Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

PHYSICAL CHEMISTRY CHEMICAL PHYSICS

Electronic Supplementary Information

Conical Intersections and Intersystem Crossings Explain Product Formation in Photochemical Reactions of Aryl Azides

by

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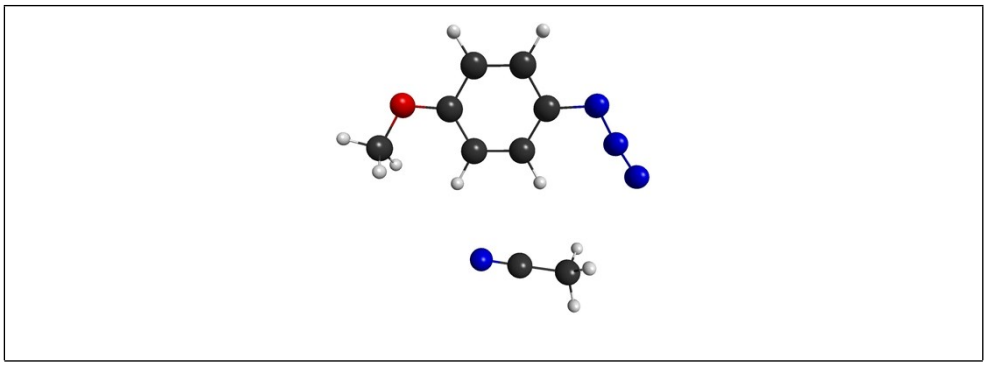
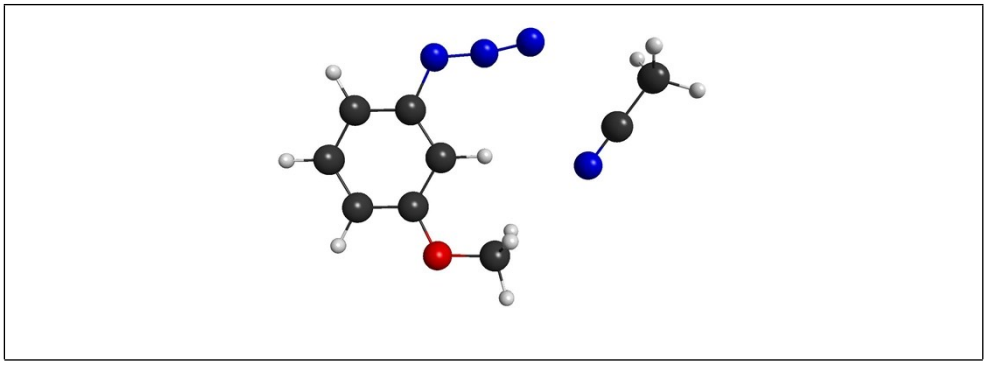
TableS1. Adiabatic excitation energies in eV of the singlet states of 4-methoxyphenyl azide (C_s, MS-CASPT2, IPEA=0.25) with explicit interaction of one molecule of solvent (acetonitrile).[a,b]



Transition	ΔE	*TDM*[c]	*Configuration*[d]
1A'→ 2A'	4.38	1.042 75	26% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$ 24% $\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1$ 15% $\pi_2(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 3A'	4.91	1.547 42	44% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 4A'	6.65	0.358 38	24% $\pi_3(\text{ring})^0\pi_3^*(\text{ring})^2$ 19% $n_\pi(\text{NN})^1\pi_3^*(\text{ring})^1$
1A'→ 1A"	3.67	0.074 34	79% $\pi_3(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 2A"	6.10	0.010 55	41% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$ 21% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 3A"	6.29	0.017 44	22% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$ 40% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 4A"	8.05	0.007 09	55% $\pi_\sigma^*(\text{NN})^1\pi_2(\text{ring})^1\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1$

[a]MP2/aug-cc-pDVZ optimized geometry (C_s symmetry). [b]CAS-SCF wavefunction including four roots in each symmetry block. IPEA=0.25, imaginary shift = 0.1. [c]Transition dipole moment (position operator) in atomic units. [d]MS-CASPT2 main electronic configurations of the excited states referred to the ground state configuration (see text). Only contributions with weight greater than 15% are included.

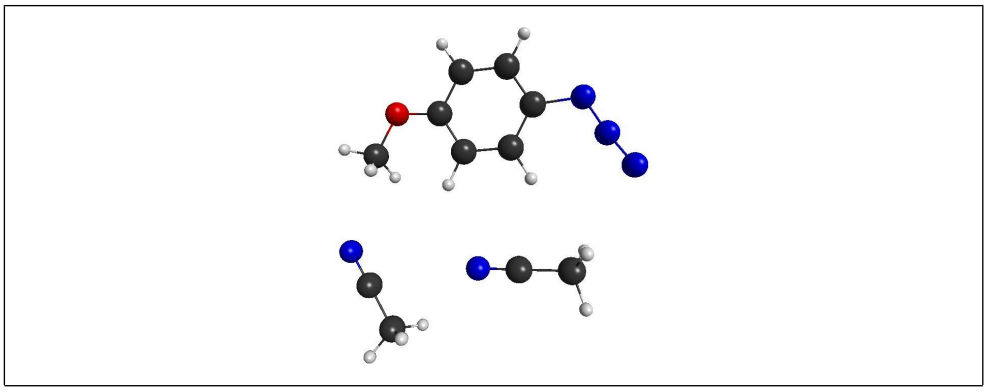
Table S2. Adiabatic excitation energies in eV of the singlet states of 3-methoxyphenyl azide (C_s, MS-CASPT2, IPEA=0.25) with explicit interaction of one molecule of solvent (acetonitrile).[a,b]



Transition	ΔE	*TDM*[c]	*Configuration*[d]
1A'→ 2A'	4.44	1.367 93	32% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 3A'	5.03	1. 430 08	35% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$ 24% $\pi_2(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 4A'	6.53	0.164 71	21% $n_\pi(\text{NN})^1\pi_3^*(\text{ring})^1$ 35% $\pi_3(\text{ring})^0\pi_3^*(\text{ring})^2$
1A'→ 1A"	3.77	0.068 87	77% $\pi_3(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 2A"	5.57	0.011 94	69% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 3A"	6.37	0.014 86	57% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 4A"	8.05	0.008 89	36% $\pi_\sigma^*(\text{NN})^1\pi_2(\text{ring})^1\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1$

[a]MP2/aug-cc-pDVZ optimized geometry (C_s symmetry). [b]CAS-SCF wavefunction including four roots in each symmetry block. IPEA=0.25, imaginary shift = 0.1. [c]Transition dipole moment (position operator) in atomic units. [d]MS-CASPT2 main electronic configurations of the excited states referred to the ground state configuration (see text). Only contributions with weight greater than 15% are included.

