Supplementary Information: Theoretical study of the photochemistry and photophysics of aniline using *ab-initio* electronic structure calculations

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S1 CASSCF optimized orbitals

Fig. S1 displays the SA5-CASSCF optimized orbitals at the Franck-Condon (FC) geometry calculated with the CAS2 active space.

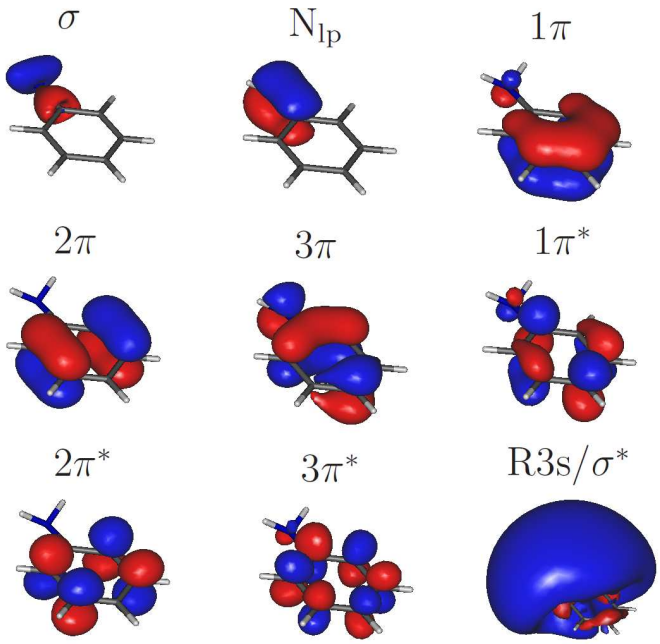

Fig. S1 Orbitals included in the CAS1 and CAS2 active spaces

We present in Tab. S1 the expansion coefficients of the main configurations for each state in the same calculation. We observe that the ground state and the two $\pi\sigma^*$ state wavefunctions are dominated by a single excitation whereas the two $\pi\pi^*$ states have a significant multireference character.

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Table S1 Wavefuction expansion coefficient of the main configurations for each state obtained from a SA5-CASSCF calculation using the CAS2 active space.

Symmetry	State	coefficients
A'	GS	0.94.(ref)
A''	$1\pi\pi^*$	$0.67(2\pi \rightarrow 1\pi^*) + 0.57(3\pi \rightarrow 2\pi^*)$
A'	$1\pi\sigma^*$	$0.92(3\pi \rightarrow \mathrm{R3s}/\sigma^*)$
A'	$2\pi\pi^*$	$0.81(3\pi \rightarrow 1\pi^*) - 0.36(2\pi \rightarrow 2\pi^*)$
A''	$2\pi\sigma^*$	$0.91(2\pi \rightarrow \mathrm{R3s}/\sigma^*)$

S2 Transition states imaginary frequencies and associated normal modes

In this section, we report the values of the imaginary frequencies at the four transition state structures optimized in this work (see Tab. S2), and display the displacement vectors associated with the corresponding normal modes in Fig. S2.

Table S2 Values of the imaginary frequencies (in cm^{-1}) at the four transition state structures optimized in this work.

$TS^1_{1\pi\pi^*/GS}$	$TS^4_{1\pi\pi^*/GS}$	$TS_{\pi\sigma^*}$	TS_{Dew}
-322.8	-329.2	-2435.2	-429.0

