Supporting Information for

Conserving Coherence and Storing Energy during Internal Conversion: Photoinduced Dynamics of *cis*- and *trans*-Azobenzene Radical Cations

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1. Molecular Orbital plots

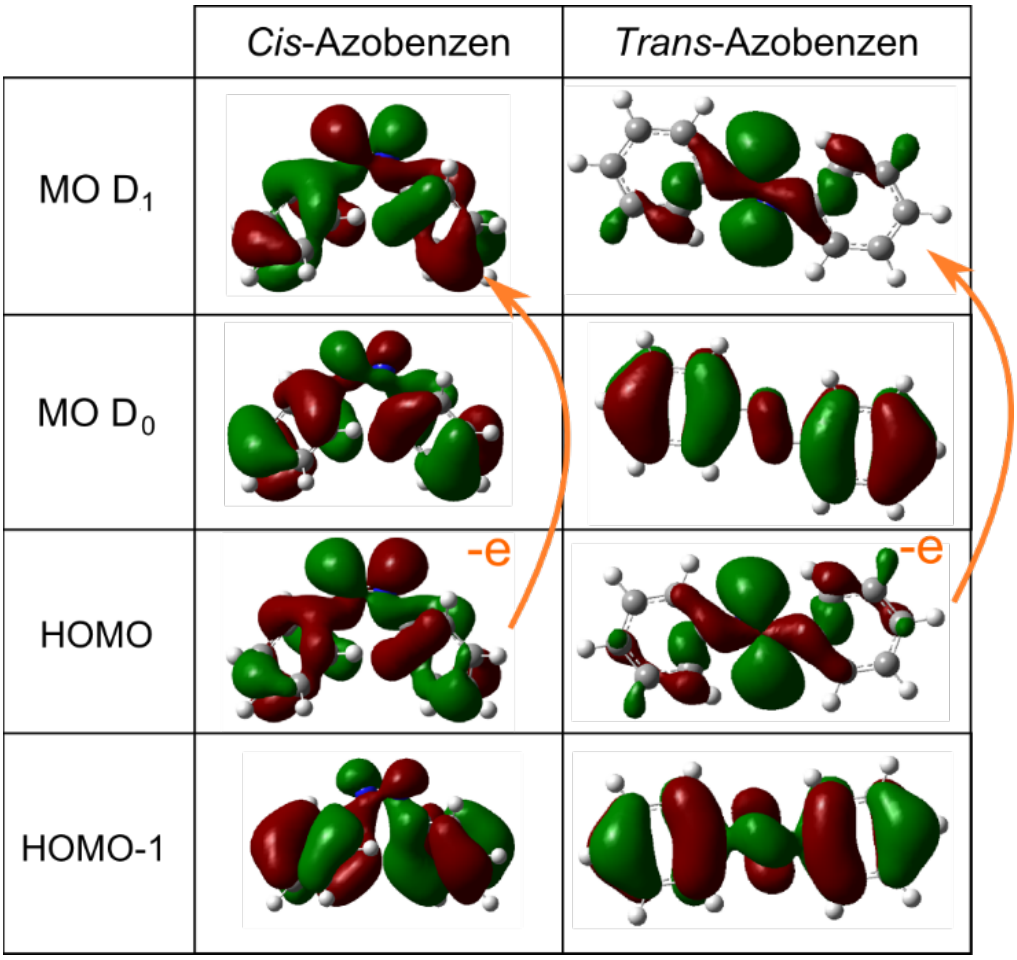

Figure S1. Orbital plots of the highest occupied molecular orbital (HOMO), HOMO-1, ground cationic state D_0, and first excited cationic state D_1 of *cis*-azobenzene (left column) and *trans*-azobenzene (right column) calculated using B3LYP/6-31+G(d).

