# Experimental and Theoretical Studies on Aqueous-Phase Reactivity of Hydroxyl Radicals with Multiple Carboxylated and Hydroxylated Benzene Compounds

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Supporting Information

Table S1 and Figure S1

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Table S1:

The energies for SOMO-1, SOMO, LUMO, and LUMO+1, and the SOMO-LUMO energy gap calculated at the level of wB97XD/cc-pVQZ and M06-2X/cc-pVQZ. Values in () are by M06-2X/cc-pVQZ. The lowest excited state and $\lambda_{max}$ with the MO contributions calculated at the level of M06-2X/cc-pVQZ.

| Compounds | | Benzoate | | | | | |
|---|---|---|---|---|---|---|---|
| Position of HO attack | | Ortho | | Meta | | Para | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy, eV | LUMO+1 | 2.97 (1.70) | 2.24 (1.23) | 2.97 (1.70) | 2.19 (1.19) | 2.98 (1.70) | 2.15 (1.15) |
| | LUMO | 1.69 (0.73) | -0.64 (-1.73) | 1.73 (0.76) | -0.73 (-1.83) | 1.64 (0.66) | -0.59 (-1.67) |
| | SOMO | -6.96 (-6.19) | -8.6 (-8.15) | -7.12 (-6.31) | -8.44 (-8.04) | -6.86 (-6.11) | -8.96 (-8.40) |
| | SOMO-1 | -8.94 (-8.54) | -9.08 (-8.74) | -8.75 (-8.41) | -9.12 (-8.77) | -9.32 (-8.79) | -9.09 (-8.84) |
| | SOMO-LUMO gap | 8.65 (6.92) | 7.97 (6.42) | 8.85 (7.07) | 7.7 (6.2) | 8.5 (6.77) | 8.37 (6.72) |
| Lowest excited state | $\lambda_{exc}$, nm | 460 | | 472 | | 440 | |
| | Energy, eV | 2.7 | | 2.63 | | 2.82 | |
| | $f$ | 0.0057 | | 0.0051 | | 0.0004 | |
| | | SOMO → LUMO (-0.486) | SOMO-3 → LUMO (0.215)<br>SOMO → LUMO (0.832) | SOMO → LUMO (-0.404) | SOMO-3 → LUMO (0.233)<br>SOMO-2 → LUMO (-0.101)<br>SOMO → LUMO (0.866) | SOMO → LUMO (-0.578) | SOMO → LUMO (0.794) |
| Excited state at $\lambda_{max}$ | $\lambda_{max}$, nm | 322 | | 324 | | 326 | |
| | Energy, eV | 3.84 | | 3.82 | | 3.79 | |
| | $f$ | 0.1189 | | 0.0476 | | 0.0776 | |
| | | SOMO → LUMO (0.844) | SOMO-1 → LUMO (-0.168)<br>SOMO → LUMO (0.485) | SOMO → LUMO (0.774) | SOMO-3 → LUMO (0.241)<br>SOMO-2 → LUMO (0.407)<br>SOMO → LUMO (0.375) | SOMO → LUMO (0.794) | SOMO-4 → LUMO (-0.130)<br>SOMO → LUMO (0.580) |
| | | | | | | 246 | |
| | | | | | | 5.03 | |
| | | | | | | 0.08 | |
| | | | | | | SOMO-1 → LUMO (-0.275) | SOMO-6 → LUMO (1.30) |
| | | | | | | SOMO → LUMO+1 (-0.146) | SOMO-5 → LUMO (0.334) |
| | | | | | | SOMO → LUMO+3 (0.187) | SOMO-2 → LUMO (0.745) |
| | | | | | | SOMO → LUMO+6 (0.165) | SOMO → LUMO (-0.319) |

