Electronic Supplementary Material (ESI) for Photochemical & Photobiological Science

# ELECTRONIC SUPPLEMENTARY INFORMATION

# THEORETICAL AND EXPERIMENTAL EVIDENCE OF THE PHOTONITRATION PATHWAY OF PHENOL AND 4-CHLOROPHENOL: A MECHANISTIC STUDY OF ENVIRONMENTAL SIGNIFICANCE

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## Optimised structures of reactions intermediates

Figure ESI 1 shows the gas-phase optimised structures of the phenoxyl and 4-chlorophenoxyl radicals in their ground state ($S_0$). The two obtained geometries were confirmed by analytical calculation of frequencies. The structures are here reported with their corresponding atoms labels, to facilitate the description of the results of our computational study.

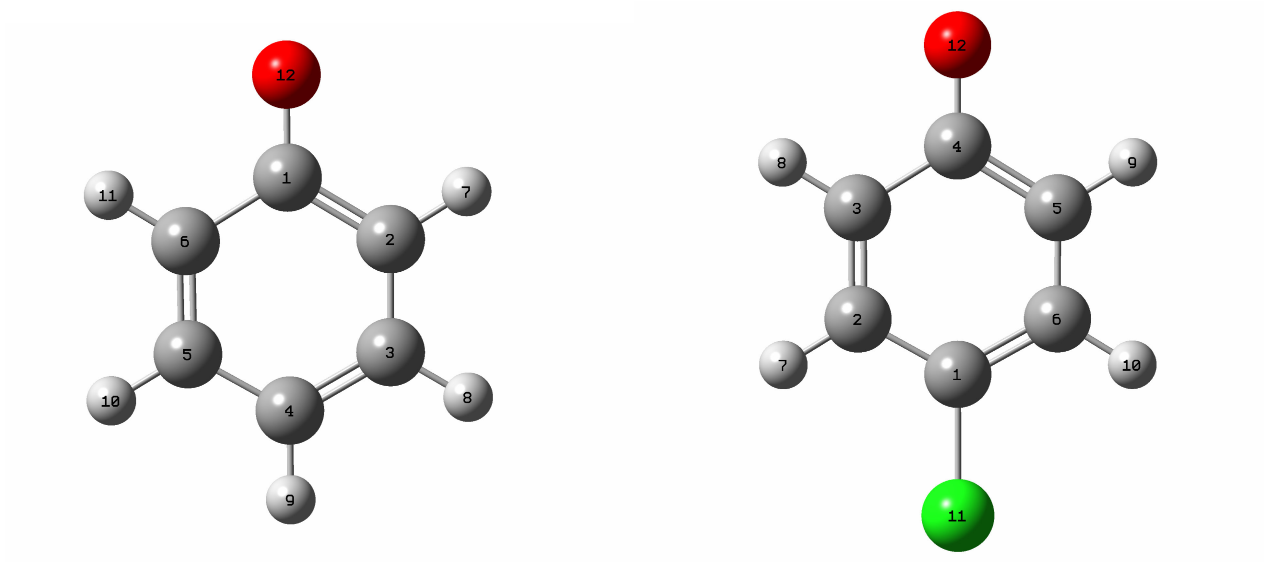

**Figure ESI 1.** Optimised structures of phenoxyl (left) and of 4-chlorophenoxyl (right) radicals.

**Table ESI 1.** Spin density distribution on phenoxyl and 4-chlorophenoxyl radicals

**Phenoxyl radical**

Mulliken atomic spin densities:

| | | |
|---|---|---|
| 1 | C | -0.104428 |
| 2 | C | 0.318164 |
| 3 | C | -0.162712 |
| 4 | C | 0.408545 |
| 5 | C | -0.162709 |
| 6 | C | 0.318146 |
| 7 | H | -0.017207 |
| 8 | H | 0.006857 |
| 9 | H | -0.022392 |
| 10 | H | 0.006857 |
| 11 | H | -0.017207 |
| 12 | O | 0.428086 |

*Sum of Mulliken spin densities= 1.00000*

**4-Chlorophenoxyl radical**

Mulliken atomic spin densities:

| | | |
|---|---|---|
| 1 | C | 0.363955 |
| 2 | C | -0.150451 |
| 3 | C | 0.300495 |
| 4 | C | -0.098136 |
| 5 | C | 0.300499 |
| 6 | C | -0.150451 |
| 7 | H | 0.006339 |
| 8 | H | -0.016398 |
| 9 | H | -0.016399 |
| 10 | H | 0.006339 |
| 11 | Cl | 0.045914 |
| 12 | O | 0.408293 |

*Sum of Mulliken spin densities= 1.00000*

It can be observed that for both radicals the spin density is mainly localised on the oxygen atom and on the *ortho* and *para* positions of the ring (the relevant atoms are highlighted in yellow and in green in Table ESI 1). In the case of the 4-chloroderivative, the electron-withdrawing inductive effect (-*I*) of the chlorine atom stabilises the unpaired resonating spin and attracts spin density from far (C3, C5) and neighbouring (C1) carbon atoms. The inductive effect also weakens the O-H bond, making the phenolic hydrogen more acidic (the $pK_a$ values for phenol and 4-chlorophenol are 9.95 and 9.38, respectively). If an homolytic cleavage of the O-H bond via hydrogen abstraction occurs, it is reasonable to suppose an influence of the chlorine substituent in the hydrogen abstraction reaction. As a consequence, there would be a small lowering of the energy barrier for the transition state in the case of hydrogen abstraction from 4-chlorophenol compared to phenol.

