**Supporting Information**

**13C NMR Chemical Shifts in Substituted Benzenes: Analysis Using Natural Perturbation Orbitals and Substitution Effects**

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Table S1. Optimised geometry parameters of benzene, aniline, and nitrobenzene when calculating the magnetic shielding tensors of *ortho*-, *meta*-, and *para*-carbons.

1. Benzene

|  |  |  |  |
| --- | --- | --- | --- |
|  | x | y | z |
| C | 1.388268 | 0.000000 | 0.000000 |
| C | 0.694134 | 1.202276 | 0.000000 |
| C | -0.694134 | 1.202276 | 0.000000 |
| C | -1.388268 | 0.000000 | 0.000000 |
| C | -0.694134 | -1.202276 | 0.000000 |
| C | 0.694134 | -1.202276 | 0.000000 |
| H | 2.471837 | 0.000000 | 0.000000 |
| H | 1.235918 | 2.140673 | 0.000000 |
| H | -1.235918 | 2.140673 | 0.000000 |
| H | -2.471837 | 0.000000 | 0.000000 |
| H | -1.235918 | -2.140673 | 0.000000 |
| H | 1.235918 | -2.140673 | 0.000000 |

Table S1 (continued).

1. Aniline

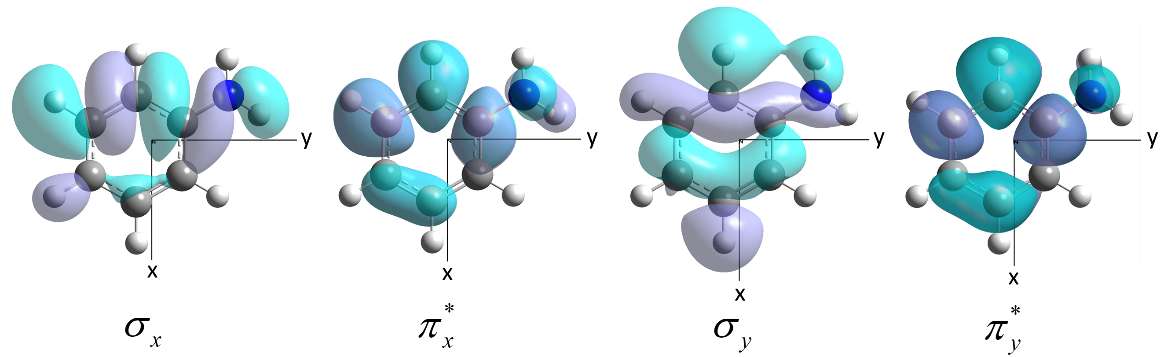
|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *ortho* | x | y | z | *meta* | x | y | z | *para* | x | y | z |
| C | 0.929524 | 1.201798 | 0.004406 | C | 1.149333 | 0.000000 | 0.004406 | C | 0.219594 | 1.200621 | 0.004406 |
| C | -0.467155 | 1.218866 | 0.003076 | C | 0.467155 | 1.218866 | 0.003076 | C | 0.933394 | 0.000000 | 0.003076 |
| C | -1.149333 | 0.000000 | 0.004406 | C | -0.929524 | 1.201798 | 0.004406 | C | 0.219594 | -1.200621 | 0.004406 |
| C | -0.451384 | -1.196271 | 0.004406 | C | -1.617911 | 0.000000 | 0.004406 | C | -1.165385 | -1.195099 | 0.004406 |
| C | 0.936596 | -1.209325 | 0.004012 | C | -0.936596 | -1.209325 | 0.004012 | C | -1.871357 | 0.000000 | 0.004012 |
| C | 1.617911 | 0.000000 | 0.004406 | C | 0.451384 | -1.196271 | 0.004406 | C | -1.165385 | 1.195099 | 0.004406 |
| H | 1.473890 | 2.140139 | 0.010419 | H | 2.234139 | -0.003493 | 0.010419 | H | 0.759505 | 2.141532 | 0.010419 |
| H | -2.234139 | -0.003493 | 0.010419 | H | -1.473890 | 2.140139 | 0.010419 | H | 0.759505 | -2.141532 | 0.010419 |
| H | -1.001728 | -2.130086 | 0.004256 | H | -2.701780 | 0.010932 | 0.004256 | H | -1.698386 | -2.138921 | 0.004256 |
| H | 1.478404 | -2.146539 | 0.003507 | H | -1.478404 | -2.146539 | 0.003507 | H | -2.953912 | 0.000000 | 0.003507 |
| H | 2.701780 | 0.010932 | 0.004256 | H | 1.001728 | -2.130086 | 0.004256 | H | -1.698386 | 2.138921 | 0.004256 |
| N | -1.163275 | 2.423006 | 0.055678 | N | 1.163275 | 2.423006 | 0.055678 | N | 2.324270 | 0.000000 | 0.055678 |
| H | -0.660946 | 3.227706 | -0.285441 | H | 2.111292 | 2.389253 | -0.285441 | H | 2.769522 | 0.837632 | -0.285441 |
| H | -2.111292 | 2.389253 | -0.285441 | H | 0.660946 | 3.227706 | -0.285441 | H | 2.769522 | -0.837632 | -0.285441 |

