

Matrix isolation and computational study of the photochemistry of *p*-azidoaniline

Elena A. Pritchina, Nina P. Gritsan, Thomas Bally

SUPPORTING INFORMATION, PART 2 (TABLES)

Table S1. Vertical excitation energies of triplet *p*-aminophenylnitrene calculated using CASPT2 method (symmetry C_s).^a

state	ΔE_{CASSCF} , eV	ΔE_{CASPT2} , eV	ref. weight	λ , nm	f	Major configurations
$1^3A''$	0.0	0.0	0.78			82% of ground configuration
$1^3A'$	3.05	2.89	0.76	429	1.3×10^{-3}	41%: $9a'' \rightarrow 19a'$ 31%: $19a' \rightarrow 11a''$
$2^3A''$	3.27	2.95	0.77	420	1.5×10^{-2}	49%: $18a' \rightarrow 19a'$ 28%: $19a' \rightarrow 20a'$
$2^3A'$	5.45	3.68	0.73	337	4.6×10^{-2}	32%: $9a'' \rightarrow 19a'$ 33%: $19a' \rightarrow 11a''$
$3^3A'$	3.89	3.96	0.76	313	2.6×10^{-10}	79%: $18a' \rightarrow 10a''$
$4^3A'$	4.36	4.15	0.76	298	1.4×10^{-2}	81%: $16a' \rightarrow 10a''$
$3^3A''$	4.62	4.45	0.77	279	3.5×10^{-3}	63%: $9a'' \rightarrow 11a''$
$4^3A''$	6.52	4.60	0.74	269	3.2×10^{-1}	26%: $18a' \rightarrow 19a'$ 30%: $19a' \rightarrow 20a'$
$5^3A''$	5.23	4.61	0.77	269	6.1×10^{-3}	39%: $9a'' \rightarrow 11a''$ 24%: $15a' \rightarrow 19a'$
$6^3A''$	4.92	4.65	0.77	267	1.5×10^{-5}	60%: $9a'' \rightarrow 10a''$ 13%: $18a' \rightarrow 19a'$ + $9a'' \rightarrow 10a''$
$7^3A''$	5.26	4.84	0.76	256	1.7×10^{-3}	77%: $16a' \rightarrow 19a'$
$5^3A'$	5.69	5.65	0.76	219	1.4×10^{-5}	67%: $19a' \rightarrow 10a''$ + $9a'' \rightarrow 11a''$

^a based on a CASSCF(12,12)/ANO-S wavefunction at the CASSCF(8,8)/6-31G(d) geometry; A' states were calculated with a level shift of 0.10 h, A'' states - with a level shift of 0.20 h.

Table S2. Dependence of energy and reference weight of CASPT2 states on the level shift for triplet *p*-aminophenylnitrene^a (C_s -symmetry).

CASPT2 states	1 ¹ A''	2 ¹ A''	3 ¹ A''	4 ¹ A''	5 ¹ A''	6 ¹ A''
level shift = 0.00 h						
E _{CASPT2} , H	-340.604311	-340.504202	-340.441194	-340.436084	-340.769466	-340.433844
ΔE _{CASPT2} , eV	0.000	2.724	4.439	4.578		4.639
Ref. Weight	0.749	0.446	0.619	0.347	0.001	0.741
level shift = 0.05 h						
E _{CASPT2} , H	-340.603963	-340.497846	-340.445576	-340.450847	-340.437480	-340.433462
ΔE _{CASPT2} , eV	0.000	2.888	4.309	4.167	4.530	4.640
Ref. Weight	0.757	0.735	0.701	0.509	0.728	0.750
level shift = 0.10 h						
E _{CASPT2} , H	-340.602988	-340.495686	-340.440384	-340.472190	-340.434696	-340.432371
ΔE _{CASPT2} , eV	0.000	2.920	4.425	3.559	4.580	4.643
Ref. Weight	0.764	0.752	0.753	0.586	0.750	0.758
level shift = 0.15 h						
E _{CASPT2} , H	-340.601477	-340.494080	-340.440179	-340.437994	-340.432406	-340.430714
ΔE _{CASPT2} , eV	0.000	2.922	4.389	4.449	4.601	4.647
Ref. Weight	0.771	0.760	0.755	0.712	0.760	0.755
level shift = 0.20 h						
E _{CASPT2} , H	-340.599503	-340.491066	-340.435909	-340.430405	-340.429910	-340.428572
ΔE _{CASPT2} , eV	0.000	2.951	4.452	4.601	4.615	4.651
Ref. Weight	0.778	0.771	0.770	0.736	0.769	0.773
level shift = 0.00 h						
CASPT2 states	7 ¹ A''	1 ¹ A'	2 ¹ A'	3 ¹ A'	4 ¹ A'	5 ¹ A'
level shift = 0.00 h						
E _{CASPT2} , H	-340.424738	-340.498338	-340.470241	-340.459211	-340.452022	-340.396714
ΔE _{CASPT2} , eV	4.885	2.884	3.648	3.948	4.144	5.649
Ref. Weight	0.568	0.437	0.659	0.654	0.737	0.743
level shift = 0.05 h						
E _{CASPT2} , H	-340.492415	-340.498154	-340.493620	-340.458554	-340.451493	-340.396499
ΔE _{CASPT2} , eV	3.035	2.879	3.003	3.957	4.149	5.645
Ref. Weight	0.392	0.746	0.534	0.755	0.751	0.750
level shift = 0.10 h						
E _{CASPT2} , H	-340.541135	-340.496880	-340.467712	-340.457530	-340.450325	-340.395271
ΔE _{CASPT2} , eV	1.683	2.887	3.681	3.958	4.154	5.652
Ref. Weight	0.393	0.757	0.728	0.763	0.760	0.760
level shift = 0.15 h						
E _{CASPT2} , H	-340.425987	-340.495693	-340.464710	-340.455969	-340.448651	-340.393637
ΔE _{CASPT2} , eV	4.775	2.895	3.722	3.960	4.159	5.656
Ref. Weight	0.746	0.765	0.742	0.771	0.768	0.768
level shift = 0.20 h						
E _{CASPT2} , H	-340.421655	-340.492858	-340.461669	-340.453944	-340.446532	-340.391531
ΔE _{CASPT2} , eV	4.840	2.902	3.751	3.961	4.163	5.659
Ref. Weight	0.761	0.773	0.751	0.778	0.775	0.775

^aThe results with level shift 0.20 h and 0.10 h for A'' and A' states are listed in Table S1 of the supporting information, respectively.

Table S3. Dependence of energy and reference weight of CASPT2 states on the level shift for triplet *p*-aminophenylnitrene^a (C_{2v} -symmetry).

