Supporting Information

(Total of 13 pages)

for

Toward the Understanding of the Photophysics and Photochemistry of 1-Nitronaphthalene under Solar Radiation: the First Theoretical Evidence of a Photodegradation Intramolecular Rearrangement Mechanism Involving the Triplet States

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Table of Contents

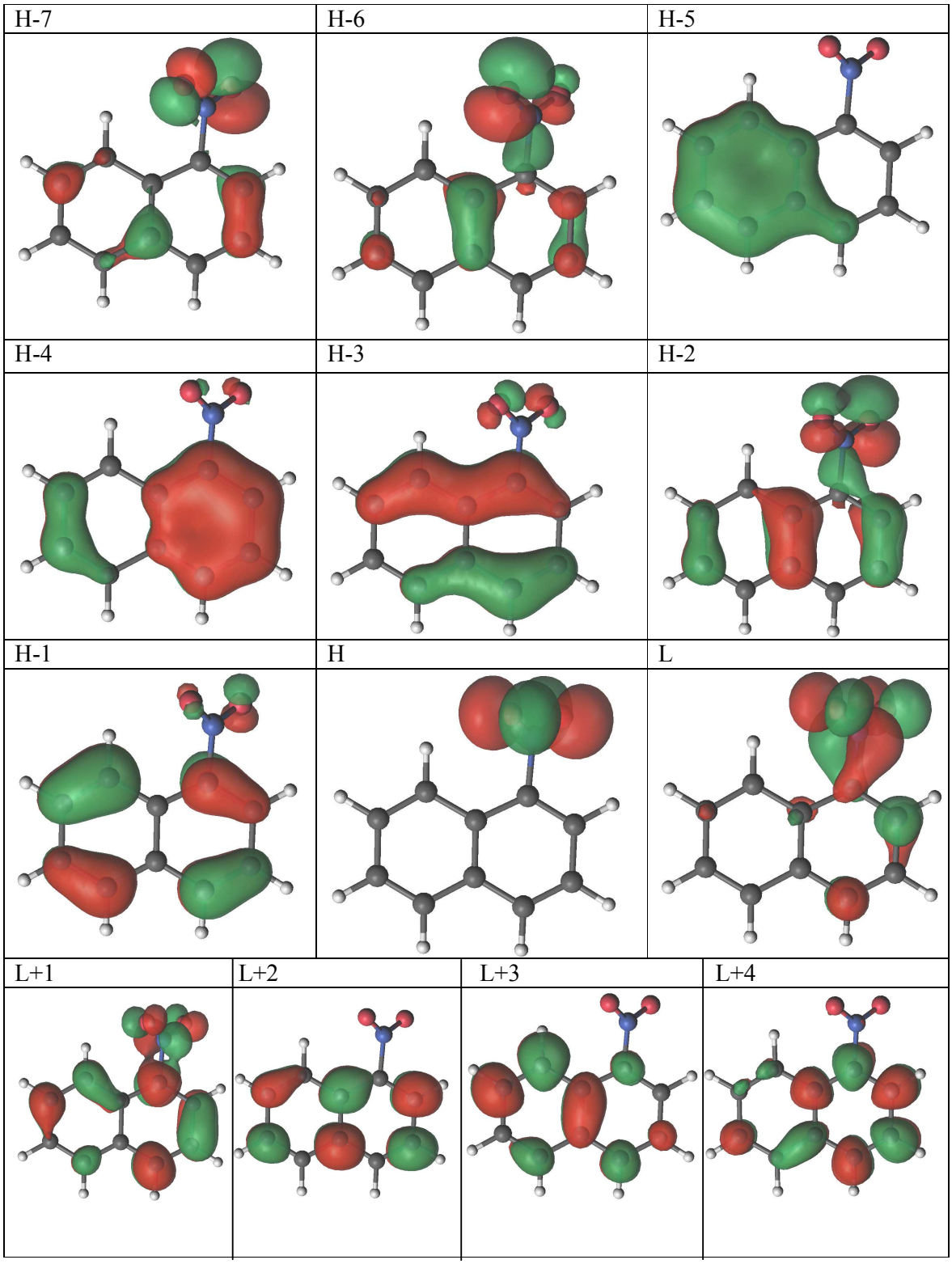

Figure S1. Active orbitals. The labels that identify each orbital have been given accordingly to the topology of the Hartree-Fock orbitals.

