**Table S1**

Second order perturbation theory analysis of Fock matrix in NBO basis of 2-Bromo-6-nitrotoluene.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Donor | Type | ED/e(qi) | Acceptor | Type | ED/e(qi) | E(2) kcal/mol | E(j)-E(i) a.u. | F(i,j) a.u. |
| C 1 - C 2 | σ | 1.97336 | C 4 - N 8 | σ\* | 0.10545 | 3.24 | 0.97 | 0.051 |
| C 1 - C 2 | π | 1.65746 | C 3 - C 5 | π\* | 0.31589 | 20.78 | 0.29 | 0.069 |
| C 1 - C 2 | π | 1.65746 | C 4 - C 6 | π\* | 0.37558 | 15.98 | 0.28 | 0.06 |
| C 1 - C 4 | σ | 1.96404 | C 2 -Br 11 | σ\* | 0.02978 | 4.26 | 0.82 | 0.053 |
| C 1 - C 7 | σ | 1.97813 | C 1 - C 2 | σ\* | 0.03515 | 2.51 | 1.16 | 0.048 |
| C 2 - C 5 | σ | 1.98169 | C 1 - C 2 | σ\* | 0.03515 | 3.09 | 1.24 | 0.056 |
| C 2 -Br 11 | σ | 1.9852 | C 1 - C 4 | σ\* | 0.02986 | 3.4 | 1.2 | 0.057 |
| C 3 - C 5 | σ | 1.97412 | C 2 -Br 11 | σ\* | 0.02978 | 4.94 | 0.8 | 0.056 |
| C 3 - C 5 | π | 1.6493 | C 4 - C 6 | π\* | 0.37558 | 22.72 | 0.26 | 0.069 |
| C 3 - C 6 | σ | 1.97749 | C 4 - N 8 | σ\* | 0.10545 | 4.15 | 0.95 | 0.057 |
| C 3 - H 12 | σ | 1.98006 | C 2 - C 5 | σ\* | 0.02418 | 3.41 | 1.04 | 0.053 |
| C 3 - H 12 | σ | 1.98006 | C 4 - C 6 | σ\* | 0.01935 | 3.54 | 1.04 | 0.054 |
| C 4 - C 6 | σ | 1.97556 | C 1 - C 4 | σ\* | 0.02986 | 4.09 | 1.23 | 0.063 |
| C 4 - C 6 | σ | 1.97556 | N 8 - O 9 | σ\* | 0.03676 | 1.64 | 1.33 | 0.042 |
| C 4 - C 6 | π | 1.66305 | C 1 - C 2 | π\* | 0.38738 | 24.7 | 0.27 | 0.074 |
| C 4 - C 6 | π | 1.66305 | C 3 - C 5 | π\* | 0.31589 | 15.99 | 0.28 | 0.06 |
| C 4 - C 6 | π | 1.66305 | N 8 - O 9 | π\* | 0.52391 | 14.91 | 0.18 | 0.049 |
| C 4 - N 8 | σ | 1.98675 | C 1 - C 2 | σ\* | 0.03515 | 1.76 | 1.32 | 0.043 |
| C 4 - N 8 | σ | 1.98675 | N 8 - O 9 | σ\* | 0.03676 | 0.56 | 1.42 | 0.025 |
| C 5 - H 13 | σ | 1.98077 | C 1 - C 2 | σ\* | 0.03515 | 3.98 | 1.05 | 0.058 |
