442,-0.6753961391\C,0.936239604,-0.05248810  
72,3.6073442683\C,-0.540962614,0.4495621478,3.6726759637\C,-1.18023093  
34,0.0059948753,2.3416248302\C,1.8592543757,0.7184797533,4.5205546638\  
C,1.4223901772,1.8908788881,5.1748461235\O,0.079911635,2.3345839557,5.  
0495766834\C,-0.51904217,1.9784750088,3.8121899959\C,3.1773501102,0.32  
45462644,4.8091917014\C,4.0007711983,1.0568299495,5.6555142872\C,3.591  
5751231,2.2744994717,6.3223121867\C,2.2155927053,2.6458838139,6.020922

0205\O,1.6981202042,3.7805645262,6.6254673425\O,4.3267869119,2.9494649  
598,7.0904291763\O,-1.2770912088,-0.0950358903,4.7627162417\O,3.616864  
2305,0.0006924048,-0.6535621826\O,1.3382307505,-0.0205251061,-2.060070  
1287\H,3.3617000333,0.0412002606,1.9684473045\H,-0.9372454403,-0.00270  
96371,-0.5723514497\H,0.9097868124,-1.1155432183,3.9045113891\H,-1.996  
095092,0.6696327592,2.021925245\H,-1.6165265025,-0.9934329329,2.484164  
4847\H,-0.91387573,0.3451158615,5.5518672272\H,0.0201293299,2.44003718  
27,2.9721530379\H,-1.5445695907,2.364637301,3.8448305546\H,5.016666934  
2,0.7216564607,5.8579382311\H,3.5577166712,-0.595574069,4.3604000768\H  
,3.3934520362,0.042050043,-1.5984874175\H,0.456600429,0.0836049303,-2.  
4463338195\H,0.7992239004,3.8643069404,6.2648758235\Version=EM64L-G03  
RevE.01\State=1-A\HF=-1068.8646458\RMSD=5.592e-09\RMSF=6.751e-06\Therm  
al=0.\Dipole=-3.7566652,-1.9244452,-5.5069063\PG=C01 [X(C16H13O6)]\@

3

1\1\GINC-X67\FOpt\RB3LYP\6-31G(d)\C16H13O6(1-)\MXN501\27-May-2011\0\#\n  
# opt b3lyp/6-31g(d) freq maxdisk=536870912\Title Card Required\ -1,1\  
C,0.0039254911,-0.0490348016,0.0064140424\C,0.0001110019,-0.03054965,1  
.4011249375\C,1.2078077007,-0.0106368039,2.1141629923\C,2.4282261907,0  
.0108954234,1.4410437123\C,2.4369365477,-0.007741448,0.0462770965\C,1.  
225801007,-0.0427258044,-0.662787871\C,0.9348953821,-0.0313339308,3.61  
64952934\C,-0.5459840502,0.4543147597,3.6759825592\C,-1.1766054148,-0.  
0097181116,2.3484631367\C,1.8647786516,0.7553312168,4.5246960697\C,1.3  
96650765,1.9075006564,5.1873868555\O,0.0553164561,2.3253880082,5.05761  
3107\C,-0.523253526,1.9821954489,3.8153092412\C,3.1799092061,0.3249762  
34,4.7430873357\C,4.0300680729,1.0464107664,5.6044841929\C,3.551234031  
2,2.1772522671,6.2385364469\C,2.2020851349,2.6702509666,6.0752360793\O  
,1.8713016825,3.7196153544,6.7371483843\O,4.2862548383,2.949588328,7.0  
944012282\O,-1.2722362156,-0.0832265294,4.7751715164\O,3.6266621429,0.  
0165594105,-0.6380034996\O,1.3501200842,-0.061444448,-2.0478742412\H,3  
.3654764561,0.0752320232,1.9845203295\H,-0.9265745269,-0.0579558334,-0  
.5623576781\H,0.928900451,-1.0856536246,3.9380583652\H,-1.9970699555,0  
.6438151938,2.0204648182\H,-1.6036585506,-1.0124920106,2.4968183295\H,  
-0.9859741473,0.4539783267,5.5376281004\H,0.030031586,2.4415758459,2.9  
816397334\H,-1.5484300317,2.3724770912,3.8300257288\H,5.0537912182,0.7  
20946392,5.7807469926\H,3.5340334714,-0.5890644405,4.2699467652\H,3.40  
22467605,0.062294093,-1.5826213979\H,0.479897981,0.1119457663,-2.43521  
93861\H,3.5813065949,3.624555927,7.3243483585\Version=EM64L-G03RevE.0  
1\State=1-A\HF=-1068.8821263\RMSD=5.381e-09\RMSF=3.853e-05\Thermal=0.\  
Dipole=-2.0328432,-2.1526526,-5.0098389\PG=C01 [X(C16H13O6)]\@

