Cyclic Voltammetric Study of 2-Hydroxybenzophenone (HBP) Derivatives and the Correspondent Change in the Orbital Energy Levels in Different Solvents

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Cyclic Voltammetric Study of 2-hydroxybenzophenone (HBP) derivatives and the correspondent change in the orbital energy levels in different solvents

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Table S1: Experimental reduction potential

Table S1: The values of peak reduction potential ($E_{pc}$ in V) in the solvents ACN, DMF and DMSO at scan rates of 0.050 – 5.00 in V/s for the five HBP derivatives

|        | ACN    | DMF    | DMSO   |
|--------|--------|--------|--------|
| 1 (5-bromo-2-hydroxybenzophenone) |        |        |        |
| 0.050  | -1.810 | -1.846 | -1.846 |
| 0.100  | -1.814 | -1.851 | -1.851 |
| 0.150  | -1.818 | -1.857 | -1.857 |
| 0.200  | -1.821 | -1.861 | -1.861 |
| 0.250  | -1.822 | -1.861 | -1.861 |
| 0.300  | -1.825 | -1.865 | -1.865 |
| 0.500  | -1.835 | -1.874 | -1.874 |
| 1.000  | -1.844 | -1.884 | -1.884 |
| 5.000  | -1.896 | -1.914 | -1.914 |
| 2 (5-chloro-2-hydroxybenzophenone) |        |        |        |
| 0.050  | -1.817 | -1.875 | -1.881 |
| 0.100  | -1.821 | -1.880 | -1.886 |
| 0.150  | -1.836 | -1.889 | -1.892 |
| 0.200  | -1.839 | -1.890 | -1.893 |
| 0.250  | -1.842 | -1.892 | -1.897 |
| 0.300  | -1.846 | -1.896 | -1.900 |
| 0.500  | -1.856 | -1.905 | -1.910 |
| 1.000  | -1.867 | -1.918 | -1.923 |
| 5.000  | -1.934 | -1.966 | -1.975 |
| 3 (2-hydroxybenzophenone) |        |        |        |
| 0.050  | -1.971 | -1.990 | -1.956 |
| 0.100  | -1.976 | -1.997 | -1.963 |
| 0.150  | -1.980 | -2.006 | -1.969 |
| 0.200  | -1.986 | -2.028 | -1.976 |
| 0.250  | -1.993 | -2.032 | -1.980 |
| 0.300  | -1.997 | -2.039 | -1.985 |
| 0.500  | -2.004 | -2.056 | -2.002 |
| 1.000  | -2.022 | -2.074 | -2.018 |
| 5.000  | -2.083 | -2.166 | -2.072 |
| Solvent | Molecule | experimental | TDDFT calculated |
|---------|----------|--------------|-----------------|
|         |          | HOMO | LUMO | HOMO | LUMO | HOMO | LUMO | HOMO | LUMO |
| ACN     | 1 (5-Br) | -6.487 | -3.076 | -7.235 | -7.159 | -6.332 | -2.278 | -0.888 | -0.612 |
| ACN     | 2 (5-Cl) | -6.486 | -3.069 | -7.234 | -7.157 | -6.382 | -2.272 | -0.877 | -0.602 |
| ACN     | 3 (H)    | -6.236 | -2.941 | -7.196 | -7.108 | -6.416 | -2.132 | -0.743 | -0.553 |
| ACN     | 4 (4-OMe)| -6.061 | -2.865 | -7.067 | -6.775 | -6.281 | -1.932 | -0.625 | -0.508 |
| ACN     | 5 (4-Oct)| -6.050 | -2.858 | -7.061 | -6.750 | -6.260 | -1.921 | -0.619 | -0.505 |
| DMF     | 1 (5-Br) | -6.418 | -3.038 | -7.233 | -7.155 | -6.328 | -2.274 | -0.887 | -0.610 |
| DMF     | 2 (5-Cl) | -6.420 | -3.034 | -7.23 | -7.153 | -6.377 | -2.267 | -0.876 | -0.601 |
| DMF     | 3 (H)    | -6.173 | -2.910 | -7.194 | -7.102 | -6.409 | -2.125 | -0.741 | -0.551 |
| DMF     | 4 (4-OMe)| -6.023 | -2.819 | -7.06 | -6.775 | -6.274 | -1.923 | -0.623 | -0.506 |
| DMF     | 5 (4-Oct)| -6.017 | -2.818 | -7.054 | -6.744 | -6.252 | -1.912 | -0.617 | -0.502 |
| DMSO    | 1 (5-Br) | -6.414 | -3.038 | -7.231 | -7.154 | -6.327 | -2.272 | -0.885 | -0.609 |
| DMSO    | 2 (5-Cl) | -6.413 | -3.033 | -7.23 | -7.152 | -6.377 | -2.266 | -0.874 | -0.599 |
| DMSO    | 3 (H)    | -6.223 | -2.948 | -7.193 | -7.102 | -6.409 | -2.124 | -0.740 | -0.550 |
| DMSO    | 4 (4-OMe)| -6.125 | -2.879 | -7.06 | -6.775 | -6.274 | -1.924 | -0.622 | -0.505 |
| DMSO    | 5 (4-Oct)| -6.115 | -2.872 | -7.054 | -6.744 | -6.252 | -1.913 | -0.616 | -0.502 |

