Supplementary Material (ESI) for PCCP


# Molecular mechenisms of the photostability of indigo

# Electronic Supplementary Information

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Table S1: Cartesian coordinates of $S_0$ equilibrium geometries of **1** (indigo) and **2** (bispyrroleindigo), optimized with the MP2 method (in au)

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| | | **1** | | | | **2** | |
| N | -2.809356032 | -2.136201129 | 0.000000000 | N | -2.280029126 | -2.675317506 | 0.000000000 |
| N | 2.809356032 | 2.136201129 | 0.000000000 | N | 2.280029126 | 2.675317506 | 0.000000000 |
| C | -1.301843628 | -0.009815915 | 0.000000000 | C | -1.263590542 | -0.279591898 | 0.000000000 |
| C | 1.301843628 | 0.009815915 | 0.000000000 | C | 1.263590542 | 0.279591898 | 0.000000000 |
| C | -2.943214174 | 2.281515511 | 0.000000000 | C | -3.400321140 | 1.590094240 | 0.000000000 |
| C | 2.943214174 | -2.281515511 | 0.000000000 | C | 3.400321140 | -1.590094240 | 0.000000000 |
| C | -5.544505528 | 1.250772444 | 0.000000000 | C | -5.674635403 | 0.008290374 | 0.000000000 |
| C | 5.544505528 | -1.250772444 | 0.000000000 | C | 5.674635403 | -0.008290374 | 0.000000000 |
| C | -5.344215265 | -1.423313712 | 0.000000000 | C | -4.885632747 | -2.471504701 | 0.000000000 |
| C | 5.344215265 | 1.423313712 | 0.000000000 | C | 4.885632747 | 2.471504701 | 0.000000000 |
| O | -2.182857197 | 4.493285409 | 0.000000000 | O | -3.107311445 | 3.915377121 | 0.000000000 |
| O | 2.182857197 | -4.493285409 | 0.000000000 | O | 3.107311445 | -3.915377121 | 0.000000000 |
| H | -2.081191232 | -3.914292816 | 0.000000000 | H | -1.196958206 | -4.261877027 | 0.000000000 |
| H | 2.081191232 | 3.914292816 | 0.000000000 | H | 1.196958206 | 4.261877027 | 0.000000000 |
| C | -7.906867246 | 2.450478636 | 0.000000000 | H | -7.621960503 | 0.670531332 | 0.000000000 |
| C | 7.906867246 | -2.450478636 | 0.000000000 | H | 7.621960503 | -0.670531332 | 0.000000000 |
| C | -10.083966409 | 0.936527366 | 0.000000000 | H | -6.034905953 | -4.185037047 | 0.000000000 |
| C | 10.083966409 | -0.936527366 | 0.000000000 | H | 6.034905953 | 4.185037047 | 0.000000000 |
| C | -9.876646602 | -1.726132550 | 0.000000000 | | | | |
| C | 9.876646602 | 1.726132550 | 0.000000000 | | | | |
| C | -7.516726464 | -2.944874535 | 0.000000000 | | | | |
| C | 7.516726464 | 2.944874535 | 0.000000000 | | | | |
| H | -8.014656092 | 4.516777293 | 0.000000000 | | | | |
| H | 8.014656092 | -4.516777293 | 0.000000000 | | | | |
| H | -11.957325863 | 1.812320884 | 0.000000000 | | | | |
| H | 11.957325863 | -1.812320884 | 0.000000000 | | | | |
| H | -11.596275721 | -2.878244083 | 0.000000000 | | | | |
| H | 11.596275721 | 2.878244083 | 0.000000000 | | | | |
| H | -7.384432288 | -5.009650621 | 0.000000000 | | | | |
| H | 7.384432288 | 5.009650621 | 0.000000000 | | | | |

Table S2: Cartesian coordinates of $CI_{SPT}$ geometries of **1** (indigo) and **2** (bispyrroleindigo), optimized with the CASSCF method (in au)

