**Supplementary Table 1**

**Optimised geometrical parameters of the three Isomers of title compound at B3LYP and CAM-B3LYP/6-311 G (d, p) level along with experimental values**

|  |  |  |  |
| --- | --- | --- | --- |
| **Bond Length** | **Exp.** | **B3LYP** | **CAM-B3LYP** |
| **Isomer I** | **Isomer II** | **Isomer III** | **Isomer I** | **Isomer II** | **Isomer III** |
| (C1=C2) | 1.401 | 1.402 | 1.405 | 1.404 | 1.395 | 1.397 | 1.396 |
| (C1-C6) | 1.378 | 1.388 | 1.383 | 1.383 | 1.382 | 1.378 | 1.378 |
| (C1-H7) | - | 1.084 | 1.082 | 1.082 | 1.084 | 1.082 | 1.081 |
| (C2-C3) | 1.384 | 1.399 | 1.399 | 1.400 | 1.391 | 1.391 | 1.392 |
| (C2-C13) | 1.482 | 1.499 | 1.466 | 1.466 | 1.495 | 1.466 | 1.467 |
| (C3=C4) | 1.369 | 1.387 | 1.390 | 1.389 | 1.382 | 1.385 | 1.384 |
| (C3-H8) | - | 1.083 | 1.082 | 1.082 | 1.082 | 1.082 | 1.081 |
| (C4-C5) | 1.393 | 1.398 | 1.396 | 1.397 | 1.392 | 1.390 | 1.390 |
| (C4-H9) | - | 1.086 | 1.086 | 1.086 | 1.085 | 1.085 | 1.085 |
| (C5=C6) | 1.394 | 1.397 | 1.400 | 1.400 | 1.391 | 1.394 | 1.393 |
| (C5-O11) | 1.360 | 1.361 | 1.362 | 1.361 | 1.355 | 1.356 | 1.355 |
| (C6-H10) | - | 1.083 | 1.083 | 1.083 | 1.082 | 1.082 | 1.082 |
| (O11-H12) | - | 0.963 | 0.963 | 0.963 | 0.961 | 0.961 | 0.961 |
| (C13=O14) | 1.238 | 1.214 | - | - | 1.208 | - | - |
| (C13-O14) | - | - | 1.345 | 1.337 | - | 1.337 | 1.329 |
| (C13-N15) | 1.373 | 1.388 | - | 1.302 | 1.380 | - | - |
| (C13=N15) | - | - | 1.297 | - | - | 1.286 | 1.292 |
| (O14-H18) | - | - | - | 0.986 | - | - | 0.984 |
| (O14-H28) | - | - | 0.978 | - | - | 0.976 | - |
| (N15-N16) | 1.380 | 1.358 | 1.388 | 1.395 | 1.356 | 1.388 | 1.394 |
| (N16=C17) | - | - | 1.289 | 1.293 | - | 1.277 | 1.282 |
| (N15-H17) | - | 1.015 | - | - | 1.013 | - | - |
| (N16=C18) | 1.278 | 1.284 | - | - | 1.273 | - | - |
| (C17-C20) | - | - | 1.434 | - | - | 1.437 | - |
| (C17-C22) | - | - | - | 1.435 | - | - | 1.437 |
| (C17-H27) | - | - | 1.091 | - | - | 1.090 | - |
| (C17-H28) | - | - | - | 1.087 | - | - | 1.087 |
| (C18=C19) | - | - | 1.383 | - | - | 1.375 | - |
| (C18-C21) | 1.440 | 1.439 | 1.413 | - | 1.442 | 1.414 | - |
| (C18-H28) | - | 1.096 | - | - | 1.095 | - | - |
| (C18-H25) | - | - | 1.078 | - | - | 1.078 | - |
| (C19=C20) | 1.380 | 1.382 | - | 1.388 | 1.375 | - | 1.380 |
| (C19-C20) | - | - | - | - | - | - | - |
| (C19-N23) | - | - | - | 1.358 | - | - | 1.353 |
| (C19-H25) | - | - | - | 1.078 | - | - | 1.078 |
| (C19-N22) | 1.406 | 1.416 | 1.365 | - | 1.414 | 1.360 | - |
| (C19-H26) | - | 1.078 | 1.078 | - | 1.078 | 1.078 | - |
| (C20=C21) | - | - | 1.391 | - | - | 1.381 | - |
| (C20-N22) | - | - | 1.378 | - | - | 1.371 | - |
| (C20-N23) | 1.353 | 1.365 | - | - | 1.360 | - | - |
| (C20-H26) | - | - | - | 1.079 | - | - | 1.078 |
| (C20-H27) | - | 1.078 | - | - | 1.078 | - | - |
| (C21=C22) | 1.392 | 1.389 | - | 1.396 | 1.379 | - | 1.386 |
| (C21-N23) | 1.374 | 1.376 | - | - | 1.368 | - | - |
| (C21-H24) | - | - | 1.079 | - | - | 1.079 | - |
| (C21-H27) | - | - | - | 1.079 | - | - | 1.079 |
| (N22-H23) | - | - | 1.007 | 1.378 | - | 1.006 | 1.371 |
| (C22-H25) | - | 1.079 | - | - | 1.079 | - | - |
| (N23-H24) | - | 1.009 | - | 1.013 | 1.008 | - | 1.012 |

