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

Supporting Information
(Total of 10 pages)
for

Similar chemical structures, dissimilar triplet quantum yields; CASPT2 model rationalizing the trend of triplet quantum yield in nitroaromatic systems.

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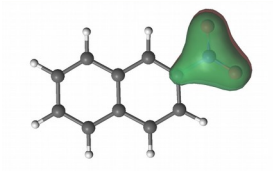	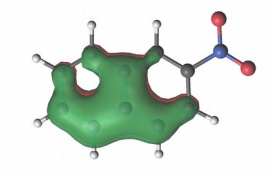	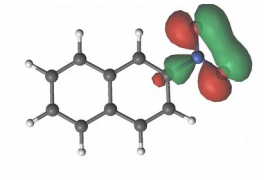	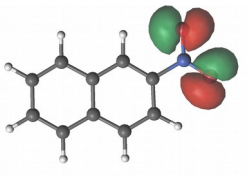
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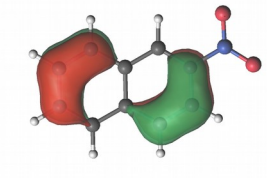	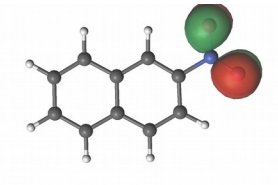	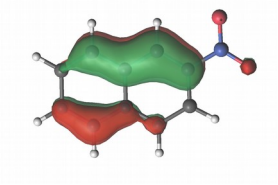	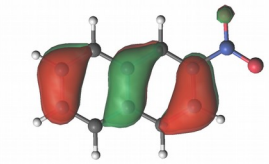
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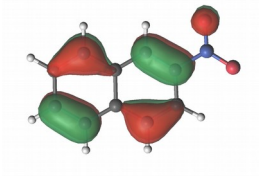	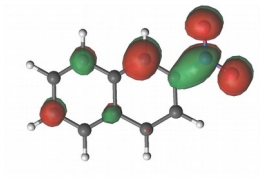	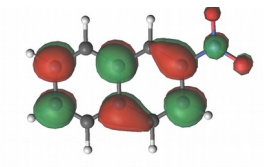	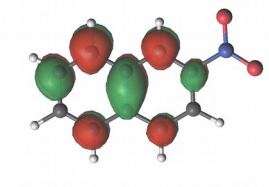
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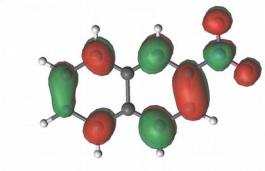		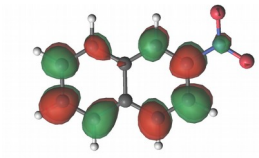	

Figure S1. CAS(18,14) active space for 2NN, labeled accordingly to the topology of the Hartree-Fock orbitals. Topologically equivalent orbitals were used for 1NN and 2M1NN.

Tabla S1. Main configuration state functions (CSF) describing the low-lying excited states of 2NN at its ground state minimum.

STATE	CSF	Weigth
T_1 $^3(\pi\pi^*)$	H -> L+3	47%
T_2 $^3(n_A\pi^*)$	H-5 -> L	71%
T_3 $^3(\pi_O\pi^*)$	H -> L H-3 -> L	12% 69%
S_1 $^1(n_A\pi^*)$	H-5 -> L	63%
T_4 $^3(\pi\pi^*)$	H-> L H-1 -> L+3	20% 28%
S_2 $^1(L_b\pi\pi^*)$	H-1 -> L H -> L+1 H-1 -> L+3	22% 22% 16%
T_5 $^3(n_B\pi^*)$	H-6 -> L H-5, H-3 --> L	68% 12%
S_3 $^1(n_B\pi^*)$	H-6 -> L	61%
S_4 $^1(L_a\pi\pi^*)$	H -> L H -> L+3	28% 11%