Table S2: The experimental HOMO (H) and LUMO (L) values with the computed HOMO-2 – LUMO+2 for all the models in ACN, DMF and DMSO solvents. All values in eV.
Coordinates of optimized geometries

1. 5-bromo-2-hydroxybenzophenone (1), neutral

../hbp-oct/hbp-oct-red.log  Energy: -678430.7790958

O          3.47325       -2.70476        1.13840
H          4.46036       -2.36691       -1.03065
O          5.51930       -1.47660        0.63849
C          2.77526       -1.78660        0.45876
C          3.41998       -0.60670       -0.03999
C          2.61585        0.24480       -0.82859
H          3.07213        1.09861       -1.31101
C          1.26162        0.01815       -1.05359
H          0.67529        0.69407       -1.66571
C          0.64867       -1.10654       -0.49503
C          1.40682       -2.01214        0.24757
H          0.98744       -2.91564        0.66953
C          4.85224       -0.42650        0.23841
C          5.57299        0.82470        0.10179
C          4.98792        2.12299        0.05389
H          3.91576        2.23316        0.14561
C          5.76466        3.27037       -0.03876
H          5.27231        4.23954       -0.05543
C          7.16486        3.20022       -0.09058
H          7.76593        4.09976       -0.17064
C          7.76521        1.93280       -0.01452
H          8.84917        1.84999       -0.03516
C          7.00020        0.78224        0.08944
H          7.47072       -0.19010        0.16309
O         -0.70277       -1.25464       -0.74480
C         -1.36828       -2.37664       -0.20046
H         -0.92519       -3.30546       -0.58695
H         -1.25875       -2.38896        0.89436
C         -2.84161       -2.29646       -0.58515
H         -3.32553       -3.22612       -0.25775
H         -2.91700       -2.26846       -1.67916
C         -3.57578       -1.09218        0.01578
H         -3.49193       -1.13011        1.11045
H         -3.07006       -0.17362       -0.29921
C         -5.05611       -1.02801       -0.37699
H         -5.55788       -1.95573        0.06750
H         -5.13825       -0.98972       -1.47184
C         -5.79866        0.17069        0.22523
H         -5.71830        0.13312        1.31997
H         -5.29705        1.09733        0.08335
C         -7.27836        0.24027       -0.17049
H         -7.77987       -0.68746        0.13759
H         -7.35836        0.27886       -1.26541
C         -8.02122        1.43866        0.43161
H         -7.94225        1.40142        1.52668
2. 5-bromo-2-hydroxybenzophenone (1), reduced

```
.\hbp-br/hbp-br-red.log Energy: -2022675.4090312
O               0.00783   3.52320   0.23047
H               0.97516   3.25344  -0.01552
O               2.07332   2.32182   0.18134
C               -0.65697   2.35884   0.18134
C               0.05613   1.12112  -0.00657
C               -0.73366  -0.04893  -0.13611
H               -0.26031  -0.98813  -0.38034
C               -2.11313  -0.00498  -0.00154
C               -2.79334   1.18409   0.24341
H               -3.86964   1.19943   0.35866
C               -2.04490   2.36404   0.31909
H               -2.53512   3.31810   0.48177
C               -1.51181   1.16714  -0.11957
C               -2.38847   0.00142  -0.01904
C               -3.71086   0.11769  -0.52906
H               -3.98777   1.05749  -0.98983
C               -4.62016  -0.92654  -0.44430
H               -5.61613  -0.80013  -0.86080
C               -4.27247  -2.13650   0.17205
H               -4.98469  -2.95227   0.23905
C               -2.98764  -2.26002   0.71507
H               -2.70317  -3.17395   1.22930
C               -2.06734  -1.22180   0.62468
H               -1.10466  -1.34302   1.10288
Br              -3.11409  -1.61785  -0.18067
```

3. 5-chloro-2-hydroxybenzophenone (2), neutral

```
.\hbp-cl/ch3cn-hbp-cl-oxd.log Energy: -697510.9345265
O               -1.45224   3.04149   0.26445
H               -0.48556   3.16796   0.09904
O               -0.99616   2.45478  -0.16808
C               -1.69087   1.73108   0.16644
C               -0.65022   0.77671  -0.01374
C               -0.99881  -0.58067  -0.17703
H               -0.22949  -1.31481  -0.37123
C               -2.32075  -0.97914  -0.11965
C               -3.33889  -0.04405   0.10830
H               -4.36996  -0.37251   0.15872
```
4. 5-chloro-2-hydroxybenzophenone (2), reduced