| Compounds | | Phthalic acid (1,2-Di) | | | | Terephthalic acid (1,4-Di) | |
|---|---|---|---|---|---|---|---|
| Position of HO attack | | 3 position | | 4 position | | 2 or 3 position | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy | LUMO+1 | 2.86 (1.63) | 1.66 (0.79) | 2.23 (1.03) | 1.32 (0.64) | 2.85 (1.71) | 1.78 (0.68) |
| | LUMO | 1.13 (0.33) | -0.58 (-1.80) | 1.28 (0.20) | -1.09 (-2.47) | 1.28 (0.19) | -0.71 (-1.68) |
| | SOMO | -6.91 (-6.24) | -8.56 (-7.96) | -6.35 (-6.42) | -6.32 (-6.37) | -7.01 (-6.14) | -8.35 (-8.11) |
| | SOMO-1 | -8.89 (-8.33) | -8.96 (-8.52) | -8.61 (-6.75) | -8.60 (-7.94) | -8.65 (-8.49) | -8.86 (-8.70) |
| | SOMO-LUMO gap | 8.04 (6.57) | 7.98 (6.15) | 7.62 (6.61) | 5.23 (3.89) | 8.29 (6.34) | 7.64 (6.44) |
| Lowest excited state | $\lambda$, nm | 490.73 | | 1230 | | 474.24 | |
| | Energy, eV | 2.5265 | | 1.0079 | | 2.61 | |
| | $f$ | 0.0035 | | 0.0008 | | 0.0006 | |
| | | SOMO → LUMO (0.483) | SOMO-6 → LUMO (0.111)<br>SOMO-5 → LUMO (-0.204)<br>SOMO → LUMO (0.824) | | SOMO → LUMO (0.945)<br>SOMO → LUMO+2 (-0.159)<br>SOMO → LUMO+3 (0.148) | SOMO → LUMO (0.611) | SOMO-6 → LUMO (-0.192)<br>SOMO → LUMO (0.739) |
| Excited state at $\lambda_{max}$ | $\lambda_{max}$, nm | 341 | | 300 | | 348 | |
| | Energy, eV | 3.63 | | 4.13 | | 3.56 | |
| | $f$ | 0.09 | | 0.0618 | | 0.108 | |
| | | SOMO → LUMO (0.745) | SOMO-1 → LUMO (0.453)<br>SOMO → LUMO (-0.420) | SOMO-1 → LUMO (0.659)<br>SOMO-1 → LUMO+1 (-0.386) | SOMO-5 → LUMO (0.261)<br>SOMO-6 → LUMO (0.145) | SOMO → LUMO (0.755) | SOMO-6 → LUMO (-0.146)<br>SOMO → LUMO (-0.613) |

| Compounds | | Trimesic acid (1,3,5-Tri) | | 1,2,3,4,5-Penta | | Pyromellitic acid (1,2,4,5-Tetra) | |
|---|---|---|---|---|---|---|---|
| Position of HO attack | | 2 or 4 position | | | | | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy | LUMO+1 | 2.42 (1.46) | 1.65 (0.68) | 2.28 (1.28) | 1.85 (0.87) | 2.90 (1.68) | 1.59 (0.53) |
| | LUMO | 1.30 (0.31) | -1.10 (-2.20) | 1.60 (0.59) | -0.90 (-2.04) | 1.21 (0.10) | -0.78 (-1.79) |
| | SOMO | -7.04 (-6.33) | -8.48 (-8.05) | -6.91 (-6.22) | -7.90 (-7.80) | -6.94 (6.11) | -8.13 (-7.80) |
| | SOMO-1 | -8.75 (-8.40) | -8.79 (-8.45) | -8.20 (-7.90) | -8.48 (-8.33) | -8.46 (-8.14) | -8.61 (-8.33) |
| | SOMO-LUMO gap | 8.31 (6.64) | 7.37 (5.85) | 8.51 (6.82) | 7 (5.55) | 8.15 (6.21) | 7.35 (6.00) |
| Lowest excited state | $\lambda$, nm | 504.73 | | 521 | | 502.91 | |
| | Energy, eV | 2.4564 | | 2.38 | | 2.4653 | |
| | $f$ | 0.01696 | | 0.211 | | 0.0003 | |
| | | SOMO → LUMO (0.351) | SOMO → LUMO (-0.202)<br>SOMO → LUMO (0.890) | SOMO → LUMO (0.287) | SOMO-15 → LUMO (0.207)<br>SOMO → LUMO (0.917) | SOMO → LUMO (-0.577) | SOMO → LUMO (-0.201)<br>SOMO-12 → LUMO (0.771) |
| Excited state at $\lambda_{max}$ | $\lambda_{max}$, nm | 340 | | 334 | | 366 | |
| | Energy, eV | 3.64 | | 3.711 | | 3.38 | |
| | $f$ | 0.125 | | 0.0828 | | 0.15 | |
| | | SOMO → LUMO (0.875) | SOMO-4 → LUMO (0.107)<br>SOMO-2 → LUMO (0.115)<br>SOMO → LUMO (-0.369) | SOMO-1 → LUMO+1 (0.109)<br>SOMO → LUMO (0.899) | SOMO-3 → LUMO (0.206)<br>SOMO → LUMO (-0.296) | SOMO → LUMO (0.785) | SOMO-1 → LUMO (-0.135)<br>SOMO → LUMO (0.577) |