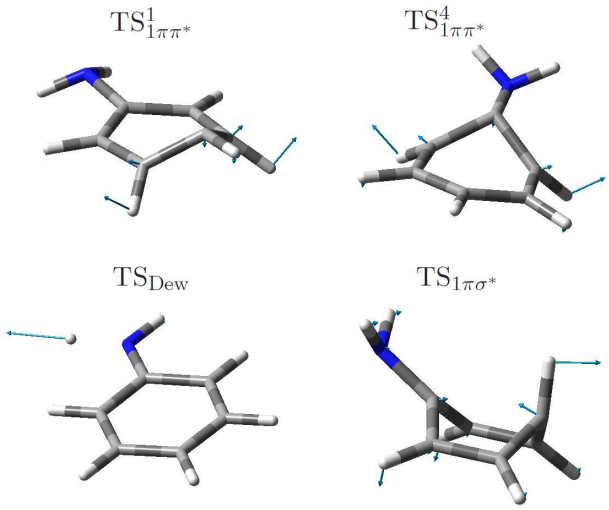

Fig. S2 Displacement vectors associated with the imaginary frequency normal modes for the four transition state structures optimized in this work.

S3 Branching plane vectors for the optimized minimum energy conical intersections

We show in Fig. S3 the derivative coupling and gradient difference vectors associated with all the minimum energy conical intersection structures optimized in this work.