Table S1 (continued).

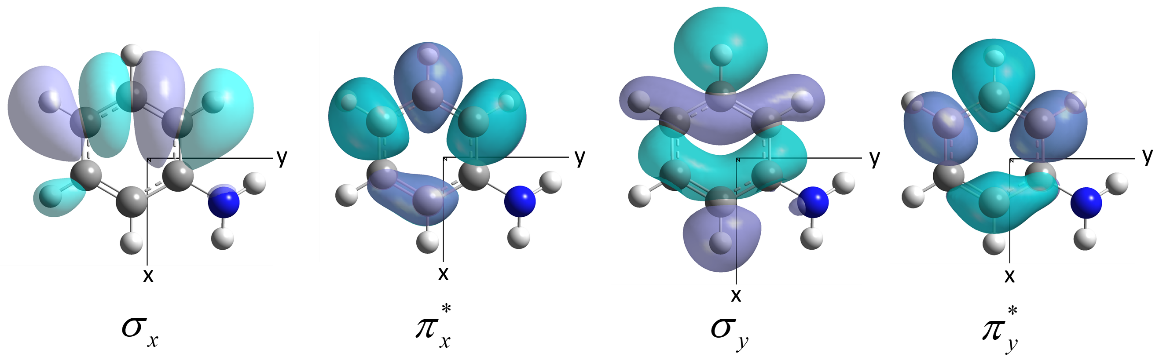
1. Nitrobenzene

|  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| *ortho* | x | y | z | *meta* | x | y | z | *para* | x | y | z |
| C | 1.264507 | 1.206166 | 0.000000 | C | 0.840747 | 0.000000 | 0.000000 | C | -0.426213 | 1.213150 | 0.000000 |
| C | -0.119004 | 1.180611 | 0.000000 | C | 0.119004 | 1.180611 | 0.000000 | C | 0.239386 | 0.000000 | 0.000000 |
| C | -0.840747 | 0.000000 | 0.000000 | C | -1.264507 | 1.206166 | 0.000000 | C | -0.426213 | -1.213150 | 0.000000 |
| C | -0.145057 | -1.198252 | 0.000000 | C | -1.946383 | 0.000000 | 0.000000 | C | -1.811756 | -1.205190 | 0.000000 |
| C | 1.243905 | -1.198224 | 0.000000 | C | -1.243905 | -1.198224 | 0.000000 | C | -2.502215 | 0.000000 | 0.000000 |
| C | 1.946383 | 0.000000 | 0.000000 | C | 0.145057 | -1.198252 | 0.000000 | C | -1.811756 | 1.205190 | 0.000000 |
| H | 1.777408 | 2.157049 | 0.000000 | H | 1.920455 | 0.038427 | 0.000000 | H | 0.143876 | 2.130889 | 0.000000 |
| H | -1.920455 | 0.038427 | 0.000000 | H | -1.777408 | 2.157049 | 0.000000 | H | 0.143876 | -2.130889 | 0.000000 |
| H | -0.689690 | -2.133869 | 0.000000 | H | -3.028970 | -0.003332 | 0.000000 | H | -2.352824 | -2.142873 | 0.000000 |
| H | 1.782362 | -2.138052 | 0.000000 | H | -1.782362 | -2.138052 | 0.000000 | H | -3.585364 | 0.000000 | 0.000000 |
| H | 3.028970 | -0.003332 | 0.000000 | H | 0.689690 | -2.133869 | 0.000000 | H | -2.352824 | 2.142873 | 0.000000 |
| N | -0.852588 | 2.461015 | 0.000000 | N | 0.852588 | 2.461015 | 0.000000 | N | 1.715049 | 0.000000 | 0.000000 |
| O | -0.197823 | 3.483690 | 0.000000 | O | 2.065976 | 2.413367 | 0.000000 | O | 2.276907 | 1.076521 | 0.000000 |
| O | -2.065976 | 2.413367 | 0.000000 | O | 0.197823 | 3.483690 | 0.000000 | O | 2.276907 | -1.076521 | 0.000000 |