| Compounds | | Salicylic acid (2hydroxybenzoic acid) | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Position of HO attack | | 3 position | | 4 position | | 5 position | | 6 position | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy | LUMO+1 | 2.72 (1.44) | 2.46 (1.36) | 2.66 (1.62) | 2.12 (1.10) | 2.83 (1.73) | 1.87 (0.87) | 3.05 (1.73) | 1.62 (0.67) |
| | LUMO | 1.92 (0.95) | -0.43 (-1.53) | 1.75 (0.75) | -0.89 (-1.99) | 1.36 (0.40) | -0.55 (-1.63) | 1.27 (0.30) | -0.92 (-2.01) |
| | SOMO | -6.66 (-5.89) | -8.14 (-7.68) | -7.09 (-6.34) | -8.78 (-8.23) | -6.91 (-6.12) | -8.60 (-8.21) | -7.18 (-6.39) | -8.78 (-8.25) |
| | SOMO-1 | -8.55 (-8.14) | -9.21 (-8.89) | -9.18 (-8.66) | -9.03 (-8.89) | -8.83 (-8.52) | -9.17 (-8.83) | -9.06 (-8.74) | -9.07 (-8.83) |
| | SOMO-LUMO gap | 8.58 (6.85) | 7.71 (6.14) | 8.83 (7.09) | 7.89 (6.24) | 8.27 (6.52) | 8.05 (6.58) | 8.45 (6.69) | 7.86 (6.24) |
| | λmax | 477.94 | | 470.83 | | 439 (449.88) | | 479.21 | |
| Lowest | Energy | 2.594 | | 2.6333 | | 2.8237 (2.7559) | | 2.59 | |
| excited | f | 0.0096 | | 0.0084 | | 0.0001 (0.0003) | | 0.0077 | |
| state | | SOMO → LUMO (0.431) | SOMO-3 → LUMO (-0.160) SOMO → LUMO (0.875) | SOMO → LUMO (0.361) | SOMO → LUMO (0.915) | SOMO → LUMO (-0.639) | SOMO-3 → LUMO (-0.224) SOMO → LUMO (0.708) | SOMO → LUMO (-0.460) | SOMO → LUMO (0.868) |
| Excited | $\lambda_{max}$, nm | 334 | | 315 | | 336 | | 340 | |
| state | Energy, eV | 3.71 | | 3.93 | | 3.684 | | 3.64 | |
| at λmax | *f* | 0.104 | | 0.054 | | 0.0764 | | 0.086 | |
| | | SOMO → LUMO (0.885) | SOMO → LUMO (-0.434) | SOMO → LUMO (0.788) | SOMO-4 → LUMO (-0.147) SOMO-1 → LUMO (-0.439) SOMO → LUMO (-0.321) | SOMO → LUMO (0.747) | SOMO-3 → LUMO (-0.161) SOMO → LUMO (0.623) | SOMO → LUMO (0.681) | SOMO-2 → LUMO (0.174) SOMO-1 → LUMO (-0.525) SOMO-1 → LUMO+1 (-0.153) SOMO → LUMO (-0.400) |