2. Field calculations

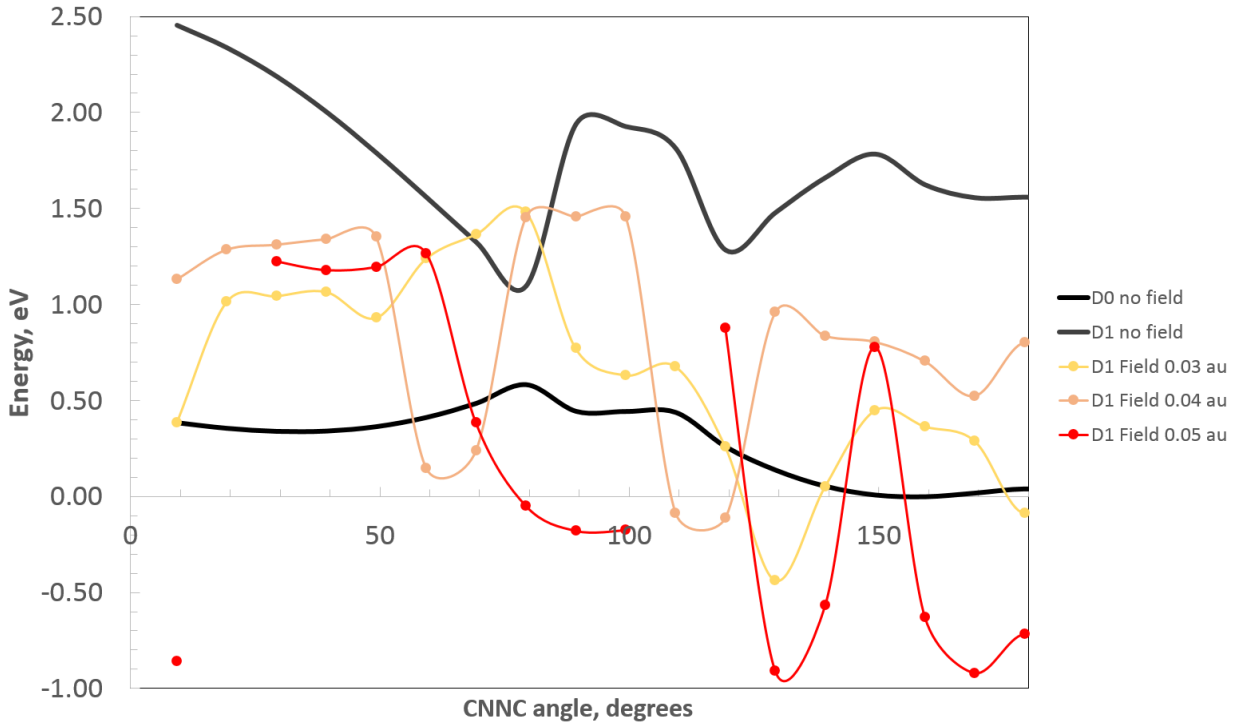

Figure S2. Plot of the CNNC dihedral relaxed scan of D_0 and D_1 without field keyword in DFT calculations are shown as black lines. Yellow, orange and red lines are D_1 with field keyword applied in the DFT calculations.

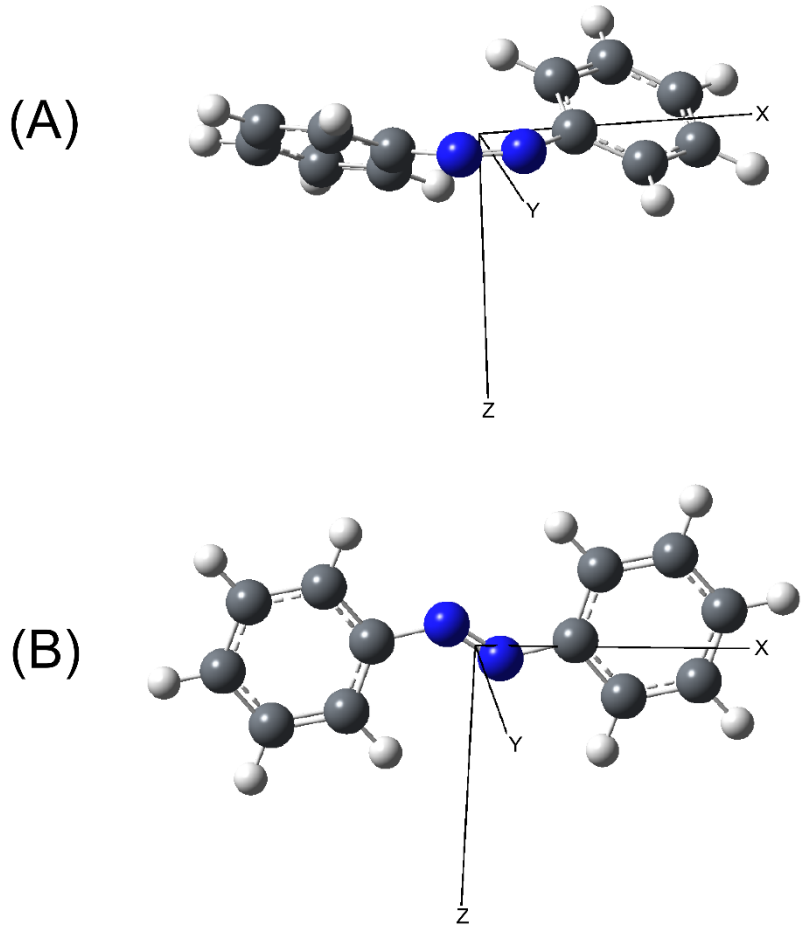

Figure S3. *Cis*- and *trans*-azobenzene geometries showing the Cartesian axes. Field calculations were calculated along the X-axis.