CASPT2 states	1^3A_2	2^3A_2	3^3A_2	4^3A_2	5^3A_2
level shift = 0.00 h					
$E_{\text{CASPT2}}, \text{H}$	-340.601508	-340.488557	-340.438401	-340.439107	-340.425794
$\Delta E_{\text{CASPT2}}, \text{eV}$	0.000	3.074	4.438	4.419	4.4781
Ref. Weight	0.749	0.468	0.499	0.722	0.160
level shift = 0.05 h					
$E_{\text{CASPT2}}, \text{H}$	-340.601158	-340.496922	-340.443155	-340.510687	-340.693264
$\Delta E_{\text{CASPT2}}, \text{eV}$	0.000	2.836	4.300	2.462	
Ref. Weight	0.757	0.732	0.584	0.363	0.140
level shift = 0.10 h					
$E_{\text{CASPT2}}, \text{H}$	-340.600179	-340.494251	-340.536053	-340.437865	-340.444394
$\Delta E_{\text{CASPT2}}, \text{eV}$	0.000	2.882	1.745	4.417	4.239
Ref. Weight	0.765	0.754	0.446	0.754	0.643
level shift = 0.15 h					
$E_{\text{CASPT2}}, \text{H}$	-340.598662	-340.492112	-340.444793	-340.435890	-340.424790
$\Delta E_{\text{CASPT2}}, \text{eV}$	0.000	2.899	4.187	4.429	4.731
Ref. Weight	0.772	0.764	0.704	0.763	0.743
level shift = 0.20 h					
$E_{\text{CASPT2}}, \text{H}$	-340.596683	-340.489715	-340.434337	-340.433508	-340.418413
$\Delta E_{\text{CASPT2}}, \text{eV}$	0.000	2.911	4.418	4.440	4.851
Ref. Weight	0.779	0.772	0.736	0.771	0.764
CASPT2 states	1^3B_1	2^3B_1	3^3B_1	4^3B_1	5^3B_1
level shift = 0.00 h					
$E_{\text{CASPT2}}, \text{H}$	-340.498726	-340.467576	-340.448562	-340.418487	-340.401337
$\Delta E_{\text{CASPT2}}, \text{eV}$	2.797	3.645	4.162	4.980	5.447
Ref. Weight	0.737	0.682	0.740	0.704	0.348
level shift = 0.05 h					
$E_{\text{CASPT2}}, \text{H}$	-340.498309	-340.466572	-340.448113	-340.419420	-340.410328
$\Delta E_{\text{CASPT2}}, \text{eV}$	2.799	3.662	4.150	4.945	5.193
Ref. Weight	0.747	0.723	0.751	0.716	0.673
level shift = 0.10 h					
$E_{\text{CASPT2}}, \text{H}$	-340.497135	-340.465083	-340.447001	-340.418085	-340.403779
$\Delta E_{\text{CASPT2}}, \text{eV}$	2.804	3.676	4.168	4.955	5.344
Ref. Weight	0.756	0.735	0.759	0.737	0.730
level shift = 0.15 h					
$E_{\text{CASPT2}}, \text{H}$	-340.495401	-340.462821	-340.445355	-340.416231	-340.399988
$\Delta E_{\text{CASPT2}}, \text{eV}$	2.810	3.696	4.172	4.963	5.405
Ref. Weight	0.764	0.745	0.767	0.747	0.748

^aThe results with level shift 0.20 h and 0.10 h for A_2 and B_1 states are listed in Table 1 of the manuscript, respectively.

Table S4. Dependence of energy and reference weight of CASPT2 states on the level shift for *cis-p*-aminophenylnitroso oxide^a (geometry CASSCF(12,12)/6-31G(d))

CASPT2 states	1 ¹ A'	2 ¹ A'	3 ¹ A'	4 ¹ A'	5 ¹ A'	6 ¹ A'
level shift = 0.00 h						
E _{CASPT2} , H	-490.619194	-490.511776	-490.480913	-490.475284	-490.443425	-490.432613
ΔE _{CASPT2} , eV	0.000	2.923	3.763	3.330	4.783	5.077
Ref. Weight	0.695	0.659	0.573	0.650	0.547	0.391
level shift = 0.05 h						
E _{CASPT2} , H	-490.618753	-490.511002	-490.480231	-490.509758	-490.445726	-490.448055
ΔE _{CASPT2} , eV	0.000	2.932	3.769	2.966	4.708	4.645
Ref. Weight	0.704	0.673	0.689	0.439	0.665	0.565
level shift = 0.10 h						
E _{CASPT2} , H	-490.617517	-490.509080	-490.478751	-490.480038	-490.443147	-490.442568
ΔE _{CASPT2} , eV	0.000	2.951	3.776	3.741	4.745	4.761
Ref. Weight	0.712	0.685	0.702	0.684	0.683	0.642
level shift = 0.15 h						
E _{CASPT2} , H	-490.615598	-490.506314	-490.476100	-490.473761	-490.439299	-490.439840
ΔE _{CASPT2} , eV	0.000	2.974	3.796	3.860	4.797	4.783
Ref. Weight	0.720	0.696	0.713	0.710	0.698	0.665
level shift = 0.20 h						
E _{CASPT2} , H	-490.613088	-490.502874	-490.473139	-490.470035	-490.435617	-490.430968
ΔE _{CASPT2} , eV	0.000	2.999	3.808	3.893	4.829	4.956
Ref. Weight	0.728	0.706	0.721	0.721	0.709	0.694
level shift = 0.25 h						
E _{CASPT2} , H	-490.610066	-490.498882	-490.469707	-490.466308	-490.431529	-490.422442
ΔE _{CASPT2} , eV	0.000	3.025	3.819	3.912	4.858	5.106
Ref. Weight	0.735	0.715	0.729	0.730	0.718	0.713

^aThe results with level shift 0.20 h are listed in Table 2 of the manuscript.

Table S5. Vertical excitation energies of *cis-p*-aminophenylnitrosooxide calculated using CASPT2 method at the RB3LYP/6-31G(d) geometry.^a

state	ΔE_{CASSCF} , eV	ΔE_{CASPT2} , eV	ref. weight	λ , nm	f	Major configurations
1A'	0.0	0.0	0.70			65% of ground state configuration
1 ¹ A''	1.41	2.58	0.72	481	2.0×10^{-5}	82%: 30a' → 7a''
2 ¹ A'	4.34	2.58	0.68	480	3.4×10^{-1}	13% of ground state configuration 45%: 6a'' → 7a'' 12%: 6a'' → 7a'' + 4a'' → 7a''
3 ¹ A'	3.62	3.56	0.70	349	2.0×10^{-2}	15%: 6a'' → 8a'' 13%: 2 (6a'') → 2 (7a'') 10%: 4a'' → 7a''
4 ¹ A'	3.66	3.63	0.70	341	1.1×10^{-2}	15%: 6a'' → 8a'' 12%: 5a'' → 7a'' 10%: 6a'' → 7a'' + 5a'' → 7a''
5 ¹ A'	5.54	4.62	0.68	269	1.5×10^{-2}	14%: 6a'' → 8a'' 14%: 6a'' → 7a'' + 5a'' → 8a'' 13%: 5a'' → 7a''
6 ¹ A'	5.89	5.03	0.69	246	4.2×10^{-2}	13%: 6a'' → 8a'' 12%: 6a'' → 7a'' + 5a'' → 8a'' 11%: 5a'' → 7a''
2 ¹ A''	4.32	5.12	0.71	242	1.4×10^{-5}	47%: 30a' → 7a'' + 6a'' → 7a'' 34%: 30a' → 9a''

^a based on a CASSCF(16,14)/ANO-S wavefunction at the B3LYP/6-31G(d) geometry; A' and A'' states were calculated with a level shift of 0.15 h.

