Supporting information

# Theoretical Study on the Reaction Mechanism of the Thermal *cis* - *trans* Isomerization of Fluorine Substituted Azobenzene Derivatives

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Table S1. The absorption wavelength of the *trans* azobenzene (E-AB).

| E-AB | 6-311g* | |
|---|---|---|
| | $\lambda\pi\rightarrow\pi$ [nm] | $\lambda n\rightarrow\pi^*$[nm] |
| M06 | 342 | 497 |
| M06L | 360 | 494 |
| M06-2X | 301 | 488 |
| PBE0 | 380 | 558 |
| B3LYP | 344 | 482 |
| Expt[1] | 317 | 444 |

Table S2. The absorption band of the *trans* azobenzene (E-AB).

| E-AB | B3LYP | |
|---|---|---|
| | $\lambda\pi\rightarrow\pi$ [nm] | $\lambda n\rightarrow\pi^*$[nm] |
| 6-31+g(d) | 353 | 476 |
| 6-31+g(d,p) | 354 | 477 |
| 6-311+g(2d,p) | 350 | 479 |
| 6-311+g(d) | 351 | 480 |
| 6-311+g(d,p) | 351 | 481 |
| 6-311g* | 344 | 482 |
| Expt.[1] | 317 | 444 |

Table S3. Absorption properties, including vertical transtion energies (in nm/eV), oscillator strengths (*f*) and molecular orbitals involved in the excitation features of the azobenzene compounds.

| | Isomer | State | | Transition(CI) | λ/E | f |
|---|---|---|---|---|---|---|
| **AB** | Z | $S_1$ | n→π* | H→L(0.93) | 477(2.60) | 0.0500 |
| | Z | $S_2$ | π→π* | H-1→L(0.90) | 310 (4.01) | 0.0705 |
| | E | $S_1$ | n→π* | H-1→L(0.99) | 482 (2.57) | 0.0000 |
| | E | $S_2$ | π→π* | H→L(0.99) | 344 (3.60) | 0.8933 |
| **1a** | Z | $S_1$ | n→π* | H→L(0.93) | 470 (2.64) | 0.0467 |
| | Z | $S_2$ | π→π* | H-1→L(0.91) | 317 (3.91) | 0.0274 |
| | E | $S_1$ | n→π* | H-1→L(0.99) | 486 (2.55) | 0.0000 |
| | E | $S_2$ | π→π* | H→L(0.99) | 350 (3.54) | 0.8853 |
| **1b** | Z | $S_1$ | n→π* | H→L(0.93) | 471 (2.63) | 0.0538 |
| | Z | $S_2$ | π→π* | H-1→L(0.91) | 312 (3.97) | 0.0120 |
| | E | $S_1$ | n→π* | H→L(0.95) | 495 (2.50) | 0.0004 |
| | E | $S_2$ | π→π* | H-1→L(0.94) | 341 (3.64) | 0.8714 |
| **2a** | Z | $S_1$ | n→π* | H→L(0.92) | 466 (2.66) | 0.0521 |
| | Z | $S_2$ | π→π* | H-1→L(0.96) | 322 (3.85) | 0.0166 |
| | E | $S_1$ | n→π* | H→L(0.94) | 500 (2.48) | 0.0003 |
| | E | $S_2$ | π→π* | H-1→L(0.91) | 346 (3.58) | 0.8477 |
| **2b** | Z | $S_1$ | n→π* | H→L(0.92) | 466 (2.66) | 0.0582 |
| | Z | $S_2$ | π→π* | H-1→L(0.97) | 319 (3.88) | 0.0048 |
| | E | $S_1$ | n→π* | H→L(0.85) | 506 (2.45) | 0.0120 |
| | E | $S_2$ | π→π* | H-1→L(0.82) | 336 (3.70) | 0.7512 |
| **2c** | Z | $S_1$ | n→π* | H→L(0.92) | 463(2.68) | 0.0496 |
| | Z | $S_2$ | π→π* | H-1→L(0.92) | 315(3.94) | 0.0128 |
| | E | $S_1$ | n→π* | H→L(0.88) | 502(2.47) | 0.0016 |
| | E | $S_2$ | π→π* | H-1→L(0.88) | 343(3.62) | 0.9310 |
| **2d** | Z | $S_1$ | n→π* | H→L(0.92) | 457 (2.71) | 0.0449 |
| | Z | $S_2$ | π→π* | H-1→L(0.93) | 319 (3.89) | 0.0262 |
| | E | $S_1$ | n→π* | H-1→L(0.99) | 491 (2.53) | 0.0000 |
| | E | $S_2$ | π→π* | H→L(0.98) | 355(3.49) | 0.8826 |
| **2e** | Z | $S_1$ | n→π* | H→L(0.92) | 478(2.59) | 0.0575 |
| | Z | $S_3$ | π→π* | H-1→L(0.92) | 300(4.14) | 0.0267 |
| | E | $S_1$ | n→π* | H-1→L(0.99) | 470(2.64) | 0.0000 |
| | E | $S_2$ | π→π* | H→L(1.00) | 350(3.54) | 0.9120 |