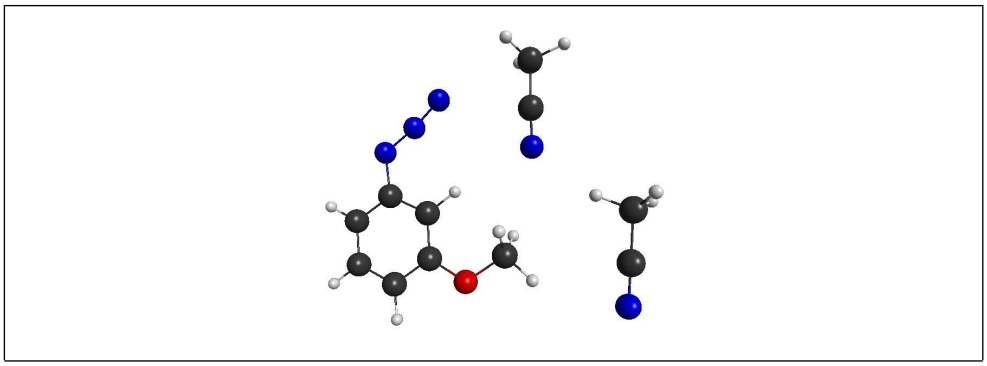
Table S3. Adiabatic excitation energies in eV of the singlet states of 4-methoxyphenyl azide (C_s, MS-CASPT2, IPEA=0.25) with explicit interaction of two molecules of solvent (acetonitrile).[a,b]



Transition	ΔE	*TDM*[c]	*Configuration*[d]
1A'→ 2A'	4.34	1.130 82	30% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$ 22% $\pi_3(\text{ring})^1\pi_2^*(\text{ring})$
1A'→ 3A'	4.86	1. 493 65	40% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 4A'	6.63	0.388 67	18% $n_\pi(\text{NN})^1\pi_3^*(\text{ring})^1$ 24% $\pi_3(\text{ring})^0\pi_3^*(\text{ring})^2$
1A'→ 1A"	3.62	0.073 81	79% $\pi_3(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 2A"	6.02	0.012 83	39% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$ 24% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 3A"	6.21	0.018 25	25% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$ 39% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 4A"	7.99	0.007 46	54% $\pi_\sigma^*(\text{NN})^1\pi_2(\text{ring})^1\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1$ 18% $\pi_\sigma^*(\text{NN})^1\pi_1(\text{ring})^1$

[a]MP2/aug-cc-pDVZ optimized geometry (C_s symmetry). [b]CAS-SCF wavefunction including four roots in each symmetry block. IPEA=0.25, imaginary shift = 0.1. [c]Transition dipole moment (position operator) in atomic units. [d]MS-CASPT2 main electronic configurations of the excited states referred to the ground state configuration (see text). Only contributions with weight greater than 15% are included.

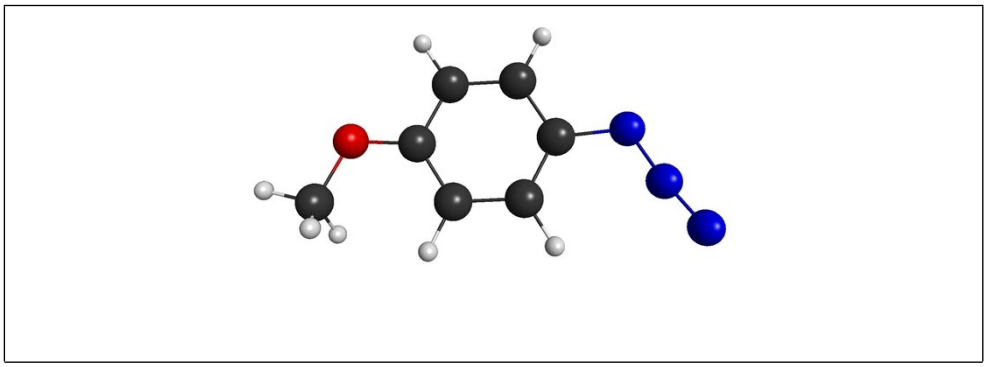
Table S4. Adiabatic excitation energies in eV of the singlet states of 3-methoxyphenyl azide (C_s, MS-CASPT2, IPEA=0.25) with explicit interaction of two molecules of solvent (acetonitrile).[a,b]



Transition	ΔE	*TDM*[c]	*Configuration*[d]
1A'→ 2A'	4.43	1.394 95	34% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 3A'	5.02	1. 372 61	33% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$ 23% $\pi_2(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 4A'	6.53	0.180 71	21% $n_\pi(\text{NN})^1\pi_3^*(\text{ring})^1$ 25% $\pi_3(\text{ring})^0\pi_3^*(\text{ring})^2$
1A'→ 1A"	3.74	0.068 96	77% $\pi_3(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 2A"	5.49	0.013 12	70% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 3A"	6.31	0.015 46	57% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 4A"	8.02	0.009 06	36% $\pi_\sigma^*(\text{NN})^1\pi_2(\text{ring})^1\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1$ 18% $\pi_\sigma^*(\text{NN})^1\pi_1(\text{ring})^1$

[a]MP2/aug-cc-pDVZ optimized geometry (C_s symmetry). [b]CAS-SCF wavefunction including four roots in each symmetry block. IPEA=0.25, imaginary shift = 0.1. [c]Transition dipole moment (position operator) in atomic units. [d]MS-CASPT2 main electronic configurations of the excited states referred to the ground state configuration (see text). Only contributions with weight greater than 15% are included.

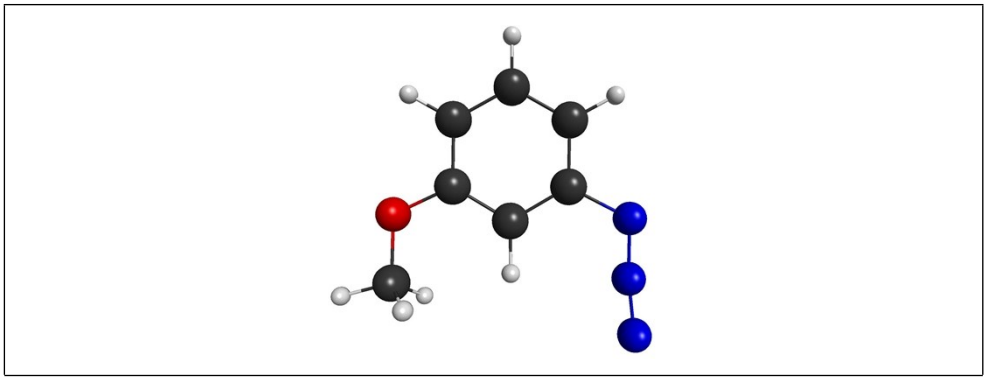
Table S5. Adiabatic excitation energies in eV of the singlet states of isolated 4-methoxyphenyl azide (C_s, MS-CASPT2, IPEA=0.0).[a,b]



Transition	ΔE	*TDM*[c]	*Configuration*[d]
1A'→ 2A'	3.92	1.039 42	26% $\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1$ 15% $\pi_2(\text{ring})^1\pi_3^*(\text{ring})^1$ 24% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 3A'	4.50	1.644 80	47% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 4A'	6.19	0.214 38	15% $n_\pi(\text{NN})^1\pi_3^*(\text{ring})^1$ 24% $\pi_3(\text{ring})^0\pi_3^*(\text{ring})^2$ 15% $\pi_3(\text{ring})^1\pi^*(\text{NNN})^1$
1A'→ 1A"	3.51	0.074 30	79% $\pi_3(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 2A"	5.83	0.010 50	33% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$ 26% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 3A"	6.12	0.012 74	26% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$ 32% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 4A"	7.65	0.007 89	56% $\pi_2(\text{ring})^1\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1\pi_\sigma^*(\text{NN})^1$

[a]C_s MP2/aug-cc-pDVZ optimized geometry [b]CAS-SCF wavefunction including four roots state average CAS-SCF wavefunctions (C_s symmetry). (IPEA=0), (Imaginary shift = 0.1). [c]Transition dipole moment (position operator). [d]MS-CASPT2 main electronic configurations of the excited states referred to the ground state configuration (see text). Only contributions with weight greater than 15% are included.