3. TDDFT calculations

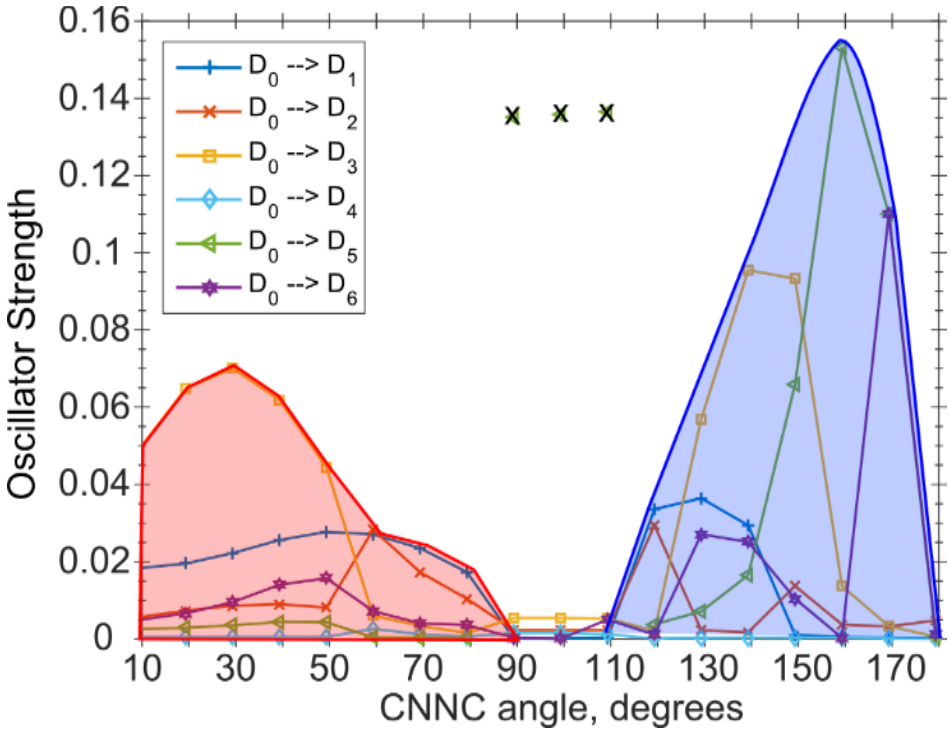

Figure S4. Calculated oscillator strengths associated with the surfaces in S5 for photon absorption of D_0 to D_1-D_6 at each point on the CNNC potential energy surface. The red colored area indicates that the oscillator strengths in the *cis* valley which are less intense than the overall oscillator strengths in the *trans* valley indicated under the blue colored area.

4. XYZ coordinates of Optimized Structures

Cis-azobenzene D_0 optimized

Sum of electronic and zero-point Energies= -572.091370
Sum of electronic and thermal Energies= -572.080394
Sum of electronic and thermal Enthalpies= -572.079450
Sum of electronic and thermal Free Energies= -572.130873

N	-0.58730900	-1.50758000	0.09310200
N	0.58728300	-1.50757300	-0.09319600
C	-1.63501500	-0.59703000	-0.01895200
C	-1.51902500	0.55930500	-0.81109200
C	-2.83035300	-0.94040700	0.62690500
C	-2.61701100	1.39273500	-0.91364100
H	-0.59807200	0.78335800	-1.33859300
C	-3.91079200	-0.07917400	0.52689800
H	-2.88580200	-1.86262200	1.19541200
C	-3.80407400	1.07988200	-0.24142200
H	-2.55749100	2.28829400	-1.52285600
H	-4.84038200	-0.31615600	1.03252400
H	-4.65787900	1.74394900	-0.33096900
C	1.63500500	-0.59705200	0.01890300
C	2.83031700	-0.94038100	-0.62702600
C	1.51905600	0.55920700	0.81116200
C	3.91076900	-0.07917000	-0.52697300
H	2.88573700	-1.86254200	-1.19562400
C	2.61705600	1.39261400	0.91375500
H	0.59812300	0.78321800	1.33871600
C	3.80409200	1.07981200	0.24146500
H	4.84033900	-0.31611400	-1.03265300
H	2.55756800	2.28811400	1.52306000
H	4.65790800	1.74386000	0.33104700