*o*-NH2



*m*-NH2



*p*-NH2

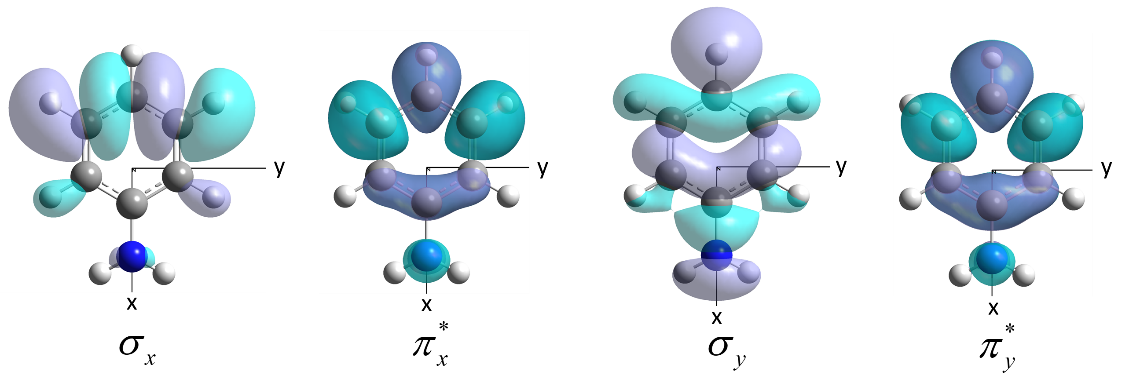
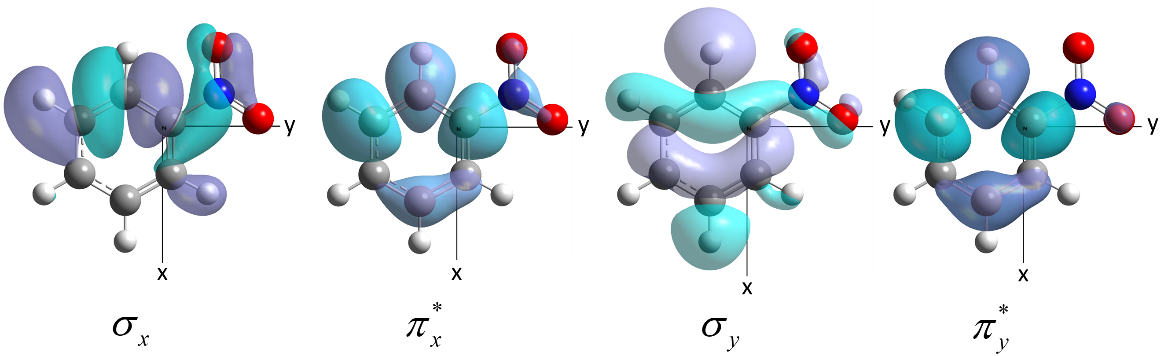
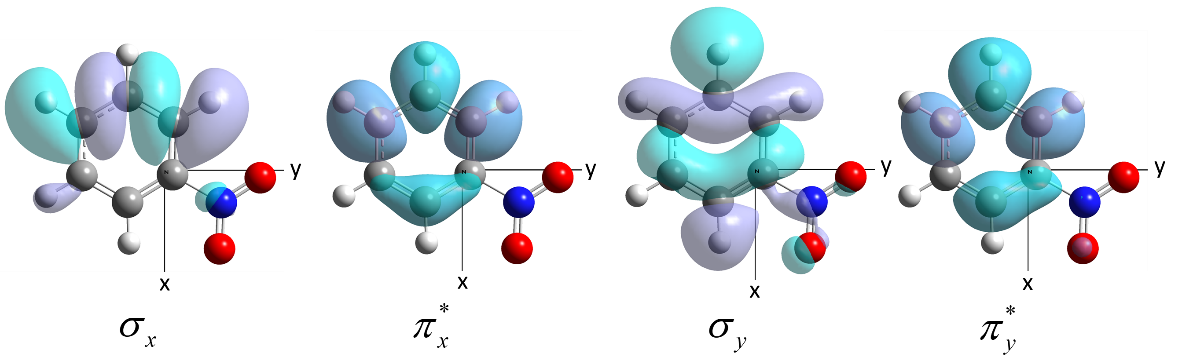