**Supplementary Table 2**

**Polarizability and ﬁrst hyperpolarizability data for 4HBH and the three Isomers of title compound calculated at 6-311 G (d, p)**

|  |  |
| --- | --- |
| **Parameters**  |  **Polarizability** |
| **4HBH** | **Isomer I** | **Isomer II** | **Isomer III** |
| **B3LYP** | **B3LYP** | **CAM-B3LYP** | **B3LYP** | **CAM****-B3LYP** | **B3LYP** | **CAM-B3LYP** |
| αxx | -49.3079 | -74.3664 | -76.7147 | -72.8100 | -74.9082 | -75.5030 | -76.5533 |
| αxy | -5.5029 | -3.5662 | -4.0223 | -3.1991 | -3.5473 | 2.6741 | -2.2737 |
| αyy | -59.8218 | -95.1766 | -94.7748 | -89.0573 | -88.8631 | -93.8017 | -93.7898 |
| αyz | 2.3029 | -0.6645 | -0.6909 | 0.0050 | 0.0055 | -0.4319 | 0.4983 |
| αzz | -63.4829 | -102.2838 | -102.4635 | -103.9933 | -104.1745 | -103.6719 | -103.7938 |
| αzx | 4.8247 | 4.9030 | 4.8318 | -0.0028 | -0.0033 | -2.2710 | -2.5327 |
| α | -57.5375 | -90.6089 | -91.3176 | -88.6202 | -89.3152 | -90.9922 | -91.3789 |
|  | **Hyperpolarizability** |
| βxxx | 49.8478 | -107.4875 | -114.4099 | -70.8050 | -74.0321 | 132.8504 | -133.2511 |
| βxxy | -58.9907 | 86.4829 | 87.8430 | 88.8542 | 89.8751 | 28.9769 | 32.4795 |
| βxyy | -14.5516 | 15.1008 | 14.2825 | 17.6045 | 17.4885 | -24.5779 | 24.6468 |
| βyyy | -22.1283 | -9.9111 | -9.8577 | 5.6924 | 5.6490 | -2.1903 | -0.7961 |
| βzzz | 4.1706 | 1.8770 | 1.8465 | 0.0025 | 0.0009 | 0.1805 | -0.2319 |
| βxxz | 6.26 | -21.5976 | -21.7170 | 0.0543 | 0.0503 | -13.7895 | 14.7455 |
| βxzz | 9.0307 | -15.1689 | -15.4456 | -11.9637 | -12.0557 | 12.5529 | -12.7795 |
| βyzz | -2.8536 | 3.7090 | -3.6485 | 4.2632 | 4.2631 | 4.9612 | 5.1998 |
| βyyz | 2.3076 | -2.0170 | -2.0901 | 0.0031 | 0.0036 | -1.2995 | 1.3603 |
| βxyz | -4.0292 | 18.5450 | 18.7084 | 0.0332 | 0.0172 | -2.9786  | -3.1799 |
| βtotal | 95.8047 | 135.9671 | 140.8815  | 118.3596 | 121.0923 | 125.8132 | 127.8529 |

