**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](mailto: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 (), chemical hardness (), chemical softness (), and electrophilicity index () (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 ) 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) |
|  | 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 |
|  | 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 |
|  | 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 |
|  | 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 (), the anisotropy of linear polarizability (), the second-order hyperpolarizabilities (), and total hyperpolarizability () (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 ) 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) |
|  | 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 |
|  | 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 |
|  | 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 |
|  | 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 |