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| Compounds | | 3-hydroxybenzoic acid | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Position of HO attack | | 2 position | | 4 position | | 5 position | | 6 position | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy | LUMO+1 | 2.91 (1.61) | 1.60 (0.63) | 2.37 (1.32) | 2.24 (1.20) | 3.00 (1.7) | 2.37 (1.37) | 3.03 (1.71) | 1.57 (0.60) |
| | LUMO | 1.14 (0.18) | -0.84 (-1.92) | 1.75 (0.78) | -0.96 (-2.04) | 2.01 (1.02) | -0.83 (-1.96) | 1.06 (0.10) | -0.59 (-1.64) |
| | SOMO | -7.03 (-6.24) | -8.87 (-8.29) | -7.09 (-6.32) | -8.87 (-8.29) | -7.21 (-6.42) | -8.12 (-7.65) | -6.60 (-5.86) | -8.90 (-8.52) |
| | SOMO-1 | -9.12 (-8.75) | -9.09 (-8.92) | -8.98 (-8.72) | -8.95 (-8.83) | -8.60 (-8.13) | -9.10 (-8.82) | -8.93 (-8.78) | -9.10 (-8.81) |
| | SOMO-LUMO gap | 8.17 (6.42) | 8.03 (6.36) | 8.84 (7.10) | 7.91 (6.25) | 9.22 (7.44) | 7.27 (5.69) | 7.66 (5.94) | 8.31 (6.87) |
| | λmax | 474.39 | | 452.89 (468.17) | | 544.07 (548.24) | | 457.6 (468.13) | |
| Lowest | Energy | 2.6135 | | 2.7376 (2.6483) | | 2.2788 (2.2615) | | 2.709 (2.6485) | |
| excited | f | 0.0013 | | 0.009 (0.0096) | | 0.0154 (0.0147) | | 0.0249 (0.0283) | |
| state | | SOMO → LUMO (-0.583) | SOMO → LUMO (0.793) | SOMO → LUMO (-0.369) | SOMO-2 → LUMO (0.122) SOMO → LUMO (0.906) | SOMO → LUMO (0.245) | SOMO → LUMO (0.953) | SOMO → LUMO (0.871) | SOMO → LUMO (-0.454) |
| Excited | $\lambda_{max}$, nm | 351 | | 303 | | 298 | | 344 | |
| state | Energy, eV | 3.53 | | 4.084 | | 4.16 | | 3.603 | |
| at λmax | *f* | 0.1652 | | 0.0364 | | 0.071 | | 0.127 | |
| | | SOMO → LUMO (0.791) | SOMO → LUMO (0.585) | SOMO-1 → LUMO (-0.214) SOMO → LUMO (0.379) SOMO → LUMO+1 (-0.420) SOMO → LUMO+2 (-0.191) | SOMO-5 → LUMO (0.505) SOMO-4 → LUMO (0.185) SOMO-2 → LUMO (0.427) SOMO → LUMO (0.104) | SOMO → LUMO (0.867) | SOMO-4 → LUMO (0.106) SOMO-2 → LUMO (-0.137) SOMO-1 → LUMO (0.34) SOMO → LUMO (-0.246) | SOMO → LUMO (0.165) | SOMO-3 → LUMO (0.-0.102) SOMO-1 → LUMO (0.850) SOMO → LUMO+1 (0.211) |

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| Compounds | | 4-hydroxybenzoic acid | | | |
|---|---|---|---|---|---|
| Position of HO attack | | 2 position | | 3 position | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy | LUMO+1 | 3.10 (1.79) | 1.71 (0.74) | 2.84 (1.65) | 1.80 (0.82) |
| | LUMO | 1.35 (0.34) | -1.09 (-2.20) | 1.20 (0.28) | -0.50 (-1.58) |
| | SOMO | -7.30 (-6.51) | -8.31 (-7.81) | -6.70 (-5.93) | -8.54 (7.96) |
| | SOMO-LUMO gap | 8.64 (6.88) | 7.22 (5.61) | 7.9 (6.21) | 8.05 (6.38) |
| | λmax | 551.1 (561.14) | | 464.21 (479.39) | |
| Lowest | Energy | 2.2498 (2.2095) | | 2.67 (2.5863) | |
| excited | f | 0.0201 (0.0183) | | 0.0002 (0.0001) | |
| state | | SOMO → LUMO (-0.261) | SOMO → LUMO (0.948) | SOMO → LUMO (0.596) | SOMO → LUMO (0.776) |
| Excited | $\lambda_{max}$, nm | 298 | | 344 | |
| state | Energy, eV | 4.16 | | 3.603 | |
| at λmax | *f* | 0.066 | | 0.127 | |
| | | SOMO-4 → LUMO (-0.126) SOMO-1 → LUMO (0.292) SOMO → LUMO (-0.347) SOMO → LUMO+5 (0.136) | SOMO-5 → LUMO (0.512) SOMO-4 → LUMO (-0.299) SOMO-2 → LUMO (-0.380) SOMO-2 → LUMO+1 (0.153) | SOMO → LUMO (0.476) | SOMO-3 → LUMO (-0.102) SOMO → LUMO (0.850) |