**‬‬‬**

**Supplementary Table 3**

**Calculated Thermodynamic Properties of 4-HBH, I, II and III by B3LYP/CAM-B3LYP/ 6-311 G (d, p) methods**

|  |
| --- |
| **I** |
| **Parameters**  | **E (Thermal) (kcalmol-1)** | **CV (cal K-1mol-1)** | **S (cal K-1mol-1)** |
| **B3LYP** | **CAM-B3LYP** | **B3LYP** | **CAM-B3LYP** | **B3LYP** | **CAM-B3LYP** |
| **Total** | 146.314 | 146.314 | 55.562 | 55.562 | 123.740 | 123.740 |
| **Translational**  | 0.889 | 0.889 | 2.981 | 2.981 | 42.189 | 42.189 |
|  **Rotational**  | 0.889 | 0.889 | 2.981 | 2.981 | 33.290 | 33.290 |
| **Vibrational**  | 144.537 | 144.537 | 49.600 | 49.600 | 48.260 | 48.260 |
| **II** |
| **Total** | 144.655 | 144.655 | 55.943 | 55.943 | 122.966 | 122.966 |
| **Translational**  | 0.889 | 0.889 | 2.981 | 2.981 | 42.189 | 42.189 |
|  **Rotational**  | 0.889 | 0.889 | 2.981 | 2.981 | 33.236 | 33.236 |
| **Vibrational**  | 142.877 | 142.877 | 49.981 | 49.981 | 47.541 | 47.541 |
| **III** |
| **Total** | 144.815 | 144.815 | 54.984 | 54.984 | 121.267 | 121.267 |
| **Translational**  | 0.889 | 0.889 | 2.981 | 2.981 | 42.189 | 42.189 |
|  **Rotational**  | 0.889 | 0.889 | 2.981 | 2.981 | 33.403 | 33.403 |
| **Vibrational**  | 143.037 | 143.037 | 49.022 | 49.022 | 45.675 | 45.675 |
| **4 - Hydroxy Benzo Hydrazide** |
| **Total** | 100.792 | 100.792 | 37.308 | 37.308 | 97.896 | 97.896 |
| **Translational**  | 0.889 | 0.889 | 2.981 | 2.981 | 40.967 | 40.967 |
|  **Rotational**  | 0.889 | 0.889 | 2.981 | 2.981 | 30.246 | 30.246 |
| **Vibrational**  | 99.014 | 99.014 | 31.346 | 31.346 | 26.683 | 26.683 |