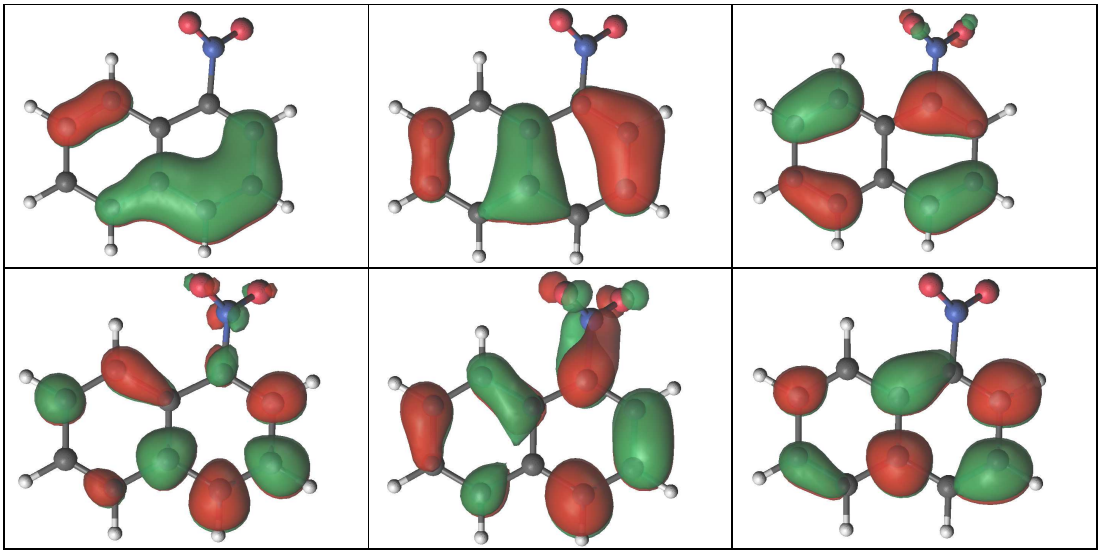

Figure S2. Active orbitals used for the optimization of ππ* states.

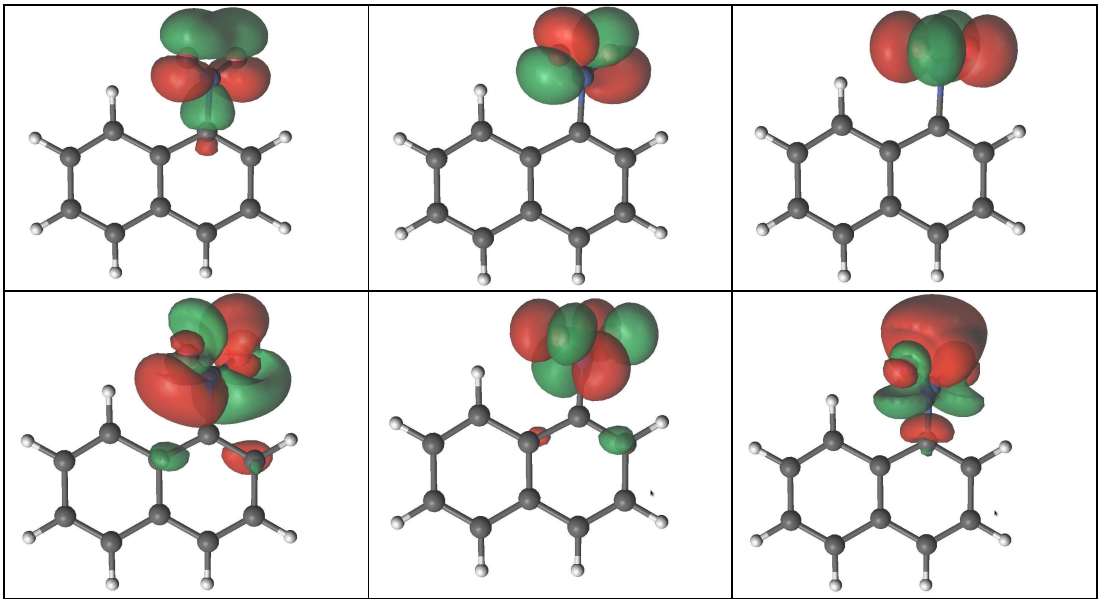

Figure S3. Active orbitals used for the optimization of nπ* states.

