

**Figure 1S:** Valence-prime structures of the isomers in the mono- and bis-oxidised states

|  |  |
| --- | --- |
| –0.02 / 0.64 | –0.00 / 0.94 |
| **p-CH3TNH● (-state)**  –326.204527 hartree | **p-CH3TNH. (-state)**  –326.145215 hartree |
| 0.65 / 0.02 | 0.96 / –0.00 |
| **m-CH3TNH● (-state)**  –326.203661 hartree | **p-CH3TNH● (-state)**  –326.147076 hartree |
| –0.01 / 0.62 | 0.00 / 0.96 |
| **o-CH3TNH● (-state)**  –326.206300 hartree | **p-CH3TNH● (-state)**  –326.149204 hartree |

**Figure 2S:** The gas-phase electron B3LYP energies, Mulliken spin density distribution in the toluidine isomers in their different oxidised radical states. The depicted iso-surface value is 0.30 atomic units. The spin densities for nitrogen atom / carbon atoms of substitutents are in atomic units.

**Table 1S.** Reaction M062x Gibb´s free energies for selected acido-basic steps calculated for the gas-phase and solvents (energies in kJ mol–1).

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Reaction No.** | **Acid-base reaction** |  |  |  |  |  |  |  |  |  |  |  |
|  |  |  | **gas** |  |  |  | **DMSO** |  |  |  | **water** |  |
| a | **ANH3+**→ **ANH2** + **H+** |  | 850.4 |  |  |  | –53.5 |  |  |  | –31.1 |  |
| b | **ANH2** → **ANH-** + **H+** |  | 1505.9 |  |  |  | 165.9 |  |  |  | 183.1 |  |
| c | **ANH2+●** → **ANH●** + **H+** |  | 925.5 |  |  |  | –4.5 |  |  |  | 16.3 |  |
|  |  | ***ortho*** | ***meta*** | ***para*** |  | ***ortho*** | ***meta*** | ***para*** |  | ***ortho*** | ***meta*** | ***para*** |
| 1 | **CH3TNH3+**→ **CH3TNH2** + **H+** | 857.1 | 857.6 | 862.2 |  | –52.4 | –51.7 | –47.1 |  | –29.6 | –30.9 | –26.4 |
| 2 | **CH3TNH2** → **CH3TNH2**–+ **H+** | 1503.3 | 1509.4 | 1510.2 |  | 167.9 | 169.8 | 170.8 |  | 185.0 | 186.7 | 188.2 |
| (*G*1 – *G*2) |  | –646.2 | –651.8 | –648.0 |  | –220.3 | –221.5 | –217.9 |  | –214.7 | –217.2 | –215.4 |
| 3 | **CH3TNH3+-** → **CH2TNH3**+--+ **H+** | 1128.9 | 1181.4 | 1186.4 |  | 166.5 | 188.2 | 193.2 |  | 188.4 | 208.2 | 212.4 |
| 4 | **CH3TNH2** → **CH2TNH2**–+ **H+** | 1571.1 | 1572.2 | 1589.2 |  | 236.9 | 234.8 | 254.0 |  | 254.0 | 251.9 | 270.5 |
| 5 | **CH3TNH**– → **CH2TNH2**2-+ **H+** | 1991.1 | 1952.9 | 1984.2 |  | 296.7 | 272.3 | 314.7 |  | 318.5 | 288.4 | 328.8 |
| (*G*2 – *G*4) |  | –67.8 | –62.8 | –79.0 |  | –69.0 | –65.0 | –83.2 |  | –69.0 | –65.2 | –82.3 |
| 6 | **CH2TNH3+**– → **CH2TNH2**–+ **H+** | 1299.3 | 1248.4 | 1265.0 |  | 17.9 | –5.1 | 13.8 |  | 35.9 | 13.2 | 31.6 |
| 7 | **CH2TNH2**– → **CH2TNH**2-+ **H+** | 1923.3 | 1890.2 | 1905.2 |  | 227.7 | 207.3 | 231.5 |  | 249.5 | 223.4 | 246.5 |
| (*G*6 – *G*7) |  | –624.0 | –641.8 | –640.2 |  | –209.8 | –212.4 | –217.7 |  | –213.6 | –210.2 | –214.9 |

**Table 1S (continued).** Reaction M062x Gibb´s free energies for selected acido-basic steps calculated for the gas-phase and solvents (energies in kJ mol–1).