| | Isomer | State | | Transition(CI) | λ/E | f |
|---|---|---|---|---|---|---|
| **3a** | Z | $S_1$ | n→π* | H→L(0.92) | 460 (2.69) | 0.0559 |
| | Z | $S_2$ | π→π* | H-1→L(0.97) | 323(3.83) | 0.0209 |
| | E | $S_1$ | n→π* | H→L(0.83) | 507 (2.45) | 0.0269 |
| | E | $S_2$ | π→π* | H-1→L(0.80) | 333 (3.72) | 0.6934 |
| **3b** | Z | $S_1$ | n→π* | H→L(0.92) | 454 (2.73) | 0.0484 |
| | Z | $S_2$ | π→π* | H-1→L(0.97) | 323 (3.84) | 0.0141 |
| | E | $S_1$ | n→π* | H→L(0.99) | 508 (2.44) | 0.0000 |
| | E | $S_2$ | π→π* | H-1→L(0.98) | 349 (2.56) | 0.9149 |
| **4** | Z | $S_1$ | n→π* | H→L(0.92) | 452 (2.74) | 0.0534 |
| | Z | $S_2$ | π→π* | H-1→L(0.98) | 327 (3.80) | 0.0147 |
| | E | $S_1$ | n→π* | H→L(0.84) | 514 (2.41) | 0.0355 |
| | E | $S_2$ | π→π* | H-1→L(0.83) | 330 (3.76) | 0.9359 |
| **5** | Z | $S_1$ | n→π* | H→L(0.91) | 453 (2.74) | 0.0621 |
| | Z | $S_3$ | π→π* | H-1→L(0.97) | 310 (4.00) | 0.0102 |
| | E | $S_1$ | n→π* | H→L(0.74) | 505 (2.45) | 0.0208 |
| | E | $S_2$ | π→π* | H-1→L(0.75) | 338 (3.67) | 1.0079 |
| **6** | Z | $S_1$ | n→π* | H→L(0.88) | 469(2.64) | 0.1294 |
| | Z | $S_2$ | π→π* | H-1→L(0.94) | 331 (3.75) | 0.0524 |
| | E | $S_1$ | n→π* | H-1→L(0.98) | 490 (2.53) | 0.0007 |
| | E | $S_2$ | π→π* | H→L(0.99) | 373 (3.33) | 1.3464 |
| **7** | Z | $S_1$ | n→π* | H→L(0.88) | 465 (2.66) | 0.1053 |
| | Z | $S_2$ | π→π* | H-1→L(0.94) | 325 (3.81) | 0.0477 |
| | E | $S_1$ | n→π* | H-1→L(0.90) | 490 (2.53) | 0.0053 |
| | E | $S_2$ | π→π* | H→L(0.91) | 364 (3.41) | 1.1881 |
| **8** | Z | $S_1$ | n→π* | H→L(0.91) | 468 (2.65) | 0.0825 |
| | Z | $S_2$ | π→π* | H-1→L(0.98) | 340 (3.65) | 0.0232 |
| | E | $S_1$ | n→π* | H→L(0.86) | 549 (2.26) | 0.0776 |
| | E | $S_4$ | π→π* | H-1→L(0.76) | 344 (3.61) | 1.1258 |
| **9** | Z | $S_1$ | n→π* | H→L(0.86) | 480 (2.58) | 0.0968 |
| | Z | $S_2$ | π→π* | H-1→L(0.97) | 350 (3.55) | 0.0261 |
| | E | $S_1$ | n→π* | H→L(0.87) | 580 (2.14) | 0.0819 |
| | E | $S_5$ | π→π* | H-1→L(0.84) | 359 (3.45) | 1.0895 |