Table S6. Dependence of energy and reference weight of CASPT2 states on the level shift for *cis-p*-aminophenylnitroso oxide^a (geometry B3LYP/6-31G(d))

CASPT2 states	1 ¹ A'	2 ¹ A'	3 ¹ A'	4 ¹ A'	5 ¹ A'	6 ¹ A'
level shift = 0.00 h						
E _{CASPT2} , H	-490.632642	-490.540052	-490.501941	-490.498361	-490.468144	-490.448990
ΔE _{CASPT2} , eV	0.000	2.520	3.557	3.654	4.476	4.997
Ref. weight	0.677	0.637	0.633	0.650	0.560	0.597
level shift = 0.05 h						
E _{CASPT2} , H	-490.632136	-490.539147	-490.512715	-490.512495	-490.468479	-490.448921
ΔE _{CASPT2} , eV	0.000	2.530	3.250	3.256	4.453	4.985
Ref. weight	0.687	0.653	0.606	0.590	0.625	0.651
level shift = 0.10 h						
E _{CASPT2} , H	-490.630727	-490.536894	-490.501473	-490.498434	-490.462349	-490.451518
ΔE _{CASPT2} , eV	0.000	2.553	3.517	3.600	4.582	4.877
Ref. Weight	0.696	0.666	0.681	0.685	0.672	0.654
level shift = 0.15 h						
E _{CASPT2} , H	-490.628551	-490.533671	-490.497912	-490.495120	-490.458942	-490.443611
ΔE _{CASPT2} , eV	0.000	2.582	3.555	3.631	4.615	5.033
Ref. Weight	0.704	0.678	0.695	0.698	0.684	0.685
level shift = 0.20 h						
E _{CASPT2} , H	-490.625720	-490.529694	-490.494218	-490.491671	-490.455005	-490.439456
ΔE _{CASPT2} , eV	0.000	2.613	3.578	3.648	4.645	5.069
Ref. Weight	0.713	0.688	0.705	0.707	0.695	0.696
level shift = 0.25 h						
E _{CASPT2} , H	-490.622325	-490.525110	-490.490132	-490.487805	-490.450570	-490.435038
ΔE _{CASPT2} , eV	0.000	2.645	3.597	3.661	4.674	5.096
Ref. weight	0.720	0.698	0.714	0.716	0.705	0.706

^aThe results with level shift 0.15 h are listed in Table S5.

Table S7. Dependence of energy and reference weight of CASPT2 states on the level shift for *trans-p*-aminophenylnitroso oxide^a (geometry CASSCF(12,12)/6-31G(d))

CASPT2 states	1 ¹ A'	2 ¹ A'	3 ¹ A'	4 ¹ A'	5 ¹ A'	6 ¹ A'
level shift = 0.00 h						
$E_{\text{CASPT2}}, \text{H}$	-490.624626	-490.524977	-490.498810	-490.489627	-490.439511	-490.438708
$\Delta E_{\text{CASPT2}}, \text{eV}$	0.000	2.712	3.424	3.674	5.037	5.059
Ref. weight	0.685	0.648	0.644	0.656	0.153	0.526
level shift = 0.05 h						
$E_{\text{CASPT2}}, \text{H}$	-490.624139	-490.524175	-490.497694	-490.563936	-490.442497	-490.445863
$\Delta E_{\text{CASPT2}}, \text{eV}$	0.000	2.720	3.441	1.638	4.943	4.851
Ref. weight	0.694	0.662	0.677	0.365	0.626	0.624
level shift = 0.10 h						
$E_{\text{CASPT2}}, \text{H}$	-490.622781	-490.522098	-490.495694	-490.492007	-490.471108	-490.447413
$\Delta E_{\text{CASPT2}}, \text{eV}$	0.000	2.740	3.458	3.559	4.127	4.772
Ref. weight	0.703	0.675	0.690	0.687	0.560	0.640
level shift = 0.15 h						
$E_{\text{CASPT2}}, \text{H}$	-490.620685	-490.519071	-490.492988	-490.487884	-490.437407	-490.433960
$\Delta E_{\text{CASPT2}}, \text{eV}$	0.000	2.765	3.475	3.614	4.987	5.081
Ref. weight	0.711	0.686	0.700	0.703	0.682	0.695
level shift = 0.20 h						
$E_{\text{CASPT2}}, \text{H}$	-490.617958	-490.515303	-490.489664	-490.484311	-490.431658	-490.430006
$\Delta E_{\text{CASPT2}}, \text{eV}$	0.000	2.793	3.491	3.637	5.070	5.114
Ref. weight	0.719	0.696	0.710	0.713	0.700	0.706
level shift = 0.25 h						
$E_{\text{CASPT2}}, \text{H}$	-490.614689	-490.510940	-490.485819	-490.480481	-490.426337	-490.425778
$\Delta E_{\text{CASPT2}}, \text{eV}$	0.000	2.823	3.507	3.652	5.125	5.141
Ref. weight	0.727	0.706	0.719	0.722	0.712	0.715

^aThe results with level shift 0.15 h are listed in Table 3 of the manuscript.

Table S8. Vertical excitation energies of *trans-p*-aminophenylnitroso oxide calculated using CASPT2 method at the RB3LYP/6-31G(d) geometry.^a

state	ΔE_{CASSCF} , eV	ΔE_{CASPT2} , eV	ref. weight	λ nm	f	Major configurations
1A'	0.0	0.0	0.71			61% of ground state configuration 10%: 6a'' → 7a''
1 ¹ A''	1.89	2.40	0.69	516	1.2×10 ⁻⁵	83%: 30a' → 7a''
2 ¹ A'	4.33	2.87	0.69	432	4.7×10 ⁻¹	17% of ground state configuration 49%: 6a'' → 7a''
3 ¹ A'	3.49	3.31	0.70	375	1.7×10 ⁻²	22%: 2(6a'') → 2(7a'') 18%: 4a'' → 7a'' 17%: 6a'' → 9a'' 13%: 6a'' → 7a'' + 4a'' → 7a''
4 ¹ A'	3.60	3.37	0.70	368	2.2×10 ⁻²	29%: 6a'' → 8a'' 16%: 5a'' → 7a'' 15%: 6a'' → 7a'' + 5a'' → 7a''
5 ¹ A'	5.80	4.34	0.69	285	8.2×10 ⁻²	21%: 5a'' → 7a'' 19%: 6a'' → 8a''
6 ¹ A'	5.49	4.90	0.69	253	8.2×10 ⁻³	24%: 6a'' → 7a'' + 5a'' → 8a''

^a based on a CASSCF(16,14)/ANO-S wavefunction at the B3LYP/6-31G(d) geometry; A' states were calculated with a level shift of 0.15 h, A'' states were calculated with no level shift.

