**DFT investigation on the linear and nonlinear optical properties of the tautomers and derivatives of 2-aminobenzothiazole (ABT) in the gas phase and different solvents**

Nuha Wazzan a ‡, , Zaki Safi b, Ohoud Al-Qurashi a, c

a Department of Chemistry, Faculty of Science, King Abdulaziz University, P. O. Box 42805, Jeddah 21589, Saudi Arabia

b Department of Chemistry, Faculty of Science, Al Azhar University-Gaza, Gaza City, P. O. Box 1277, Palestine

c University of Jeddah, Chemistry Department, Faculty of Science, P.O Box 42805 Jeddah 21589, Saudi Arabia

‡ Corresponding author: E-Mail: nwazzan@kau.edu.sa; Fax: + 966 2 695 2000/63170; Tel: + 966561404754

**Supplementary data**

Table SD 1: Geometrical parameters, bond lengths (in Å), bond angles and dihedrals (in o) of the crystal structure of 1,3-benzothiazol-2-amine (T1 ABT).

|  |  |  |  |
| --- | --- | --- | --- |
| S1—C1 | 1.747 (2) | C2—C3 | 1.375 (4) |
| S1—C7 | 1.760 (2) | C3—C4 | 1.402 (3) |
| N1—C6 | 1.389 (3) | C4—C5 | 1.388 (4) |
| N1—C7 | 1.303 (3) | C5—C6 | 1.393 (3) |
| N2—C7 | 1.352 (3) | C2—H2 | 0.9500 |
| N2—H2B | 0.83 (2) | C3—H3 | 0.9500 |
| N2—H2A | 0.80 (2) | C4—H4 | 0.9500 |
| C1—C6 | 1.410 (3) | C5—H5 | 0.9500 |
| C1—C2 | 1.380 (3) |  |  |
|  |  |  |  |
| C1—S1—C7 | 88.64 (10) | N1—C6—C1 | 115.36 (18) |
| C6—N1—C7 | 110.53 (17) | N1—C6—C5 | 125.68 (19) |
| H2A—N2—H2B | 117 (3) | S1—C7—N1 | 116.18 (16) |
| C7—N2—H2B | 123.7 (18) | S1—C7—N2 | 118.60 (16) |
| C7—N2—H2A | 115 (2) | N1—C7—N2 | 125.1 (2) |
| C2—C1—C6 | 122.2 (2) | C1—C2—H2 | 121.00 |
| S1—C1—C6 | 109.29 (16) | C3—C2—H2 | 121.00 |
| S1—C1—C2 | 128.54 (17) | C2—C3—H3 | 120.00 |
| C1—C2—C3 | 118.3 (2) | C4—C3—H3 | 120.00 |
| C2—C3—C4 | 120.7 (2) | C3—C4—H4 | 119.00 |
| C3—C4—C5 | 121.0 (2) | C5—C4—H4 | 120.00 |
| C4—C5—C6 | 118.8 (2) | C4—C5—H5 | 121.00 |
| C1—C6—C5 | 119.0 (2) | C6—C5—H5 | 121.00 |
|  |  |  |  |
| C7—S1—C1—C2 | −179.8 (2) | S1—C1—C6—N1 | 0.0 (2) |
| C7—S1—C1—C6 | 0.41 (17) | S1—C1—C6—C5 | −179.83 (17) |
| C1—S1—C7—N1 | −0.79 (18) | C2—C1—C6—N1 | −179.8 (2) |
| C1—S1—C7—N2 | −176.53 (19) | C2—C1—C6—C5 | 0.4 (3) |
| C7—N1—C6—C1 | −0.6 (3) | C1—C2—C3—C4 | 1.4 (4) |
| C7—N1—C6—C5 | 179.2 (2) | C2—C3—C4—C5 | −0.6 (4) |
| C6—N1—C7—S1 | 0.9 (2) | C3—C4—C5—C6 | −0.3 (4) |
| C6—N1—C7—N2 | 176.3 (2) | C4—C5—C6—N1 | −179.4 (2) |
| S1—C1—C2—C3 | 179.0 (2) | C4—C5—C6—C1 | 0.4 (3) |
| C6—C1—C2—C3 | −1.2 (4) |  |  |