| C 6 - H 14 | σ | 1.9787 | C 1 - C 4 | σ\* | 0.02986 | 3.91 | 1.04 | 0.057 |
| C 7 - H 15 | σ | 1.97353 | C 1 - C 2 | π\* | 0.38738 | 4.19 | 0.49 | 0.045 |
| C 7 - H 16 | σ | 1.97358 | C 1 - C 2 | σ\* | 0.03515 | 2.08 | 1.01 | 0.041 |
| C 7 - H 16 | σ | 1.97358 | C 1 - C 2 | π\* | 0.38738 | 4.31 | 0.49 | 0.045 |
| C 7 - H 17 | σ | 1.98624 | C 1 - C 4 | σ\* | 0.02986 | 4.52 | 1.01 | 0.061 |
| N 8 - O 9 | σ | 1.99592 | C 4 - N 8 | σ\* | 0.10545 | 1.19 | 1.51 | 0.039 |
| N 8 - O 9 | σ | 1.99053 | C 4 - C 6 | π\* | 0.37558 | 2.08 | 0.52 | 0.032 |
| N 8 - O 9 | σ | 1.99053 | N 8 - O 9 | π\* | 0.52391 | 3.35 | 0.42 | 0.039 |
| N 8 - O 10 | σ | 1.99362 | C 1 - C 4 | σ\* | 0.02986 | 0.65 | 1.46 | 0.028 |
| O 9 | LP ( 1) | 1.97748 | C 4 - N 8 | σ\* | 0.10545 | 1.9787 | 1.03 | 0.064 |
| O 9 | LP ( 1) | 1.97748 | N 8 - O 10 | σ\* | 0.08973 | 1.93 | 1.08 | 0.041 |
| O 9 | LP ( 2) | 1.84902 | C 4 - N 8 | σ\* | 0.10545 | 19.56 | 0.56 | 0.094 |
| O 9 | LP ( 2) | 1.84902 | N 8 - O 10 | σ\* | 0.08973 | 29.99 | 0.6 | 0.122 |
| O 10 | LP ( 1) | 1.98569 | C 4 - N 8 | σ\* | 0.10545 | 3.33 | 1.06 | 0.054 |
| O 10 | LP ( 1) | 1.98569 | N 8 - O 9 | σ\* | 0.03676 | 2.03 | 1.43 | 0.048 |
| O 10 | LP ( 2) | 1.93003 | C 4 - N 8 | σ\* | 0.10545 | 9.45 | 0.52 | 0.063 |
| O 10 | LP ( 2) | 1.93003 | N 8 - O 9 | σ\* | 0.03676 | 10.51 | 0.89 | 0.087 |
| O 10 | LP ( 2) | 1.93003 | N 8 - O 9 | π\* | 0.52391 | 0.58 | 0.18 | 0.01 |
| O 10 | LP ( 3) | 1.51386 | N 8 - O 9 | π\* | 0.52391 | 93.55 | 0.17 | 0.112 |
| Br 11 | LP ( 1) | 1.9927 | C 1 - C 2 | σ\* | 0.03515 | 1.78 | 1.52 | 0.047 |
| Br 11 | LP ( 1) | 1.9927 | C 2 - C 5 | σ\* | 0.02418 | 1.7 | 1.51 | 0.046 |
| Br 11 | LP ( 2) | 1.96249 | C 1 - C 2 | σ\* | 0.03515 | 3.84 | 0.82 | 0.05 |
| Br 11 | LP ( 2) | 1.96249 | C 2 - C 5 | σ\* | 0.02418 | 3.81 | 0.81 | 0.05 |