Table S4. Molecular orbital energies (eV) of n, π and π* orbitals.

| | E | | | Z | | |
|---|---|---|---|---|---|---|
| | π* | n | π | π* | n | π |
| **AB** | -2.63 | -6.60 | -6.59 | -2.35 | -6.14 | -7.18 |
| **1a** | -2.73 | -6.67 | -6.63 | -2.45 | -6.28 | -7.17 |
| **1b** | -2.65 | -6.53 | -6.64 | -2.44 | -6.26 | -7.18 |
| **2a** | -2.75 | -6.61 | -6.68 | -2.55 | -6.39 | -7.15 |
| **2b** | -2.67 | -6.43 | -6.79 | -2.54 | -6.37 | -7.19 |
| **2c** | -2.75 | -6.58 | -6.71 | -2.53 | -6.40 | -7.25 |
| **2d** | -2.84 | -6.74 | -6.67 | -2.51 | -6.43 | -7.20 |
| **2e** | -2.65 | -6.68 | -6.51 | -2.41 | -6.16 | -7.31 |
| **3a** | -2.75 | -6.47 | -6.95 | -2.64 | -6.51 | -7.23 |
| **3b** | -2.85 | -6.66 | -6.74 | -2.61 | -6.54 | -7.22 |
| **4** | -2.84 | -6.50 | -7.08 | -2.72 | -6.65 | -7.27 |
| **5** | -2.86 | -6.57 | -6.95 | -2.78 | -6.66 | -7.55 |
| **6** | -2.52 | -6.41 | -6.11 | -2.50 | -6.10 | -6.87 |
| **7** | -2.54 | -6.45 | -6.17 | -2.51 | -6.16 | -6.98 |
| **8** | -3.39 | -6.78 | -7.51 | -3.20 | -6.95 | -7.55 |
| **9** | -3.86 | -7.03 | -7.81 | -3.67 | -7.23 | -7.86 |

Table S5. The size and direction of dipole moment in the *cis*, *trans* and **TS** configurations in each

azobenzene derivative are shown. X, Y, Z represent the three directions of the axis.