**Hydrogen-bond geometry (Å, º)**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
| N2—H2*B*···N1i | 0.83 (2) | 2.14 (2) | 2.964 (3) | 172 (2) |
| N2—H2*A*···N2ii | 0.80 (2) | 2.46 (2) | 3.217 (3) | 157 (2) |

|  |
| --- |
| Symmetry codes: (i) −*x*, −*y*+1, −*z*; (ii) −*x*, *y*−1/2, −*z*+1/2. |

Table SD 2: The electronegativity ($χ$), chemical hardness ($η$), chemical softness ($σ$), and electrophilicity index ($ω$) (in eV unit) for ABT in its tautomeric forms, T1, T2, and T3, in the gas phase and in solvents of different polarities (dielectric constant $ε$) as calculated at the B3LYP/PCMB3LYP/6-311++G(d,p) levels of theory.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | Gas(1.0) | CCl4(2.24) | THF(7.58) | EtOH (24.5) | MeOH (32.7) | DMSO(46.7) | H2O(80.1) |
| $$χ$$ | T1 | -3.395 | -3.449 | -3.488 | -3.508 | -3.509 | -3.511 | -3.511 |
|  | T2 | -3.395 | -3.382 | -3.390 | -3.397 | -3.398 | -3.398 | -3.398 |
|  | T3 | -3.391 | -3.379 | -3.388 | -3.396 | -3.397 | -3.398 | -3.398 |
| $$η$$ | T1 | 2.532 | 2.670 | 2.668 | 2.666 | 2.666 | 2.666 | 2.666 |
|  | T2 | 2.532 | 2.554 | 2.573 | 2.580 | 2.581 | 2.582 | 2.582 |
|  | T3 | 2.528 | 2.552 | 2.574 | 2.582 | 2.583 | 2.584 | 2.584 |
| $$σ$$ | T1 | 0.395 | 0.375 | 0.375 | 0.375 | 0.375 | 0.375 | 0.375 |
|  | T2 | 0.395 | 0.392 | 0.389 | 0.388 | 0.387 | 0.387 | 0.387 |
|  | T3 | 0.396 | 0.392 | 0.389 | 0.387 | 0.387 | 0.387 | 0.387 |
| $$ω$$ | T1 | 2.275 | 2.228 | 2.279 | 2.307 | 2.309 | 2.312 | 2.311 |
|  | T2 | 2.275 | 2.239 | 2.233 | 2.236 | 2.236 | 2.236 | 2.237 |
|  | T3 | 2.275 | 2.238 | 2.231 | 2.233 | 2.234 | 2.234 | 2.234 |

Table SD 3: The average linear polarizability ($\left〈α\right〉x10^{-23}$), the anisotropy of linear polarizability ($∆αx10^{-23}$), the second-order hyperpolarizabilities ($\left〈γ\right〉x10^{-35}$), and total hyperpolarizability ($β\_{tot}x10^{-30}$) (in esu unit) for ABT in its tautomeric forms, T1, T2, and T3, in the gas phase and in solvents of different polarity (dielectric constant $ε$) as calculated at the B3LYP/6-311++G(d,p) and PCM/B3LYP/6-311++G(d,p) levels of theory. Note: For comparison reason, similar data for pNA are calculated in this work at the same level of theory are included.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Parameter | Molecule | Gas(1.0) | CCl4(2.24) | THF(7.58) | EtOH (24.5) | MeOH (32.7) | DMSO(46.7) | H2O(80.1) |
| $$\left〈α\right〉$$ | T1 | 1.73 | 2.01 | 2.28 | 2.40 | 2.42 | 2.43 | 2.44 |
|  | T2 | 1.73 | 2.01 | 2.28 | 2.40 | 2.41 | 2.43 | 2.44 |
|  | T3 | 1.72 | 1.99 | 2.27 | 2.38 | 2.39 | 2.41 | 2.42 |
|  | pNA | 1.51 | 1.79 | 2.10 | 2.24 | 2.25 | 2.27 | 2.29 |
| $$Δα$$ | T1 | 1.36 | 1.62 | 1.83 | 1.89 | 1.90 | 1.90 | 1.91 |
|  | T2 | 1.42 | 1.70 | 1.92 | 1.99 | 2.00 | 2.01 | 2.01 |
|  | T3 | 1.40 | 1.68 | 1.90 | 1.97 | 1.98 | 1.98 | 1.99 |
|  | pNA | 1.33 | 1.74 | 2.19 | 2.41 | 2.44 | 2.46 | 2.49 |
| $$\left〈γ\right〉$$ | T1 | 1.70 | 2.56 | 3.78 | 4.43 | 4.51 | 4.59 | 4.67 |
|  | T2 | 1.61 | 2.52 | 3.79 | 4.46 | 4.55 | 4.63 | 4.70 |
|  | T3 | 1.59 | 2.47 | 3.72 | 4.37 | 4.45 | 4.53 | 4.60 |
|  | pNA | 1.51 | 2.58 | 4.08 | 4.83 | 4.91 | 5.00 | 5.08 |
| $$β\_{tot}$$ | T1 | 4.03 | 6.87 | 10.35 | 11.99 | 12.20 | 12.39 | 12.57 |
|  | T2 | 4.46 | 6.62 | 9.06 | 10.17 | 10.29 | 10.42 | 10.53 |
|  | T3 | 4.65 | 6.69 | 9.00 | 10.01 | 10.13 | 10.24 | 10.24 |
|  | pNA | 14.27 | 27.60 | 47.06 | 57.43 | 58.68 | 59.93 | 61.13 |