..../hbp-cl/hbp-cl-red.log Energy: -697573.4504899

| C  | -3.02372 | 1.29684 | 0.24849 |
|----|----------|---------|---------|
| H  | -3.79722 | 2.03910 | 0.40499 |
| C  | 0.74889  | 1.24549 | -0.06525|
| C  | 1.90109  | 0.29376 | 0.00608 |
| C  | 3.01142  | 0.54107 | -0.81488|
| H  | 2.98190  | 1.38038 | -1.49961|
| C  | 4.13169  | -0.28211| -0.74903|
| H  | 4.97824  | -0.09408| -1.40004|
| C  | 4.16916  | -1.34146| 0.16104 |
| H  | 5.04617  | -1.97680| 0.21914 |
| C  | 3.08064  | -1.57589| 1.00169 |
| H  | 3.11356  | -2.38455| 1.72328 |
| C  | 1.94585  | -0.76964| 0.91881 |
| H  | 1.11156  | -0.94880| 1.58662 |
| Cl | -2.73491 | -2.66694| -0.33665|

5. 2-hydroxybenzophenone (3), neutral

..../hbp/ch3cn-hbp-oxd.log Energy: -409109.5474374

| O  | -2.52040 | 1.97556 | 0.43827 |
|----|----------|---------|---------|
| H  | -1.61966 | 2.37404 | 0.34872 |
| O  | 0.00512  | 2.12950 | 0.08058 |
6. 2-hydroxybenzophenone (3), reduced

Energy: -409169.3321677
7. 2-hydroxy-4-methoxybenzophenone (4), neutral

..../hbp-och3/ch3cn-hbp-och3-oxd.log Energy: -480986.3350929
O  1.42470  2.49539  0.40171
H  0.46296  2.73214  0.32448
O  -1.08600  2.24699  0.10000
C  1.50818  1.18453  0.16542
C  0.34751  0.38283  -0.04054
C  0.54721  -0.98445  -0.34787
H  -0.31282  -1.60452  -0.56466
C  1.80277  -1.54547  -0.40830
H  1.94822  -2.58984  -0.65374
C  2.93522  -0.74101  -0.15287
C  2.78870  0.61437  0.12842
H  3.63181  1.26702  0.30606
C  -0.97153  1.01030  0.03094
C  -2.23122  0.19763  0.02405
C  -2.39722  -0.94156  0.82336
H  -1.58521  -1.28371  1.45428
C  -3.61844  -1.61543  0.84267
H  -3.74262  -2.48482  1.47900
C  -4.67656  -1.17084  0.04940
H  -5.62225  -1.70183  0.05784
C  -4.51849  -0.03447  -0.74762
H  -5.34042  0.31816  -1.36099
C  -3.30889  0.65489  -0.74791
H  -3.18510  1.55249  -1.34236
O  4.12541  -1.37575  -0.21914
C  5.31600  -0.63567  0.01700
H  5.32253  -0.20868  1.02579
H  6.13400  -1.34847  -0.08229
H  5.43663  0.16501  -0.72082

8. 2-hydroxy-4-methoxybenzophenone (4), reduced

..../hbp-och3/hbp-och3-red.log Energy: -481042.3413528
O  1.29907  2.45649  0.37988
H  0.27964  2.58994  0.17204
O  -1.06518  2.20404  -0.15989
C  1.47482  1.14982  0.14727
C  0.34975  0.30120  -0.11712
C  0.56501  -1.03684  -0.44901
H  -0.14595  -1.69777  -0.75161
C  1.95047  -1.54430  -0.44709
H  2.14765  -2.57789  -0.70794
C  3.01823  -0.70531  -0.11764
C  2.78163  0.63946  0.16655
H  3.57766  1.33649  0.39243
C  -0.99286  0.90059  -0.09881
C  -2.23361  0.15435  -0.01761
C  -2.36891  -1.19306  0.42599
H  -1.49727       -1.73844        0.76197
C  -3.60847       -1.81368        0.50690
H  -3.66181       -2.83806        0.86716
C  -4.78608       -1.13826        0.15263
H  -5.75087       -1.63125        0.21060
C  -4.68061        0.20038       -0.25872
H  -5.57830        0.75419       -0.52311
C  -3.45010        0.83297       -0.33225
H  -3.37846        1.86981       -0.63572
O           4.27382       -1.28404       -0.11625
C           5.37514       -0.46348        0.19716
H           5.29242       -0.03761        1.20605
H           6.25850       -1.10402        0.14985
H           5.48851        0.35969       -0.52110