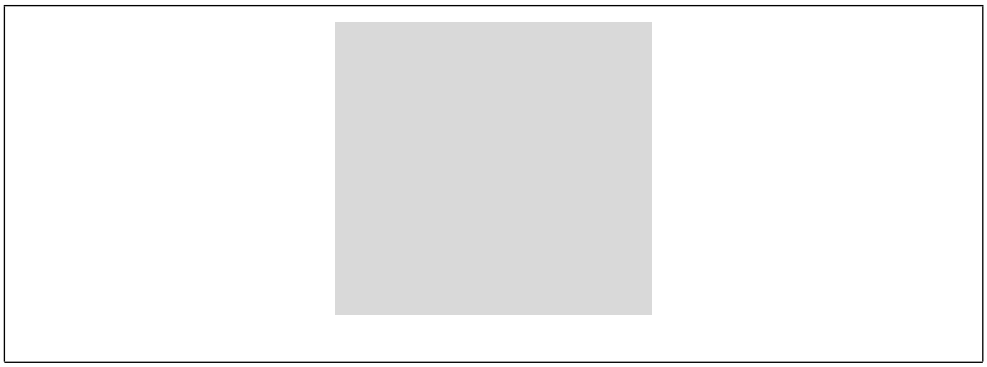
Table S6. Gas phase adiabatic excitation energies in eV of the singlet states of 3-methoxyphenyl azide (C_s, MS-CASPT2, IPEA=0.0).[a,b]



Transition	ΔE	*TDM*[c]	*Configuration*[d]
1A'→ 2A'	4.02	1.413 27	35% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 3A'	4.68	1.375 34	32% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$ 25% $\pi_2(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 4A'	6.18	0.028 48	25% $n_\pi(\text{NN})^1\pi_3^*(\text{ring})^1$ 20% $\pi_3(\text{ring})^0\pi_3^*(\text{ring})^2$
1A'→ 1A"	3.62	0.072 94	77% $\pi_3(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 2A"	5.41	0.016 35	68% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 3A"	6.09	0.012 89	56% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 4A"	7.59	0.009 13	15% $\pi_1(\text{ring})^1\pi_\sigma^*(\text{NN})^1$ 30% $\pi_2(\text{ring})^1\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1\pi_\sigma^*(\text{NN})^1$

[a]C_s MP2/aug-cc-pDVZ optimized geometry. [b]CAS-SCF wavefunction including four roots state average CAS-SCF wavefunctions (C_s symmetry). (IPEA=0.0), (Imaginary shift = 0.1). [c]Transition dipole moment (position operator) in atomic units. [d]MS-CASPT2 main electronic configurations of the excited states referred to the ground state configuration (see text). Only contributions with weight greater than 15% are included.

Table S7. Adiabatic excitation energies in eV of the singlet states of 4-methoxyphenyl azide (C_s, MS-CASPT2, IPEA=0.0) with explicit interaction of one molecule of solvent (acetonitrile).[a,b]



Transition	ΔE	*TDM*[c]	*Configuration*[d]
1A'→ 2A'	3.89	1.246 94	35% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$ 19% $\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1$
1A'→ 3A'	4.41	1.408 31	34% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$ 17% $\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1$
1A'→ 4A'	6.23	0.241 53	18% $n_\pi(\text{NN})^1\pi_3^*(\text{ring})^1$ 24% $\pi_3(\text{ring})^0\pi_3^*(\text{ring})^2$
1A'→ 1A"	3.34	0.072 14	79% $\pi_3(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 2A"	5.58	0.009 64	44% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$ 19% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 3A"	5.81	0.018 15	20% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$ 43% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 4A"	7.44	0.008 21	55% $\pi_\sigma^*(\text{NN})^1\pi_2(\text{ring})^1\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1$

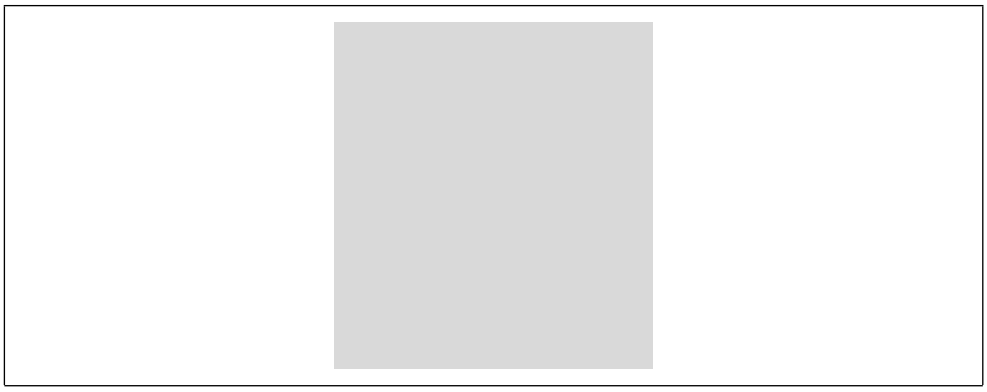
[a]C_s MP2/aug-cc-pVDZ optimized geometry. [b]CAS-SCF wavefunction including four roots in each symmetry block (IPEA=0), (Imaginary shift = 0.1). [b]Transition dipole moment (position operator). [d]MS-CASPT2 main electron configurations of the excited states referred to the ground state configuration (see text). Only contributions with weight greater than 15% are included.

Table S8. Adiabatic excitation energies in eV of the singlet states of 3-methoxyphenyl azide (C_s, MS-CASPT2, IPEA=0.0) with explicit interaction of one molecule of solvent (acetonitrile).[a,b]

Transition	ΔE	*TDM*[c]	*Configuration*[d]
1A'→ 2A'	3.97	1.508 85	39% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 3A'	4.57	1.290 94	28% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$ 27% $\pi_2(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 4A'	6.16	0.048 55	25% $n_\pi(\text{NN})^1\pi_3^*(\text{ring})^1$ 21% $\pi_3(\text{ring})^0\pi_3^*(\text{ring})^2$
1A'→ 1A"	3.52	0.068 63	77% $\pi_3(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 2A"	5.19	0.012 18	70% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 3A"	5.92	0.015 28	58% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 4A"	7.47	0.009 27	54% $\pi_\sigma^*(\text{NN})^1\pi_2(\text{ring})^1\pi_3(\text{ring})^1\pi_2^*(\text{ring})$

[a]C_s MP2/aug-cc-pVDZ optimized geometry. [b]CAS-SCF wavefunction including four roots in each symmetry block (IPEA=0), (Imaginary shift = 0.1). [b]Transition dipole moment (position operator). [d]MS-CASPT2 electronic configurations of the excited states referred to the ground state configuration (see text). Only contributions with weight greater than 15% are included.