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| | | **1** | | | | **2** | |
| N | -2.816850812 | -2.301758771 | 0.000000000 | N | -2.270766626 | -2.887718341 | 0.000000000 |
| N | 2.733943970 | 2.159444491 | 0.000000000 | N | 2.109263967 | 2.670368699 | 0.000000000 |
| C | -1.361243013 | 0.144555617 | 0.000000000 | C | -1.369320670 | -0.236604459 | 0.000000000 |
| C | 1.198692471 | 0.030425879 | 0.000000000 | C | 1.169165063 | 0.244313262 | 0.000000000 |
| C | -2.849371218 | 2.367240237 | 0.000000000 | C | -3.324870921 | 1.615673280 | 0.000000000 |
| C | 2.812350624 | -2.131628424 | 0.000000000 | C | 3.316090196 | -1.419849454 | 0.000000000 |
| C | -5.309984000 | 1.332523615 | 0.000000000 | C | -5.538230999 | 0.048164299 | 0.000000000 |
| C | 5.298884591 | -1.239583660 | 0.000000000 | C | 5.470853905 | 0.078936173 | 0.000000000 |
| C | -5.078899761 | -1.519283349 | 0.000000000 | C | -4.659235260 | -2.679496206 | 0.000000000 |
| C | 5.142701996 | 1.422991328 | 0.000000000 | C | 4.632069617 | 2.605305661 | 0.000000000 |
| O | -2.013931282 | 4.581136051 | 0.000000000 | O | -3.006462839 | 3.933338693 | 0.000000000 |
| O | 2.115959192 | -4.502892878 | 0.000000000 | O | 3.237306022 | -3.922168552 | 0.000000000 |
| H | 0.305799562 | -4.597848311 | 0.000000000 | H | 1.520682331 | -4.469889097 | 0.000000000 |
| H | 1.944611420 | 3.891176727 | 0.000000000 | H | 0.911931186 | 4.152238969 | 0.000000000 |
| C | -7.769271002 | 2.481421644 | 0.000000000 | H | -7.485271856 | 0.652859716 | 0.000000000 |
| C | 7.707351291 | -2.486698599 | 0.000000000 | H | 7.403696116 | -0.550522779 | 0.000000000 |
| C | -9.821967841 | 1.003442617 | 0.000000000 | H | -5.889194266 | -4.313153018 | 0.000000000 |
| C | 9.836983972 | -1.026616293 | 0.000000000 | H | 5.734570937 | 4.315660025 | 0.000000000 |
| C | -9.642858699 | -1.812344526 | 0.000000000 | | | | |
| C | 9.653962676 | 1.690644397 | 0.000000000 | | | | |
| C | -7.413069451 | -3.044532463 | 0.000000000 | | | | |
| C | 7.379500524 | 2.931032975 | 0.000000000 | | | | |
| H | -7.904691627 | 4.519186698 | 0.000000000 | | | | |
| H | 7.799890913 | -4.525374250 | 0.000000000 | | | | |
| H | -11.694125857 | 1.823481825 | 0.000000000 | | | | |
| H | 11.688216901 | -1.888557961 | 0.000000000 | | | | |
| H | -11.392348061 | -2.870158462 | 0.000000000 | | | | |
| H | 11.380141844 | 2.785914095 | 0.000000000 | | | | |
| H | -7.275967234 | -5.081722554 | 0.000000000 | | | | |
| H | 7.257810582 | 4.968485142 | 0.000000000 | | | | |

Table S3: Cartesian coordinates of $CI_{DPT}$ geometries of **1** (indigo) and **2** (bispyrroleindigo), optimized with the CASSCF method (in au)