Table S9. Dependence of energy and reference weight of CASPT2 states on the level shift for *trans-p*-aminophenylnitroso oxide^a (geometry RB3LYP/6-31G(d))

CASPT2 states	1 ¹ A'	2 ¹ A'	3 ¹ A'	4 ¹ A'	5 ¹ A'	6 ¹ A'
level shift = 0.00 h						
E _{CASPT2} , H	-490.630543	-490.526582	-490.505492	-490.507948	-490.473056	-490.464089
ΔE _{CASPT2} , eV	0.000	2.829	3.403	3.336	4.285	4.529
Ref. weight	0.684	0.653	0.620	0.662	0.641	0.078
level shift = 0.05 h						
E _{CASPT2} , H	-490.630056	-490.525837	-490.515487	-497.406897	-492.374681	-490.453606
ΔE _{CASPT2} , eV	0.000	2.836	3.118			4.801
Ref. weight	0.694	0.667	0.641	0.007	0.025	0.650
level shift = 0.10 h						
E _{CASPT2} , H	-490.628700	-490.523893	-490.580320	-490.505418	-490.470132	-490.469713
ΔE _{CASPT2} , eV	0.000	2.852	3.276	3.355	4.315	4.326
Ref. weight	0.703	0.678	0.690	0.692	0.676	0.604
level shift = 0.15 h						
E _{CASPT2} , H	-490.626605	-490.521033	-490.505028	-490.502761	-490.466952	-490.446501
ΔE _{CASPT2} , eV	0.000	2.873	3.308	3.370	4.344	4.901
Ref. weight	0.711	0.689	0.703	0.702689	0.688	0.693
level shift = 0.20 h						
E _{CASPT2} , H	-490.623879	-490.517445	-490.501635	-490.499522	-490.463207	-490.442268
ΔE _{CASPT2} , eV	0.000	2.896	3.326	3.384	4.372	4.942
Ref. weight	0.719	0.699	0.713	0.711	0.698	0.705
level shift = 0.25 h						
E _{CASPT2} , H	-490.620610	-490.513265	-490.497869	-490.495764	-490.458929	-490.437975
ΔE _{CASPT2} , eV	0.000	2.921	3.340	3.397	4.400	4.970
Ref. weight	0.727	0.708	0.721	0.720	0.707	0.715

^aThe results with level shift 0.15 h are listed in Table S8.

Table S10. Summary of CBS-QB3 calculations

	H(0 K), kcal/mol	H(298 K), kcal/mol	G(298 K), kcal/mol	$\Delta H(0\text{ K})$, kcal/mol	$\Delta H(298\text{ K})$, kcal/mol	$\Delta G(298\text{ K})$, kcal/mol
$^3\text{NH}_2\text{PhN} + \text{O}_2$	-491.230477	-491.219401	-491.281987	0.0	0.0	0.0
<i>cis</i> -NH ₂ PhNOO, singlet	-491.262193	-491.252574	-491.295769	-19.9	-20.8	-8.6
<i>syn</i> -NH ₂ PhNOO, triplet	-491.235343	-491.225302	-491.270560	-3.1	-3.7	+7.2
<i>trans</i> -NH ₂ PhNOO, singlet	-491.260009	-491.250282	-491.293680	-18.5	-19.4	-7.3
<i>anti</i> -NH ₂ PhNOO, triplet	-491.235184	-491.225032	-491.270886	-3.0	-3.5	+7.0
NH ₂ PhNOO dioxaziridine	-491.244113	-491.234578	-491.277756	-8.6	-9.5	+2.7
NH ₂ PhNO ₂	-491.364963	-491.355637	-491.398421	-84.4	-85.5	-73.1
$^3\text{PhN} + \text{O}_2$	-435.947759	-435.938169	-435.996933	0.0	0.0	0.0
<i>cis</i> -PhNOO, singlet	-435.977727	-435.969765	-436.009602	-18.8	-19.8	-7.9
<i>syn</i> -PhNOO, triplet	-435.949080	-435.940554	-435.982765	-0.8	-1.5	+8.9
<i>trans</i> -PhNOO, singlet	-435.977817	-435.969658	-436.009890	-18.9	-19.8	-8.1
<i>anti</i> -PhNOO, triplet	-435.949819	-435.941218	-435.983845	-1.3	-1.9	+8.2
PhNOO dioxaziridine	-435.963739	-435.955735	-435.995808	-10.0	-11.0	+0.7
PhNO ₂	-436.083418	-436.075597	-436.115455	-85.1	-86.2	-74.4

Table S11. Summary of G2M(CC5, MP2) calculations

	H(0 K), kcal/mol	$\Delta H(0 K)$, kcal/mol
$^3\text{NH}_2\text{PhN} + \text{O}_2$	-491.188632	0.0
<i>cis</i> -NH ₂ PhNOO, singlet	-491.234750	-28.9
<i>syn</i> -NH ₂ PhNOO, triplet	-491.195054	-4.0
<i>trans</i> -NH ₂ PhNOO, singlet	-491.231816	-27.1
<i>anti</i> -NH ₂ PhNOO, triplet	-491.195029	-4.0
NH ₂ PhNOO dioxaziridine	-491.214032	-15.9
NH ₂ PhNO ₂	-491.334128	-91.3
$^3\text{PhN} + \text{O}_2$	-435.909331	0.0
<i>cis</i> -PhNOO, singlet	-435.953061	-27.4
<i>syn</i> -PhNOO, triplet	-435.912864	-2.2
<i>trans</i> -PhNOO, singlet	-435.952217	-26.9
<i>anti</i> -PhNOO, triplet	-435.912008	-1.7
PhNOO dioxaziridine	-435.936772	-17.2
PhNO ₂	-436.055984	-92.0

Table S12. Summary of B3LYP/6-311G(d,p) calculations

	H(0 K), kcal/mol	H(298 K), kcal/mol	G(298 K), kcal/mol	$\Delta H(0 K)$, kcal/mol	$\Delta H(298 K)$, kcal/mol	$\Delta G(298 K)$, kcal/mol
$^3\text{NH}_2\text{PhN} + \text{O}_2$	-492.008411	-491.997397	-492.059881	0.0	0.0	0.0
<i>cis</i> -NH ₂ PhNOO, singlet	-492.023609	-492.014069	-492.057111	-9.5	-10.5	+1.7
<i>syn</i> -NH ₂ PhNOO, triplet	-492.005848	-491.995879	-492.041002	+1.6	+1.0	+11.8
<i>trans</i> -NH ₂ PhNOO, singlet	-492.017436	-492.007781	-492.051045	-5.7	-6.5	+5.5
<i>anti</i> -NH ₂ PhNOO, triplet	-492.006226	-491.996145	-492.041863	+1.4	+0.8	+11.3
NH ₂ PhNOO dioxaziridine	-491.994358	-491.984895	-492.027944	+8.8	+7.8	+20.0
NH ₂ PhNO ₂	-492.123543	-492.114287	-492.156945	-72.2	-73.3	-60.9
$^3\text{PhN} + \text{O}_2$	-436.647277	-436.637732	-436.696426	0.0	0.0	0.0
<i>cis</i> -PhNOO, singlet	-436.657222	-436.649317	-436.689056	-6.2	-7.3	+4.6
<i>syn</i> -PhNOO, triplet	-436.641064	-436.632596	-436.674701	+3.9	+3.2	+13.6
<i>trans</i> -PhNOO, singlet	-436.654088	-436.645979	-436.686133	-4.3	-5.2	+6.5
<i>anti</i> -PhNOO, triplet	-436.641794	-436.633246	-436.675799	+3.4	+2.8	+12.9
PhNOO dioxaziridine	-436.634596	-436.626649	-436.666622	+8.0	+7.0	+18.7
PhNO ₂	-436.761942	-436.754176	-436.793939	-72.0	-73.1	-61.2