**Table - 4**

**Second–order perturbation theory analysis of the Fock matrix, in the NBO basis for intermolecular interactions with in I: Stabilization energy of interactions (E(2)), Energy difference between donor (i) and acceptor (j) NBO orbitals (Ej– Ei), Fock matrix element between i and j NBO orbitals (Fij)**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Donor****NBO(i)** | **Occupancy****(i)** | **Acceptor NBO(j)** | **Occupancy****(j)** | **E(2)****(kcal/mol** | **(Ej–Ei) a.u** | **F(i,j)****a.u** |
| σ(C1-C2) | 1.97416 | σ\*(C2-C3) | 0.02249 | 4.63 | 1.27 | 0.068 |
| π(C1-C6) | 1.70461 | π\*(C2-C3) | 0.37469 | 16.51 | 0.29 | 0.063 |
| π(C1-C6) | 1.70461 | π\*(C4-C5) | 0.39178 | 22.79 | 0.28 | 0.073 |
| π(C2-C3) | 1.63635 | π\*(C1-C6) | 0.32819 | 24.04 | 0.27 | 0.073 |
| π(C2-C3) | 1.63635 | π\*(C4-C5) | 0.39178 | 17.75 | 0.27 | 0.062 |
| π(C2-C3) | 1.63635 | π\*(C13-O14) | 0.28335 | 18.20 | 0.30 | 0.067 |
| σ(C4-C5) | 1.63375 | σ\*(C5-C6) | 0.02617 | 4.39 | 1.27 | 0.067 |
| π(C4-C5) | 1.63375 | π\*(C1-C6) | 0.32819 | 16.48 | 0.29 | 0.062 |
| π(C4-C5) | 1.63375 | π\*(C2-C3) | 0.37469 | 24.78 | 0.30 | 0.077 |
| π(N16-C18) | 1.93335 | π\*(C21-C22) | 0.40523 | 10.01 | 0.37 | 0.060 |
| π(C19-C20) | 1.80384 | π\*(C21-C22) | 0.40523 | 18.95 | 0.29 | 0.070 |
| σ(C19-C22) | 1.97292 | σ\*(C18-C21) | 0.02694 | 6.27 | 1.16 | 0.076 |
| π(C21-C22) | 1.76143 | π\*(C21-C22) | 0.40523 | 22.12 | 0.26 | 0.068 |
| π(C21-C22) | 1.76143 | π\*(N16-C18) | 0.23587 | 19.21 | 0.28 | 0.067 |
| lp(1)N15 | 1.67850 | σ\*(C13-O14) | 0.01727 | 44.30 | 0.32 | 0.107 |
| lp(1)N15 | 1.67850 | π\*(N16-C18) | 0.23587 | 28.03 | 0.29 | 0.082 |
| lp(2)O11 | 1.97986 | σ\*(C4-C5) | 0.02893 | 29.67 | 0.35 | 0.097 |
| Lp(2)O14 | 1.85820 | σ\*(C2-C13) | 0.06943 | 18.73 | 0.66 | 0.101 |
| Lp(2)O14 | 1.85820 | σ\*(C13-N15) | 0.08456 | 28.20 | 0.67 | 0.124 |
| lp(1)N23 | 1.57608 | π\*(C19-C20) | 0.34638 | 39.09 | 0.28 | 0.096 |
| lp(1)N23 | 1.57608 | π\*(C22-C21) | 0.40523 | 38.89 | 0.29 | 0.095 |