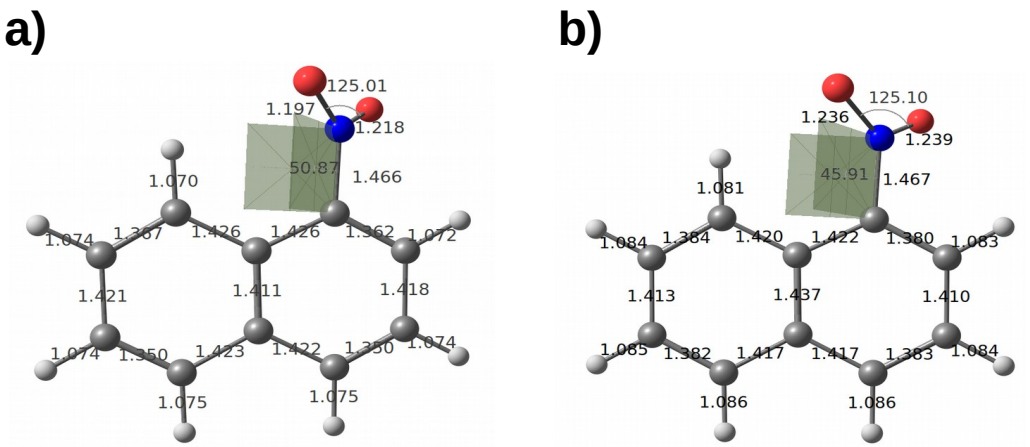

Figure S2. a) 1NN optimized geometry at the CASSCF level (J. Chem. Theory Comput. 2014, 10, 3987.); b) 1NN optimized geometry at the CASPT2(18,14) level. Selected bond lengths (in Å), angles, and dihedral angles (in degrees) are also reported.

Table S2. CASSCF(18,14) dipole moments for the singlet states of the three nitronaphthalene molecules at the corresponding ground state minima.

2NN		1NN		2M1NN	
State	μ(D)	State	μ(D)	State	μ(D)
S_0	4.71	S_0	4.05	S_0	3.68
S_1 $^1(n_A\pi^*)$	2.53	S_1 $^1(n_A\pi^*)$	2.86	S_1 $^1(n_A\pi^*)$	3.21
S_2 $^1(L_b\pi\pi^*)$	2.45	S_2 $^1(L_b\pi\pi^*)$	2.86	S_2 $^1(L_b\pi\pi^*)$	2.80
S_3 $^1(n_B\pi^*)$	5.49	S_3 $^1(n_B\pi^*)$	3.86	S_3 $^1(n_B\pi^*)$	3.31
S_4 $^1(L_a\pi\pi^*)$	4.15	S_4 $^1(L_a\pi\pi^*)$	8.67	S_4 $^1(L_a\pi\pi^*)$	5.88

Table S3. Geometrical parameters characterizing the nitro group at the obtained critical points. For each $^1(n_A\pi^*)$ minimum and CI, the difference with respect to the ground state minimum are also reported (in blue in case of a negative value, in red for a positive value).

	$^1(gs)_{min}$				$^1(n_A\pi^*)_{min}$				$(^1n_A\pi^*/gs)_{CI}$			
	CN (Å)	NO_{12} (Å)	NO_{13} (Å)	ONO (degrees)	CN (Å)	NO_{12} (Å)	NO_{13} (Å)	ONO (degrees)	CN (Å)	NO_{12} (Å)	NO_{13} (Å)	ONO (degrees)
2NN	1.472	1.239	1.240	124.76	1.414 -0.058	1.247 +0.008	1.393 +0.153	110.88 -13.88	1.227 -0.245	1.320 +0.081	1.318 +0.078	93.48 -31.28
1NN	1.467	1.236	1.239	125.10	1.436 -0.031	1.251 +0.015	1.372 +0.133	108.09 -17.01	1.226 -0.241	1.318 +0.082	1.318 +0.079	93.54 -31.56
2M1NN	1.468	1.241	1.240	125.46	1.437 -0.031	1.379 +0.138	1.244 +0.004	109.27 -16.19	1.277 -0.191	1.318 +0.077	1.318 +0.078	93.25 -32.21

Table S4. Cartesian coordinates x, y, z (in Å) of the optimized structures.