**Figure ESI 2** shows the gas-phase optimised structure of the transition state TS4 (see the main article) in the case of phenol, for the water-assisted rearomatisation process of the intermediate **3** to give product **5** (2-nitrophenol). The obtained geometry was confirmed by analytical calculation of frequencies. The structure is here reported with its corresponding atoms labels, to facilitate the description of the results of our computational study.

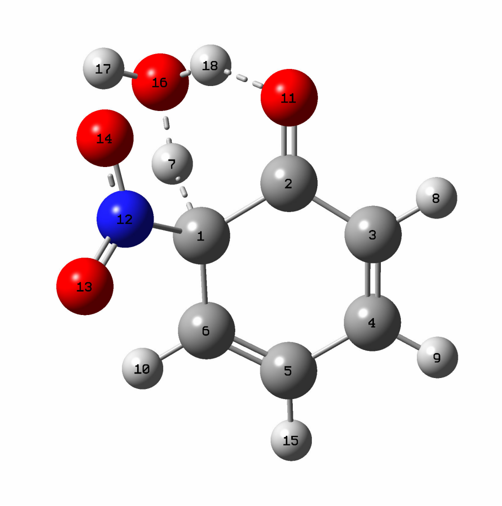

**Figure ESI 2.** Optimised structure of the transition state TS4.

**Table ESI 2.** Z-matrix data of TS4.

| **Row** | **Tag** | **Symbol** | **NA** | **NB** | **NC** | **Bond** | **Angle** | **Dihedral** |
|---|---|---|---|---|---|---|---|---|
| 1 | 1 | C | | | | | | |
| 2 | 2 | C | 1 | | | 1.4969939 | | |
| 3 | 3 | C | 2 | 1 | | 1.4416128 | 115.8316422 | |
| 4 | 4 | C | 3 | 2 | 1 | 1.3622396 | 121.6195984 | 5.9539021 |
| 5 | 5 | C | 4 | 3 | 2 | 1.4312933 | 122.1578178 | -2.7914251 |
| 6 | 6 | C | 5 | 4 | 3 | 1.3564303 | 119.6181063 | -4.1200767 |
| 7 | 7 | H | 1 | 6 | 5 | 1.4596872 | 118.8364280 | 102.9262830 |
| 8 | 8 | H | 3 | 2 | 1 | 1.0831658 | 116.1705186 | -177.0730627 |
| 9 | 9 | H | 4 | 3 | 2 | 1.0852427 | 119.1695191 | 177.3626916 |
| 10 | 10 | H | 6 | 5 | 4 | 1.0823749 | 121.1282227 | -172.4215219 |
| 11 | 11 | O | 2 | 1 | 6 | 1.2520337 | 121.8156277 | 169.6014931 |
| 12 | 12 | N | 1 | 6 | 5 | 1.4902951 | 113.5034509 | -146.8860289 |
| 13 | 13 | O | 12 | 1 | 6 | 1.2221270 | 117.8470747 | 10.7197060 |
| 14 | 14 | O | 12 | 1 | 6 | 1.2337444 | 118.4098152 | -167.7236472 |
| 15 | 15 | H | 5 | 4 | 3 | 1.0826514 | 119.6556313 | 179.3313934 |
| 16 | 16 | O | 11 | 2 | 1 | 2.4941001 | 88.5867236 | -36.8801011 |
| 17 | 17 | H | 16 | 11 | 2 | 0.9703271 | 109.3854731 | 107.9360422 |
| 18 | 18 | H | 16 | 11 | 2 | 1.0344458 | 18.9266791 | -179.2508190 |

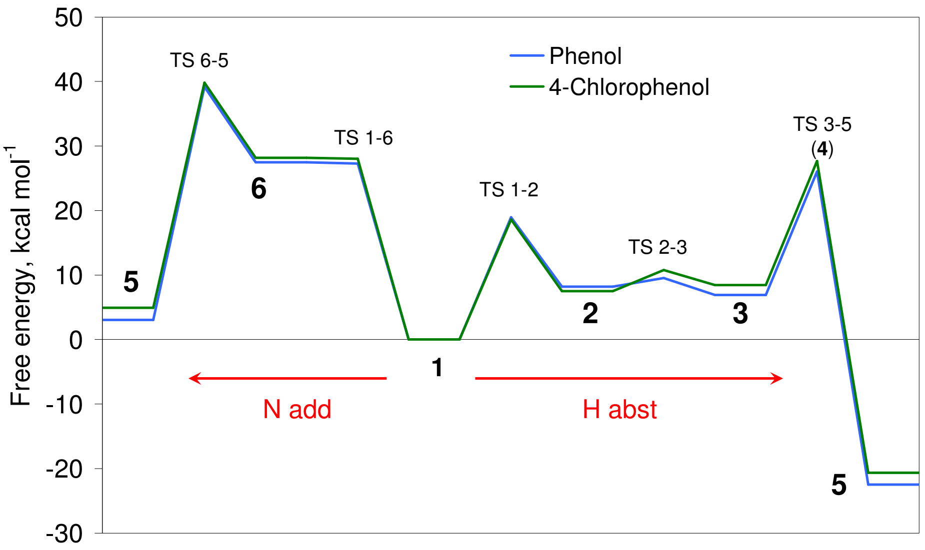

**Figure ESI 3**. Free energy diagram for the reaction of phenol and of 4-chlorophenol (4CP) with nitrogen dioxide via two pathways: hydrogen abstraction (H abst, *i.e.* Path A) and nitrogen dioxide addition (N add, *i.e.* Path B).