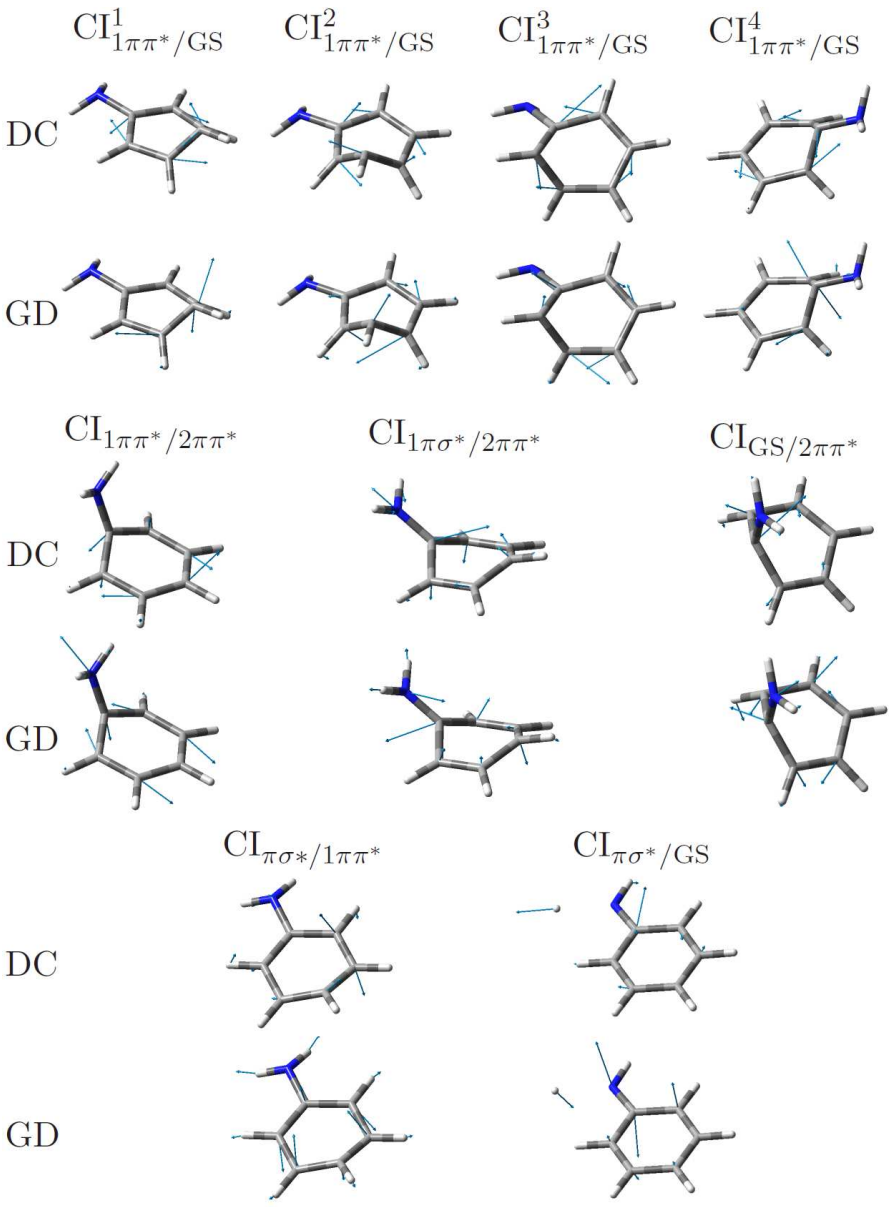

Fig. S3 Derivative coupling (DC) and gradient difference (GD) vectors for the minimum energy conical intersection optimized in this work.

S4 Cartesian coordinates and geometrical parameters

In this section, we provide cartesian coordinates (tables S3–S19) and relevant geometrical parameters (tables S20–S22) for all the stationary points (minima, transition states and minimum energy conical intersections) optimized in this work.

Table S3 Cartesian coordinates of the ground state equilibrium geometry (Min_{GS}) optimized with SS-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	-1.870536	0.000002	-0.001205
C2	-1.163973	1.201614	-0.001846
C3	0.229173	1.203776	-0.005204
C4	0.941415	-0.000015	-0.011824
C5	0.229157	-1.203799	-0.005160
C6	-1.163986	-1.201621	-0.001816
N7	2.344791	-0.000038	0.053612
H8	0.764622	2.137782	0.005951
H9	0.764599	-2.137807	0.006045
H10	-1.693166	-2.138103	0.001446
H11	-2.945471	0.000008	0.001032
H12	-1.693140	2.138104	0.001392
H13	2.760786	0.816718	-0.337551
H14	2.760775	-0.816643	-0.337875

Table S4 Cartesian coordinates of the $1\pi\pi^*$ state equilibrium geometry ($Min_{1\pi\pi^*}$) optimized with SS-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	-1.886185	0.000193	0.015637
C2	-1.181842	1.243506	0.015032
C3	0.250287	1.246237	0.010113
C4	0.955832	-0.000095	-0.004011
C5	0.250021	-1.246287	0.009735
C6	-1.182086	-1.243255	0.014642
N7	2.339202	-0.000254	0.060508
H8	0.797612	2.169898	0.029834
H9	0.797151	-2.170069	0.029158
H10	-1.724250	-2.169030	0.020147
H11	-2.960430	0.000296	0.022014
H12	-1.723815	2.169388	0.020842
H13	2.784155	0.826058	-0.271728
H14	2.783970	-0.826587	-0.271921

Table S5 Cartesian coordinates of the $CI^{1}_{1\pi\pi^*/GS}$ geometry optimized with SA2-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	0.080865	0.043654	-0.796651
C2	0.135997	1.172070	0.119065
C3	1.294071	2.065421	0.166885
C4	2.540599	1.441914	0.110358
C5	2.436259	0.052292	0.172731
C6	1.075450	-0.483739	0.123966
N7	3.760211	2.133464	-0.017112
H8	1.164753	3.126482	0.279218
H9	3.280469	-0.602499	0.289976
H10	0.831456	-1.344509	0.724411
H11	-0.850291	-0.485002	-0.914172
H12	-0.729584	1.406838	0.716263
H13	3.723968	3.050416	0.374298
H14	4.527515	1.634277	0.379596

Table S6 Cartesian coordinates of the $TS^{1}_{1\pi\pi^*/GS}$ geometry optimized with SS-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	0.062294	0.033485	-0.705081
C2	0.074791	1.279878	0.048835
C3	1.282746	2.078940	0.151458
C4	2.521641	1.430912	0.096863
C5	2.442133	0.035171	0.156957
C6	1.136637	-0.592075	0.054178
N7	3.747308	2.125687	-0.005481
H8	1.203562	3.141678	0.300625
H9	3.313419	-0.577432	0.310251
H10	0.933421	-1.465457	0.652729
H11	-0.871753	-0.496558	-0.784336
H12	-0.780690	1.556252	0.643919
H13	3.702147	3.036950	0.399242
H14	4.504083	1.623650	0.408675