Table S13. Vertical excitation energies of *p*-aminophenyl dioxaziridine calculated using CASPT2 method.^a

state	ΔE_{CASSCF} , eV	ΔE_{CASPT2} , eV	ref. weight	λ , nm	f	Major configurations
1 ¹ A'	0.0	0.0	0.74			82% of ground state configuration
2 ¹ A'	6.17	3.94	0.71	315	5.8×10^{-2}	29%: 8a" → 9a" 32%: 5a" → 9a" 12%: 5a" → 12a"
3 ¹ A'	4.72	4.21	0.72	294	3.9×10^{-3}	41%: 8a" → 10a" 18%: 7a" → 9a"
4 ¹ A'	6.74	4.70	0.71	264	1.6×10^{-1}	38%: 8a" → 9a" 18%: 5a" → 9a"
1 ¹ A"	8.55	5.11	0.70	243	1.2×10^{-2}	84%: 28a' → 9a"
2 ¹ A"	7.20	5.56	0.72	223	9.0×10^{-3}	80%: 8a" → 29a'

^a based on a CASSCF(12,12)/ANO-S wavefunction at the B3LYP/6-31G(d) geometry; all states were calculated with a level shift of 0.25 h.

Table S14. Dependence of energy and reference weight of CASPT2 states on the level shift for *p*-aminophenyl dioxaziridine^a

CASPT2 states	1 ¹ A'	2 ¹ A'	3 ¹ A'	4 ¹ A'	1 ¹ A''	2 ¹ A''
level shift = 0.00 h						
E _{CASPT2} , H	-490.537678	-490.405533	-490.381358	-490.290141	-490.354769	-490.334763
ΔE _{CASPT2} , eV	0.000	3.596	4.254	6.736	4.977	5.522
Ref. weight	0.697	0.031	0.498	0.081	0.640	0.674
level shift = 0.05 h						
E _{CASPT2} , H	-490.537253	-490.400771	-490.402785	-490.396054	-490.353806	-490.334449
ΔE _{CASPT2} , eV	0.000	3.727	3.659	3.842	4.992	5.519
Ref. weight	0.706	0.640	0.581	0.537	0.659	0.684
level shift = 0.10 h						
E _{CASPT2} , H	-490.536054	-490.395558	-490.387242	-490.378363	-490.351769	-490.333671
ΔE _{CASPT2} , eV	0.000	3.823	4.049	4.291	5.015	5.507
Ref. weight	0.714	0.674	0.674	0.638	0.671	0.692
level shift = 0.15 h						
E _{CASPT2} , H	-490.534183	-490.392068	-490.382141	-490.367590	-490.348895	-490.330725
ΔE _{CASPT2} , eV	0.000	3.867	4.137	4.533	5.042	5.536
Ref. weight	0.722	0.687	0.703	0.677	0.682	0.704
level shift = 0.20 h						
E _{CASPT2} , H	-490.531725	-490.388236	-490.378142	-490.361560	-490.345302	-490.327783
ΔE _{CASPT2} , eV	0.000	3.905	4.179	4.630	5.073	5.550
Ref. weight	0.729	0.697	0.714	0.694	0.692	0.712
level shift = 0.25 h						
E _{CASPT2} , H	-490.528757	-490.383927	-490.374031	-490.356055	-490.341094	-490.324314
ΔE _{CASPT2} , eV	0.000	3.941	4.210	4.699	5.107	5.563
Ref. weight	0.736	0.707	0.724	0.706	0.701	0.720
level shift = 0.30 h						
E _{CASPT2} , H	-490.525342	-490.379169	-490.369663	-490.350569	-490.336365	-490.320368
ΔE _{CASPT2} , eV	0.000	3.978	4.236	4.756	5.142	5.578
Ref. weight	0.743	0.716	0.732	0.716	0.709	0.728

^aThe results with level shift 0.25 h are listed in Table S13.

Matrix isolation and computational study of the photochemistry of *p*-azidoaniline

Elena A. Pritchina, Nina P. Gritsan, Thomas Bally

SUPPORTING INFORMATION, PART 3 (FIGURES)

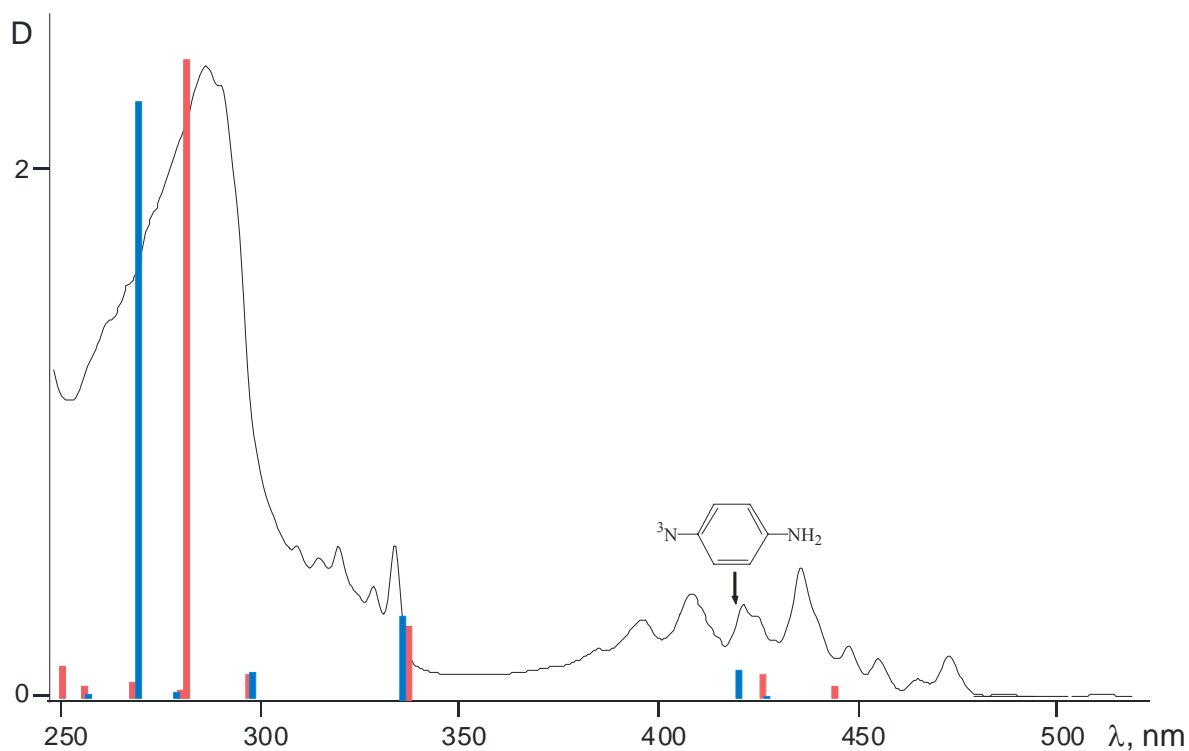


Figure S1

The electronic absorption spectrum of *p*-aminophenylnitrene (**4**) in an Ar matrix at 12 K and comparison of the positions and relative oscillator strengths of the electronic transitions of nitrene **4** calculated for planar (symmetry C_{2v} - **red bars**, cf. Table 1) and non-planar (symmetry C_s - **blue bars**, cf. Table S1) geometry of *p*-aminophenylnitrene.