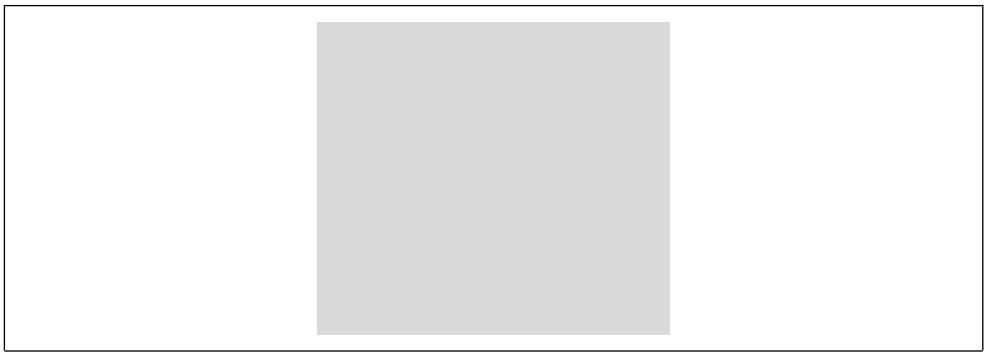
Table S9. Adiabatic excitation energies in eV of the singlet states of 4-methoxyphenyl azide (C_s, MS-CASPT2, IPEA=0.0) with explicit interaction of two molecules of solvent (acetonitrile).[a,b]



Transition	ΔE	*TDM*[c]	*Configuration*[d]
1A'→ 2A'	3.89	1.239 96	35% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$ 20% $\pi_3(\text{ring})^1\pi_2^*(\text{ring})$
1A'→ 3A'	4.42	1. 419 43	35% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 4A'	6.22	0.251 24	18% $n_\pi(\text{NN})^1\pi_3^*(\text{ring})^1$ 24% $\pi_3(\text{ring})^0\pi_3^*(\text{ring})^2$
1A'→ 1A"	3.39	0.073 95	79% $\pi_3(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 2A"	5.64	0.011 55	40% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$ 23% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 3A"	5.86	0.018 21	24% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$ 40% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 4A"	7.49	0.007 78	55% $\pi_\sigma^*(\text{NN})^1\pi_2(\text{ring})^1\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1$ 13% $\pi_\sigma^*(\text{NN})^1\pi_1(\text{ring})^1$

[a]MP2/aug-cc-pDVZ optimized geometry (C_s symmetry). [b]CAS-SCF wavefunction including four roots in each symmetry block. IPEA=0.0, imaginary shift = 0.1. [c]Transition dipole moment (position operator) in atomic units. [d]MS-CASPT2 main electronic configurations of the excited states referred to the ground state configuration (see text). Only contributions with weight greater than 15% are included.

Table S10. Adiabatic excitation energies in eV of the singlet states of 3-methoxyphenyl azide (C_s, MS-CASPT2, IPEA=0.0) with explicit interaction of two molecules of solvent (acetonitrile).[a,b]



Transition	ΔE	*TDM*[c]	*Configuration*[d]
1A'→ 2A'	3.97	1.508 85	39% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 3A'	4.56	1. 290 94	28% $\pi_3(\text{ring})^1\pi_3^*(\text{ring})^1$ 27% $\pi_2(\text{ring})^1\pi_3^*(\text{ring})^1$
1A'→ 4A'	6.26	0.048 55	21% $n_\pi(\text{NN})^1\pi_3^*(\text{ring})^1$ 25% $\pi_3(\text{ring})^0\pi_3^*(\text{ring})^2$
1A'→ 1A"	3.51	0.068 63	77% $\pi_3(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 2A"	5.18	0.012 18	70% $\pi_2(\text{ring})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 3A"	5.92	0.015 28	57% $n_\pi(\text{NN})^1\pi_\sigma^*(\text{NN})^1$
1A'→ 4A"	7.44	0.009 27	36% $\pi_\sigma^*(\text{NN})^1\pi_2(\text{ring})^1\pi_3(\text{ring})^1\pi_2^*(\text{ring})^1$ 17% $\pi_\sigma^*(\text{NN})^1\pi_1(\text{ring})^1$

[a]MP2/aug-cc-pDVZ optimized geometry (C_s symmetry). [b]CAS-SCF wavefunction including four roots in each symmetry block. IPEA=0.0, imaginary shift = 0.1. [c]Transition dipole moment (position operator) in atomic units. [d]MS-CASPT2 main electronic configurations of the excited states referred to the ground state configuration (see text). Only contributions with weight greater than 15% are included.