|  |  |
| --- | --- |
|  |  |
| (a) | (b) |
|  |  |
| (c) | (d) |

Figure SD 1: Graphical representations of the relationships between the solvent dielectric constant and linear and nonlinear polarizabilities included (a) average linear polarizability, (b) anisotropy of linear polarizability, (c) second-order hyperpolarizability, and (d) total hyperpolarizability for the six derivatives of T1ABT.

**Cartesian coordinates of the optimized geometries**

|  |  |  |  |
| --- | --- | --- | --- |
| **T1** |  |  |  |
| C | 0.40168 | -0.64737 | -0.00015 |
| C | 0.33443 | 0.76472 | -0.00397 |
| C | 1.52371 | 1.50015 | -0.00306 |
| C | 2.73974 | 0.82532 | 0.00221 |
| C | 2.78876 | -0.57431 | 0.00746 |
| C | 1.61560 | -1.32655 | 0.00722 |
| C | -1.83941 | 0.37688 | 0.00162 |
| H | 1.47723 | 2.58244 | -0.00649 |
| H | 3.66421 | 1.39140 | 0.00228 |
| H | 3.74669 | -1.08109 | 0.01133 |
| H | 1.65313 | -2.40935 | 0.01075 |
| S | -1.23414 | -1.30423 | -0.00985 |
| N | -3.18835 | 0.60915 | -0.05647 |
| H | -3.45722 | 1.56427 | 0.13348 |
| H | -3.80824 | -0.09285 | 0.31619 |
| N | -0.94261 | 1.30511 | 0.00248 |

|  |  |  |  |
| --- | --- | --- | --- |
| **T2** |  |  |  |
| C | -0.37004 | -0.65121 | 0.00000 |
| C | -0.34508 | 0.75289 | 0.00000 |
| C | -1.53462 | 1.47714 | 0.00000 |
| C | -2.74274 | 0.77937 | 0.00000 |
| C | -2.76626 | -0.61584 | 0.00001 |
| C | -1.57343 | -1.34292 | 0.00000 |
| C | 1.99143 | 0.36024 | 0.00000 |
| H | -1.51950 | 2.56114 | 0.00000 |
| H | -3.67400 | 1.33350 | 0.00000 |
| H | -3.71307 | -1.14219 | 0.00001 |
| H | -1.58755 | -2.42627 | 0.00001 |
| S | 1.27755 | -1.30629 | 0.00000 |
| N | 3.21067 | 0.71421 | 0.00001 |
| H | 3.85650 | -0.06845 | 0.00001 |
| N | 0.94388 | 1.26245 | -0.00001 |
| H | 1.15944 | 2.24837 | 0.00000 |

