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" →19a' 31%: 19a' →11a"
$2^3A''$	3.27	2.95	0.77	420	1.5×10^{-2}	49%: 18a' →19a' 28%: 19a' →20a'
$2^3A'$	5.45	3.68	0.73	337	4.6×10^{-2}	32%: 9a" →19a' 33%: 19a' →11a"
$3^3A'$	3.89	3.96	0.76	313	2.6×10^{-10}	79%: 18a' →10a"
$4^3A'$	4.36	4.15	0.76	298	1.4×10^{-2}	81%: 16a' →10a"
$3^3A''$	4.62	4.45	0.77	279	3.5×10^{-3}	63%: 9a" →11a"
$4^3A''$	6.52	4.60	0.74	269	3.2×10^{-1}	26%: 18a' →19a' 30%: 19a' →20a'
$5^3A''$	5.23	4.61	0.77	269	6.1×10^{-3}	39%: 9a" →11a" 24%: 15a' →19a'
$6^3A''$	4.92	4.65	0.77	267	1.5×10^{-5}	60%: 9a" →10a" 13%: 18a' →19a' + 9a" →10a"
$7^3A''$	5.26	4.84	0.76	256	1.7×10^{-3}	77%: 16a' →19a'
$5^3A'$	5.69	5.65	0.76	219	1.4×10^{-5}	67%: 19a' →10a" + 9a" →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	$1^1A"$	$2^1A"$	$3^1A"$	$4^1A"$	$5^1A"$	$6^1A"$
			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

CASPT2 states	$7^1A"$	$1^1A'$	$2^1A'$	$3^1A'$	$4^1A'$	$5^1A'$
			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

[a]The 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_{CASPT2}, H	-340.601508	-340.488557	-340.438401	-340.439107	-340.425794
ΔE_{CASPT2}, 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_{CASPT2}, H	-340.601158	-340.496922	-340.443155	-340.510687	-340.693264
ΔE_{CASPT2}, 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_{CASPT2}, H	-340.600179	-340.494251	-340.536053	-340.437865	-340.444394
ΔE_{CASPT2}, 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_{CASPT2}, H	-340.598662	-340.492112	-340.444793	-340.435890	-340.424790
ΔE_{CASPT2}, 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_{CASPT2}, H	-340.596683	-340.489715	-340.434337	-340.433508	-340.418413
ΔE_{CASPT2}, 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_{CASPT2}, H	-340.498726	-340.467576	-340.448562	-340.418487	-340.401337
ΔE_{CASPT2}, 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_{CASPT2}, H	-340.498309	-340.466572	-340.448113	-340.419420	-340.410328
ΔE_{CASPT2}, 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_{CASPT2}, H	-340.497135	-340.465083	-340.447001	-340.418085	-340.403779
ΔE_{CASPT2}, 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_{CASPT2}, H	-340.495401	-340.462821	-340.445355	-340.416231	-340.399988
ΔE_{CASPT2}, eV	2.810	3.696	4.172	4.963	5.405
Ref. Weight	0.764	0.745	0.767	0.747	0.748

[a]The 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	$1^1A'$	$2^1A'$	$3^1A'$	$4^1A'$	$5^1A'$	$6^1A'$
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

[a]The 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
1^1A"	1.41	2.58	0.72	481	2.0×10^{-5}	82%: 30a' →7a"
2^1A'	4.34	2.58	0.68	480	3.4×10^{-1}	13% of ground state configuration 45%: 6a" →7a" 12%: 6a" →7a" + 4a" →7a"
3^1A'	3.62	3.56	0.70	349	2.0×10^{-2}	15%: 6a" →8a" 13%: 2(6a") →2(7a") 10%: 4a" →7a"
4^1A'	3.66	3.63	0.70	341	1.1×10^{-2}	15%: 6a" →8a" 12%: 5a" →7a" 10%: 6a" →7a" + 5a" →7a"
5^1A'	5.54	4.62	0.68	269	1.5×10^{-2}	14%: 6a" →8a" 14%: 6a" →7a" + 5a" →8a" 13%: 5a" →7a"
6^1A'	5.89	5.03	0.69	246	4.2×10^{-2}	13%: 6a" →8a" 12%: 6a" →7a" + 5a" →8a" 11%: 5a" →7a"
2^1A"	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	$1^1A'$	$2^1A'$	$3^1A'$	$4^1A'$	$5^1A'$	$6^1A'$
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