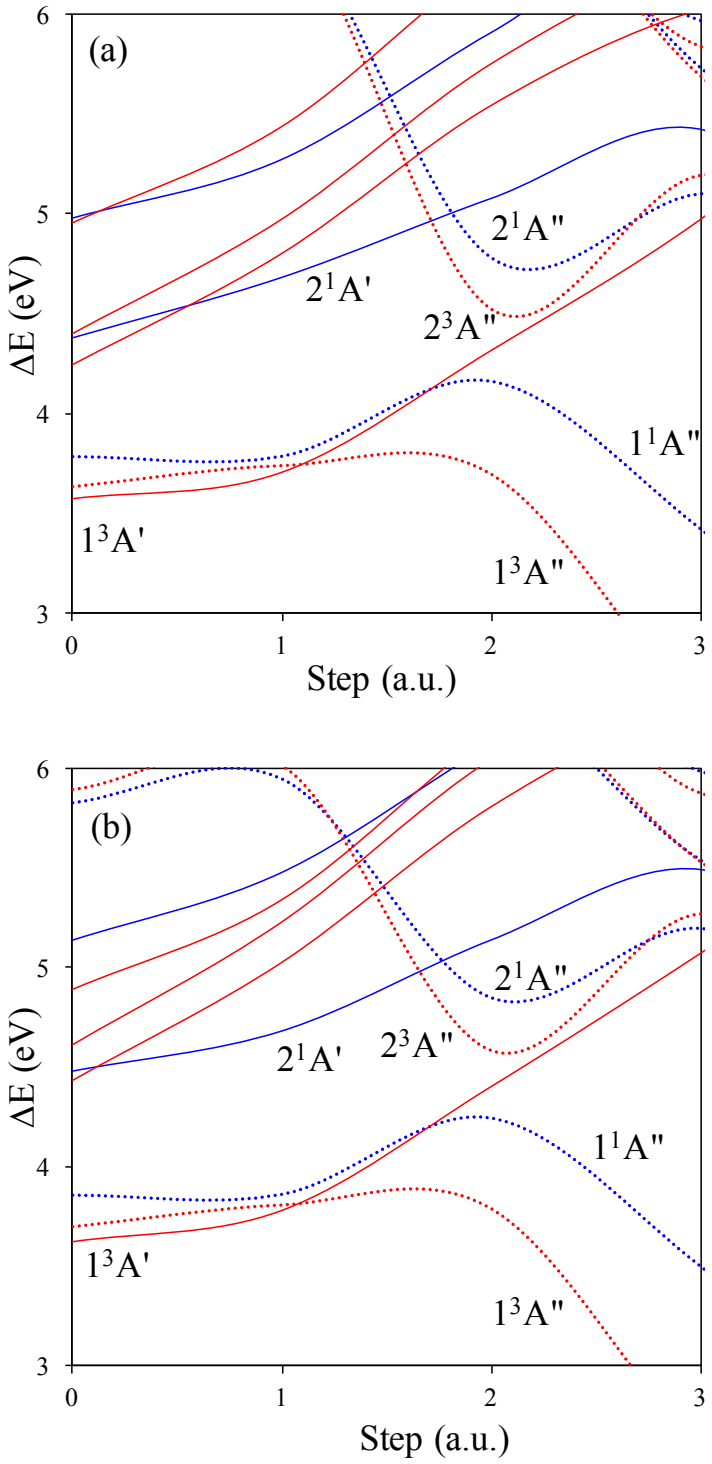
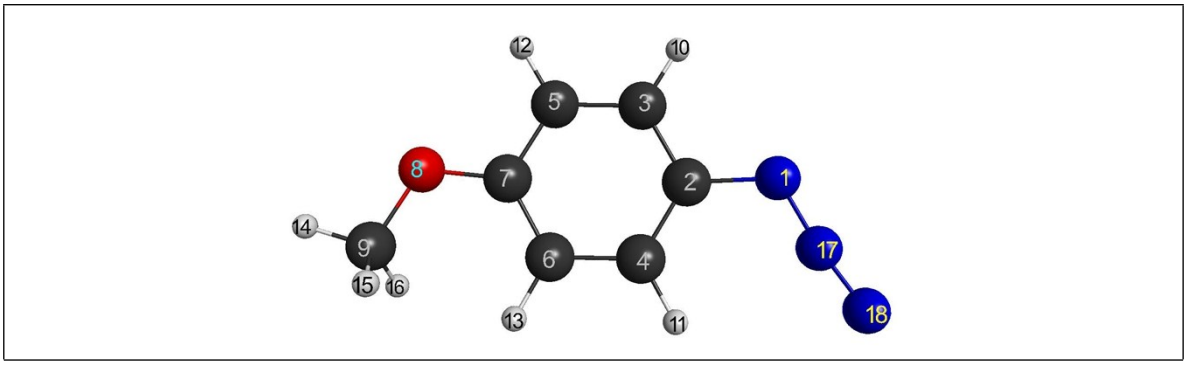


Fig. S1. Expanded view of the critical region of the potential energy surfaces (Fig. 3). MS-CASPT2/ANO-RCC[4*s*3*p*2*d*1*f*/3*s*2*p*1*d*] (C_s symmetry) potential energy curves of the ground and low-lying singlet and triplet excited states for dissociation into methoxyphenyl nitrene and N_2, (a) 4-methoxyphenyl azide and (b) 3-methoxyphenyl azide. SA-CASSCF reference wavefunction. Blue solid line: singlet A'; red solid line: triplet A'; blue dotted line: singlet A"; red dotted line: triplet A". Reference geometry: MP2/aug-cc-pVDZ.

Table S11. CAS-SCF internal coordinates of the conical intersections on the potential energy surfaces of 4-methoxyphenyl azide.[a]



Coordinate	4M1[c]	4CI0	4CI1	4CI2t	4CI2s	4CI3	4CI2b
	$1^1A'$	$3^1A'/2^1A''$	$2^1A'/2^1A''$	$2^3A'/1^3A''$	$2^1A'/1^1A''$	$1^1A''/1^1A'$	S_3/S_2
R2,1	1.421	1.348	1.303	1.334	1.400	1.422	1.308
R3,2	1.398	1.439	1.453	1.430	1.429	1.406	1.430
A3,2,1	115.451	115.475	114.149	114.630	114.917	110.852	115.986
R4,2	1.384	1.447	1.434	1.423	1.434	1.370	1.461
A4,2,1	125.422	126.224	128.090	127.263	124.030	129.916	127.357
Dh4,2,1,3	180.000	-180.000	180.000	180.000	-179.976	180.000	179.886
R5,3	1.379	1.409	1.359	1.371	1.434	1.381	1.412
A5,3,2	120.420	119.534	120.421	120.689	119.424	120.177	121.137
Dh5,3,2,4	0.000	0.000	-0.000	0.000	-0.005	0.001	1.263
R6,4	1.399	1.413	1.389	1.387	1.430	1.412	1.412
A6,4,2	120.581	121.153	120.356	120.470	119.215	120.460	120.635
Dh6,4,2,3	0.000	0.000	0.000	0.000	0.002	0.000	-0.680
R7,5	1.399	1.424	1.426	1.412	1.420	1.398	1.411
A7,5,4	60.498	59.665	59.408	59.594	59.295	60.871	60.000
Dh7,5,4,2	180.000	180.000	180.000	180.000	-179.999	180.000	-179.640
R8,7	1.351	1.350	1.345	1.344	1.349	1.360	2.432
A8,7,5	115.844	114.995	114.938	115.373	115.152	115.676	148.089
Dh8,7,5,6	180.000	-180.000	180.000	180.000	179.997	180.000	-0.363

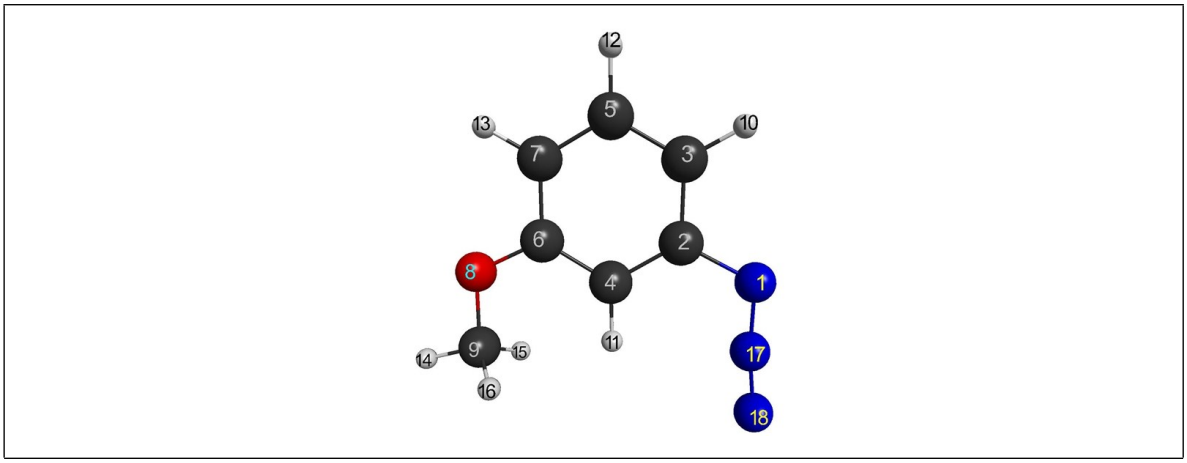
(continue)