|  |  |  |  |
| --- | --- | --- | --- |
| **T3** |  |  |  |
| C | -0.36891 | -0.65042 | 0.00000 |
| C | -0.34334 | 0.75285 | 0.00000 |
| C | -1.52775 | 1.48336 | 0.00000 |
| C | -2.73955 | 0.79084 | 0.00000 |
| C | -2.76664 | -0.60405 | 0.00000 |
| C | -1.57665 | -1.33569 | 0.00000 |
| C | 1.99267 | 0.33341 | 0.00000 |
| H | -1.50887 | 2.56755 | 0.00000 |
| H | -3.66868 | 1.34844 | 0.00000 |
| H | -3.71531 | -1.12715 | 0.00000 |
| H | -1.59555 | -2.41901 | 0.00000 |
| S | 1.27300 | -1.31406 | 0.00000 |
| N | 3.25105 | 0.50111 | 0.00000 |
| H | 3.51868 | 1.48423 | 0.00000 |
| N | 0.95358 | 1.25652 | 0.00000 |
| H | 1.15036 | 2.24575 | 0.00000 |

|  |  |  |  |
| --- | --- | --- | --- |
| **−C2H5** |  |  |  |
| C | 0.62566 | 1.08671 | -0.00119 |
| C | -0.05768 | -0.14762 | -0.00024 |
| C | -1.46684 | -0.17530 | 0.00308 |
| C | -2.12699 | 1.05364 | 0.00658 |
| C | -1.43506 | 2.27310 | 0.00751 |
| C | -0.04456 | 2.30665 | 0.00446 |
| C | 2.00362 | -0.95842 | 0.00174 |
| H | -3.20973 | 1.07511 | 0.00839 |
| H | -1.99186 | 3.20318 | 0.01022 |
| H | 0.49228 | 3.24747 | 0.00438 |
| S | 2.36365 | 0.78958 | -0.01088 |
| N | 3.03000 | -1.85998 | -0.05689 |
| H | 2.77281 | -2.81492 | 0.15030 |
| H | 3.93547 | -1.57785 | 0.28561 |
| N | 0.75042 | -1.27748 | 0.00564 |
| C | -2.17763 | -1.51312 | 0.00247 |
| H | -1.82331 | -2.08727 | -0.86101 |
| C | -3.70629 | -1.46606 | -0.00860 |
| H | -4.10454 | -0.95478 | 0.87244 |
| H | -4.09106 | -0.95618 | -0.89642 |
| H | -4.11075 | -2.48137 | -0.01073 |
| H | -1.83597 | -2.08199 | 0.87475 |

|  |  |  |  |
| --- | --- | --- | --- |
| **−CF3** |  |  |  |
| C | 1.16909 | 1.15956 | -0.00048 |
| C | 0.23849 | 0.09384 | -0.00158 |
| C | -1.13330 | 0.40591 | -0.00076 |
| C | -1.53110 | 1.74171 | 0.00210 |
| C | -0.58968 | 2.77399 | 0.00418 |
| C | 0.77461 | 2.49149 | 0.00380 |
| C | 2.07404 | -1.13114 | 0.00169 |
| H | -2.58616 | 1.98043 | 0.00241 |
| H | -0.92500 | 3.80371 | 0.00600 |
| H | 1.50436 | 3.29205 | 0.00522 |
| S | 2.80102 | 0.49897 | -0.00564 |
| N | 2.87230 | -2.22853 | -0.04792 |
| H | 2.42078 | -3.11589 | 0.12104 |
| H | 3.83841 | -2.15717 | 0.22821 |
| N | 0.77794 | -1.17496 | 0.00288 |
| C | -2.15365 | -0.69785 | -0.00082 |
| F | -2.04777 | -1.50461 | -1.08433 |
| F | -2.05385 | -1.49791 | 1.08911 |
| F | -3.42187 | -0.21828 | -0.00547 |