E(2) means energy of hyper conjugative interaction( stabilization energy).

bE(j)-E(i) is the energy difference between donor I and acceptor j.

c F(i,j) is the Fock matrix element between I and j NBO orbital’s.

 **Table S2**

Second order perturbation theory analysis of Fock matrix in NBO basis of 2-Bromo-6-nitrotoluene for different solvents.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Donor | Type | ED/e | Acceptor | Type | ED/e | E(2)a kcal/mol | E(j)-E(i)b a.u. | F(i,j)c a.u. |
|  |  |  | Water |  |  |  |  |  |
| C 1 - C 2 | π | 1.6582 | C 3 - C 5 | π\* | 0.3056 | 20.67 | 0.29 | 0.07 |
| C 1 - C 4 | σ | 1.96385 | C 2 -Br 11 | σ\* | 0.02981 | 4.22 | 0.82 | 0.053 |
| C 1 - C 7 | σ | 1.97808 | C 4 - C 6 | σ\* | 0.01949 | 3.14 | 1.15 | 0.054 |
| C 2 - C 5 | σ | 1.98191 | C 1 - C 2 | σ\* | 0.03511 | 3.08 | 1.24 | 0.055 |
| C 3 - C 6 | σ | 1.97722 | C 4 - N 8 | σ\* | 0.10152 | 4.31 | 0.94 | 0.058 |
| C 4 - C 6 | π | 1.66499 | C 1 - C 2 | π\* | 0.38396 | 24.75 | 0.28 | 0.075 |
| C 7 - H 15 | σ | 1.97298 | C 1 - C 2 | π\* | 0.38396 | 4.25 | 0.49 | 0.045 |
| O 9 | LP ( 1) | 1.97787 | C 4 - N 8 | σ\* | 0.10152 | 4.78 | 1.04 | 0.064 |
| O 9 | LP ( 2) | 1.85196 | C 4 - N 8 | σ\* | 0.10152 | 18.54 | 0.57 | 0.093 |
| Br 11 | LP ( 3) | 1.92749 | C 1 - C 2 | π\* | 0.38396 | 11.06 | 0.3 | 0.056 |
|  |  |  | Benzene |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
| C 4 - C 6 | π | 1.96396 | C 1 - C 2 | π\* | 0.38587 | 24.74 | 0.27 | 0.074 |
| C 7 - H 16 | σ | 1.6435 | C 1 - C 2 | π\* | 0.38587 | 4.32 | 0.49 | 0.045 |
| C 7 - H 17 | σ | 1.66412 | C 1 - C 4 | σ\* | 0.02983 | 4.53 | 1.01 | 0.061 |
| C 1 - C 4 | σ | 1.97355 | C 2 -Br 11 | σ\* | 0.02978 | 4.25 | 0.82 | 0.053 |
| C 1 - C 2 | π | 1.98616 | C 3 - C 5 | π\* | 0.02978 | 20.72 | 0.29 | 0.069 |
| C 3 - C 5 | π | 1.97766 | C 4 - C 6 | π\* | 0.37919 | 23.2 | 0.26 | 0.07 |
| C 3 - C 6 | σ | 1.93255 | C 4 - N 8 | σ\* | 0.10359 | 4.23 | 0.94 | 0.057 |
| O 10 | LP ( 2) | 1.92673 | N 8 - O 9 | σ\* | 0.03645 | 10.53 | 0.89 | 0.087 |
| Br 11 | LP ( 2) | 1.96264 | C 1 - C 2 | σ\* | 0.03514 | 3.84 | 0.82 | 0.05 |
| Br 11 | LP ( 3) | 1.97737 | C 1 - C 2 | π\* | 0.38587 | 11.13 | 0.3 | 0.056 |
|  |  |  | DMSO |  |  |  |  |  |
|  |  |  |  |  |  |  |  |  |
| C 1 - C 2 | π | 1.97355 | C 3 - C 5 | π\* | 0.30573 | 20.67 | 0.29 | 0.07 |
| C 3 - C 5 | π | 1.98607 | C 4 - C 6 | π\* | 0.38349 | 23.74 | 0.26 | 0.07 |
| C 3 - C 6 | σ | 1.85192 | C 4 - N 8 | σ\* | 0.10157 | 4.31 | 0.94 | 0.058 |
| C 7 - H 15 | σ | 1.65819 | C 1 - C 2 | π\* | 0.38401 | 4.25 | 0.49 | 0.045 |
| C 7 - H 16 | σ | 1.63656 | C 1 - C 2 | π\* | 0.38401 | 4.33 | 0.49 | 0.045 |
| C 7 - H 17 | σ | 1.97298 | C 1 - C 4 | σ\* | 0.02979 | 4.53 | 1.01 | 0.061 |
| O 9 | LP ( 2) | 1.98615 | C 4 - N 8 | σ\* | 0.10157 | 18.55 | 0.57 | 0.093 |
| O 9 | LP ( 2) | 1.92747 | N 8 - O 10 | σ\* | 0.09138 | 30.56 | 0.6 | 0.123 |
| O 10 | LP ( 3) | 1.54582 | N 8 - O 9 | π\* | 0.5065 | 87.07 | 0.18 | 0.112 |
| Br 11 | LP ( 3) | 1.97722 | C 1 - C 2 | π\* | 0.38401 | 11.07 | 0.3 | 0.056 |
|  |  |  |  |  |  |  |  |  |

E(2) means energy of hyper conjugative interaction( stabilization energy).

bE(j)-E(i) is the energy difference between donor I and acceptor j.

c F(i,j) is the Fock matrix element between I and j NBO orbital’s.