[a]The 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	$1^1A'$	$2^1A'$	$3^1A'$	$4^1A'$	$5^1A'$	$6^1A'$
level shift = 0.00 h						
E_{CASPT2}, H	-490.624626	-490.524977	-490.498810	-490.489627	-490.439511	-490.438708
ΔE_{CASPT2}, 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_{CASPT2}, H	-490.624139	-490.524175	-490.497694	-490.563936	-490.442497	-490.445863
ΔE_{CASPT2}, 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_{CASPT2}, H	-490.622781	-490.522098	-490.495694	-490.492007	-490.471108	-490.447413
ΔE_{CASPT2}, 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_{CASPT2}, H	-490.620685	-490.519071	-490.492988	-490.487884	-490.437407	-490.433960
ΔE_{CASPT2}, 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_{CASPT2}, H	-490.617958	-490.515303	-490.489664	-490.484311	-490.431658	-490.430006
ΔE_{CASPT2}, 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_{CASPT2}, H	-490.614689	-490.510940	-490.485819	-490.480481	-490.426337	-490.425778
ΔE_{CASPT2}, 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

[a]The 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"
1^1A"	1.89	2.40	0.69	516	1.2×10^{-5}	83%: 30a' →7a"
2^1A'	4.33	2.87	0.69	432	4.7×10^{-1}	17% of ground state configuration 49%: 6a" →7a"
3^1A'	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"
4^1A'	3.60	3.37	0.70	368	2.2×10^{-2}	29%: 6a" →8a" 16%: 5a" →7a" 15%: 6a" →7a" + 5a" →7a"
5^1A'	5.80	4.34	0.69	285	8.2×10^{-2}	21%: 5a" →7a" 19%: 6a" →8a"
6^1A'	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	$1^1A'$	$2^1A'$	$3^1A'$	$4^1A'$	$5^1A'$	$6^1A'$
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