9.  2-hydroxy-4-(octyloxy)benzophenone (5), neutral

53
../hbp-oct/ch3cn-hbp-oct-oxd.log  Energy:  -678375.0763102
O          3.46525       -2.81057       1.15947
H          4.41637       -2.52478       1.17906
O          5.54578       -1.38578       0.83717
C          2.79781       -1.85028       0.51564
C          3.43743       -0.65107       0.08497
C          2.65582        0.27615       -0.64543
H          3.12790        1.16915       -1.03394
C          1.32039        0.06499       -0.90294
H          0.73223        0.77423       -1.47151
C          0.69595       -1.10892       -0.42416
C          1.43252       -2.06075        0.27705
H          0.99843       -2.98192        0.63885
C          4.85733       -0.45858        0.37455
C          5.53970        0.85364       -0.12865
C          4.98516        2.07742       -0.52736
C          4.01250        2.10129        1.00473
C          5.69724        3.26369        0.34958
H          5.26711        4.20331        0.67867
C          6.95874        3.24106       -0.24595
H          7.50690        4.16538       -0.39269
C          7.51836        2.02428       -0.64317
H          8.50137        2.00141       -1.10071
C          6.82028        0.83650       -0.44235
H          7.25709       -0.11477       -0.72283
O          -0.61669       -1.22654       -0.70951
C          -1.33244       -2.38775       -0.27658
H          -0.87532        3.27968       -0.72210
H          -1.26111       -2.47135        0.81577
C          -2.78309       -2.24826       -0.71574
H          -3.28287       -3.19992       -0.49604
H          -2.80966       -2.12380       -1.80469
C          -3.53659       -1.09871       -0.03514
H          -3.49768       -1.23811        1.05378
H          -3.02196       -0.15450       -0.24445
10. 2-hydroxy-4-(octyloxy)benzophenone (5), reduced

../hbp-oct/hbp-oct-red.log  Energy: -678430.7790958

O  3.47325  -2.70476    1.13840
H  4.46036  -2.36691    1.03065
O  5.51930  -1.47660    0.63849
C  2.77526  -1.78660    0.45876
C  3.41998  -0.60670   -0.03999
C  2.61585   0.24480   -0.82859
C  1.26162   0.01815   -1.05359
C  0.67529   0.69407   -1.66571
C  0.64867  -1.10654   -0.49503
C  1.40682  -2.01214    0.24757
C  0.98744  -2.91564    0.66953
C  4.85224  -0.42650    0.23841
C  5.57299   0.82470    0.10179
C  4.98792   2.12299    0.05389
C  3.91576   2.23316    0.14561
C  5.76466   3.27037   -0.03876
C  5.27231   4.23954   -0.05543
C  7.16486   3.20002   -0.09058
C  7.76593   4.09976   -0.17064
C  7.76521   1.93280   -0.01452
C  8.84917   1.84899   -0.03516
C  7.00020   0.78224    0.08944
H  7.47072  -0.19010    0.16309
O -0.70277  -1.25464   -0.74480
C -1.36828  -2.37664   -0.20046
H -0.92519  -3.30546   -0.58695
H -1.25875  -2.38896    0.89436
C -2.84161  -2.29646   -0.58515
| Atom | X         | Y         | Z         |
|------|-----------|-----------|-----------|
| H    | -3.32553  | -3.22612  | -0.25775  |
| H    | -2.91700  | -2.26846  | -1.67916  |
| C    | -3.57578  | -1.09218  | 0.01578   |
| H    | -3.49193  | -1.13011  | 1.11045   |
| H    | -3.07006  | -0.17362  | -0.29921  |
| C    | -5.05611  | -1.02801  | -0.37699  |
| H    | -5.55788  | -1.95573  | -0.06750  |
| H    | -5.13825  | -0.98972  | -1.47184  |
| C    | -5.79866  | 0.17069   | 0.22523   |
| H    | -5.71830  | 0.13312   | 1.31997   |
| H    | -5.29705  | 1.09733   | -0.08335  |
| C    | -7.27836  | 0.24027   | -0.17049  |
| H    | -7.77987  | -0.68746  | 0.13759   |
| H    | -7.55386  | 0.27886   | -1.26541  |
| C    | -8.02122  | 1.43866   | 0.43161   |
| H    | -7.94225  | 1.40142   | 1.52668   |
| H    | -7.52118  | 2.36688   | 0.12365   |
| C    | -9.50099  | 1.50894   | 0.03597   |
| H    | -10.00137 | 0.58192   | 0.34420   |
| H    | -9.58036  | 1.54737   | -1.05801  |
| C    | -10.23481 | 2.71016   | 0.64255   |
| H    | -10.20190 | 2.68131   | 1.73708   |
| H    | -9.77789  | 3.65347   | 0.32450   |
| H    | -11.28704 | 2.73238   | 0.34196   |