| Atom | x | y | z | Atom | x | y | z |
|---|---|---|---|---|---|---|---|
| | | **1** | | | | **2** | |
| N | -2.773130529 | -2.213800824 | 0.000000000 | N | -2.229999775 | -2.721041984 | 0.000000000 |
| N | 2.675093975 | 2.155905124 | 0.000000000 | N | 2.148831937 | 2.711301380 | 0.000000000 |
| C | -1.350320055 | 0.031243082 | 0.000000000 | C | -1.347751291 | -0.226453580 | 0.000000000 |
| C | 1.344076516 | 0.053251209 | 0.000000000 | C | 1.351600252 | 0.393742331 | 0.000000000 |
| C | -2.848922224 | 2.134003378 | 0.000000000 | C | -3.307316429 | 1.397082705 | 0.000000000 |
| C | 2.956055992 | -2.178891462 | 0.000000000 | C | 3.457979740 | -1.386160213 | 0.000000000 |
| C | -5.418460504 | 1.256998067 | 0.000000000 | C | -5.661701825 | -0.191889452 | 0.000000000 |
| C | 5.425528340 | -1.263863260 | 0.000000000 | C | 5.670185482 | 0.095139847 | 0.000000000 |
| C | -5.212247401 | -1.465176084 | 0.000000000 | C | -4.827642462 | -2.643308247 | 0.000000000 |
| C | 5.152053395 | 1.393010610 | 0.000000000 | C | 4.831306325 | 2.568390908 | 0.000000000 |
| O | -2.143618635 | 4.515943868 | 0.000000000 | O | -3.352951329 | 3.894454712 | 0.000000000 |
| O | 2.196868076 | -4.549927407 | 0.000000000 | O | 3.301440725 | -3.888083698 | 0.000000000 |
| H | 0.393291808 | -4.608663858 | 0.000000000 | H | 1.572735363 | -4.386691050 | 0.000000000 |
| H | -0.327275727 | 4.565932241 | 0.000000000 | H | -1.646181914 | 4.488652458 | 0.000000000 |
| C | -7.763457950 | 2.447565130 | 0.000000000 | H | -7.572741817 | 0.512475657 | 0.000000000 |
| C | 7.857629071 | -2.425621215 | 0.000000000 | H | 7.590133311 | -0.576857006 | 0.000000000 |
| C | -9.889916549 | 0.950960721 | 0.000000000 | H | -5.911381595 | -4.364522413 | 0.000000000 |
| C | 9.947322595 | -0.880787302 | 0.000000000 | H | 5.927038959 | 4.283187529 | 0.000000000 |
| C | -9.728208705 | -1.743959731 | 0.000000000 | | | | |
| C | 9.666391132 | 1.805384671 | 0.000000000 | | | | |
| C | -7.409878163 | -2.972583323 | 0.000000000 | | | | |
| C | 7.314549600 | 2.951944662 | 0.000000000 | | | | |
| H | -7.904300118 | 4.484860870 | 0.000000000 | | | | |
| H | 8.033934130 | -4.460182452 | 0.000000000 | | | | |
| H | -11.739641038 | 1.819456685 | 0.000000000 | | | | |
| H | 11.826244339 | -1.684103446 | 0.000000000 | | | | |
| H | -11.456325252 | -2.833019813 | 0.000000000 | | | | |
| H | 11.346931904 | 2.970843154 | 0.000000000 | | | | |
| H | -7.273021083 | -5.009274827 | 0.000000000 | | | | |
| H | 7.114451856 | 4.984190755 | 0.000000000 | | | | |

Table S4: Cartesian coordinates of $CI_{twist}$ geometry of **2** (bispyrroleindigo), optimized with the CASSCF method (in au)

| Atom | x | y | z |
|---|---|---|---|
| N | -2.576490694 | -1.342423037 | -2.469518258 |
| N | 2.920087491 | 1.680255573 | -2.101523640 |
| C | -1.257887585 | 0.034223679 | -0.705918351 |
| C | 1.440024595 | 0.152001271 | -0.521780208 |
| C | -3.121035352 | 1.010893778 | 1.097701181 |
| C | 2.986981909 | -0.943235954 | 1.464906371 |
| C | -5.577985439 | 0.010801141 | 0.239518173 |
| C | 5.397607540 | -0.895481510 | 0.036160131 |
| C | -5.133070868 | -1.402434083 | -1.843489663 |
| C | 5.299677159 | 1.283188501 | -1.782207664 |
| O | -2.696762709 | 2.417366912 | 2.874311733 |
| O | 2.409583524 | -2.055087718 | 3.355082047 |
| H | -1.747373434 | -2.635887730 | -3.558584832 |
| H | 2.209009416 | 3.178146184 | -3.040426243 |
| H | -7.375518163 | 0.371758187 | 1.121915774 |
| H | 6.028617399 | -2.705825194 | -0.683477918 |
| H | -6.442440779 | -2.428882951 | -3.018146373 |
| H | 6.702585478 | 2.713260379 | -2.169042882 |