Table S11. (continuation)

Coordinate	4M1[c]	4Cl0	4Cl1	4Cl2t	4Cl2s	4Cl3	4Cl2b
	$1^1A'$	$3^1A'/2^1A''$	$2^1A'/2^1A''$	$2^3A'/1^3A''$	$2^1A'/1^1A''$	$1^1A''/1^1A'$	S_3/S_2
R9,8	1.395	1.399	1.402	1.402	1.400	1.395	1.400
A9,8,7	119.693	119.755	119.759	119.970	120.373	119.128	91.751
Dh9,8,7,5	180.000	180.000	-180.000	180.000	-179.994	-180.000	-179.227
R10,3	1.072	1.071	1.073	1.073	1.071	1.075	1.072
A10,3,2	119.038	119.299	118.175	118.297	119.266	120.136	118.287
Dh10,3,2,5	180.000	-180.000	-180.000	180.000	179.998	180.000	179.406
R11,4	1.073	1.071	1.069	1.071	1.072	1.072	1.070
A11,4,2	121.007	120.153	119.733	119.700	121.302	121.328	119.838
Dh11,4,2,6	180.000	-180.000	180.000	180.000	179.997	180.000	-179.570
R12,5	1.072	1.073	1.074	1.073	1.071	1.074	1.073
A12,5,7	118.759	118.175	118.119	118.441	119.182	118.983	118.822
Dh12,5,7,3	180.000	180.000	180.000	180.000	-180.000	180.000	179.974
R13,6	1.070	1.071	1.072	1.072	1.070	1.072	1.072
A13,6,7	121.340	121.765	120.868	120.931	121.288	121.524	121.046
Dh13,6,7,4	180.000	180.000	-180.000	180.000	180.000	180.000	179.787
R14,9	1.078	1.080	1.080	1.080	1.080	1.081	1.080
A14,9,8	106.506	106.327	106.240	106.177	106.234	106.489	106.278
Dh14,9,8,7	180.000	-180.000	-180.000	180.000	179.997	-180.000	179.961
R15,9	1.085	1.086	1.085	1.085	1.085	1.087	1.086
A15,9,8	111.561	111.428	111.261	111.292	111.484	111.523	111.377
Dh15,9,8,14	-118.768	-118.674	-118.703	-118.662	-118.599	-118.773	-118.684
R16,9	1.085	1.086	1.085	1.085	1.085	1.087	1.086
A16,9,8	111.561	111.428	111.261	111.292	111.484	111.522	111.371
Dh16,9,8,14	118.768	118.674	118.703	118.662	118.599	118.773	118.663
R17,1	1.258	1.509	1.637	1.558	1.252	1.998	1.458
A17,1,2	114.361	111.380	106.380	110.314	115.946	105.628	113.902
Dh17,1,2,3	180.000	-179.998	180.000	180.000	179.993	179.999	-179.094
R18,17	1.115	1.130	1.165	1.171	1.121	1.093	1.179
A18,17,1	173.605	176.836	168.849	179.139	173.881	163.649	130.596
Dh18,17,1,2	180.000	-179.996	180.000	-179.998	179.954	-179.994	-82.293

[a]Numbering for coordinate definition given in the molecular geometry on top of the table. [b]R: internuclear distance in Å; A: valence bond in degrees; Dh: dihedral angle in degrees. [c]MP2/aug-cc-pVDZ S_0 minimum.

Table S12. CAS-SCF internal coordinates of the conical intersections on the potential energy surfaces of 3-methoxyphenyl azide.[a]



Coordinate[b]	3M1[c]	3CI0	3CI1	3CI2"	3CI2s	3CI3	3CI2b
	$1^1A'$	$2^1A'/2^1A''$	$2^1A'/2^1A'$	$2^3A''/1^3A''$	$2^1A'/1^1A''$	$1^1A''/1^1A'$	S_3/S_2
R2,1	1.433	1.314	1.300	1.333	1.400	1.416	1.307
R3,2	1.404	1.435	1.456	1.425	1.435	1.394	1.443
A3,2,1	116.262	118.233	113.525	114.105	114.825	111.194	116.135
R4,2	1.412	1.473	1.440	1.433	1.430	1.385	1.441
A4,2,1	122.145	124.022	127.544	126.442	124.068	128.192	126.488
Dh4,2,1,3	180.000	180.000	-180.000	180.000	180.000	180.000	-179.803
R5,3	1.407	1.390	1.368	1.383	1.430	1.391	1.399
A5,3,2	118.562	119.358	119.679	119.857	120.129	118.948	120.495
Dh5,3,2,4	0.000	0.000	-0.000	0.000	-0.000	-0.000	0.532
R6,4	1.409	1.413	1.374	1.372	1.436	1.402	1.413
A6,4,2	118.773	120.629	119.277	119.314	117.722	119.360	120.137
Dh6,4,2,3	0.000	0.000	0.000	0.000	0.000	-0.000	-0.242
R7,5	1.403	1.437	1.410	1.395	1.428	1.387	1.399
A7,5,4	60.296	60.165	59.244	59.341	59.717	60.833	60.527
Dh7,5,4,2	180.000	180.000	180.000	180.000	-180.000	-180.000	-179.856
R8,6	1.373	1.349	1.346	1.347	1.349	1.356	1.340
A8,6,4	123.868	122.961	124.177	124.563	123.167	123.070	123.032
Dh8,6,4,7	180.000	180.000	180.000	180.000	-180.000	180.000	-179.945

(continue)

Table S12. (continuation)