| Dipole moment | X | Y | Z | Total |
|---|---|---|---|---|
| | | [D] | | |
| AB-Z | 0.0000 | 0.0000 | -4.2870 | 4.2870 |
| AB-TS | -3.7588 | 2.0166 | 0.0000 | 4.2656 |
| AB-E | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 1a-Z | 0.8747 | -4.4815 | -1.1409 | 4.7064 |
| 1a-TS | -2.4644 | 0.7160 | 2.4475 | 3.5463 |
| 1a-E | -0.3407 | -1.6026 | 0.0000 | 1.6384 |
| 1b-Z | -1.0209 | 5.4809 | 0.5681 | 5.6040 |
| 1b-TS | -3.0155 | 3.9726 | 0.0000 | 4.9874 |
| 1b-E | -0.8905 | -1.4833 | -0.0238 | 1.7302 |
| 2a-Z | -2.0850 | 5.9604 | 0.4017 | 6.3273 |
| 2a-TS | 1.3882 | 3.1247 | -2.7303 | 4.3756 |
| 2a-E | 0.6390 | -3.0516 | 0.0105 | 3.1178 |
| 2b-Z | 0.0000 | 6.5542 | 0.0000 | 6.5542 |
| 2b-TS | -1.3297 | 3.1573 | -2.7258 | 4.3780 |
| 2b-E | 0.0000 | 0.0000 | -0.5159 | 0.5159 |
| 2c-Z | 0.0303 | 4.3701 | 3.4613 | 5.5748 |
| 2c-TS | 1.4246 | -2.2163 | 2.1021 | 3.3705 |
| 2c-E | -1.4398 | -0.1036 | 0.0144 | 1.4436 |
| 2d-Z | 0.0000 | 0.0002 | -4.6064 | 4.6064 |
| 2d-TS | -3.3981 | -0.7124 | -1.6670 | 3.8514 |
| 2d-E | 0.0000 | 0.0000 | 0.5999 | 0.5999 |
| 2e-Z | 0.0000 | 0.0000 | -1.5225 | 1.5225 |
| 2e-TS | 4.0754 | -0.1500 | 0.0000 | 4.0782 |
| 2e-E | 0.0000 | 0.0000 | 0.0000 | 0.0000 |
| 3a-Z | -1.1902 | -5.8806 | 3.4281 | 6.9102 |
| 3a-TS | 0.3215 | -4.2031 | 2.5308 | 4.9168 |
| 3a-E | -0.2628 | -1.5374 | -0.4121 | 1.6133 |
| 3b-Z | 1.0040 | 3.5354 | -4.6420 | 5.9207 |
| 3b-TS | -2.1598 | -3.0499 | -1.7035 | 4.1071 |
| 3b-E | 1.2186 | 1.4563 | 0.0000 | 1.8989 |
| 4-Z | 0.0000 | 0.0000 | 6.9046 | 6.9046 |
| 4-TS | -0.9906 | -4.1549 | -1.2504 | 4.4506 |
| 4-E | 0.0000 | 0.0000 | 0.2133 | 0.2133 |
| 5-Z | 0.0000 | 0.0000 | 4.1550 | 4.1550 |
| 5-TS | -0.6991 | -2.2886 | -0.5002 | 2.4447 |
| 5-E | -0.0001 | 0.0000 | 0.1223 | 0.1223 |
| 6-Z | 0.0011 | 7.5437 | -0.0004 | 7.5437 |
| 6-TS | 1.0124 | -3.4341 | -0.3413 | 3.5965 |
| 6-E | 3.2778 | -0.8594 | 1.4534 | 3.6871 |
| 7-Z | -1.0225 | 4.9081 | -1.9877 | 5.3931 |
| 7-TS | 1.0311 | -2.6314 | -2.6314 | 2.8388 |

| | | | | |
|---|---|---|---|---|
| 7-E | 0.0076 | -0.0042 | -0.6004 | 0.6005 |
| 8-Z | 0.2623 | 3.2925 | 0.0920 | 3.3042 |
| 8-TS | -6.7258 | 0.3628 | -1.8764 | 6.9920 |
| 8-E | 0.0000 | 0.0001 | 1.2116 | 1.2116 |
| 9-Z | -0.2844 | -1.3981 | 0.0826 | 1.4292 |
| 9-TS | -8.0549 | 2.2812 | 0.6421 | 8.3963 |
| 9-E | -0.5885 | 0.1069 | -0.0382 | 0.5994 |

