Supporting information

Phenylazopyridine as switch in photochemical reactions. A detailed computational description of the mechanism of its photoisomerization

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Parameters of the force field that determine the topology of the methanol molecule in the MD calculations run with the Gromacs 4.5 package.

id	at type	res nr	res name	at name	cg nr	charge	mass
1	CT	1	SOL	C1	1	0.1166	12.01000
2	OH	1	SOL	O2	1	-0.6497	16.00000
3	HO	1	SOL	H3	1	0.4215	1.00800
4	HC	1	SOL	H4	1	0.0372	1.00800
5	HC	1	SOL	H5	1	0.0372	1.00800
6	HC	1	SOL	H6	1	0.0372	1.00800

FLEXIBLE

bonds

i	j	funct	length	force_constant	length	force_constant
1	2	1	0.14100	133977.6	0.14100	133977.6
2	3	1	0.10100	181707.1	0.10100	181707.1
1	4	1	0.10980	142351.2	0.10980	142351.2
1	5	1	0.10980	142351.2	0.10980	142351.2
1	6	1	0.10980	142351.2	0.10980	142351.2

angles

i	j	k	funct	angle	force_constant	angle	force_constant
1	2	3	1	108.0	230.274	108.0	230.274
4	1	2	1	109.5	146.538	109.5	146.538
5	1	2	1	109.5	146.538	109.5	146.538
6	1	2	1	109.5	146.538	109.5	146.538
4	1	5	1	109.5	146.538	109.5	146.538
4	1	6	1	109.5	146.538	109.5	146.538
5	1	6	1	109.5	146.538	109.5	146.538

dihedrals

i	j	k	l	funct	angle	force_constant	m
4	1	2	3	1	10.5	43.9614	2
5	1	2	3	1	10.5	43.9614	2
6	1	2	3	1	10.5	43.9614	2

Figure S1. Active orbitals.

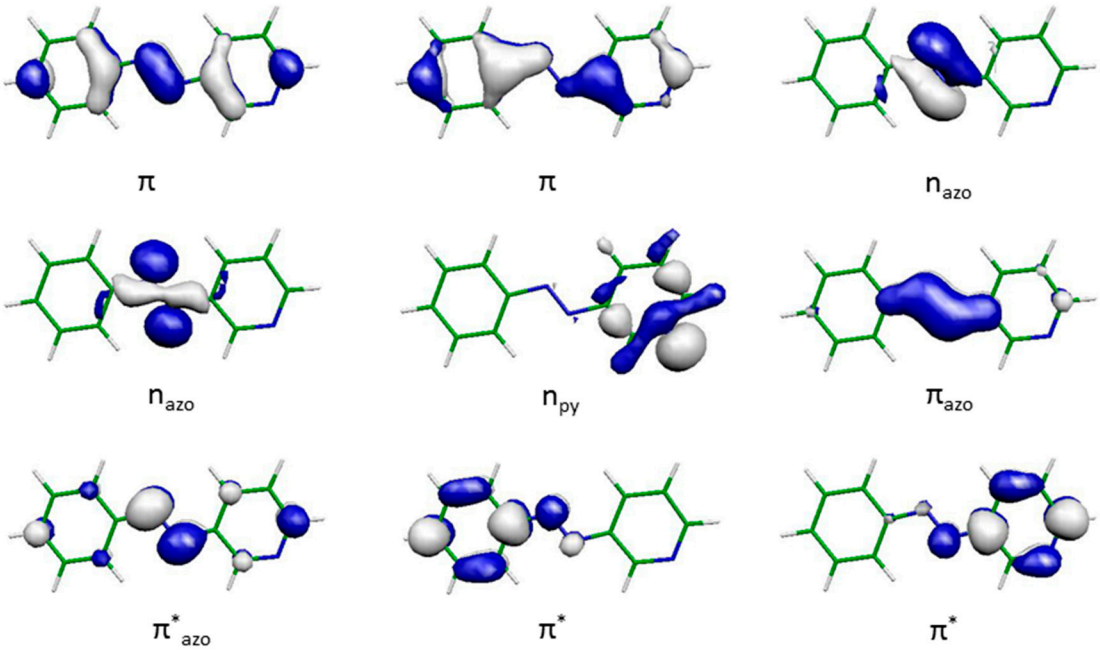

Figure S2. Test calculations using different basis sets for the relative energies of the first two singlet roots along the rotational path. Basis 1: 6-31G*; Basis 2: ANO-rcc-vdzp; Basis 3: ANO-rcc-vtzp.