**Table - 5**

**Second–order perturbation theory analysis of the Fock matrix, in the NBO basis for intermolecular interactions with in II: Stabilization energy of interactions (E(2)), Energy difference between donor (i) and acceptor (j) NBO orbitals (Ej– Ei), Fock matrix element between i and j NBO orbitals (Fij)**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Donor****NBO(i)** | **Occupancy****(i)** | **Acceptor NBO(j)** | **Occupancy****(j)** | **E(2)****(kcal/mol)** | **(Ej–Ei) a.u** | **F(i,j)****a.u** |
| σ(C1-H7) | 1.97704 | σ \*(C2-C3) | 0.02356 | 4.61 | 1.09 | 0.063 |
| σ(C1-H7) | 1.97704 | σ\*(C5-C6) | 0.02702 | 4.06 | 1.07 | 0.059 |
| π(C1-C6) | 1.70070 | π\*(C2-C3) | 0.38719 | 16.64 | 0.29 | 0.063 |
| π(C1-C6) | 1.70070 | π\*(C4-C5) | 0.38954 | 24.22 | 0.28 | 0.075 |
| π(C4-C5) | 1.64716 | π\*(C1-C6) | 0.28931 | 14.94 | 0.30 | 0.061 |
| π(C4-C5) | 1.64716 | π\*(C2-C3) | 0.38719 | 23.96 | 0.30 | 0.076 |
| σ(O11-H12) | 1.98824 | σ\*(C5-C6) | 0.02702 | 4.46 | 1.31 | 0.068 |
| σ (C1-C2) | 1.97051 | σ \*(C2-C3) | 0.02356 | 5.06 | 1.27 | 0.072 |
| σ(N15-N16) | 1.97241 | σ\*(C13-C2) | 0.03909 | 5.11 | 1.25 | 0.072 |
| π(C20-C21) | 1.75318 | π\*(C18-C19) | 0.34445 | 19.35 | 0.28 | 0.067 |
| π(C20-C21) | 1.75318 | π\*(N16-C17) | 0.22644 | 23.12 | 0.27 | 0.071 |
| lp(1)N15 | 1.93742 | π\*(C13-N15) | 0.29225 | 43.60 | 0.35 | 0.113 |
| lp(1)N15 | 1.93742 | σ\*(C13-O14) | 0.04027 | 13.16 | 0.76 | 0.090 |
| lp(1)N16 | 1.92381 | σ\*(C17-H27) | 0.02984 | 7.98 | 0.82 | 0.073 |
| lp(1)O11 | 1.97982 | π \*(C4-C5) | 0.38954 | 30.11 | 0.35 | 0.098 |
| Lp(2)O11 | 1.97982 | σ \*(C4-C5) | 0.02901 | 6.26 | 1.17 | 0.077 |
| lp(1)N22 | 1.58041 | π\*(C18-C19) | 0.34445 | 39.31 | 0.29 | 0.097 |
| lp(1)N22 | 1.58041 | π\*(C20-C21) | 0.39868 | 38.02 | 0.30 | 0.095 |

**Table - 6**

**Second–order perturbation theory analysis of the Fock matrix, in the NBO basis for intermolecular interactions with in III: Stabilization energy of interactions (E(2)), Energy difference between donor (i) and acceptor (j) NBO orbitals (Ej– Ei), Fock matrix element between i and j NBO orbitals (Fij)**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Donor****NBO(i)** | **Occupancy****(i)** | **Acceptor NBO(j)** | **Occupancy****(j)** | **E(2)****(kcal/mol** | **(Ej–Ei) a.u** | **F(i,j)****a.u** |
| σ(C1-H7) | 1.97754 | σ\*(C2-C3) | 0.02343 | 4.45 | 1.09 | 0.062 |
| σ(C1-H7) | 1.97754 | σ\*(C5-C6) | 0.02695 | 4.00 | 1.08 | 0.059 |
| π(C1-C6) | 1.70495 | π\*(C2-C3) | 0.38635 | 16.52 | 0.29 | 0.063 |
| π(C1-C6) | 1.70495 | π\*(C4-C5) | 0.38812 | 23.67 | 0.28 | 0.074 |
| π(C4-C5) | 1.64192 | π\*(C1-C6) | 0.29664 | 15.32 | 0.30 | 0.062 |
| π(C4-C5) | 1.64192 | π\*(C2-C3) | 0.38635 | 24.32 | 0.30 | 0.077 |
| σ(O11-H12) | 1.98809 | σ\*(C5-C6) | 0.02695 | 4.48 | 1.31 | 0.069 |
| σ (C1-C2) | 1.97087 | σ \*(C5-C6) | 0.02695 | 13.37 | 0.29 | 0.056 |
| σ(N15-N16) | 1.97518 | σ\*(C13-C2) | 0.03904 | 5.29 | 1.24 | 0.073 |
| σ(C19-C20) | 1.77943 | σ\*(N23-H24) | 0.03107 | 4.17 | 1.13 | 0.061 |
| σ(C2-C3) | 1.97146 | Lp(1)C21) | 1.05480 | 42.27 | 0.15 | 0.093 |
| π(C19-C20) | 1.77943 | π\*(C22-N23) | 0.79660 | 10.96 | 0.23 | 0.053 |
| π(C22-N23) | 1.77943 | Lp(1)(C21) | 1.05480 | 14.20 | 0.22 | 0.068 |
| π(C22-N23) | 1.77943 | π\*(N16-C17) | 0.79660 | 9.07 | 0.35 | 0.052 |
| π(C22-N23) | 1.77943 | π\*(C19-C20) | 0.36031 | 20.73 | 0.36 | 0.081 |
| lp(2)N14 | 1.81336 | π\*(C13-N15) | 0.30512 | 47.65 | 0.34 | 0.116 |
| lp(1)N15 | 1.92942 | σ\*(C13-O14) | 0.03630 | 12.01 | 0.79 | 0.088 |
| lp(1)N16 | 1.91658 | σ\*(O14-H18) | 0.04407 | 11.88 | 0.78 | 0.087 |
| lp(1)O11 | 1.86199 | σ\*(C4-C5) | 0.02908 | 6.33 | 1.17 | 0.077 |
| Lp(2)O11 | 1.97974 | π\*(C4-C5) | 0.3881 | 30.39 | 0.35 | 0.099 |
| lp(1)C21 | 1.05480 | π\*(C19-C20) | 0.36031 | 58.85 | 0.13 | 0.094 |
| lp(1)C21 | 1.05480 | π\*(C22-N23) | 0.79660 | 234.74 | 0.08 | 0.124 |