Table S7 Cartesian coordinates of the $CI^{2}_{1\pi\pi^*/GS}$ geometry optimized with SA2-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	0.273121	0.001575	0.074748
C2	0.068374	1.441072	-0.012445
C3	1.207234	2.228482	0.104164
C4	2.390958	1.486982	0.086104
C5	2.231813	0.035049	0.143164
C6	1.233645	-0.564158	1.013860
N7	3.662780	2.047184	-0.005975
H8	1.189954	3.302361	0.139402
H9	2.904485	-0.588464	-0.424795
H10	1.246588	-1.627227	1.181041
H11	-0.330300	-0.659529	-0.525358
H12	-0.909284	1.840294	-0.207669
H13	3.716552	2.866185	-0.571379
H14	4.385820	1.401277	-0.231635

Table S8 Cartesian coordinates of the $CI^{3}_{1\pi\pi^*/GS}$ geometry optimized with SA2-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	0.067266	0.112545	-0.129845
C2	-0.108072	1.455514	0.152536
C3	1.104194	2.153645	0.242590
C4	2.313486	1.341422	0.168974
C5	2.392183	0.052776	0.859933
C6	1.472049	-0.340594	-0.188813
N7	3.468684	1.945475	-0.363443
H8	1.187149	3.222840	0.294820
H9	3.352646	-0.435113	0.913946
H10	1.766679	-1.066015	-0.929190
H11	-0.741798	-0.576379	-0.289428
H12	-1.067859	1.920663	0.274715
H13	3.362986	2.259603	-1.304548
H14	4.287452	1.384810	-0.279202

Table S9 Cartesian coordinates of the $CI^{4}_{1\pi\pi^*/GS}$ geometry optimized with SA2-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	-0.047556	-0.028034	-0.272743
C2	-0.008951	1.343889	-0.026915
C3	1.312586	1.883742	0.282678
C4	2.475124	1.454037	-0.487677
C5	2.284549	0.229918	0.283704
C6	1.169469	-0.661838	-0.024843
N7	3.682892	2.164026	-0.346938
H8	1.436111	2.651590	1.028031
H9	3.015158	-0.035025	1.029628
H10	1.286452	-1.728685	0.016301
H11	-0.940260	-0.552751	-0.557804
H12	-0.883865	1.965585	0.012624
H13	3.625749	3.073200	-0.756821
H14	4.449589	1.671534	-0.756194

Table S10 Cartesian coordinates of the $TS^{4}_{1\pi\pi^*/GS}$ geometry optimized with SS-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	-0.022385	-0.013311	-0.258611
C2	-0.011309	1.367674	-0.029169
C3	1.263665	2.021932	0.194443
C4	2.465362	1.448553	-0.415440
C5	2.381267	0.120101	0.195254
C6	1.189357	-0.675493	-0.028308
N7	3.677812	2.161108	-0.281438
H8	1.350195	2.812401	0.921885
H9	3.113679	-0.188514	0.923150
H10	1.241261	-1.746855	0.046263
H11	-0.926456	-0.544685	-0.490107
H12	-0.922037	1.934407	0.044716
H13	3.617333	3.066293	-0.700055
H14	4.439302	1.667580	-0.699552

Table S11 Cartesian coordinates of the equilibrium geometry of the quasi-bound well of the R3s/1$\pi\sigma^*$ state Min$_{\pi\sigma^*}$ geometry optimized with SS-CASSCF using the CAS2 active space.