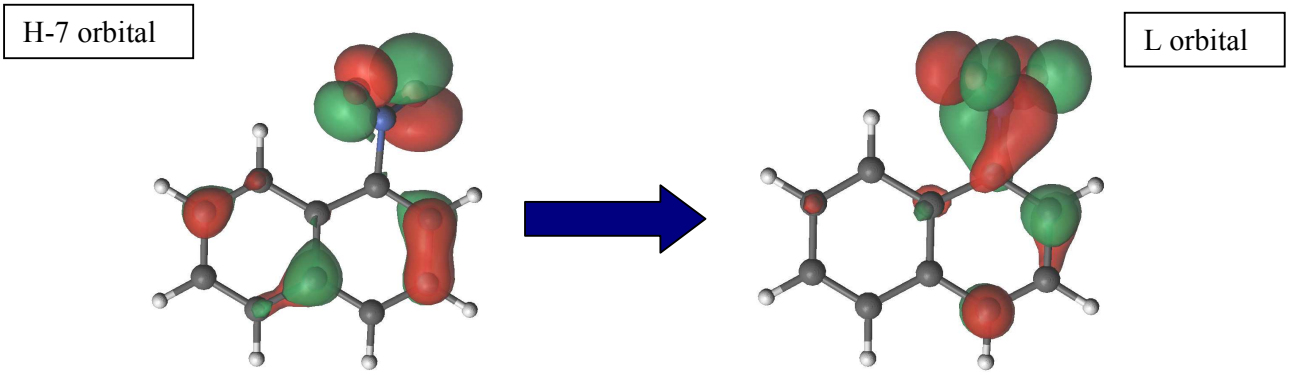

Figure S4. Orbitals mainly involved in the $^{1,3}(n_A\pi^*)$ states.

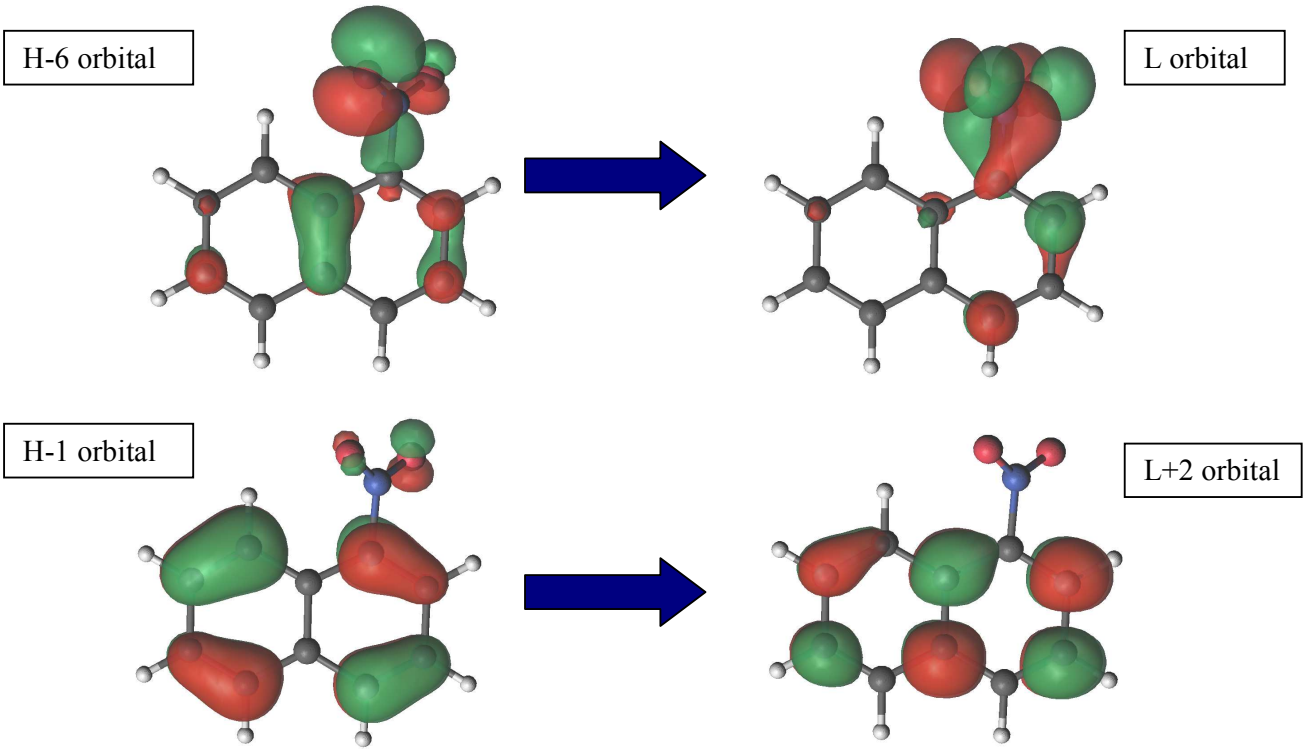

Figure S5. Orbitals mainly involved in the $^{1}(L_b\ \pi\pi^*)$ state.