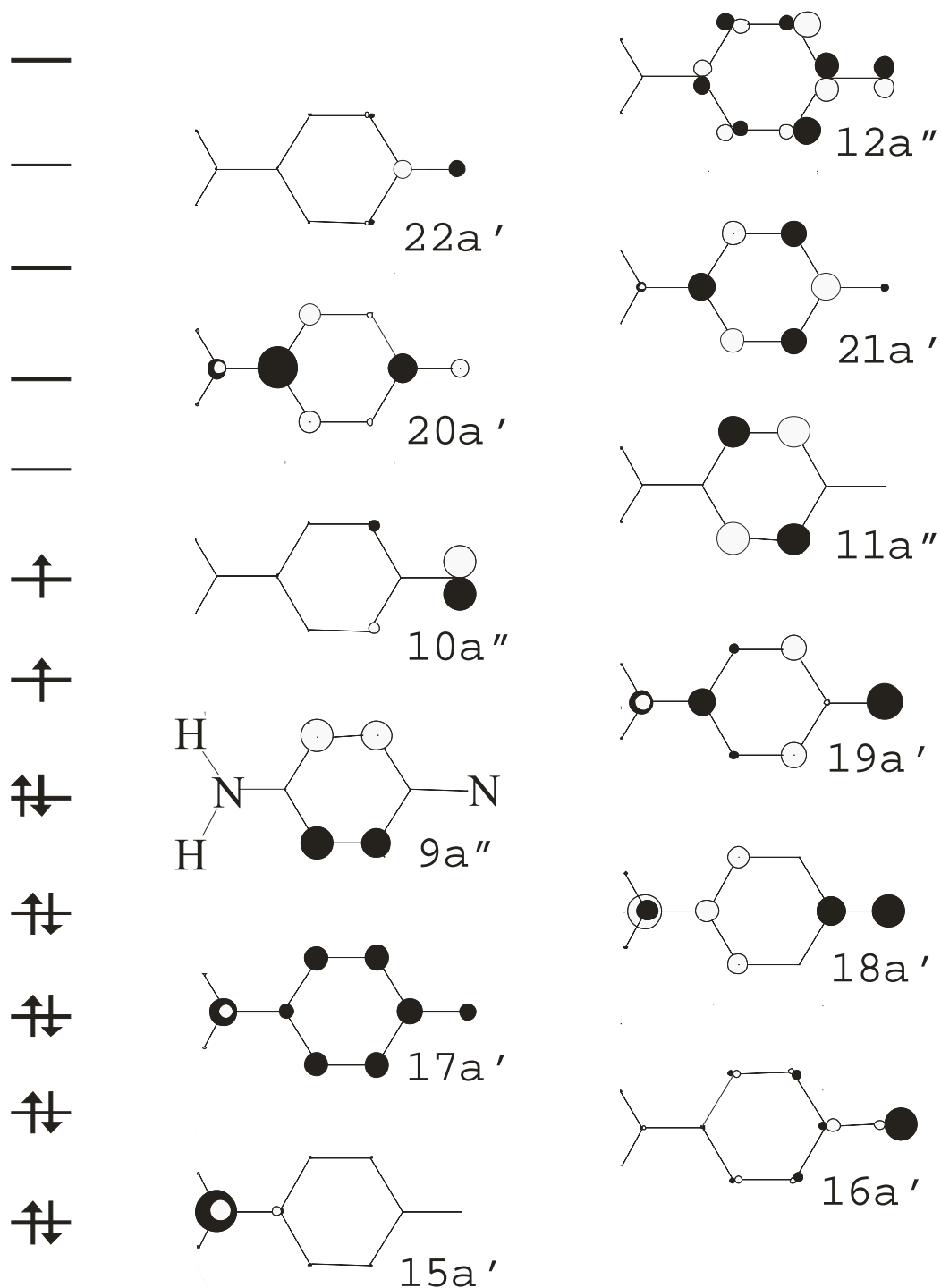


Figure S2

Active space used in the CASSCF/CASPT2 calculations of the electronic transitions of the triplet *p*-aminophenylnitrene (symmetry C_s , cf. Table S1).

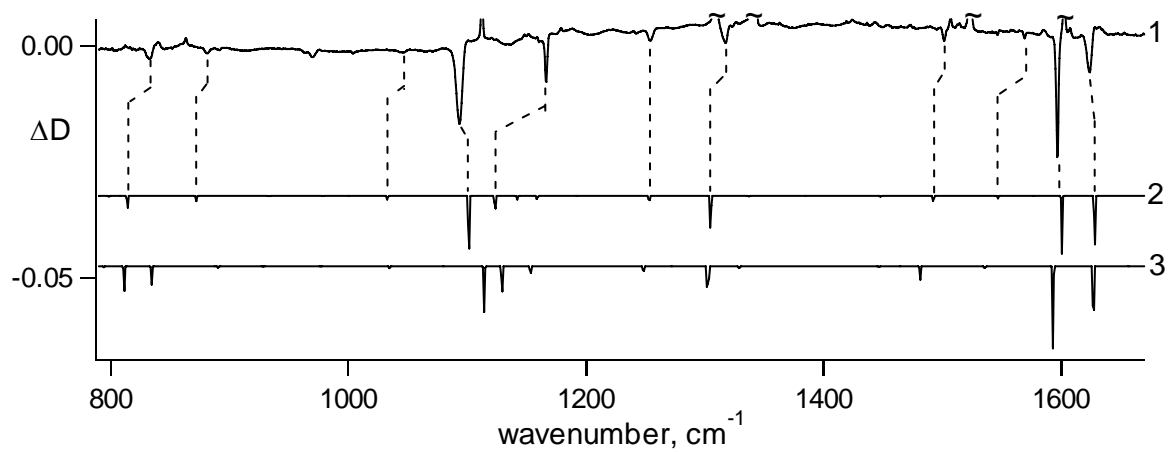


Figure S3

Difference IR spectra produced by bleaching of the adducts of nitrene **4** with oxygen in an Ar matrix at 12 K to >515 nm for 30 s (spectrum 1). The traces 2 and 3 show the IR spectra of *trans*-**(8)** *p*-aminophenylnitroso oxides calculated by RB3LYP and UB3LYP, respectively, and scaled by 0.9614.