[a]The 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	ΔH(0 K), kcal/mol	ΔH(298 K), kcal/mol	ΔG(298 K), kcal/mol
$^3NH_2PhN + O_2$	-491.230477	-491.219401	-491.281987	0.0	0.0	0.0
cis-NH_2PhNOO, singlet	-491.262193	-491.252574	-491.295769	-19.9	-20.8	-8.6
syn-NH_2PhNOO, triplet	-491.235343	-491.225302	-491.270560	-3.1	-3.7	+7.2
trans-NH_2PhNOO, singlet	-491.260009	-491.250282	-491.293680	-18.5	-19.4	-7.3
anti-NH_2PhNOO, triplet	-491.235184	-491.225032	-491.270886	-3.0	-3.5	+7.0
NH_2PhNOO dioxaziridine	-491.244113	-491.234578	-491.277756	-8.6	-9.5	+2.7
NH_2PhNO_2	-491.364963	-491.355637	-491.398421	-84.4	-85.5	-73.1
$^3PhN + O_2$	-435.947759	-435.938169	-435.996933	0.0	0.0	0.0
cis-PhNOO, singlet	-435.977727	-435.969765	-436.009602	-18.8	-19.8	-7.9
syn-PhNOO, triplet	-435.949080	-435.940554	-435.982765	-0.8	-1.5	+8.9
trans-PhNOO, singlet	-435.977817	-435.969658	-436.009890	-18.9	-19.8	-8.1
anti-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	ΔH(0 K), kcal/mol
$^3NH_2PhN + O_2$	-491.188632	0.0
cis-NH_2PhNOO, singlet	-491.234750	-28.9
syn-NH_2PhNOO, triplet	-491.195054	-4.0
trans-NH_2PhNOO, singlet	-491.231816	-27.1
anti-NH_2PhNOO, triplet	-491.195029	-4.0
NH_2PhNOO dioxaziridine	-491.214032	-15.9
NH_2PhNO_2	-491.334128	-91.3
$^3PhN + O_2$	-435.909331	0.0
cis-PhNOO, singlet	-435.953061	-27.4
syn-PhNOO, triplet	-435.912864	-2.2
trans-PhNOO, singlet	-435.952217	-26.9
anti-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	ΔH(0 K), kcal/mol	ΔH(298 K), kcal/mol	ΔG(298 K), kcal/mol
$^3NH_2PhN + O_2$	-492.008411	-491.997397	-492.059881	0.0	0.0	0.0
cis-NH_2PhNOO, singlet	-492.023609	-492.014069	-492.057111	-9.5	-10.5	+1.7
syn-NH_2PhNOO, triplet	-492.005848	-491.995879	-492.041002	+1.6	+1.0	+11.8
trans-NH_2PhNOO, singlet	-492.017436	-492.007781	-492.051045	-5.7	-6.5	+5.5
anti-NH_2PhNOO, triplet	-492.006226	-491.996145	-492.041863	+1.4	+0.8	+11.3
NH_2PhNOO dioxaziridine	-491.994358	-491.984895	-492.027944	+8.8	+7.8	+20.0
NH_2PhNO_2	-492.123543	-492.114287	-492.156945	-72.2	-73.3	-60.9
$^3PhN + O_2$	-436.647277	-436.637732	-436.696426	0.0	0.0	0.0
cis-PhNOO, singlet	-436.657222	-436.649317	-436.689056	-6.2	-7.3	+4.6
syn-PhNOO, triplet	-436.641064	-436.632596	-436.674701	+3.9	+3.2	+13.6
trans-PhNOO, singlet	-436.654088	-436.645979	-436.686133	-4.3	-5.2	+6.5
anti-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
$1^1A'$	0.0	0.0	0.74			82% of ground state configuration
$2^1A'$	6.17	3.94	0.71	315	5.8×10^{-2}	29%: 8a" →9a" 32%: 5a" →9a" 12%: 5a" →12a"
$3^1A'$	4.72	4.21	0.72	294	3.9×10^{-3}	41%: 8a" →10a" 18%: 7a" →9a"
$4^1A'$	6.74	4.70	0.71	264	1.6×10^{-1}	38%: 8a" →9a" 18%: 5a" →9a"
$1^1A"$	8.55	5.11	0.70	243	1.2×10^{-2}	84%: 28a' →9a"
$2^1A"$	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	$1^1A'$	$2^1A'$	$3^1A'$	$4^1A'$	$1^1A''$	$2^1A''$
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

[a]The 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)