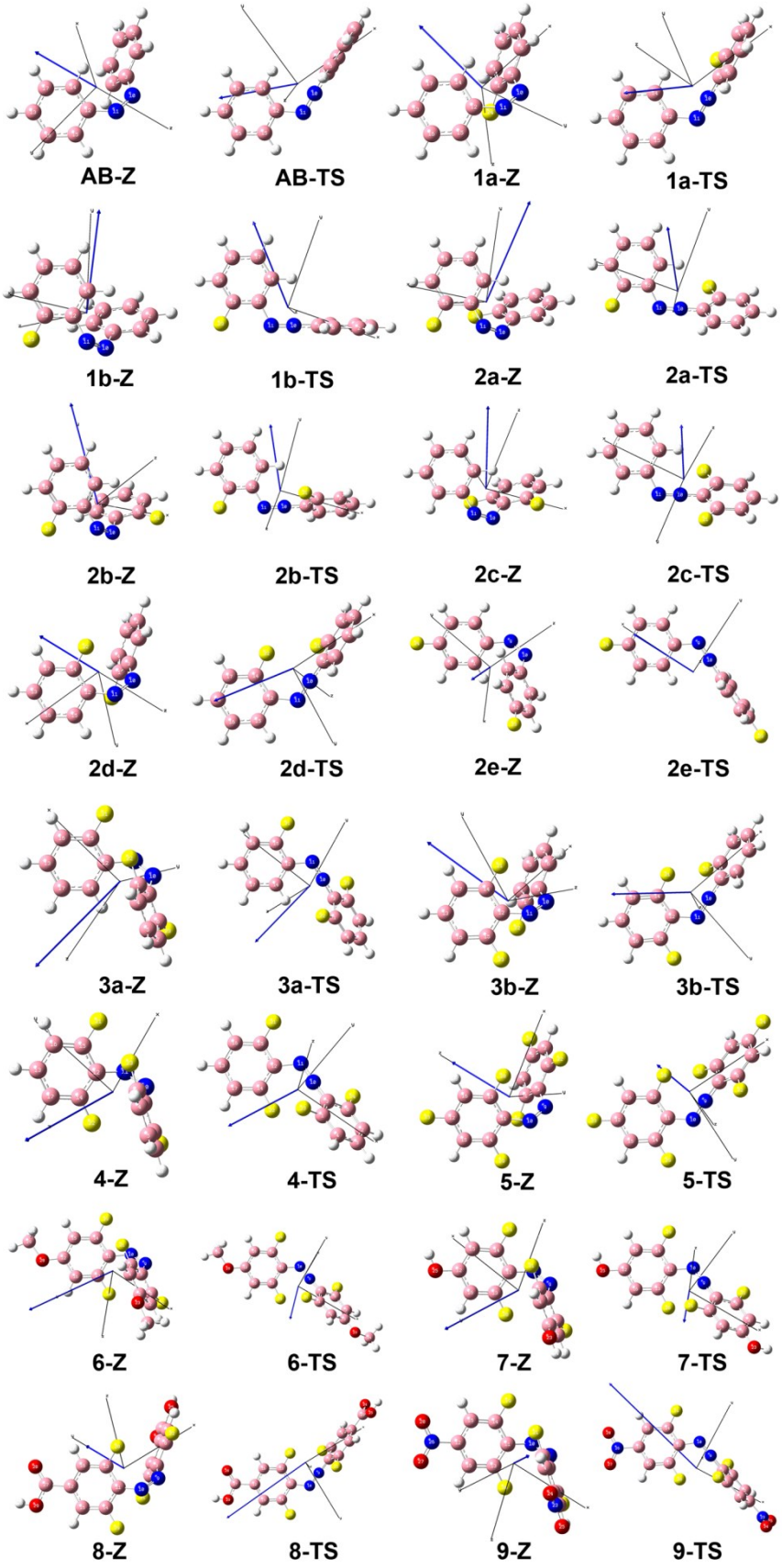


Figure S1 The dipole moments of the *cis* and **TS** configurations for each molecule. The blue arrow represents the dipole direction.

Reference

[1] C. Knie, M. Utecht, F. Zhao, H. Kulla, S. Kovalenko, A.M. Brouwer, P. Saalfrank, S. Hecht, D. Bleger, ortho-Fluoroazobenzenes: Visible Light Switches with Very Long-Lived Z Isomers, Chemistry-a European Journal, 20 (2014) 16492-16501.