Trans-azobenzene D_0 optimized

Sum of electronic and zero-point Energies= -572.102988
Sum of electronic and thermal Energies= -572.092027
Sum of electronic and thermal Enthalpies= -572.091083
Sum of electronic and thermal Free Energies= -572.142077

N	-0.59268100	-0.84130300	0.11416200
N	0.59268200	-0.84123400	-0.11420800
C	-1.64551100	-1.05558800	-0.75522200
C	-1.45424600	-1.67876100	-2.00339600
C	-2.91611400	-0.65718600	-0.31176500
C	-2.55479600	-1.87680300	-2.81297800
H	-0.45992900	-1.98311100	-2.31329300

C	-4.00538000	-0.86319100	-1.14087700
H	-3.02225000	-0.19271400	0.66282300
C	-3.82447500	-1.47038700	-2.38404200
H	-2.43432900	-2.34733100	-3.78288500
H	-4.99522400	-0.55554300	-0.82244200
H	-4.68159700	-1.63272500	-3.02987000
C	1.64553400	-1.05551400	0.75515300
C	2.91609900	-0.65694400	0.31173800
C	1.45432900	-1.67883900	2.00326000
C	4.00538500	-0.86293600	1.14082600
H	3.02219000	-0.19235700	-0.66280000
C	2.55489800	-1.87686500	2.81281900
H	0.46004000	-1.98331600	2.31312500
C	3.82453800	-1.47028400	2.38392500
H	4.99519900	-0.55516100	0.82242300
H	2.43447700	-2.34750900	3.78267500
H	4.68167600	-1.63261200	3.02973500

Cis-azobenzene S_0 optimized

Sum of electronic and zero-point Energies= -572.242080
Sum of electronic and thermal Energies= -572.231423
Sum of electronic and thermal Enthalpies= -572.230479
Sum of electronic and thermal Free Energies= -572.279925

N	-0.62007700	-2.01649600	-0.00760800
N	0.62006200	-2.01650200	0.00748800
C	-1.40703700	-0.81905300	-0.09442000
C	-1.23145400	0.12243400	-1.10907500
C	-2.48572900	-0.71386300	0.78203200
C	-2.11643300	1.18952900	-1.21348600
H	-0.41372200	0.01677500	-1.81375800
C	-3.34649600	0.37388700	0.69163400
H	-2.63612800	-1.48809100	1.52827200
C	-3.16540400	1.32763400	-0.30742900
H	-1.98327800	1.91884900	-2.00698900
H	-4.17327600	0.46564000	1.38963900
H	-3.84884200	2.16721700	-0.38995600
C	1.40703200	-0.81907100	0.09436200
C	2.48572100	-0.71384100	-0.78208900
C	1.23146100	0.12236000	1.10907000
C	3.34649700	0.37389800	-0.69163400
H	2.63611200	-1.48802700	-1.52837300
C	2.11644800	1.18944300	1.21353700
H	0.41373000	0.01666800	1.81375000
C	3.16541700	1.32759000	0.30748400
H	4.17327500	0.46568400	-1.38963600
H	1.98330300	1.91871900	2.00708200

H	3.84886200	2.16716300	0.39005500

***Trans*-azobenzene S_0 optimized**

Sum of electronic and zero-point Energies= -572.266547
Sum of electronic and thermal Energies= -572.255807
Sum of electronic and thermal Enthalpies= -572.254863
Sum of electronic and thermal Free Energies= -572.305041

C	-5.81443600	-2.82300500	-0.00144100
C	-4.42352600	-2.78942400	0.00091400
C	-3.76088400	-1.56624000	0.00187200
C	-4.48837000	-0.37731000	0.00046000
C	-5.88667900	-0.40808900	-0.00189600
C	-6.54161200	-1.63086900	-0.00283300
H	-6.33574900	-3.77575800	-0.00218900
H	-3.85448900	-3.71413900	0.00201100
H	-2.67683400	-1.51102800	0.00370600
H	-6.43707400	0.52543300	-0.00295500
H	-7.62734100	-1.65973000	-0.00465900
C	-3.59013700	3.06465600	0.00172600
C	-4.31787500	4.25343600	0.00044000
C	-2.19183000	3.09576500	0.00394400
C	-3.65551300	5.47677300	0.00135900
H	-5.40191300	4.19798500	-0.00127200
C	-1.53717500	4.31869600	0.00484300
H	-1.64121800	2.16237700	0.00492500
C	-2.26461300	5.51067100	0.00355900
H	-4.22475800	6.40136000	0.00035400
H	-0.45145200	4.34780200	0.00656000
H	-1.74351600	6.46354200	0.00428200
N	-3.71207300	0.81399100	0.00163100
N	-4.36623400	1.87315600	0.00062600

5. Complete Gaussian Reference

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