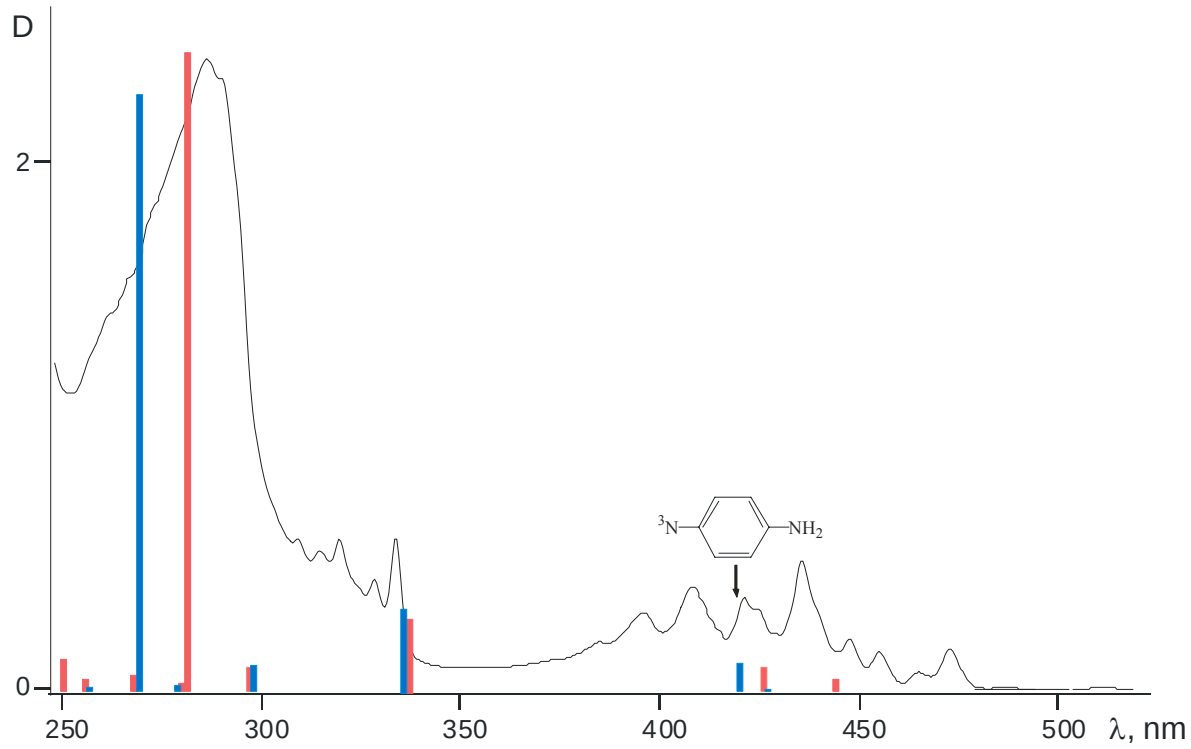

Figure S1

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.