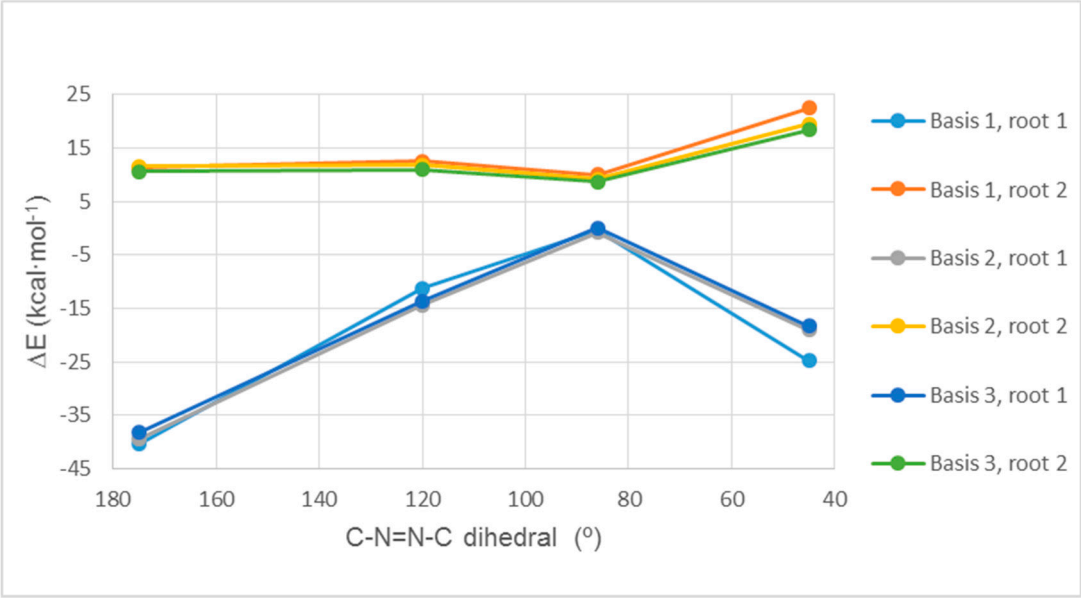

Figure S3. Distribution, in the geometries selected to reproduce the absorption spectra of 3-PAPy, of the values of the CNNC dihedral angle, the CNN angle and the N-N distance.

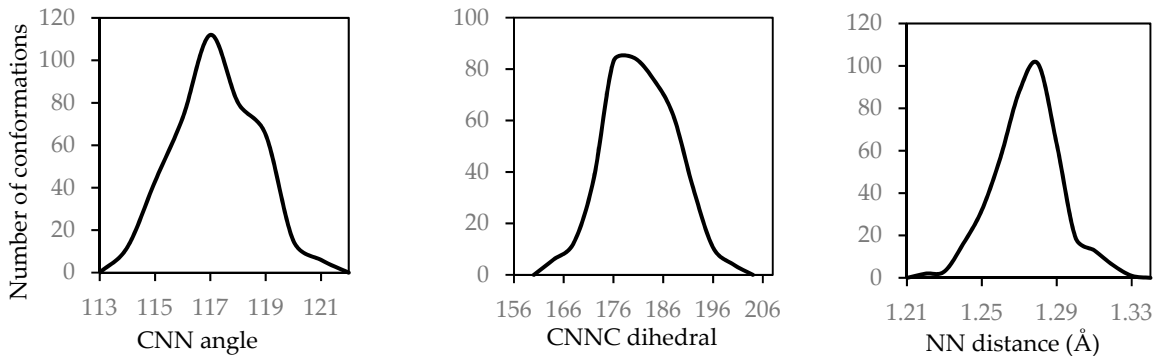

Figure S4. $^1(n\pi^*)$ optimized geometry at CASSCF level.

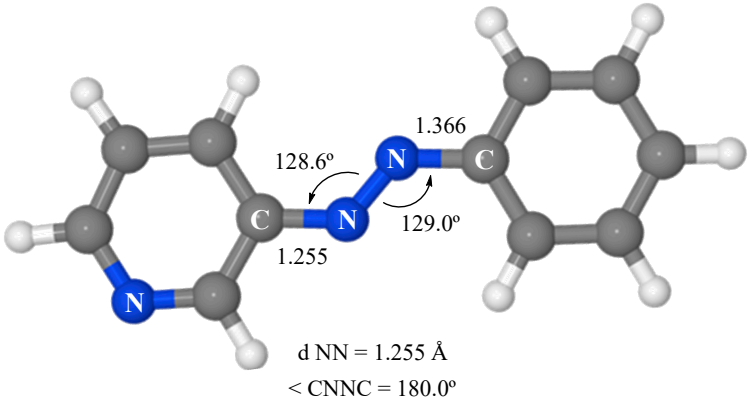

Table S1. MS-CASPT2 energies (in kcal·mol^{-1}) relative to the ground state minimum of the lowest states of 3-PAPy at the $n\pi^*$ state minima optimized at CASSCF level and at MS-CASPT2 level.

State	CASSCF optimization	Osc. strength	CASPT2 optimization	Osc. Strength
GS	16.3		42.4	
$^1(n\pi^*)$	**52.5**	**< 10^{-7}**	**48.4**	**0.91·10^{-3}**
$^1(n_{py}\pi^*)$	100.5	0.31·10^{-3}	-	-
$^1(\pi\pi^*)$	106.1	1.11	110.7	0.43·10^{-1}
$^1(n^2\pi^{*2})$	117.6	0.28·10-^{3}	62.0	0.73·10^{-3}

Figure S5. n⊚*/⊚⊚* conical intersection geometries located at MS-CASPT2 level at (a) rotated and (b) planar geometries.