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| Compounds | | 2,3-dihydroxybenzoic acid | | | | | |
|---|---|---|---|---|---|---|---|
| Position of HO attack | | 4 position | | 5 position | | 6 position | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy | LUMO+1 | 2.57 (1.26) | 2.49 (1.21) | 2.85 (1.49) | 1.97 (0.98) | 2.99 (1.61) | 1.79 (0.83) |
| | LUMO | 2.09 (1.08) | -0.7 (-1.8) | 1.54 (0.58) | -0.58 (-1.68) | 1.39 (0.41) | -0.53 (-1.60) |
| | SOMO | -6.75 (-6.03) | -7.98 (-7.46) | -6.95 (-6.17) | -8.24 (-7.77) | -6.63 (-5.89) | -8.35 (-7.88) |
| | SOMO-1 | -8.53 (-7.99) | -8.94 (-8.80) | -8.67 (-8.19) | -9.06 (-8.84) | -8.61 (-8.19) | -8.88 (-8.72) |
| | SOMO-LUMO gap | 8.84 (7.11) | 7.28 (5.66) | 8.49 (6.75) | 7.65 (6.09) | 8.02 (6.31) | 7.82 (6.28) |
| | λmax | 530.68 (544.71) | | 483.81 (484.91) | | 460.66 (459.41) | |
| Lowest | Energy | 2.3363 (2.2761) | | 2.5627 (2.5568) | | 2.6915 (2.6988) | |
| excited | f | 0.0269 (0.0279) | | 0.0089 (0.0066) | | 0.0075 (0.0048) | |
| state | | SOMO → LUMO (-0.191) SOMO → LUMO+1 (0.127) | SOMO → LUMO (0.959) | SOMO → LUMO (-0.387) | SOMO → LUMO (0.896) | SOMO → LUMO (0.612) | SOMO-4 → LUMO (0.113) SOMO → LUMO (0.755) |
| Excited | $\lambda_{max}$, nm | 307 | | 306 | | 365 | |
| state | Energy, eV | 4.03 | | 4.048 | | 3.39 | |
| at λmax | *f* | 0.0408 | | 0.0474 | | 0.1208 | |
| | | SOMO → LUMO (-0.214) SOMO → LUMO (0.379) SOMO → LUMO+1 (-0.420) SOMO → LUMO+2 (-0.191) | SOMO-2 → LUMO (0.214) SOMO-1 → LUMO (0.599) SOMO-1 → LUMO+4 (-0.119) SOMO-1 → LUMO+5 (-0.118) | SOMO-1 → LUMO (-0.286) SOMO → LUMO (0.387) SOMO → LUMO+1 (-0.101) SOMO → LUMO+2 (0.211) | SOMO-4 → LUMO (-0.445) SOMO-2 → LUMO (0.522) SOMO-1 → LUMO+1 (-0.251) SOMO → LUMO (0.179) | SOMO-1 → LUMO (0.135) SOMO → LUMO (0.742) | SOMO-4 → LUMO (0.132) SOMO → LUMO (-0.605) SOMO → LUMO+1 (-0.122) |