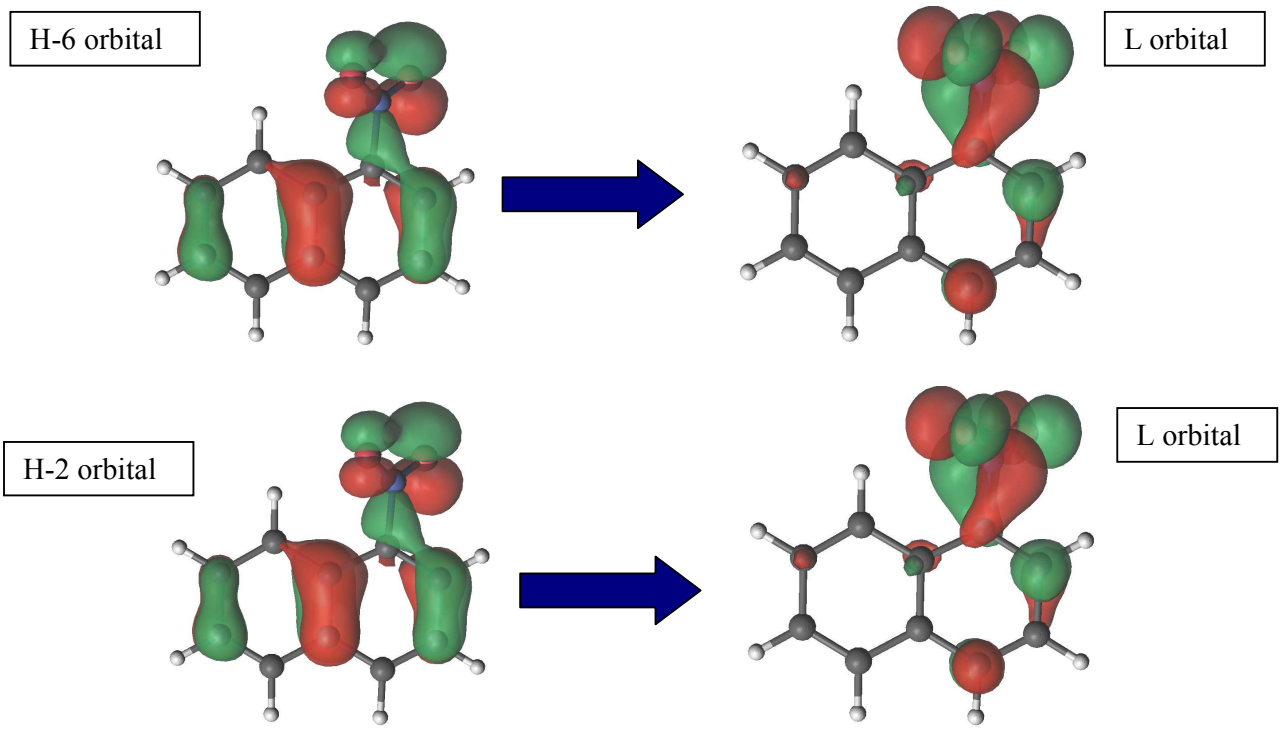

Figure S6. Orbitals mainly involved in the $^{1,3}(n_B\pi^*)$ states.