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Reaction No.** | **Acid-base reaction** |  | **DFT** |  |  |  | **DFT** |  |  |  | **DFT** |  |
|  |  |  | gas |  |  |  | DMSO |  |  |  | water |  |
|  |  | ***ortho*** | ***meta*** | ***para*** |  | ***ortho*** | ***meta*** | ***para*** |  | ***ortho*** | ***meta*** | ***para*** |
| 8 | **CH3TNH2+●** →**CH3TNH●** + **H+** | 935.9 | 939.5 | 947.7 |  | –3.6 | –0.6 | 6.6 |  | 17.2 | 20.0 | 27.1 |
| 9 | **CH3TNH2+●** →**CH2TNH2●** + **H+** | 930.7 | 932.1 | 940.8 |  | –11.7 | –9.2 | –1.2 |  | 9.2 | 11.4 | 19.3 |
| (*G*8 – *G*9) |  | 5.2 | 7.4 | 6.9 |  | 8.1 | 8.6 | 7.8 |  | 8.0 | 8.6 | 7.8 |
| 11 | **CH3TNH22+**→**CH3TNH**++ **H+** | 397.9 | 404.5 | 431.5 |  | –151.2 | –147.0 | –129.8 |  | –126.7 | –122.0 | –105.2 |
| 10 | **CH3TNH22+**→**CH2TNH2+** + **H+** | 274.6 | 312.2 | 280.3 |  | –273.8 | –228.8 | –276.8 |  | –249.3 | –203.7 | –251.9 |
| (*G*11 – *G*10) |  | 123.3 | 92.3 | 151.2 |  | 122.6 | 81.8 | 147.0 |  | 122.6 | 81.7 | 146.7 |

**Table 2S** The predicted pKa values from the G4(IEF-PCM) calculations.

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| **Reaction No.** | **Acid-base reaction** |  |  |  |  |  |  |  |  |
|  |  |  |  | **DMSO** |  |  |  | **water** |  |
| a | **ANH3+**→ **ANH2** + **H+** |  |  | –6.7 |  |  |  | –3.0 |  |
| b | **ANH2** → **ANH**–+ **H+** |  |  | 30.9 |  |  |  | 33.9 |  |
| c | **ANH2+●** → **ANH●** + **H+** |  |  | 0.2 |  |  |  | 3.9 |  |
|  |  |  | **ortho** | **meta** | **para** |  | **ortho** | **meta** | **para** |
| 1 | **CH3TNCH2** + **H+** → **CH3TNCH3+** |  | –6.1 | –6.6 | –6.1 |  | –2.3 | –2.8 | –2.8 |
| 2 | **CH3TNCH2** → **CH3TNH**–+ **H+** |  | 32.2 | 31.4 | 31.1 |  | 34.3 | 34.5 | 34.1 |
| 3 | **CH3TNCH3+**  → **CH2TNH3+**–+ **H+** |  | 37.1 | 35.9 | 32.7 |  | 36.5 | 39.6 | 35.9 |
| 4 | **CH3TNCH2** → **CH2TNH2**–+ **H+** |  | 48.0 | 44.2 | 44.0 |  | 47.2 | 47.2 | 47.1 |
| 5 | **CH3TNH**– → **CH2TNH**––+ **H+** |  | 56.1 | 51.3 | 54.0 |  | 59.5 | 53.8 | 56.4 |
| 6 | **CH2TNH3+**– → **CH2TNH2**–+ **H+** |  | 4.9 | 1.7 | 5.22 |  | 8.4 | 4.8 | 8.4 |
| 7 | **H2NTCH2**– → –**HNTCH2**–+ **H+** |  | 40.3 | 38.6 | 41.1 |  | 46.6 | 41.1 | 43.5 |
| 8 | **CH3TNH2+●** →**CH3TNH●** + **H+** |  | 1.0 | 0.8 | 0.5 |  | 4.1 | 4.5 | 4.1 |
| 9 | **CH3TNH2+●** →**CH2TNH2●** + **H+** |  | 0.9 | 0.3 | –0.1 |  | 3.6 | 4.0 | 3.6 |
| 10 | **CH3TNH22+**→**CH2TNH2+** + **H+** |  | –45.2 | –35.7 | –44.8 |  | –40.4 | –31.1 | –40.4 |
| 11 | **CH3TNH22+**→**CH3TNH+** + **H+** |  | –24.0 | –22.9 | –20.2 |  | –19.6 | –18.4 | –19.6 |