Atom	x	y	z
C1	2.419687	1.425600	-0.000059
C2	1.191012	2.125198	0.000068
C3	-0.002050	1.447720	0.000229
C4	-0.000001	0.003311	0.000264
C5	1.261012	-0.701085	0.000136
C6	2.433269	0.011759	-0.000024
N7	-1.122080	-0.656246	0.000407
H8	-0.943945	1.961902	0.000328
H9	1.252094	-1.774154	0.000165
H10	3.370934	-0.511754	-0.000123
H11	3.345150	1.969573	-0.000183
H12	1.189709	3.199106	0.000039
H13	-2.022785	-0.198065	0.000492
H14	-1.159857	-1.666073	0.000428

Table S12 Cartesian coordinates of the transition state on the R3s/1$\pi\sigma^*$ state TS$_{\pi\sigma^*}$ geometry optimized with SS-CASSCF using the CAS2 active space.

Atom	x	y	z
C1	2.426057	1.426807	0.000003
C2	1.194585	2.119909	0.000083
C3	0.000540	1.439727	0.000110
C4	-0.007916	-0.011449	0.000289
C5	1.269774	-0.702323	0.000130
C6	2.441837	0.011234	-0.000034
N7	-1.143090	-0.639941	0.000526
H8	-0.943889	1.947274	0.000215
H9	1.273678	-1.777272	-0.000043
H10	3.382246	-0.509231	-0.000271
H11	3.350985	1.972220	-0.000065
H12	1.192003	3.194559	0.000101
H13	-2.317065	-0.071072	0.000367
H14	-1.130682	-1.645310	0.000755

Table S13 Cartesian coordinates of CI$_{\pi\sigma*/1\pi\pi^*}$ geometry optimized with SA2-CASSCF using the CAS2 active space.

Atom	x	y	z
C1	2.405221	1.417702	-0.142856
C2	1.206196	2.134852	0.170205
C3	-0.014451	1.416008	0.058134
C4	0.010152	0.009267	0.015284
C5	1.227332	-0.696979	0.047837
C6	2.449728	0.018924	0.159391
N7	-1.117674	-0.652162	-0.273001
H8	-0.948984	1.910038	0.040639
H9	1.204176	-1.753649	0.022822
H10	3.376037	-0.499553	0.172527
H11	3.290345	1.939291	-0.419533
H12	1.203957	3.196252	0.191391
H13	-1.951869	-0.200750	-0.016876
H14	-1.128023	-1.602448	-0.023797

Table S14 Cartesian coordinates of $CI_{\pi\sigma^*/GS}$ geometry optimized with SA2-CASSCF using the CAS2 active space.

Atom	x	y	z
C1	2.461682	1.439253	-0.002750
C2	1.215625	2.096291	-0.002351
C3	0.042180	1.369270	-0.000012
C4	0.050269	-0.055034	0.001964
C5	1.312513	-0.702641	0.001030
C6	2.488760	0.034911	-0.001095
N7	-1.125942	-0.683728	0.004108
H8	-0.912918	1.870049	0.000283
H9	1.352974	-1.780698	0.002298
H10	3.431248	-0.485279	-0.001336
H11	3.378507	2.002309	-0.004337
H12	1.172872	3.171928	-0.003823
H13	-2.761687	0.175084	0.002814
H14	-1.151652	-1.683427	0.005404

Table S15 Cartesian coordinates of $CI_{1\pi\pi^*/2\pi\pi^*}$ geometry optimized with SA2-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	0.374985	-0.000052	-1.649388
C2	0.034003	-1.221032	-1.022338
C3	-0.478645	-1.235382	0.301328
C4	-0.285562	0.000046	1.077764
C5	-0.478436	1.235483	0.301289
C6	0.034209	1.221006	-1.022376
N7	0.603914	-0.000012	2.132210
H8	-1.001896	-2.086084	0.698375
H9	-1.001546	2.086286	0.698309
H10	0.103625	2.141950	-1.575306
H11	0.759333	-0.000100	-2.652079
H12	0.103264	-2.142006	-1.575240
H13	1.116306	-0.839408	2.293550
H14	1.116447	0.839302	2.293524

Table S16 Cartesian coordinates of $CI_{1\pi\sigma^*/2\pi\pi^*}$ geometry optimized with SA2-CASSCF using the CAS2 active space.