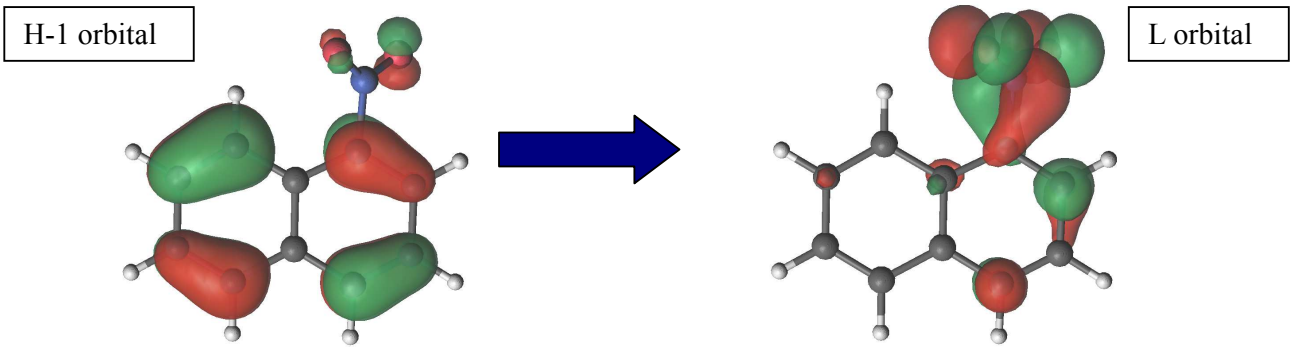

Figure S7. Orbitals mainly involved in the $^{1}(L_a\ \pi\pi^*)$ state.

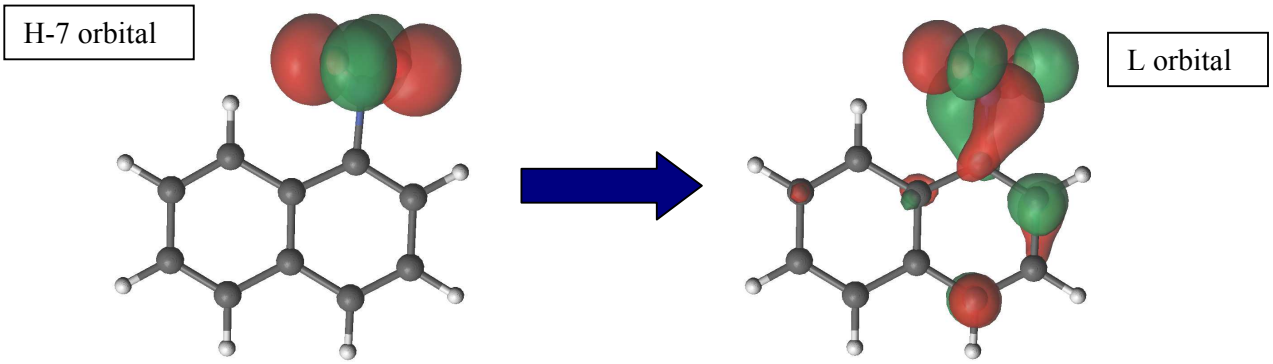

Figure S8. Orbitals mainly involved in the $^3(\pi_O\pi^*)$ state.

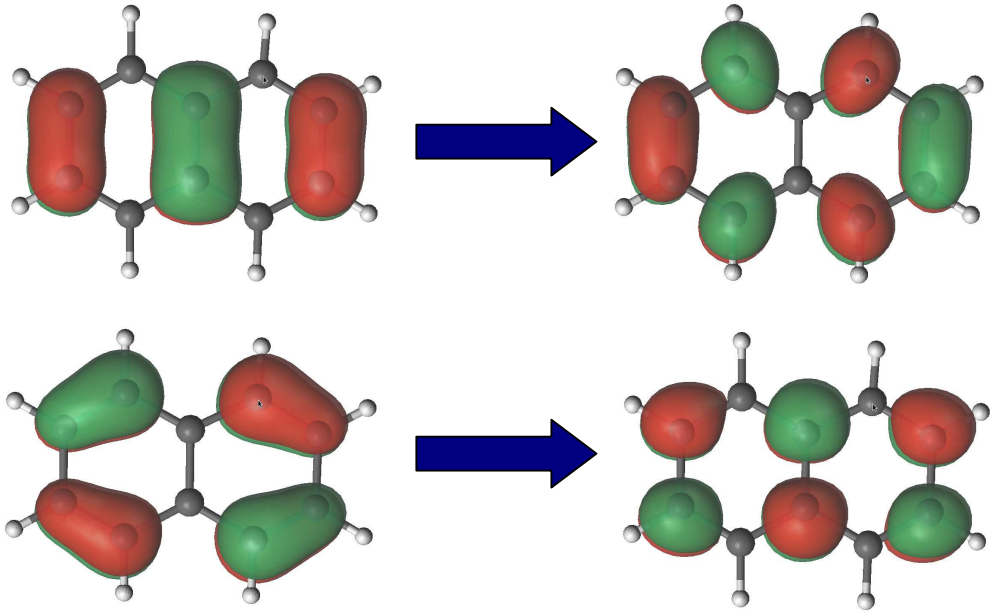

Figure S9. Orbitals mainly involved in the $^1(L_b\ \pi\pi^*)$ state of naphthalene.