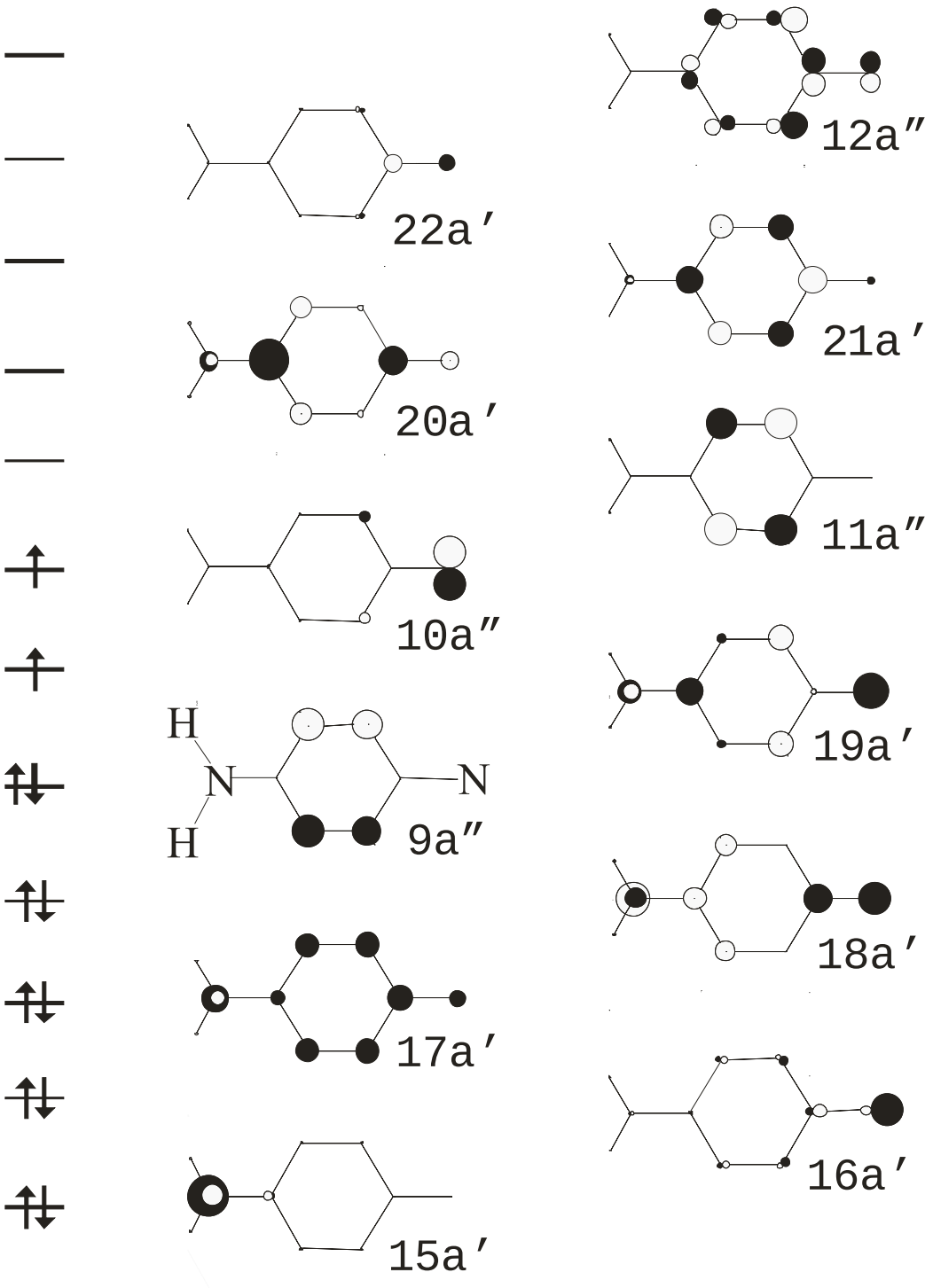

Figure S2

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

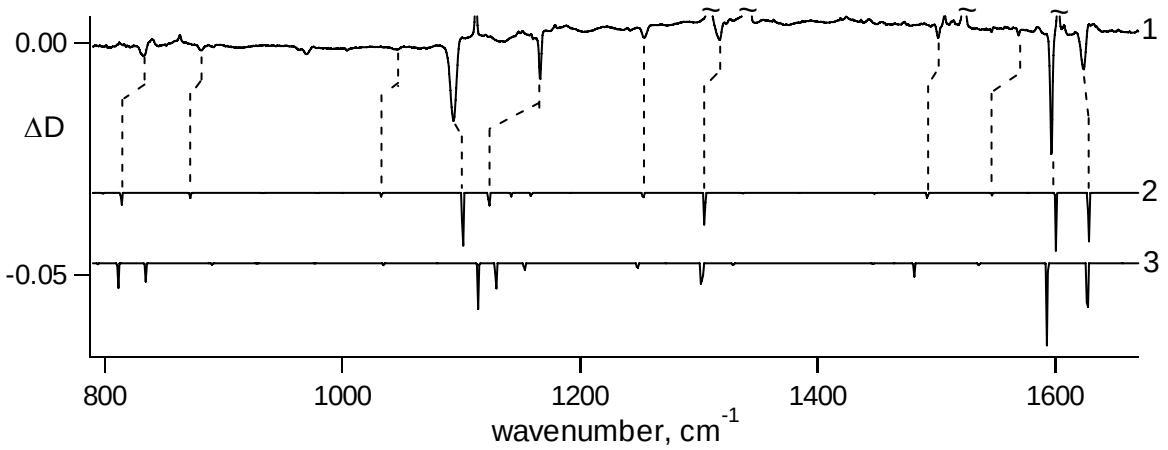

Figure S3

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.