**−CN**

|  |  |  |  |
| --- | --- | --- | --- |
| C | -0.31266 | -1.10392 | -0.00055 |
| C | 0.23377 | 0.20092 | -0.00194 |
| C | 1.63623 | 0.33984 | -0.00088 |
| C | 2.44094 | -0.80900 | 0.00169 |
| C | 1.87115 | -2.08013 | 0.00373 |
| C | 0.48374 | -2.24078 | 0.00353 |
| C | -1.88856 | 0.79047 | 0.00172 |
| H | 3.51770 | -0.69585 | 0.00222 |
| H | 2.51111 | -2.95368 | 0.00562 |
| H | 0.04539 | -3.23127 | 0.00533 |
| S | -2.06969 | -0.98624 | -0.00475 |
| N | -2.98669 | 1.58293 | -0.04388 |
| H | -2.83892 | 2.56999 | 0.10912 |
| H | -3.88886 | 1.21367 | 0.20872 |
| N | -0.66880 | 1.23761 | 0.00202 |
| C | 2.23175 | 1.63680 | -0.00088 |
| N | 2.73985 | 2.67543 | -0.00008 |

|  |  |  |  |
| --- | --- | --- | --- |
| **−NH2** |  |  |  |
| C | 0.09044 | -0.97061 | -0.00480 |
| C | 0.28943 | 0.42109 | -0.00688 |
| C | 1.59918 | 0.94257 | -0.00849 |
| C | 2.66114 | 0.03064 | -0.00074 |
| C | 2.43563 | -1.34948 | 0.00383 |
| C | 1.14690 | -1.87981 | -0.00152 |
| C | -1.92058 | 0.47221 | -0.00015 |
| H | 0.97944 | -2.94915 | 0.00105 |
| H | 3.28635 | -2.02149 | 0.01033 |
| H | 3.67861 | 0.40729 | -0.00509 |
| S | -1.64473 | -1.29160 | 0.00669 |
| N | -3.19930 | 0.95804 | 0.06872 |
| H | -3.94417 | 0.37874 | -0.28763 |
| H | -3.29075 | 1.94104 | -0.14763 |
| N | -0.85630 | 1.20643 | -0.00575 |
| N | 1.79118 | 2.31810 | -0.07305 |
| H | 2.65796 | 2.66310 | 0.31233 |
| H | 0.98641 | 2.86839 | 0.19274 |

|  |  |  |  |
| --- | --- | --- | --- |
| **−NO2** |  |  |  |
| C | 0.74991 | 1.15525 | 0.03354 |
| C | 0.00542 | -0.05462 | 0.01310 |
| C | -1.39579 | 0.07138 | 0.01607 |
| C | -2.00800 | 1.32288 | 0.02323 |
| C | -1.23990 | 2.48254 | 0.06028 |
| C | 0.15433 | 2.40728 | 0.06612 |
| C | 2.01636 | -0.95151 | -0.06244 |
| H | -3.08809 | 1.37197 | 0.01030 |
| H | -1.72780 | 3.44865 | 0.08513 |
| H | 0.75342 | 3.30942 | 0.08973 |
| S | 2.46740 | 0.77322 | -0.00820 |
| N | 2.97539 | -1.90090 | -0.16176 |
| H | 2.68222 | -2.85975 | -0.04390 |
| H | 3.93598 | -1.68374 | 0.04737 |
| N | 0.74295 | -1.21012 | -0.04615 |
| N | -2.26675 | -1.11010 | 0.01732 |
| O | -3.36096 | -1.00437 | -0.53537 |
| O | -1.87518 | -2.12180 | 0.58253 |

|  |  |  |  |
| --- | --- | --- | --- |
| **−OH** |  |  |  |
| C | 0.08265 | -0.95017 | 0.00025 |
| C | 0.27584 | 0.44697 | -0.00141 |
| C | 1.59235 | 0.94059 | -0.00029 |
| C | 2.65448 | 0.03904 | 0.00230 |
| C | 2.42918 | -1.34280 | 0.00469 |
| C | 1.13777 | -1.86041 | 0.00489 |
| C | -1.92956 | 0.48301 | 0.00181 |
| H | 3.67167 | 0.41844 | 0.00229 |
| H | 3.27748 | -2.01708 | 0.00600 |
| H | 0.96404 | -2.92892 | 0.00613 |
| S | -1.64809 | -1.28183 | -0.00711 |
| N | -3.20836 | 0.96311 | -0.06003 |
| H | -3.30261 | 1.94936 | 0.13949 |
| H | -3.95415 | 0.38374 | 0.29348 |
| N | -0.87034 | 1.22373 | 0.00429 |
| O | 1.76285 | 2.29485 | -0.00141 |
| H | 2.70469 | 2.49966 | -0.00559 |