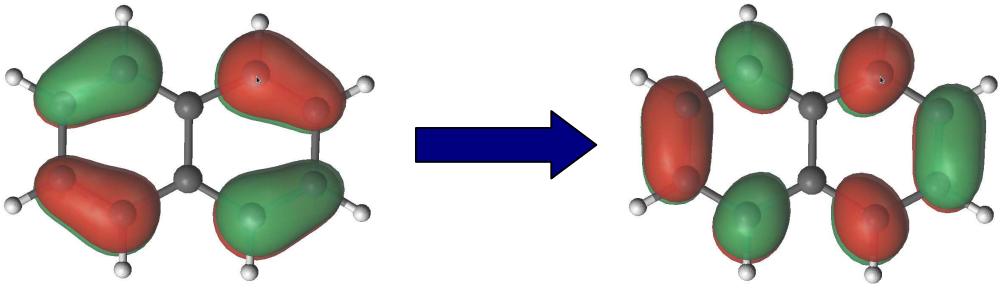

Figure S10. Orbitals mainly involved in the $^1(L_a\ \pi\pi^*)$ state of naphthalene.

Table S1. Configuration state functions mainly contributing in the CASSCF wave functions of the different calculated singlet excited states. The weight is reported in parenthesis. For all the states, all the configurations having a weight equal or greater than 10% are reported.

state	configuration state functions
$^1(n_A\pi^*)$	H-7 → L (45%)
$^1(L_b\pi\pi^*)$	H-6 → L (28%) H-1 → L+2 (20%) H-2 → L+1 (13%)
$^1(n_B\pi^*)$	H-6 → L+1 (10%) H-6 → L (18%) H-1 → L+2 (10%) H-2 → L (27%)
$^1(L_a\pi\pi^*)$	H-1 → L+1 (27%) H-1 → L (36%)

Table S2. Configuration state functions mainly contributing in the CASSCF wave functions of the different calculated triplet excited states. The weight is reported in parenthesis. For all the states, all the configurations having a weight equal or greater than 10% are reported.

state	configuration state functions
$^3(\pi\pi^*)$	H-1 → L+1 (38%) H-1 → L (16%)
$^3(n_A\pi^*)$	H-6 → L (15%) H-7 → L(36%)
$^3(\pi_O\pi^*)$	H → L (78%)
$^3(\pi\pi^*)$	H-1 → L+2 (25%) H-6 → L+1 (31%)
$^3(n_B\pi^*)$	H-2 → L (65%)

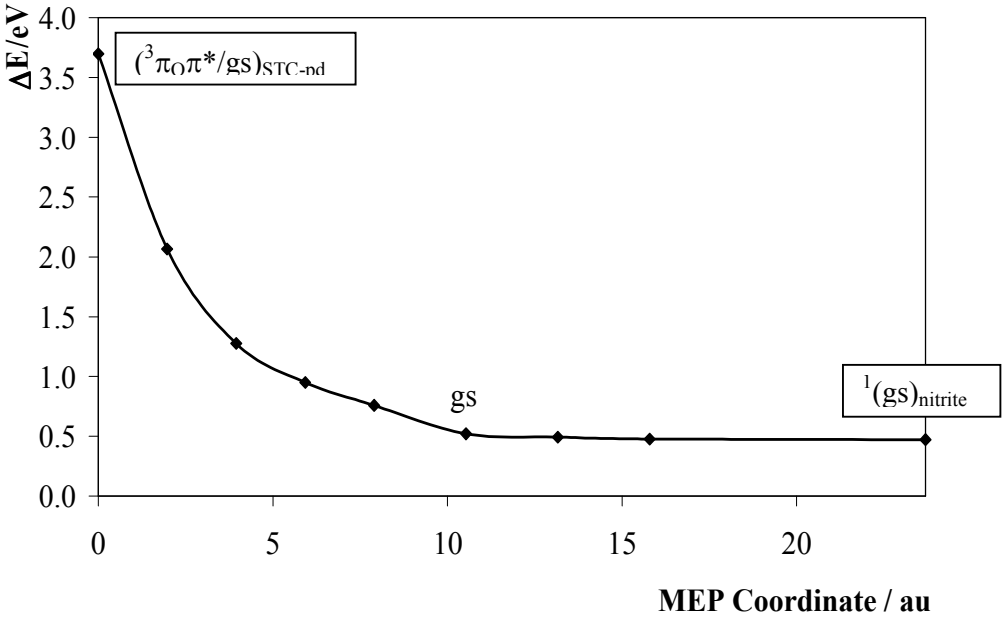

Figure S11. MEP on the gs state from the $(^3\pi_O\pi^*/gs)_{STC\text{-}pd}$ geometry computed at the CASPT2(16,13)///CASSCF(6,6)/ANO-L C,N[4s,3p,1d]/H[2s1p] level.