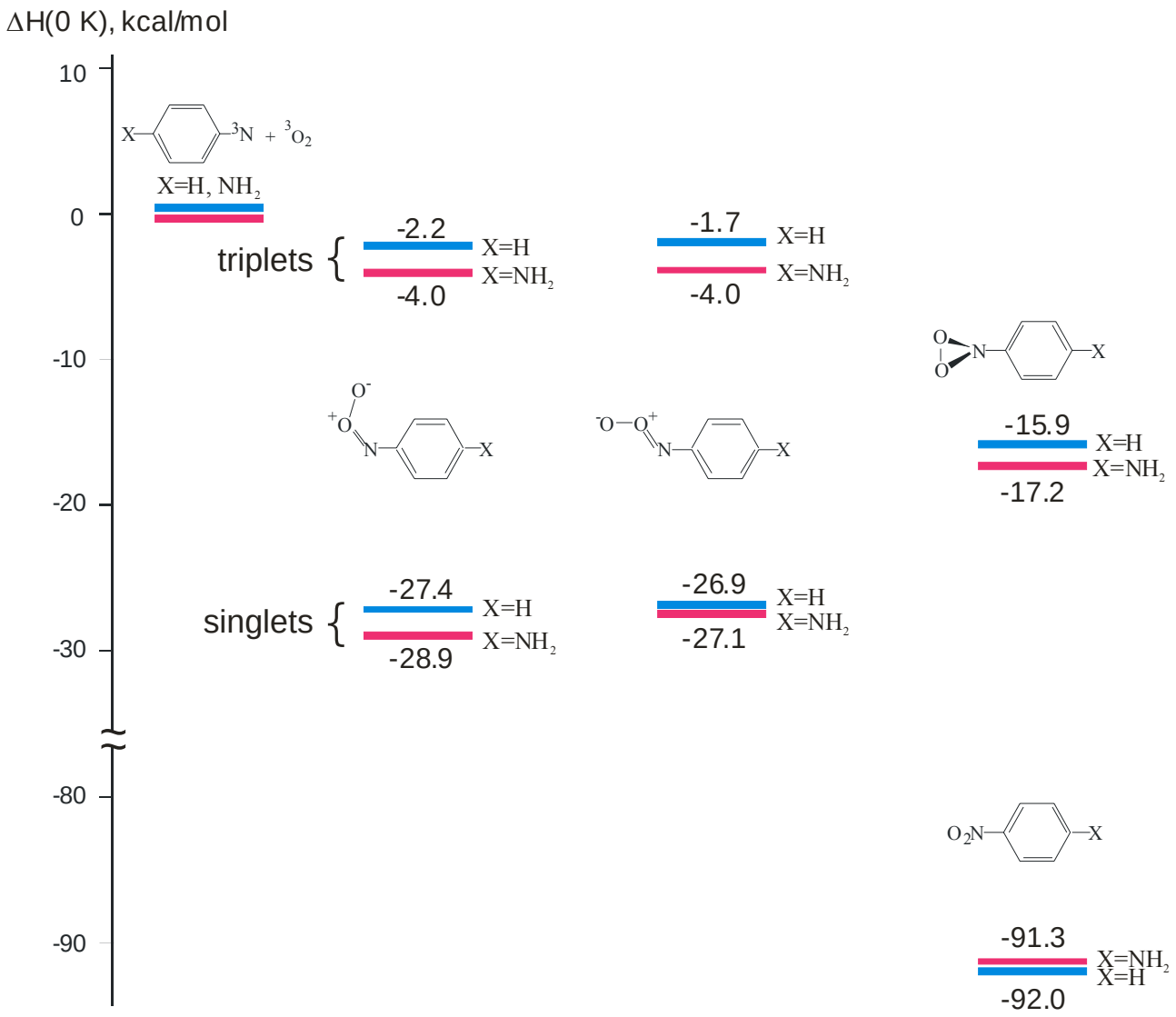

Figure S4

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

Method G2M(CC5, MP2):[a]

$E_{G2M(CC5, MP2)}$ = CCSD(T)/6-311G(d,p) + ΔE(+3d2p) + ΔE(HLC,CC5) + ZPE
ΔE(+3d2p) = E[PMP2/6-311+G(3df,2p)] - E[PMP2/6-311G(d,p)]
$\Delta E(HLC,CC5) = [-5{,}30n_\beta - 0{,}19n_\alpha]/1000$

[a]A.M. Mebel, K. Morokuma, M.C. Lin. *J. Chem. Phys*., 1995, **103**, 7414.