Atom	x	y	z
C1	1.193600	-0.000707	0.131577
C2	1.865249	1.259962	-0.205601
C3	3.216698	1.256601	-0.152431
C4	3.705404	0.000105	0.462476
C5	3.217999	-1.255067	-0.156154
C6	1.866555	-1.259679	-0.209321
N7	4.684912	-0.000683	1.336445
H8	3.879764	2.067030	-0.393265
H9	3.881905	-2.064091	-0.399387
H10	1.296231	-2.120425	-0.508870
H11	0.145097	-0.001565	0.344528
H12	1.294032	2.120997	-0.502608
H13	4.939489	-0.845727	1.799107
H14	4.938613	0.843250	1.801609

Table S17 Cartesian coordinates of $CI_{GS/2\pi\pi^*}$ geometry optimized with SA2-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	1.096583	-0.038739	-0.038412
C2	1.866264	1.193797	-0.134350
C3	3.200455	1.208232	0.160264
C4	3.559289	-0.025748	0.887331
C5	3.162215	-1.269233	0.249042
C6	1.749853	-1.261377	0.027892
N7	3.488014	0.008105	2.230273
H8	3.859330	2.034641	-0.033510
H9	3.801107	-1.768550	-0.461956
H10	1.232196	-2.158656	-0.272276
H11	0.039432	0.000219	-0.231708
H12	1.382366	2.073089	-0.526852
H13	3.383528	-0.851518	2.721312
H14	3.276361	0.855739	2.707226

Table S18 Cartesian coordinates of the Dewar local minimum Min_{Dew} geometry optimized with SS-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	1.081891	-0.011213	0.995760
C2	1.828862	1.280402	0.685675
C3	2.543417	1.285945	1.822772
C4	1.943990	-0.004836	2.369443
C5	2.547310	-1.297970	1.832600
C6	1.832537	-1.303165	0.695449
N7	1.476519	-0.000211	3.718188
H8	3.336884	1.909946	2.194443
H9	3.341292	-1.917792	2.209957
H10	1.858517	-1.927710	-0.178879
H11	-0.000594	-0.013383	0.992769
H12	1.851801	1.899949	-0.192220
H13	0.929225	-0.812105	3.920787
H14	0.927621	0.812144	3.914905

Table S19 Cartesian coordinates of the Dewar transition state TS_{Dew} geometry optimized with SS-CASSCF using the CAS1 active space.

Atom	x	y	z
C1	0.046941	0.000108	0.942685
C2	1.029790	0.000077	0.507032
C3	2.326275	1.283283	1.820578
C4	1.934835	-0.000027	2.469407
C5	2.326159	-1.283331	1.820496
C6	1.838731	-1.257070	0.570359
N7	1.682064	-0.000059	3.840746
H8	2.955611	2.023997	2.291884
H9	2.955427	-2.024133	2.291756
H10	2.088666	-1.900224	-0.254629
H11	0.046941	0.000108	0.942685
H12	2.088839	1.900329	-0.254509
H13	1.233504	-0.821519	4.182675
H14	1.233579	0.821422	4.182727

Table S20 Chosen geometrical parameters for C_s symmetry optimized geometries.