Coordinate[b]	3M1[c] $1^1A'$	3Cl0 $2^1A'/2^1A''$	3Cl1 $2^1A''/2^1A'$	3Cl2t $2^3A''/1^3A''$	3Cl2s $2^1A'/1^1A''$	3Cl3 $1^1A''/1^1A'$	3Cl2b S_3/S_2
R9,8	1.433	1.401	1.403	1.403	1.400	1.397	1.405
A9,8,6	116.293	120.509	119.858	119.683	120.440	120.307	120.766
Dh9,8,6,4	0.000	0.000	0.000	0.000	-0.000	0.002	0.572
R10,3	1.092	1.072	1.073	1.073	1.072	1.075	1.072
A10,3,2	119.564	119.046	118.150	118.431	118.607	120.501	118.156
Dh10,3,2,5	180.000	180.000	-180.000	180.000	180.000	-180.000	179.815
R11,4	1.092	1.069	1.067	1.068	1.069	1.069	1.068
A11,4,2	119.747	118.561	118.948	118.880	121.046	120.389	119.073
Dh11,4,2,6	180.000	180.000	180.000	180.000	180.000	-180.000	-179.717
R12,5	1.094	1.074	1.074	1.074	1.072	1.075	1.074
A12,5,7	119.426	118.352	119.296	119.632	120.507	119.662	119.440
Dh12,5,7,3	180.000	180.000	-180.000	180.000	180.000	-180.000	179.827
R13,7	1.093	1.071	1.072	1.073	1.072	2.127	1.072
A13,7,5	121.602	121.070	121.528	121.487	121.568	26.085	119.062
Dh13,7,5,6	180.000	180.000	180.000	180.000	-180.000	-180.000	179.854
R14,9	1.096	1.080	1.080	1.080	1.080	1.081	1.080
A14,9,8	105.527	106.116	106.162	106.167	106.223	106.305	105.951
Dh14,9,8,6	180.000	180.000	-180.000	180.000	-180.000	179.999	179.524
R15,9	1.103	1.086	1.085	1.084	1.085	1.086	1.085
A15,9,8	110.968	111.491	111.278	111.435	111.487	111.617	111.284
Dh15,9,8,14	118.760	118.526	118.707	118.886	118.560	118.570	118.544
R16,9	1.103	1.086	1.085	1.084	1.085	1.086	1.084
A16,9,8	110.968	111.491	111.278	111.435	111.487	111.617	111.305
Dh16,9,8,14	-118.760	-118.526	-118.707	-118.886	-118.559	-118.570	-118.602
R17,1	1.249	1.396	1.624	1.559	1.250	1.993	1.447
A17,1,2	116.036	113.074	107.177	110.576	115.913	106.569	113.096
Dh17,1,2,3	180.000	180.000	180.000	180.000	-180.000	-180.000	-179.050
R18,17	1.166	1.159	1.164	1.171	1.122	1.093	1.179
A18,17,1	173.061	156.926	169.395	179.116	174.378	163.046	133.842
Dh18,17,1,2	180.000	180.000	180.000	180.000	179.993	180.000	-91.215

[a]Numbering for coordinate definition given in the molecular geometry on top of the table. [b]R: internuclear distance in Å; A: valence bond in degrees; Dh: dihedral angle in degrees. [c]MP2/aug-cc-pVDZ S_0 minimum.

Table S13. CAS-SCF internal coordinates of the minimum energy intersystem crossings on the potential energy surfaces of 4-methoxyphenyl azide.[a]

Coordinate[b]	**4ISC0**	**4ISC1**	**4ISC2**	**4ISC3**
	$3^1A'/2^3A''$	**$2^1A'/2^3A''$**	**$1^1A'/1^3A''$**	**$2^1A'/1^3A''$**
R2,1	1.331	1.300	1.401	1.406
R3,2	1.439	1.452	1.409	1.435
A3,2,1	116.612	114.500	112.692	114.361
R4,2	1.449	1.433	1.387	1.427
A4,2,1	125.702	127.847	129.060	123.979
Dh4,2,1,3	180.000	180.000	180.000	180.000
R5,3	1.395	1.358	1.379	1.442
A5,3,2	119.500	120.594	120.738	119.039
Dh5,3,2,4	0.000	0.000	0.000	0.000
R6,4	1.406	1.391	1.402	1.436
A6,4,2	121.504	120.126	120.887	119.092
Dh6,4,2,3	0.000	0.000	0.000	0.000
R7,5	1.425	1.422	1.399	1.415
A7,5,4	59.801	59.622	60.717	59.331
Dh7,5,4,2	180.000	180.000	180.000	180.000
R8,7	1.346	1.343	1.355	1.343
A8,7,5	114.992	115.196	115.941	115.516
Dh8,7,5,6	180.000	180.000	180.000	180.000

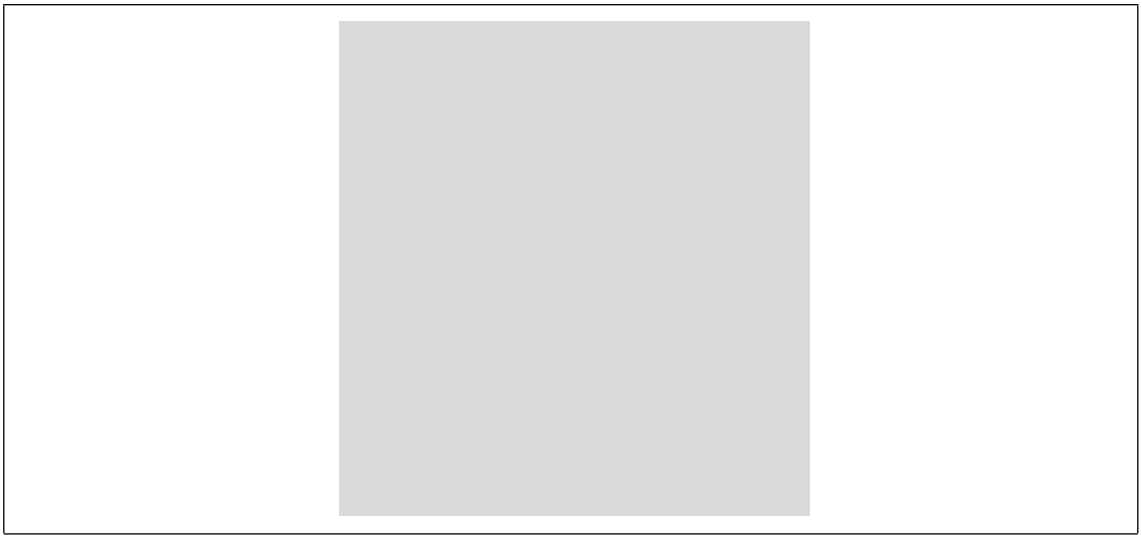
(continue)

Table S13. (continuation)

Coordinate	4ISC0	4ISC1	4ISC2	4ISC3
	$3^1A'/2^3A''$	$2^1A'/2^3A''$	$1^1A'/1^3A''$	$2^1A'/1^3A''$
R9,8	1.396	1.398	1.393	1.397
A9,8,7	119.797	119.916	119.437	120.966
Dh9,8,7,5	180.000	180.000	180.000	180.000
R10,3	1.069	1.071	1.073	1.068
A10,3,2	119.273	118.117	119.382	119.285
Dh10,3,2,5	180.000	180.000	180.000	180.000
R11,4	1.069	1.066	1.071	1.070
A11,4,2	119.784	119.910	120.989	121.529
Dh11,4,2,6	180.000	180.000	180.000	180.000
R12,5	1.071	1.072	1.072	1.069
A12,5,7	117.807	118.217	118.853	119.210
Dh12,5,7,3	180.000	180.000	180.000	180.000
R13,6	1.069	1.070	1.070	1.067
A13,6,7	121.761	120.640	121.312	121.311
Dh13,6,7,4	180.000	180.000	180.000	180.000
R14,9	1.078	1.078	1.079	1.078
A14,9,8	106.462	106.376	106.591	106.276
Dh14,9,8,7	180.000	180.000	180.000	180.000
R15,9	1.084	1.084	1.085	1.083
A15,9,8	111.454	111.359	111.617	111.572
Dh15,9,8,14	-118.765	-118.766	-118.795	-118.599
R16,9	1.084	1.084	1.085	1.083
A16,9,8	111.454	111.359	111.617	111.572
Dh16,9,8,14	118.765	118.766	118.795	118.599
R17,1	1.477	1.594	1.724	1.245
A17,1,2	111.943	106.692	107.323	115.657
Dh17,1,2,3	180.000	180.000	180.000	180.000
R18,17	1.137	1.160	1.095	1.103
A18,17,1	176.291	171.540	155.749	175.600
Dh18,17,1,2	180.000	180.000	180.000	180.000

[a]Numbering for coordinate definition given in the molecular geometry. [b]R: internuclear distance in Å; A: valence bond in degrees; Dh: dihedral angle in degrees.