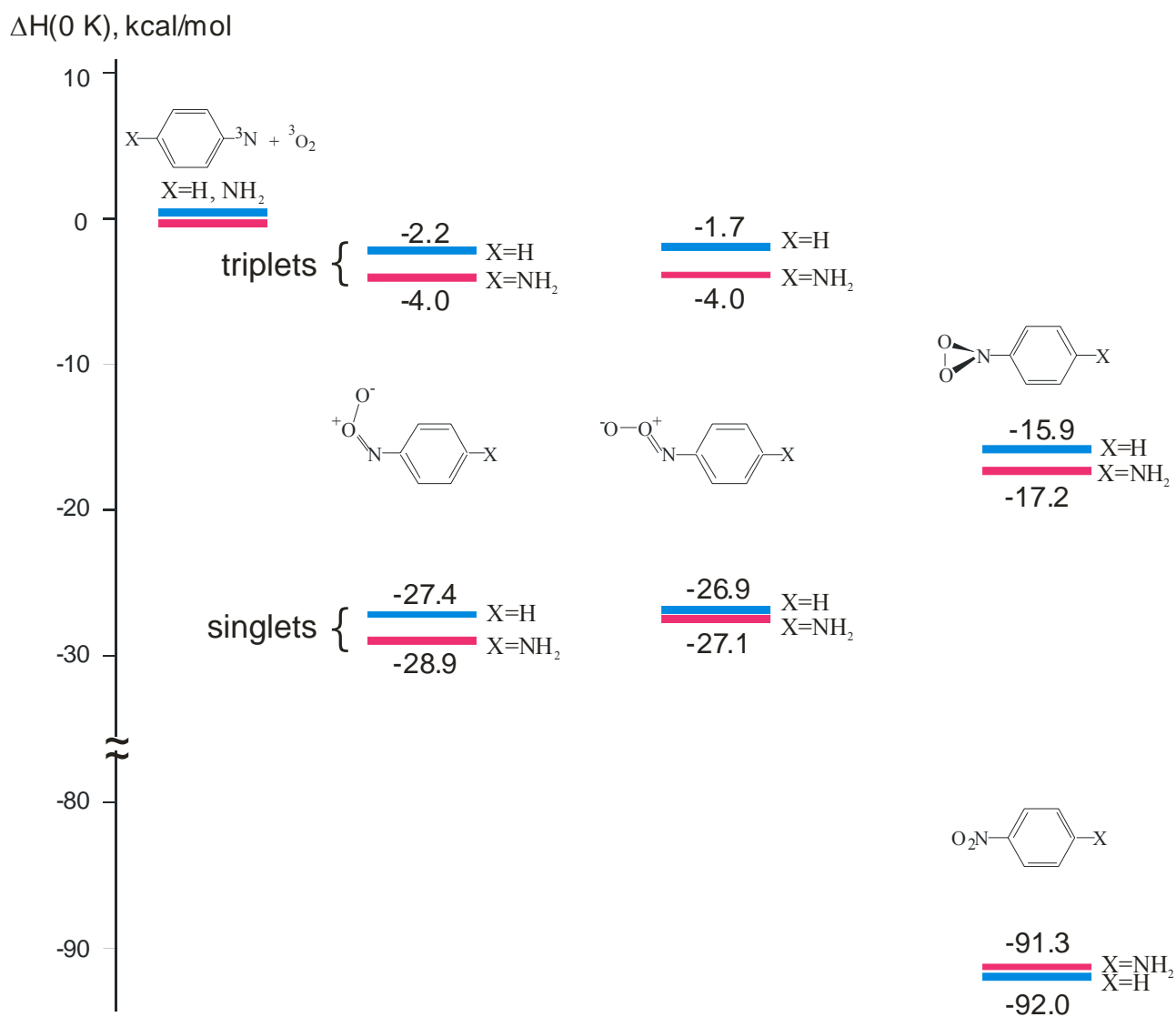


Figure S4

Relative 0 K enthalpies of the species involved in the formation and rearrangement of phenyl- and *p*-aminophenyl nitroso oxides calculated by the multi-level scheme G2M(CC5MP2).

Method G2M(CC5, MP2):^a

$$E_{\text{G2M(CC5, MP2)}} = \text{CCSD(T)/6-311G(d,p)} + \Delta E(+3d2p) + \Delta E(\text{HLC,CC5}) + \text{ZPE}$$

$$\Delta E(+3d2p) = E[\text{PMP2/6-311+G(3df,2p)}] - E[\text{PMP2/6-311G(d,p)}]$$

$$\Delta E(\text{HLC,CC5}) = [-5,30n_{\beta} - 0,19n_{\alpha}]/1000$$

^aA.M. Mebel, K. Morokuma, M.C. Lin. *J. Chem. Phys.*, 1995, **103**, 7414.

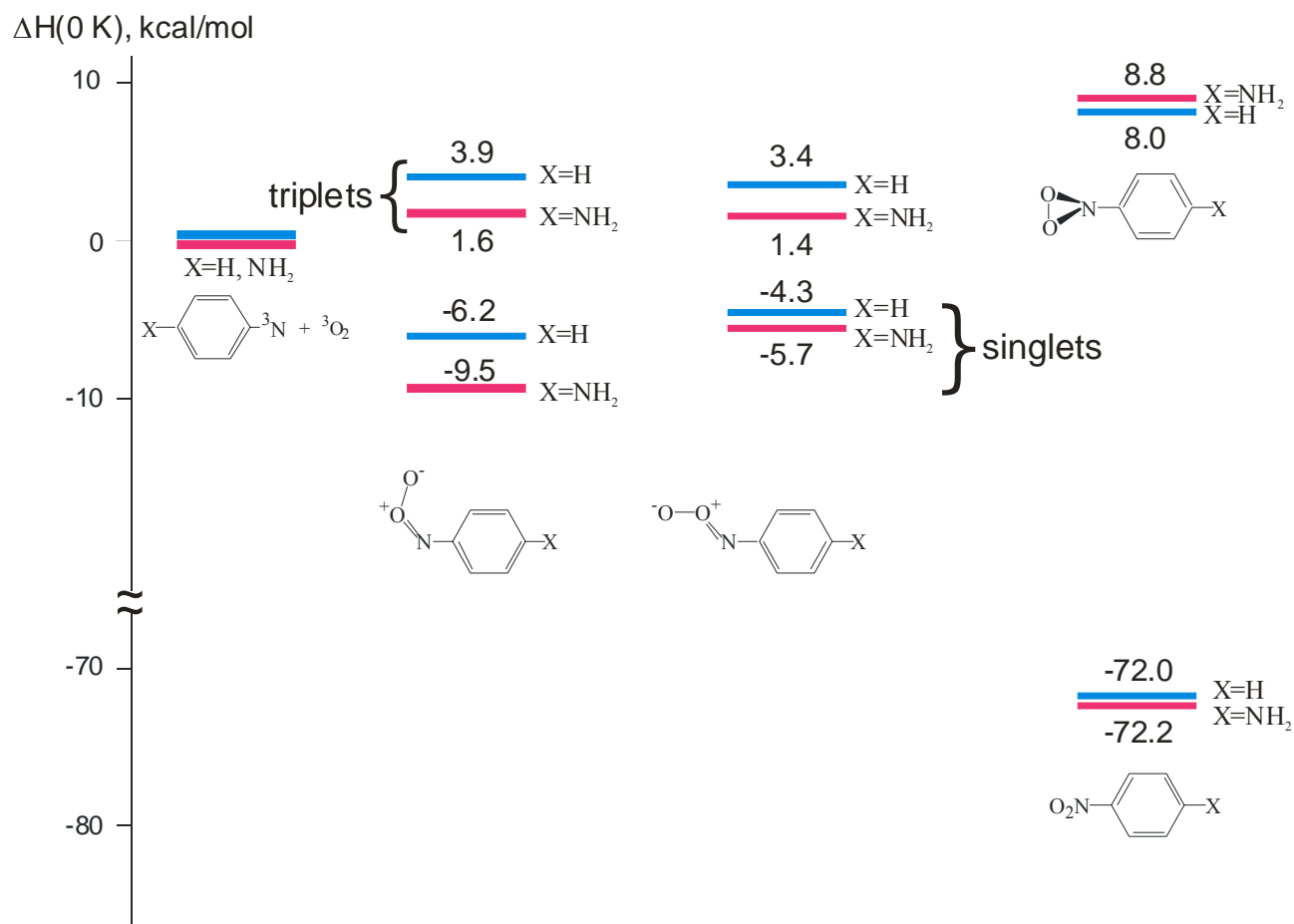


Figure S5

Relative 0 K enthalpies of the species involved in the formation and rearrangement of phenyl- and *p*-aminophenyl nitroso oxides calculated by the B3LYP/6-311G(d,p) method.