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| Compounds | | 2,4-dihydroxybenzoic acid | | | | | |
|---|---|---|---|---|---|---|---|
| Position of HO attack | | 3 position | | 5 position | | 6 position | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy | LUMO+1 | 2.67 (1.40) | 2.17 (1.18) | 2.75 (1.58) | 2.06 (1.06) | 3.05 (1.72) | 1.68 (0.73) |
| | LUMO | 1.57 (0.65) | -0.24 (-0.13) | 1.49 (0.55) | -0.28 (-1.37) | 1.43 (0.45) | -0.99 (-2.11) |
| | SOMO | -6.43 (-5.67) | -8.08 (-0.7.52) | -6.49 (-5.74) | -8.37 (-7.89) | -7.22 (-6.44) | -8.28 (-7.78) |
| | SOMO-1 | -8.40 (-7.93) | -9.02 (-8.86) | -8.67 (-8.26) | -9.17 (-.8.87) | -8.82 (-8.32) | -8.95 (-8.78) |
| | SOMO-LUMO gap | 7.99 (6.33) | 7.83 (6.18) | 7.98 (6.28) | 8.09 (6.52) | 8.66 (6.89) | 7.29 (5.67) |
| Lowest excited state | λmax | 344.47 (491.16) | | 450.25 (461.35) | | 533.66 (540.13) | |
| | Energy | 3.5992 (2.5243) | | 2.7537 (2.6874) | | 2.3233 (2.2955) | |
| | f | 0.1098 (0.0025) | | 0.0017 (0.0011) | | 0.0231 (0.0208) | |
| | | SOMO → LUMO (0.819) | SOMO → LUMO (0.537) | SOMO → LUMO (0.689) | SOMO-2 → LUMO (0.112) SOMO → LUMO (0.685) | SOMO → LUMO (0.275) | SOMO → LUMO (0.945) |
| Excited state at $\lambda_{max}$ | $\lambda_{max}$, nm | 351 | | 351 | | 317 | |
| | Energy, eV | 3.525 | | 3.532 | | 3.903 | |
| | *f* | 0.1082 | | 0.0986 | | 0.0868 | |
| | | SOMO → LUMO (0.819) | SOMO → LUMO (0.537) | SOMO → LUMO (0.704) | SOMO-2 → LUMO (-0.108) SOMO → LUMO (-0.685) | SOMO-1 → LUMO (-0.177) SOMO → LUMO (0.548) SOMO → LUMO+4 (-0.101) SOMO → LUMO+5 (0.135) | SOMO-5 → LUMO (0.186) SOMO-4 → LUMO (0.556) SOMO-3 → LUMO+1 (-0.230) SOMO-2 → LUMO (-0.307) |

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| Compounds | | 2,6-dihydroxybenzoic acid | | | |
|---|---|---|---|---|---|
| Position of HO attack | | 4 position | | 5 position | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy | LUMO+1 | 2.54 (1.47) | 2.28 (1.26) | 2.67 (1.36) | 2.53 (1.30) |
| | LUMO | 2.03 (1.03) | -1.11 (-2.24) | 1.88 (0.92) | -0.08 (-1.1) |
| | SOMO | -7.25 (-6.50) | -8.10 (-7.59) | -6.20 (-5.47) | -8.15 (-7.70) |
| | SOMO-1 | -8.72 (-8.14) | -9.21 (-9.04) | -8.46 (-8.06) | -9.20 (-8.89) |
| | SOMO-LUMO gap | 9.28 (7.53) | 3.04 (5.36) | 8.08 (6.39) | 8.06 (6.54 |
| Lowest excited state | λmax | 595.43 (601.53) | | 442.98 (448.87) | |
| | Energy | 2.0823 (2.0611) | | 2.7988 (2.7621) | |
| | f | 0.0233 (0.0229) | | 0.0033 (0.0034) | |
| | | SOMO → LUMO (0.171) | SOMO → LUMO (0.970) | SOMO → LUMO (0.712) | SOMO-2 → LUMO (0.135) SOMO → LUMO (0.656) |
| Excited state at $\lambda_{max}$ | $\lambda_{max}$, nm | 289 | | 345 | |
| | Energy, eV | 4.29 | | 3.59 | |
| | *f* | 0.0611 | | 0.1024 | |
| | | SOMO-1 → LUMO+1 (-0.101) SOMO → LUMO (0.839) SOMO → LUMO+1 (0.190) SOMO → LUMO+2 (-0.198) | SOMO-5 → LUMO (0.177) SOMO-4 → LUMO (0.316) SOMO → LUMO (-0.183) | SOMO → LUMO (-0.685) | SOMO → LUMO (0.703) |