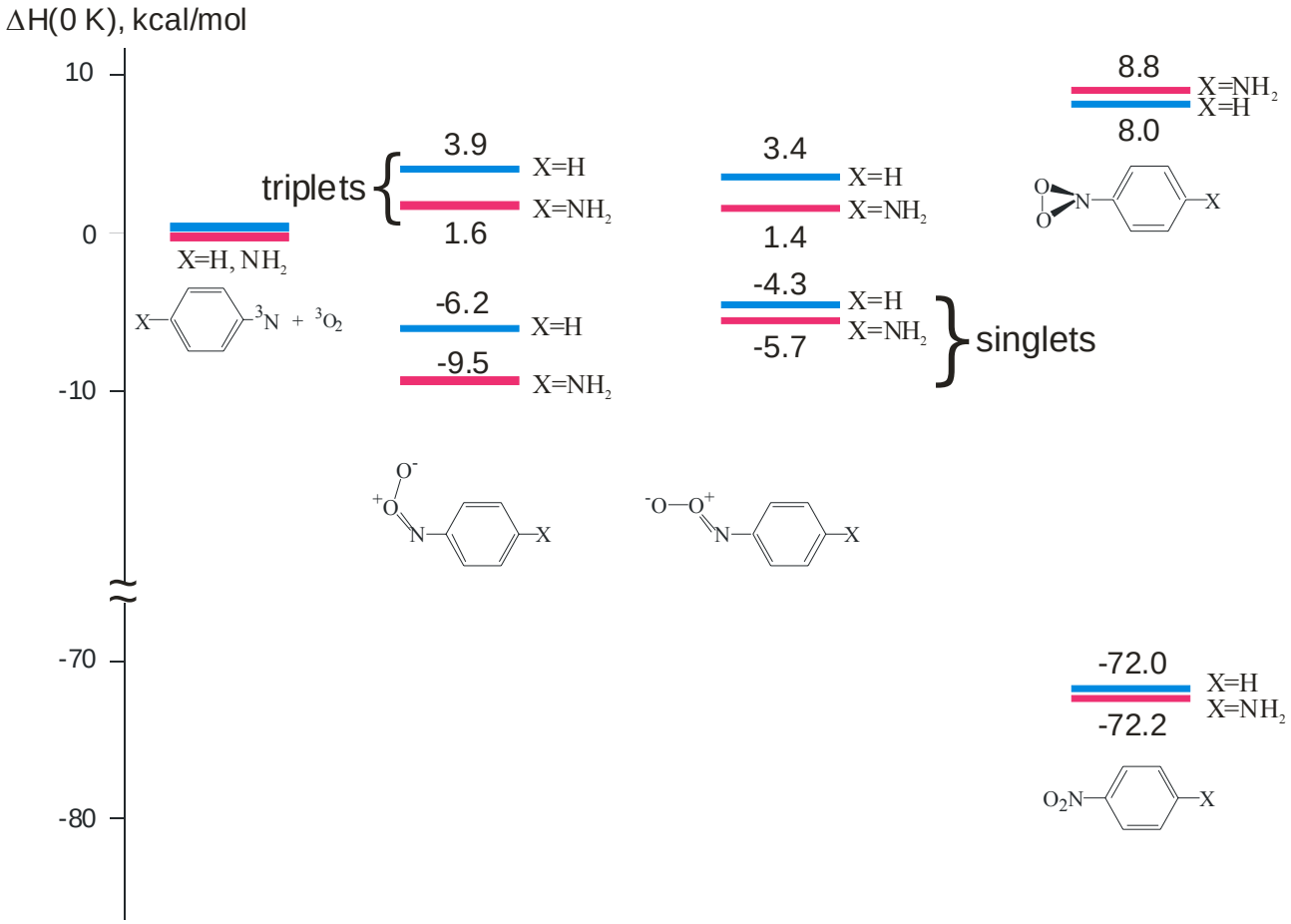

Figure S5

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.

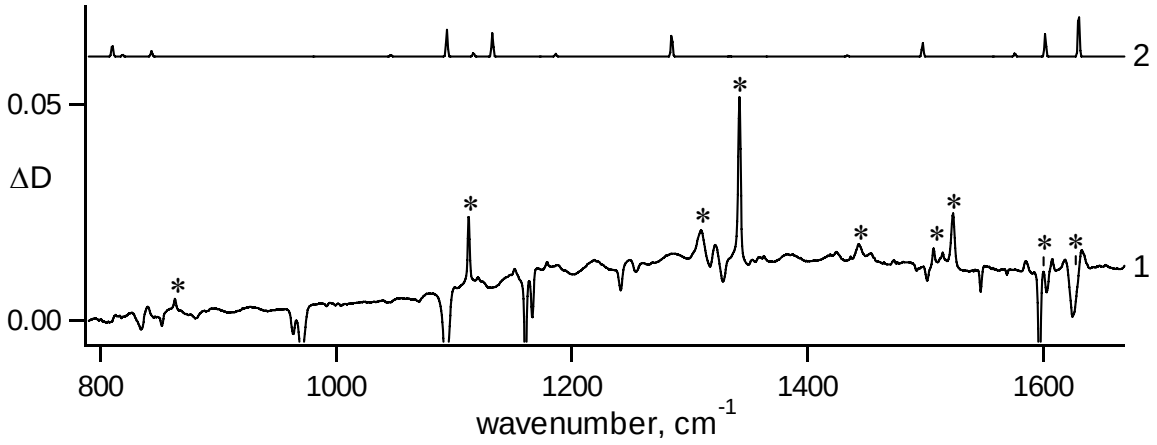

Figure S6

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.