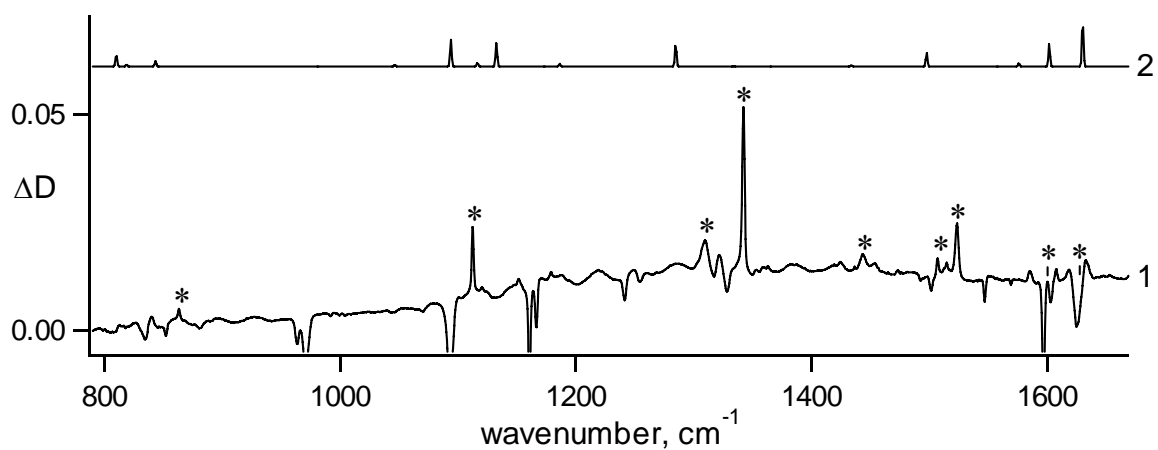


Figure S6

Difference IR spectrum produced by bleaching of the adducts of nitrene 4 with oxygen in an Ar matrix at 12 K to >515 nm for 5 min (spectrum 1). The traces 2 show the IR spectra of cyclic p-aminophenylnitroso dioxaziridine calculated by B3LYP and scaled by 0.9614. The asterisks mark the positions of experimental IR peaks of p-nitroaniline (2) in an Ar matrix at 12 K.

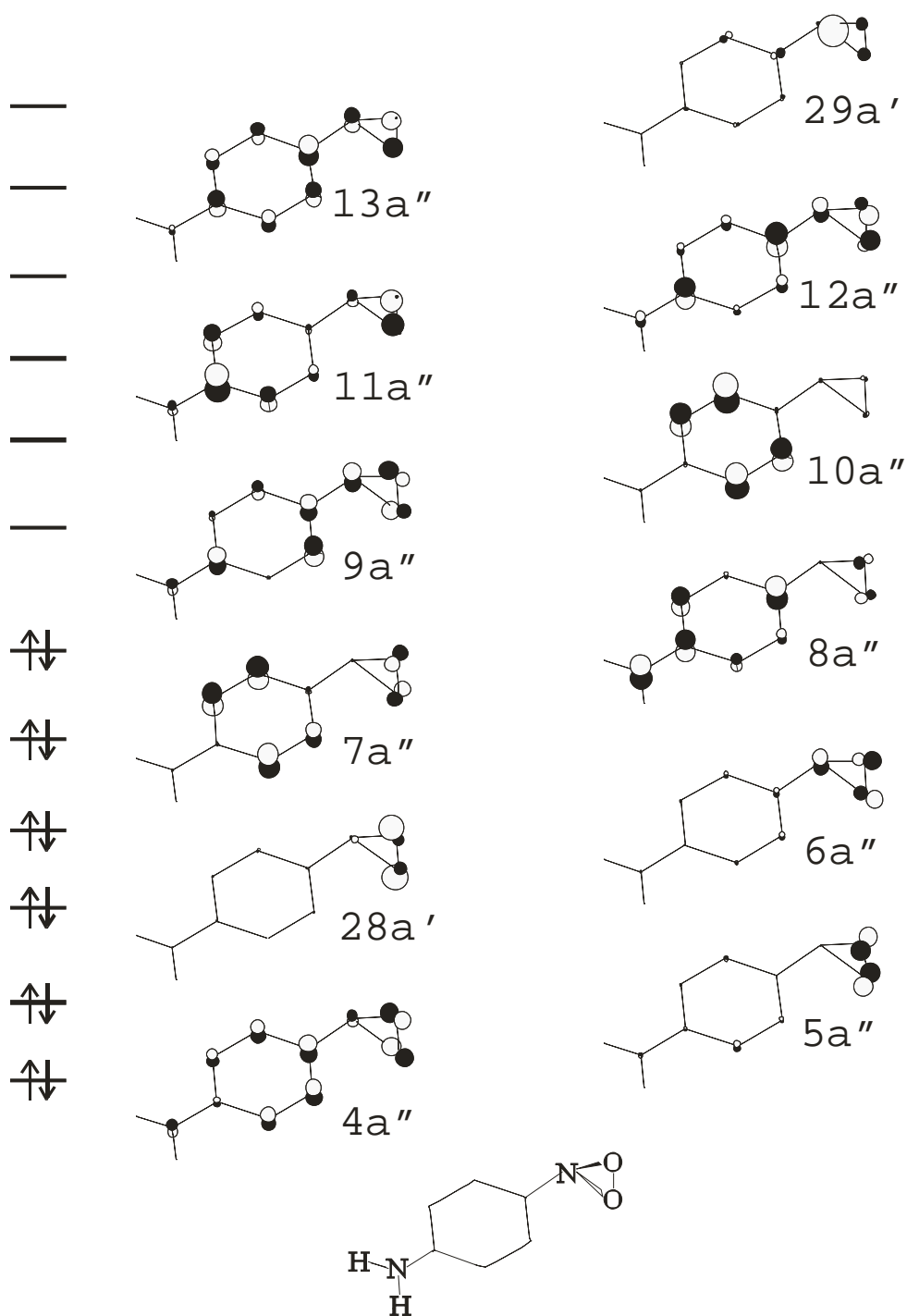


Figure S7

Active space used in the CASSCF/CASPT2 calculations of the electronic transitions of the cyclic *p*-aminophenyl dioxaziridine (cf. Table S10).