Figure S1. Isosurfaces (±0.02 a.u.) of NPOs mainly contributing to the *xx* (left) and *yy* (right) components of paramagnetic tensors for substituted benzenes. Resonance carbons are top of benzene rings.

*o*-NO2



*m*-NO2



*p*-NO2

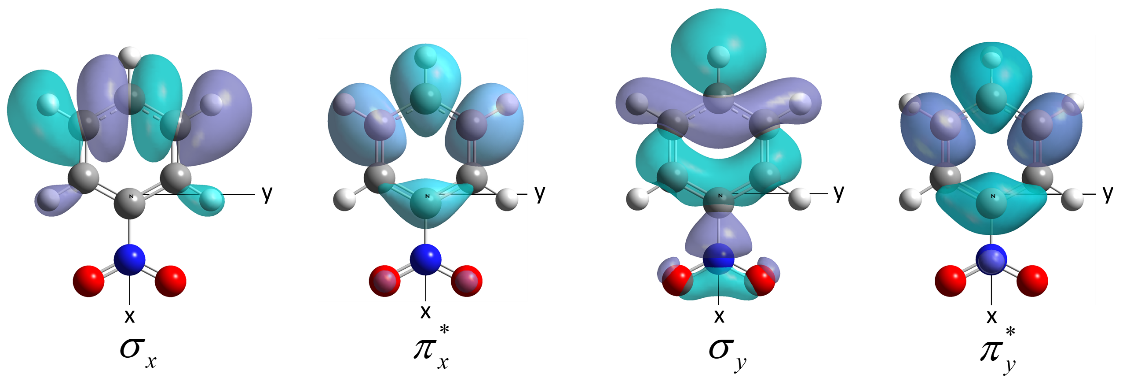


Figure S1. (continued).

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Figure S2. Contributions of and pairs to the *xx* (left) and *yy* (right) components of paramagnetic tensors for S-benzenes. Values are relative to benzene.

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Figure S3. Relationship between singular values and orbital energy gaps for the pair. Values are relative to benzene.

Table S2 *H'* (a.u.), *'* and (ppm) of the and pairs.

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | | | | | | |  |  | | | | | | |
|  | H | *o*-NH2 | *m*-NH2 | *p*-NH2 | *o*-NO2 | *m*-NO2 | *p*-NO2 |  | H | *o*-NH2 | *m*-NH2 | *p*-NH2 | *o*-NO2 | *m*-NO2 | *p*-NO2 |
| *H'* | 1.122 | 1.034 | 1.137 | 1.078 | 1.167 | 1.109 | 1.135 |  | 0.929 | 0.842 | 0.950 | 0.853 | 0.982 | 0.930 | 1.003 |
| *'* | 2.592 | 2.480 | 2.599 | 2.551 | 2.356 | 2.591 | 2.628 |  | 2.168 | 2.131 | 2.137 | 2.214 | 2.185 | 2.181 | 2.106 |
|  | -310 | -273 | -315 | -293 | -293 | -306 | -318 |  | -214 | -191 | -216 | -201 | -229 | -216 | -225 |