**Table - 7**

**Second–order perturbation theory analysis of the Fock matrix, in the NBO basis for intermolecular interactions with in 4-HBH: Stabilization energy of interactions (E(2)), Energy difference between donor (i) and acceptor (j) NBO orbitals (Ej– Ei), Fock matrix element between i and j NBO orbitals (Fij)**

|  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- |
| **Donor NBO(i)** | **occupancy(i)** | **Acceptor NBO(j)** | **occupancy(j)** | **E(2)****(kcal/mol** | **(Ej–Ei) a.u** | **F(i,j)****a.u** |
| π(C1-C2) | 1.65467 | π\*(C3-C4) | 0.29206 | 23.09 | 0.29 | 0.074 |
| π(C1-C2) | 1.65467 | π\*(C5-C6) | 0.39322 | 23.09 | 0.29 | 0.074 |
| σ (C2-C3) | 1.97089 | π\*(C12-O13) | 0.27257 | 17.47 | 0.33 | 0.069 |
| π(C3-C4) | 1.69253 | π\*(C1-C2) | 0.37593 | 16.07 | 0.29 | 0.062 |
| π(C3-C4) | 1.69253 | π\*(C5-C6) | 0.39322 | 25.16 | 0.27 | 0.076 |
| π (C5-C6) | 1.64837 | π \*(C1-C2) | 0.37593 | 24.72 | 0.30 | 0.078 |
| π(C5-C6) | 1.64837 | π\*(C3-C4) | 0.29206 | 14.58 | 0.31 | 0.060 |
| lp(2)O11 | 1.86567 | π \*(C5-C6) | 0.39322 | 30.05 | 0.35 | 0.099 |
| Lp(2)O13 | 1.86463 | σ\*(C2-C12) | 0.06822 | 18.20 | 0.68 | 0.101 |
| Lp(2)O13 | 1.86463 | σ\*(C12-N14) | 0.07590 | 23.98 | 0.70 | 0.117 |
| lp(1)N14 | 1.75191 | π\*(C12-O13) | 0.27257 | 38.27 | 0.36 | 0.105 |



**Supplementary Figure 1 - FTIR and FT-Raman spectra of 4 - Hydroxy Benzo Hydrazide**

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**Supplementary Figure 2 - Theoretical Vibrational Spectrum of 4-HBH and three isomers of title compound**

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**Supplementary Figure 3 - DOS Plots of 4-HBH and three isomers of title compound**

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**Supplementary Figure 4 - Theoretical UV spectra of 4-HBH and three isomers of title compound**