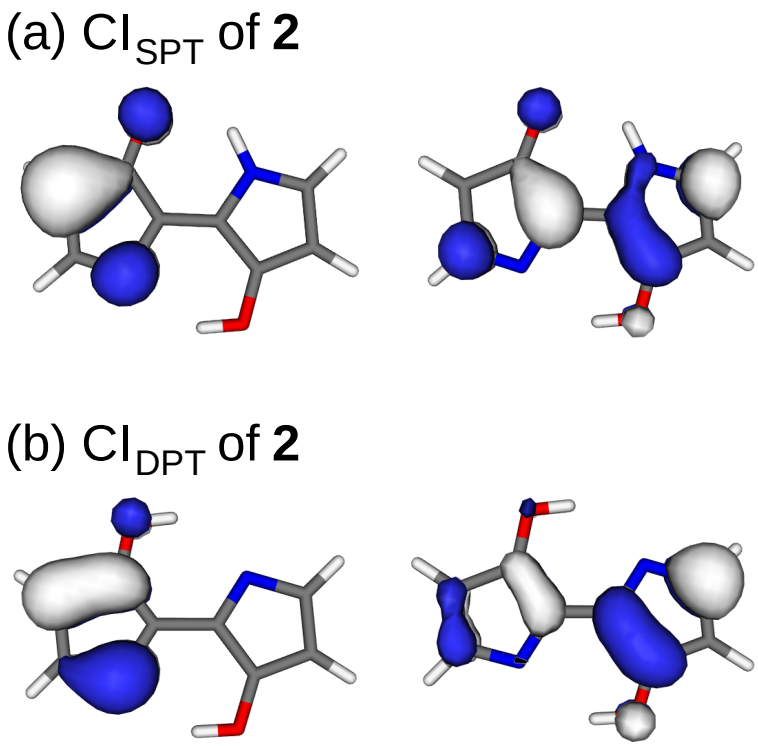
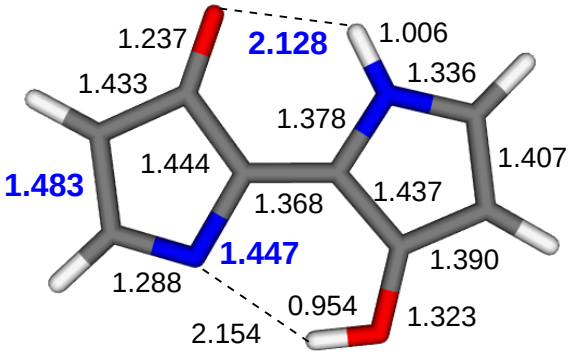



Figure S1: Singly occupied molecular orbitals at the $^1\pi\pi^*$–$S_0$ CI, calculated at the CASSCF level. (a) $CI_{SPT}$ of **2** and (b) $CI_{DPT}$ of **2**.

(a) Mono−enol minimum of **2** ($s_a$ = 0.60 Å)




(b) $CI_{SPT}$ of **2** ($s_a$ = 0.61 Å)

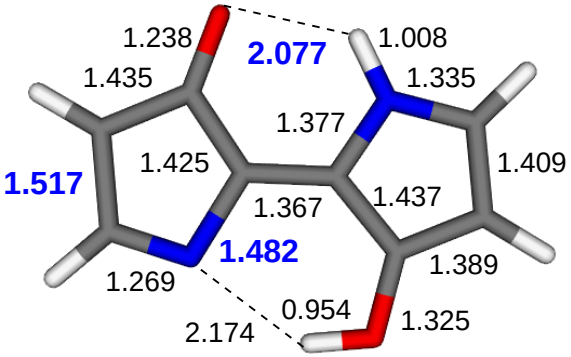



Figure S2: Bond lengths (in Å) of **2** at (a) the mono-enol minimum of the SPT path in the $^1\pi\pi^*$ state ($s_a$ = 0.60 Å) and (b) at $CI_{SPT}$ ($s_a$ = 0.61 Å). Bold blue letters indicate bond lengths which differ by more than 0.030 Å between panels a and b.