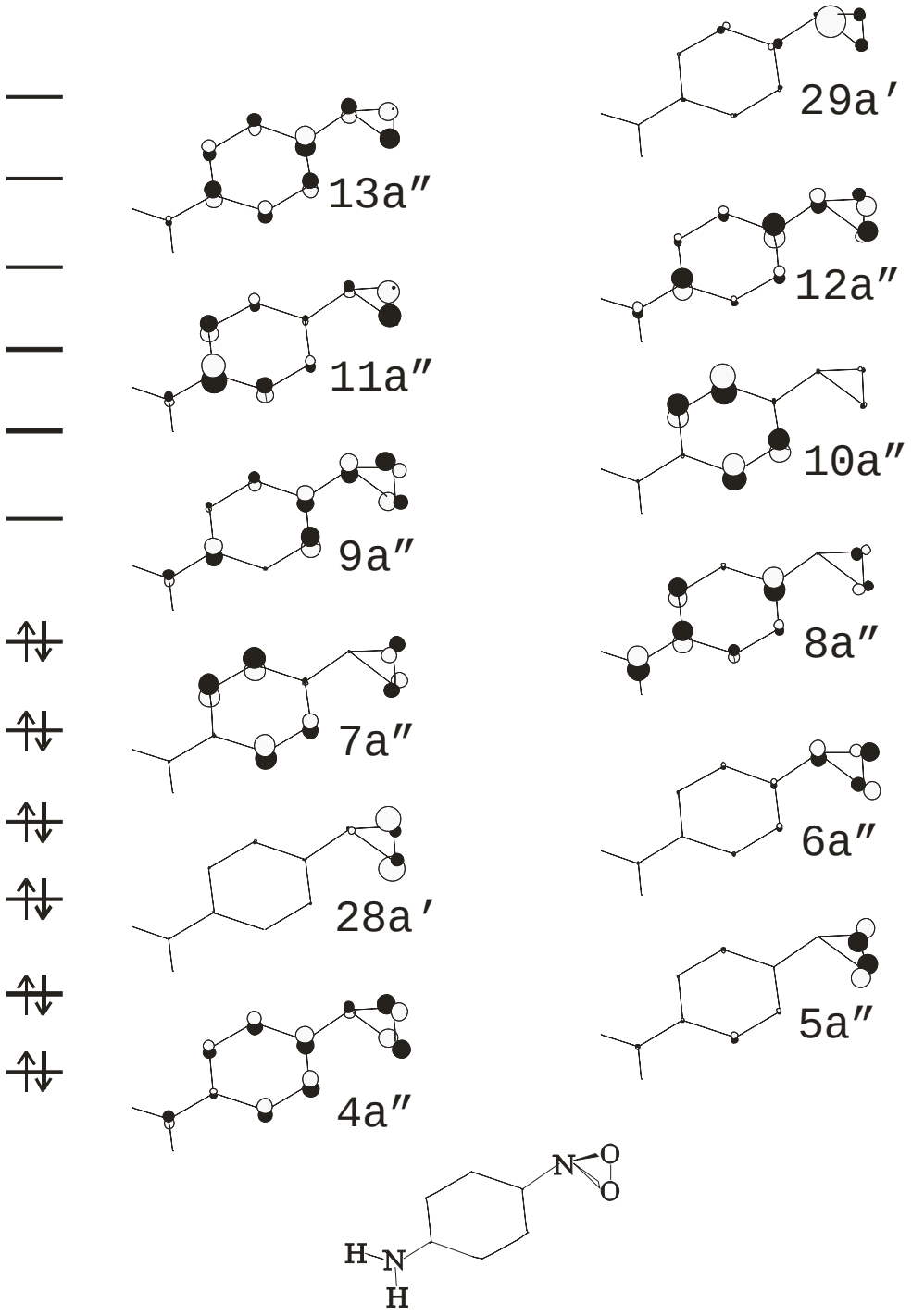

Figure S7

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