Table S14. CAS-SCF internal coordinates of the minimum energy intersystem crossings on the potential energy surfaces of 3-methoxyphenyl azide.[a]



Coordinate[b]	**3M1**	**3ISC0**	**3ISC1**	**3ISC2**	**3ISC3**
	1^1A'	**3^1A'/2^3A"**	**2^1A'/2^3A"**	**1^1A'/1^3A"**	**2^1A'/1^3A"**
R2,1	1.420	1.312	1.296	1.397	1.409
R3,2	1.386	1.439	1.458	1.399	1.430
A3,2,1	115.516	118.343	113.866	112.636	114.757
R4,2	1.399	1.467	1.437	1.400	1.435
A4,2,1	123.979	123.765	127.327	127.706	123.936
Dh4,2,1,3	180.000	180.000	180.000	180.000	180.000
R5,3	1.392	1.384	1.366	1.389	1.441
A5,3,2	119.294	119.113	119.754	119.535	120.563
Dh5,3,2,4	0.000	0.000	0.000	0.000	0.000
R6,4	1.389	1.407	1.378	1.392	1.446
A6,4,2	119.504	120.733	119.205	119.823	117.290
Dh6,4,2,3	0.000	0.000	0.000	0.000	0.000
R7,5	1.384	1.434	1.409	1.387	1.436
A7,5,4	60.354	60.101	59.348	60.581	59.603
Dh7,5,4,2	180.000	180.000	180.000	180.000	180.000
R8,6	1.350	1.345	1.342	1.352	1.342
A8,6,4	123.907	123.152	123.856	123.519	122.730
Dh8,6,4,7	180.000	180.000	180.000	180.000	180.000

(continue)

Table S14. (continuation)

Coordinate	**3M1**	**3ISC0**	**3ISC1**	**3ISC2**	**3ISC3**
	$1^1A'$	**$3^1A'/2^3A''$**	**$2^1A'/2^3A''$**	**$1^1A'/1^3A''$**	**$2^1A'/1^3A''$**
R9,8	1.395	1.398	1.400	1.393	1.398
A9,8,6	120.202	120.630	120.194	120.328	121.004
Dh9,8,6,4	0.000	0.000	0.000	0.000	0.000
R10,3	1.071	1.070	1.070	1.072	1.070
A10,3,2	119.410	119.158	118.100	119.752	118.434
Dh10,3,2,5	180.000	180.000	180.000	180.000	180.000
R11,4	1.070	1.067	1.064	1.068	1.066
A11,4,2	120.168	118.571	119.104	120.130	121.542
Dh11,4,2,6	180.000	180.000	180.000	180.000	180.000
R12,5	1.072	1.072	1.072	1.073	1.068
A12,5,7	119.582	118.218	119.329	119.574	120.891
Dh12,5,7,3	180.000	180.000	180.000	180.000	180.000
R13,7	1.072	1.069	1.070	1.071	1.069
A13,7,5	121.515	121.025	121.508	121.649	121.562
Dh13,7,5,6	180.000	180.000	180.000	180.000	180.000
R14,9	1.078	1.078	1.078	1.078	1.078
A14,9,8	106.423	106.275	106.246	106.470	106.273
Dh14,9,8,7	180.000	180.000	180.000	180.000	180.000
R15,9	1.084	1.084	1.083	1.085	1.083
A15,9,8	111.582	111.557	111.370	111.665	111.553
Dh15,9,8,14	118.691	118.605	118.748	118.663	118.567
R16,9	1.084	1.084	1.083	1.085	1.083
A16,9,8	111.582	111.557	111.370	111.665	111.553
Dh16,9,8,14	-118.691	-118.605	-118.748	-118.663	-118.567
R17,1	1.258	1.400	1.577	1.731	1.241
A17,1,2	114.670	113.251	107.712	107.813	115.477
Dh17,1,2,3	180.000	180.000	180.000	180.000	180.000
R18,17	1.115	1.152	1.158	1.095	1.103
A18,17,1	173.438	159.338	172.747	156.050	175.843
Dh18,17,1,2	180.000	180.000	180.000	180.000	180.000

[a]Numbering for coordinate definition given in the molecular geometry. [b]R: internuclear distance in Å; A: valence bond in degrees; Dh: dihedral angle in degrees.

Table S15. Relative energies (eV) of the critical points (conical intersections and intersystem crossings) in the photochemistry of 3- and 4-methoxyphenyl azide (C_s, MS-CASPT2 IPEA=0.25 and IPEA=0.0 a.u).[a]

Geometry	ΔE^b	ΔE^c	Geometry	ΔE^b	ΔE^c	*Assign.*
3ISC0	5.33	4.96	4ISC0	5.29	4.93	$3^1A'/2^3A''$
3ISC1	4.65	4.37	4ISC1	4.60	4.29	$2^1A'/2^3A''$
3ISC2	1.99	1.87	4ISC2	1.97	1.83	$1^1A'/1^3A''$
3ISC3	4.50	4.16	4ISC3	4.37	4.04	$2^1A'/1^3A''$
3CI0	5.22	4.86	4CI0	5.44	5.09	$3^1A'/2^1A''$
3CI1	4.80	4.51	4CI1	4.74	4.41	$2^1A'/2^1A''$
3CI2t	4.20	3.93	4CI2t	4.11	3.83	$2^3A''/1^3A''$
3CI2s	4.47	3.97	4CI2s	4.21	3.85	$2^1A'/1^1A''$
3CI3	2.23	2.08	4CI3	2.22	2.06	$1^1A'/1^1A''$
3CI2b	4.25	3.95	4CI2b	4.43	4.04	S_3/S_2

[a]MS-CASPT2/ANO-RCC ANO-RCC[4*s*3*p*2*d*1*f*/3*s*2*p*1*d*]; optimized geometries: SA-CASSCF ANO-RCC[3*s*2*p*1*d*/2*s*1*p*]. [b]IPEA=0.25 a. u. [c]IPEA=0.0 a.u. Reference geometry: Ground state of the respective azide optimized at the MP2/aug-cc-pVDZ level.