Table S3. Cartesian coordinates x, y, z (in Å) of the optimized structures for the 1-nitronaphthalene molecule.

$^1(gs)_{min}$

C1	-1.05734	0.22732	0.02228
C2	-1.42512	1.53805	0.05757
C3	-0.42024	2.53759	0.10612
C4	0.88286	2.18426	0.09081
C5	2.65568	0.46363	-0.01982
C6	3.03723	-0.82899	-0.09930
C7	2.05907	-1.85860	-0.13794
C8	0.72706	-1.55697	-0.08649
C9	1.27909	0.82025	0.02626
C10	0.30299	-0.19881	0.00096
N11	-2.13887	-0.76190	0.00624
O12	-2.09445	-1.65229	0.80491
O13	-3.02833	-0.59886	-0.80958
H14	-2.46301	1.80636	0.05712
H15	-0.70948	3.57038	0.15297
H16	1.64763	2.93881	0.12267
H17	3.38999	1.24814	0.00582
H18	4.07979	-1.08580	-0.13532
H19	2.37089	-2.88424	-0.20365
H20	0.00092	-2.34281	-0.10132

$^1(L_a\pi\pi^*)_{min}$

C1	-1.06482	0.16123	-0.00175
C2	-1.42410	1.57556	0.03100
C3	-0.48561	2.59532	0.04817
C4	0.91424	2.20036	0.03751
C5	2.61441	0.47490	-0.00787
C6	3.06746	-0.90378	-0.04167
C7	2.15271	-1.87540	-0.06313
C8	0.75384	-1.56559	-0.05280
C9	1.28099	0.81602	0.00353
C10	0.27929	-0.24887	-0.01928
N11	-2.16318	-0.72912	-0.01022
O12	-1.96868	-1.91211	-0.05137
O13	-3.26859	-0.25673	0.02530
H14	-2.46790	1.80515	0.03942
H15	-0.78219	3.62246	0.07122
H16	1.69217	2.93800	0.05219
H17	3.34904	1.25884	0.00882
H18	4.12016	-1.11175	-0.04899
H19	2.44045	-2.90958	-0.08858
H20	0.05665	-2.36940	-0.07120

$^1(n_A\pi^*)_{min}$

C1	-1.027444	0.180972	0.006536
C2	-1.412905	1.477047	0.074700
C3	-0.434261	2.494943	0.108618
C4	0.882189	2.173934	0.083039
C5	2.676372	0.475523	-0.018844
C6	3.061665	-0.822144	-0.096154
C7	2.090610	-1.848322	-0.145611
C8	0.767135	-1.551245	-0.112951
C9	1.302420	0.821981	0.014272
C10	0.339062	-0.201890	-0.032329
N11	-2.014196	-0.863687	-0.032887
O12	-2.381889	-1.457872	0.976350
O13	-3.138992	-0.486210	-0.886354
H14	-2.454520	1.729219	0.102235
H15	-0.745696	3.521250	0.160585
H16	1.628682	2.946579	0.113037
H17	3.409426	1.260676	0.017787
H18	4.105029	-1.076762	-0.120771
H19	2.406654	-2.873269	-0.207436
H20	0.037004	-2.335194	-0.143503

$^3(\pi_O\pi^*)_{min}$

C1	-1.041772	0.202329	-0.037594
C2	-1.410076	1.502434	0.023351
C3	-0.423419	2.511669	0.085290
C4	0.889830	2.181090	0.093333
C5	2.667527	0.467818	0.014803
C6	3.046848	-0.830752	-0.074041
C7	2.069865	-1.847767	-0.163523
C8	0.748397	-1.540206	-0.151587
C9	1.295813	0.824747	0.023990
C10	0.324225	-0.190250	-0.052209
N11	-2.043331	-0.830888	-0.111957
O12	-2.177680	-1.588011	0.982867
O13	-3.207211	-0.511216	-0.611385
H14	-2.448530	1.769390	0.019150
H15	-0.728503	3.540150	0.133488
H16	1.643048	2.945754	0.146857
H17	3.404561	1.247579	0.078008
H18	4.088887	-1.092056	-0.080004
H19	2.378640	-2.873854	-0.241031
H20	0.019223	-2.322430	-0.217487