4

1\1\GINC-X112\FOpt\RB3LYP\6-31G(d)\C16H13O6(1-)\MXN501\27-May-2011\0\#\n  
# opt b3lyp/6-31g(d) freq maxdisk=536870912\Title Card Required\ -1,1\  
\C,-0.0152575893,-0.0017557199,-0.0189475749\C,-0.0038956695,0.0159577  
171,1.3933984714\C,1.211231504,0.0152974888,2.0817577562\C,2.444553133  
9,0.0005514268,1.4157211891\C,2.4840726166,-0.0171994946,-0.0029120261  
\C,1.194008212,-0.0183355017,-0.6837260883\C,0.9396713556,-0.041234214  
3,3.5865068503\C,-0.5387733882,0.4457236916,3.6758840889\C,-1.17537616  
26,0.0039932224,2.3454079171\C,1.8609412744,0.7386170572,4.5061543264\  
C,1.405330234,1.9002269193,5.1384163299\O,0.1235934817,2.4006601236,4.  
9947231231\C,-0.5486487424,1.9713565065,3.7890551422\C,3.1682901512,0.  
326553538,4.8047988703\C,3.9911265666,1.0413978124,5.6763258268\C,3.51  
42052479,2.2029481109,6.2860449031\C,2.214074598,2.627006736,6.0147566  
09\O,1.7533461618,3.7713770313,6.6348816716\O,4.3069400513,2.923820415  
9,7.1455956259\O,-1.2620029102,-0.1065768758,4.7817300079\O,3.52074661  
53,-0.0245298628,-0.7624564137\O,1.3252151403,-0.0239956535,-2.0412273  
297\H,3.3874212261,0.0247562878,1.9570528955\H,-0.9479949027,0.0062101  
931,-0.5819737166\H,0.9440340745,-1.0901825475,3.9261136608\H,-2.00673  
10981,0.6653226481,2.0522534996\H,-1.616731811,-0.9956098676,2.4970648  
35\H,-0.8735552492,0.2839115893,5.5819464915\H,-0.0610917737,2.4223574  
882,2.9178775374\H,-1.5713674223,2.3438136891,3.8881344046\H,5.0039025

647,0.7148688034,5.8913322942\H,3.545936894,-0.5790096597,4.3389859338  
\H,2.3301377547,-0.0276314723,-2.0865143034\H,0.8761592368,3.943400800  
7,6.2486590164\H,3.7857249094,3.6987394547,7.4157705663\\Version=EM64L  
-G03RevE.01\State=1-A\HF=-1068.8923729\RMSD=4.378e-09\RMSF=2.159e-05\T  
hermal=0.\Dipole=-1.4866725,1.6726789,4.4776945\PG=C01 [X(C16H13O6)]\@