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| Compounds | | 2,5-dihydroxybenzoic acid | | | | | |
|---|---|---|---|---|---|---|---|
| Position of HO attack | | 3 position | | 4 position | | 6 position | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy | LUMO+1 | 2.66 (1.33) | 2.72 (1.30) | 2.59 (1.50) | 2.41 (1.34) | 2.80 (1.47) | 1.94 (0.98) |
| | LUMO | 2.23 (1.25) | -0.53 (-1.64) | 1.96 (0.96) | -0.90 (-1.99) | 1.55 (0.58) | -0.84 (-1.99) |
| | SOMO | -6.77 (-6.03) | -7.85 (-7.36) | -7.08 (-6.34) | -8.27 (-7.75) | -7.09 (-6.32) | -8.21 (-7.71) |
| | SOMO-1 | -8.30 (7.80) | -9.11 (8.85) | -8.73 (-8.18) | -8.99 (-.8.85) | -8.62 (-8.16) | -8.91 (-8.73) |
| | SOMO-LUMO gap | 9 (7.28) | 7.32 (5.72) | 9.04 (7.30) | 7.37 (5.76) | 8.64 (6.90) | 7.38 (5.79) |
| Lowest excited state | λmax | 528.18 (529.77) | | 522.92 (523.92) | | 518.23 (519.41) | |
| | Energy | 2.3474 (2.3404) | | 2.371 (2.3665) | | 2.3924 (2.487) | |
| | f | 0.019 (0.0181) | | 0.0143 (0.0133) | | 0.024 (0.0196) | |
| | | SOMO → LUMO (-0.251) | SOMO → LUMO (0.952) | SOMO → LUMO (0.234) | SOMO → LUMO (0.953) | SOMO → LUMO (-0.302) | SOMO → LUMO (0.934) |
| Excited state at $\lambda_{max}$ | $\lambda_{max}$, nm | 298 | | 286 | | 337 | |
| | Energy, eV | 4.15 | | 4.33 | | 3.668 | |
| | *f* | 0.0989 | | 0.0547 | | 0.0808 | |
| | | SOMO-1 → LUMO (-0.183) SOMO → LUMO (0.636) SOMO → LUMO+1 (0.108) SOMO → LUMO+8 (-0.117) | SOMO-4 → LUMO (0.310) SOMO-2→ LUMO (-0.302) SOMO-1 → LUMO+1 (0.484) SOMO → LUMO (0.175) | SOMO-1 → LUMO (0.189) SOMO-1 → LUMO+1 (-0.120) SOMO → LUMO (-0.528) SOMO → LUMO+1 (0.339) | SOMO-5 → LUMO (0.541) SOMO-4 → LUMO (-0.259) SOMO-2 → LUMO+1 (-0.120) SOMO-1 → LUMO (-0.176) | SOMO-1 → LUMO (0.154) SOMO → LUMO (0.835) SOMO → LUMO+4 (0.150) | SOMO-5 → LUMO (-0.248) SOMO-4 → LUMO (0.226) SOMO → LUMO (-0.295) SOMO → LUMO+1 (-0.150) |