$(^1n_A\pi^*/^3\pi_O\pi^*)_{STC}$

C1	-1.03689	0.17847	0.01937
C2	-1.40903	1.58722	0.04167
C3	-0.50855	2.57381	0.10628
C4	0.93371	2.18723	0.09114
C5	2.60497	0.47454	-0.01745
C6	3.03801	-0.91346	-0.10634
C7	2.12185	-1.86915	-0.13888
C8	0.73135	-1.53920	-0.07999
C9	1.28271	0.85592	0.02834
C10	0.26066	-0.20233	0.01093
N11	-2.13045	-0.75278	0.00086
O12	-2.09379	-1.65787	0.77962
O13	-3.00466	-0.58673	-0.76869
H14	-2.45943	1.81070	0.03982
H15	-0.78956	3.60126	0.17247
H16	1.69230	2.94328	0.11331
H17	3.36423	1.23700	0.01216
H18	4.08821	-1.12342	-0.14315
H19	2.39501	-2.90268	-0.20479
H20	0.01568	-2.33627	-0.09635

$(^3\pi_O\pi^*/gs)_{STC}$

C1	0.371739	-0.289461	0.062878
C2	-1.097050	0.029980	0.113064
C3	-1.477719	1.462026	0.269531
C4	-0.521855	2.456753	0.155427
C5	0.822394	2.151323	-0.013393
C6	1.289732	0.767602	-0.017369
C7	0.813442	-1.602636	0.076061
C8	2.174538	-1.880126	-0.025361
C9	3.081128	-0.846647	-0.126507
C10	2.647788	0.464896	-0.127830
N11	-1.971378	-0.772713	-0.683505
O12	-3.040439	-0.012008	-1.105669
O13	-1.959164	-0.870677	0.734666
H14	-2.460939	1.649597	0.649694
H15	-0.818636	3.483436	0.268902
H16	1.547928	2.936393	-0.111189
H17	3.361042	1.264896	-0.209820
H18	4.131624	-1.058279	-0.208517
H19	2.511761	-2.899936	-0.025613
H20	0.101395	-2.401760	0.151161

$(^3\pi_O\pi^*/gs)_{STC\text{-}pd}$

C1	0.37174	-0.28946	0.06288
C2	-1.09705	0.02998	0.11306
C3	-1.47772	1.46203	0.26953
C4	-0.52185	2.45675	0.15543
C5	0.82239	2.15132	-0.01339
C6	1.28973	0.76760	-0.01737
C7	0.81344	-1.60264	0.07606
C8	2.17454	-1.88013	-0.02536
C9	3.08113	-0.84665	-0.12651
C10	2.64779	0.46490	-0.12783
N11	-1.97138	-0.77271	-0.68351
O12	-3.04044	-0.01201	-1.10567
O13	-1.95916	-0.87068	0.73467
H14	-2.46094	1.64960	0.64969
H15	-0.81864	3.48344	0.26890
H16	1.54793	2.93639	-0.11119
H17	3.36104	1.26490	-0.20982
H18	4.13162	-1.05828	-0.20852
H19	2.51176	-2.89994	-0.02561
H20	0.10139	-2.40176	0.15116

^{1}(gs)$_{nitrite}$ CASPT2//CASSCF(16,13)/ANO-L C,N [4s,3p,1d]/H[2s1p]

C	0.32398	-0.16571	0.16468
C	-1.02703	0.22845	0.36160
C	-1.39999	1.53962	0.43139
C	-0.41852	2.55113	0.29601
C	0.89446	2.21336	0.09508
C	1.29176	0.85026	0.02756
C	0.73278	-1.53063	0.11125
C	2.04709	-1.84801	-0.08059
C	3.02147	-0.81894	-0.22652
C	2.65597	0.47754	-0.17219
N	-2.62969	-1.25988	-0.54086
O	-2.29047	-0.78998	-1.57986
O	-1.98931	-0.75412	0.54790
H	-2.43113	1.79112	0.59120
H	-0.71263	3.58247	0.35216
H	1.64155	2.97885	-0.00902
H	3.39107	1.25485	-0.27899
H	4.05153	-1.08519	-0.37752
H	2.35311	-2.87691	-0.11904
H	0.00134	-2.30563	0.23236