	Min_{GS}	$Min_{1\pi\pi^*}$	$CI^1_{1\pi\pi^*/GS}$	$TS^1_{1\pi\pi^*}$	$CI^4_{1\pi\pi^*/GS}$	$TS^4_{1\pi\pi^*}$	$Min_{1\pi\sigma^*}$	$CI_{1\pi\pi^*/1\pi\sigma^*}$
C1-C2	1.394	1.429	1.454	1.457	1.394	1.400	1.414	1.432
C2-C3	1.393	1.432	1.463	1.452	1.461	1.450	1.372	1.421
C3-C4	1.399	1.432	1.395	1.399	1.459	1.465	1.444	1.408
C4-N7	1.405	1.385	1.408	1.413	1.408	1.413	1.302	1.339
N7-H13	0.997	0.996	0.998	0.998	0.999	0.999	1.011	0.982
C6-C2	–	–	1.904	2.152	–	–	–	–
C3-C5	–	–	–	–	1.918	2.206	–	–
C6-C1-C2	119.1	120.9	81.8	95.2	113.1	115.6	120.2	118.0
C1-C2-C3	120.5	119.6	121.6	121.0	115.2	118.5	120.8	116.7
C2-C3-C4	120.5	119.4	115.7	118.6	120.0	118.7	119.5	119.5
C3-C4-C5	118.8	121.0	112.1	114.2	82.2	97.7	119.3	121.1
H13-N7-H14	110.1	112.2	109.4	109.0	108.9	108.6	114.8	111.7
φ^a	43.1	36.9	–	–	–	–	0.0	–

Table S21 Chosen geometrical parameters for C_s symmetry optimized geometries (continued).

	$CI_{1\pi\pi^*/2\pi\pi^*}$	$CI_{1\pi\sigma^*/2\pi\pi^*}$	$q^{IRC} = 2.89$	$q^{IRC} = 5.68$	$q^{IRC} = 12.55$	Min_{Dew}	TS_{Dew}
C1-C2	1.414	1.468	1.463	1.472	1.476	1.524	1.496
C2-C3	1.420	1.352	1.344	1.346	1.346	1.343	1.342
C3-C4	1.472	1.482	1.518	1.521	1.501	1.525	1.490
C4-N7	1.380	1.313	1.346	1.344	1.339	1.427	1.394
N7-H13	0.997	0.996	0.998	0.999	0.997	1.000	0.996
C1-C4	–	–	2.785	2.677	2.300	1.622	2.161
C6-C1-C2	119.4	118.3	119.6	118.3	118.9	115.9	114.3
C1-C2-C3	120.6	116.5	122.4	120.4	113.3	95.3	104.6
C2-C3-C4	115.9	110.4	115.4	112.5	104.0	95.2	107.1
C3-C4-C5	114.1	115.9	121.6	121.2	119.0	115.9	118.9
H13-N7-H14	114.8	115.9	116.4	116.4	116.8	108.6	111.1

[a] φ denotes the dihedral angle between the plane of the amino group and the plane of the phenyl ring. Specifically it is defined here as the angle between the H13–N7–H14 plane and the C2–C3–C4 plane.

Table S22 Chosen geometrical parameters for C_s' and C_1 symmetry optimized geometries.

	$CI^2_{1\pi\pi^*/GS}$	$CI^3_{1\pi\pi^*/GS}$	$TS_{1\pi\sigma^*}$	$CI_{1\pi\sigma^*/GS}$	$CI_{GS/2\pi\pi^*}$
C1-C2	1.458	1.477	1.416	1.405	1.456
C2-C3	1.454	1.450	1.372	1.388	1.366
C3-C4	1.462	1.464	1.453	1.419	1.477
C4-C5	1.397	1.459	1.451	1.424	1.453
C5-C6	1.389	1.402	1.374	1.380	1.430
C6-C1	1.457	1.383	1.413	1.409	1.388
C4-N7	1.393	1.408	1.298	1.334	1.345
N7-H13	0.995	0.996	1.005	1.000	0.995
N7-H14	0.997	0.998	1.305	1.847	0.995
C1-C3	1.960	–	–	–	–
C2-C4	–	1.914	–	–	–
C6-C1-C2	121.0	115.2	120.0	118.9	120.0
C1-C2-C3	84.6	119.4	120.7	121.0	120.7
C2-C3-C4	120.5	82.1	120.3	120.8	109.6
C3-C4-C5	115.6	120.7	118.1	117.5	115.6
C4-C5-C6	113.1	115.9	120.0	121.5	109.5
C5-C6-C1	116.1	112.8	121.0	120.4	118.5
H13-N7-H14	111.4	110.1	116.6	116.2	118.5