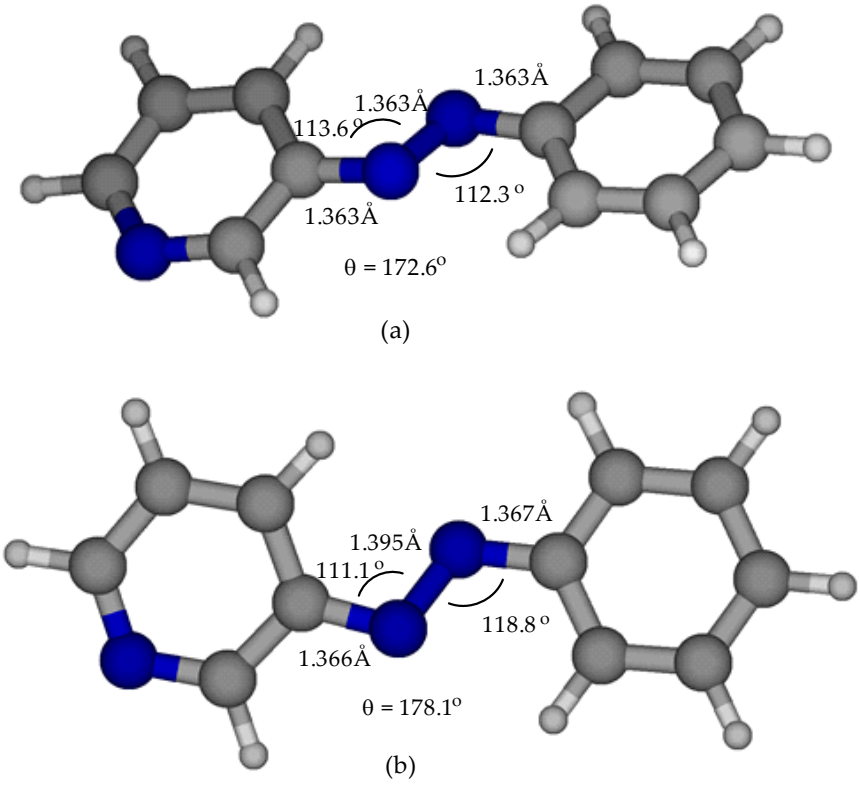

Figure S6. Energy profiles of the PES of the lowest states of PAPy along the main coordinate of the rotation mechanism path. Geometries optimized at B3LYP level for the ground state at fixed values of the CNNC dihedral angle. Geometries calculated at CASPT2(12,9) level.

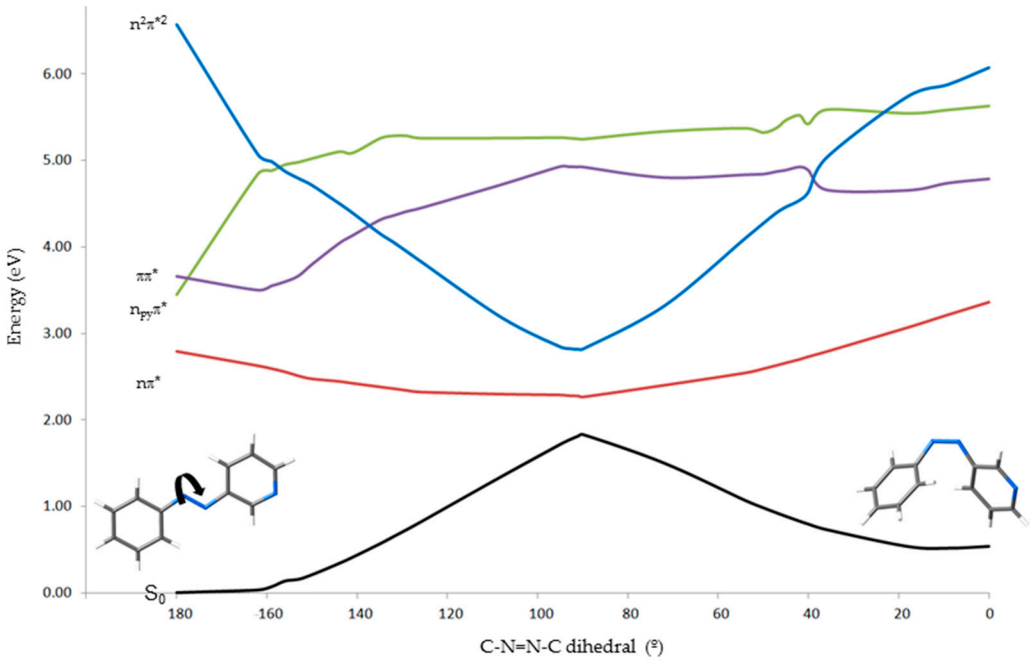

Figure S7. Energy profiles of the PES of the lowest states of PAPy along the main coordinate of the inversion mechanism path. Geometries optimized at B3LYP level for the ground state at fixed values of the NNC angle. Geometries calculated at CASPT2(12,9) level.