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| Compounds | | 3,4-dihydroxybenzoic acid | | | | | |
|---|---|---|---|---|---|---|---|
| Position of HO attack | | 2 position | | 5 position | | 6 position | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy | LUMO+1 | 2.77 (1.43) | 1.85 (0.88) | 2.83 (1.51) | 1.69 (0.70) | 2.98 (1.60) | 1.56 (0.59) |
| | LUMO | 1.43 (0.46) | -0.95 (-2.06) | 1.20 (0.27) | -0.72 (-1.83) | 1.12 (0.14) | -0.54 (-1.60) |
| | SOMO | -7.14 (-6.36) | -8.16 (-8.85) | -7.08 (-6.29) | -8.17 (-7.65) | -6.58 (-5.84) | -8.89 (-8.35) |
| | SOMO-1 | -8.68 (-8.18) | -8.98 (-8.85) | -8.72 (-8.17) | -9.01 (-8.90) | -9.07 (-8.71) | -9.04 (-8.90) |
| | SOMO-LUMO gap | 8.57 (6.82) | 7.21 (5.59) | 8.28 (6.56) | 7.45 (5.81) | 7.69 (5.98) | 8.35 (6.75) |
| Lowest excited state | λmax | 552.15 (568.52) | | 525.74 (543.49) | | 457.47 (469.36) | |
| | Energy | 2.2455 (2.1808) | | 2.3583 (2,2813) | | 2.7102 (2.6415) | |
| | f | 0.025 (0.0236) | | 0.0142 (0.0137) | | 0.0216 (0.0257) | |
| | | SOMO → LUMO (0.265) | SOMO → LUMO (0.949) | SOMO → LUMO (0.316) | SOMO → LUMO (0.930) | SOMO → LUMO (0.867) | SOMO → LUMO (0.458) |
| Excited state at $\lambda_{max}$ | $\lambda_{max}$, nm | 342 | | 360 | | 349 | |
| | Energy, eV | 3.62 | | 3.44 | | 3.543 | |
| | *f* | 0.0971 | | 0.0527 | | 0.117 | |
| | | SOMO-1 → LUMO (0.155) SOMO → LUMO (0.856) | SOMO-5 → LUMO (0.261) SOMO-4→ LUMO (-143) SOMO-2 → LUMO (0.218) SOMO → LUMO (-0.244) | SOMO-1 → LUMO (0.207) SOMO → LUMO (0.845) | SOMO-5 → LUMO (0.201) SOMO-4 → LUMO (-0.249) SOMO → LUMO (-0.301) SOMO → LUMO+1 (-0.159) | SOMO → LUMO (-0.471) | SOMO → LUMO (0.854) |

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| Compounds | | 2,3,4-trihydroxybenzoic acid | | | | 3,4,5-trihydroxybenzoic acid | |
|---|---|---|---|---|---|---|---|
| Position of HO attack | | 5 position | | 6 position | | 2 or 6 position | |
| | | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin | Alpha-spin | Beta-spin |
| energy | LUMO+1 | 2.64 (1.36) | 2.59 (1.32) | 2.81 (1.46) | 1.99 (1.03) | 2.51 (1.15) | 1.96 (0.98) |
| | LUMO | 2.13 (1.13) | -0.14 (-1.23) | 1.68 (0.70) | -0.63 (-1.71) | 1.38 (0.42) | -0.47 (-1.53) |
| | SOMO | -6.26 (-5.54) | -7.86 (-7.38) | -6.71 (5.99) | -8.14 (-7.67) | -6.37 (-5.66) | -8.40 (-7.85) |
| | SOMO-1 | -8.28 (-7.80) | -8.95 (-8.69) | -8.57 (-8.07) | -8.84 (-8.70) | -8.75 (-8.23) | -8.89 (-8.78) |
| | SOMO-LUMO gap | 8.38 (6.68) | 7.72 (6.14) | 8.39 (6.69) | 7.51 (5.60) | 7.74 (6.09) | 7.93 (6.32) |
| Lowest excited state | λmax | 457.78 (469.08) | | 494.38 (480.47) | | 462.79 (469.71) | |
| | Energy | 2.6505 (2.6432) | | 2.5079 (2.5805) | | 2.6791 (2.6396) | |
| | f | 0.0033 (0.0037) | | 0.0091 (0.0059) | | 0.0044 (0.0049) | |
| | | SOMO → LUMO (0.427) | SOMO → LUMO (0.871) | SOMO → LUMO (0.353) | SOMO → LUMO (0.916) | SOMO → LUMO (0.705) | SOMO → LUMO (-0.679) |
| | | SOMO → LUMO+1 (0.143) | | | | | |
| Excited state at $\lambda_{max}$ | $\lambda_{max}$, nm | 345 | | 338 | | 369 | |
| | Energy, eV | 3.59 | | 3.659 | | 3.356 | |
| | $f$ | 0.1021 | | 0.1102 | | 0.175 | |
| | | SOMO → LUMO (0.853) | SOMO-1 → LUMO (0.149) | SOMO-1 → LUMO (-0.134) | SOMO-4 → LUMO (-0.142) | SOMO → LUMO (0.692) | SOMO → LUMO (0.703) |
| | | SOMO → LUMO+1 (0.165) | SOMO→ LUMO (-0.442) | SOMO → LUMO (0.827) | SOMO-2 → LUMO (0.355) | | |
| | | | | | SOMO → LUMO (-0.323) | | |

Figure S1: Theoretically calculated MOs for the addition of HO• to hydroxybenzoic acids