## 5

1\1\GINC-X24\FOpt\RB3LYP\6-31G(d)\C16H13O6(1-)\MXN501\27-May-2011\0\#\  
opt b3lyp/6-31g(d) freq maxdisk=536870912\\Title Card Required\\-1,1\  
C,0.0068854088,0.01034757,-0.0167521575\C,0.0352627978,0.0203958981,1.  
3837169966\C,1.2326194722,0.0225550252,2.103197679\C,2.4678525471,0.00  
95093476,1.4167292646\C,2.4471214404,-0.0015685587,0.0366679981\C,1.21  
98997607,-0.0032676107,-0.752710765\C,0.952889341,-0.0452933219,3.5988  
07951\C,-0.5261465083,0.4462386389,3.6708770871\C,-1.1453150363,0.0070  
563772,2.3322081956\C,1.8659113401,0.7376621959,4.5266758696\C,1.40635  
5906,1.9017295653,5.1513511951\O,0.1264069517,2.4018554995,4.996073920  
5\C,-0.5341502248,1.9720166263,3.7834538023\C,3.1698117204,0.324824432  
5,4.8380245002\C,3.9875082163,1.0422026229,5.7128967904\C,3.5069671718  
,2.2064318532,6.3142720918\C,2.2090391261,2.6305270832,6.0315776079\O,  
1.7445996741,3.776695248,6.6451122217\O,4.2937271351,2.9300043346,7.17  
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## 6

1\1\GINC-X53\FOpt\RB3LYP\6-31G(d)\C16H13O6(1-)\MXN501\30-May-2011\0\#\  
opt b3lyp/6-31g(d) freq maxdisk=1342177280\\Title Card Required\\-1,1\  
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\Dipole=0.8532785,0.9568899,-2.6784808\PG=C01 [X(C16H13O6)]\@

Table S1. Zero-point energy (ZPE, kJ/mol), thermal corrections (TC, kJ/mol) and entropies (S, J/mol.K) are calculated at B3LYP/6-31G(d) level considering the scaling factors of 0.9806, 0.9989 and 1.0015, respectively, along with electronic energies (E, Hartree) calculated at MP2/GTMP2large level of theory.

<b>Species</b>	<b>ZPE</b> kJ/mol	<b>TC</b> kJ/mol	<b>S</b> J/mol.K	<b>E</b> /Hartree
catechol	280.1	20.3	336.9	-381.95873
catechol-ox	219.4	19.0	327.7	-380.70655
<b>1</b>	716.9	50.4	563.0	-1067.48862
<b>1-A-ox</b>	655.5	49.3	563.1	-1066.23538
<b>1-B-ox</b>	655.9	48.9	559.0	-1066.24101
<b>2</b>	680.8	49.9	562.6	-1066.94095
<b>3</b>	682.1	48.7	553.6	-1066.94187
<b>4</b>	683.3	48.5	552.1	-1066.95175
<b>5</b>	683.4	48.5	552.3	-1066.95229
<b>6</b>	676.7	50.5	566.7	-1066.90750

Table S2. Solvation energies (kJ/mol) calculated using COSMO-RS model of solvation at BP/TZVP level of theory.

Species	$\Delta G(\text{solv.})$ kJ/mol
catechol	-36.4
catechol-ox	-39.2
<i>1</i>	-87.3
<i>1-A-ox</i>	-104.5
<i>1-B-ox</i>	-96.4
<i>2</i>	-349.5
<i>3</i>	-312.5
<i>4</i>	-284.1
<i>5</i>	-283.3
<i>6</i>	-348.5

Table S3. G3MP2-RAD calculations for catechol and its oxidised form, catechol-ox, used for ONIOM calculations. Energies are in Hartree.

	Catechol	Catechol-ox
URCCSD(T)/6-31G*	-381.60614	-380.39708
ROMP2/6-31G*	-381.52579	-380.31447
ROMP2/GTMP2large	-381.95873	-380.70655
HLC <sup>a</sup>	-0.19767	-0.18826
G3(MP2)-RAD Energy (no ZPE)	-382.23676	-380.97742
G3(MP2)-RAD Energy (includes ZPE)	-382.13008	-380.89387

<sup>a</sup>Higher level corrections