2NN

$^1(gs)_{min}$

C -1.017644 0.217405 -0.026639
C -1.454240 1.565466 -0.004995
C -0.516787 2.573342 0.074449
C 0.872338 2.325371 0.135780
C 1.307656 1.014890 0.115245
C 0.388247 -0.065920 0.034209
C -1.939968 -0.859134 -0.107712
C -1.490872 -2.167184 -0.127449
C -0.103131 -2.447891 -0.067367
C 0.817713 -1.417898 0.012083
H -2.508741 1.806918 -0.049916
N -0.982402 3.969889 0.096144
H 1.561655 3.155800 0.197029
H 2.370220 0.798388 0.161459
H 1.880735 -1.632933 0.058332
H 0.236987 -3.477333 -0.083947

H -2.201965 -2.983318 -0.189164
H -3.001749 -0.638907 -0.153927
O -0.119638 4.858001 0.166899
O -2.203717 4.173879 0.042587

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

C -1.009301 0.213228 -0.031457
C -1.458778 1.557205 -0.037090
C -0.527485 2.570260 -0.025061
C 0.867190 2.323234 -0.018461
C 1.301216 1.020338 -0.002013
C 0.379044 -0.062384 -0.009196
C -1.932584 -0.870632 -0.036891
C -1.483928 -2.168219 -0.021462
C -0.088209 -2.442535 0.000621
C 0.817141 -1.415890 0.006192
H -2.513265 1.788683 -0.048401
N -0.973371 3.911171 -0.075566
H 1.569904 3.143367 -0.029853
H 2.361524 0.807993 0.009303
H 1.879504 -1.619062 0.023334
H 0.252796 -3.467671 0.012652
H -2.189584 -2.986554 -0.026515
H -2.992175 -0.653939 -0.053136
O -0.172196 4.823760 0.607527
O -2.164053 4.282152 -0.081330

$(^{1}n_A\pi^*/gs)_{CI}$

C 0.000607772 -0.819559 1.41833
C 0.00171572 -0.390709 0.0656317
C -0.00133083 1.01873 -0.218734
C -0.00538776 1.9415 0.857603
C -0.00637239 1.49157 2.16695
C -0.00337104 0.103577 2.44816
C 0.00576769 -1.30935 -1.01579
C 0.00679207 -0.872135 -2.32793
C 0.00372143 0.516374 -2.57282
C -0.000248041 1.45558 -1.56734
N 0.00462738 0.905306 -3.7363
O 0.00255809 2.10318 -4.28998
O 0.00801214 0.280638 -4.89707
H -0.00249354 2.51098 -1.81183
H 0.00985579 -1.5601 -3.16137
H 0.00808521 -2.37363 -0.799452
H 0.00292435 -1.884 1.63472
H -0.00420735 -0.236381 3.47923
H -0.00945849 2.20387 2.98409
H -0.00770452 3.00484 0.636786

LIIC g5

C	-2.82808231	-0.48447210	-0.02353383
C	-1.40739831	-0.48447210	-0.02353383
C	-0.71350875	0.76356454	-0.02353383
C	-1.46049017	1.97173778	-0.02310750
C	-2.83955974	1.94118396	-0.02299287
C	-3.52863387	0.70067178	-0.02311186
C	-0.65736550	-1.69070280	-0.02318236
C	0.72129936	-1.67426539	-0.02383137
C	1.37944969	-0.42413404	-0.01693937
C	0.70378349	0.77455698	-0.01913088
N	2.68925514	-0.40811206	-0.03137647
O	3.50321112	0.58934341	-0.02648298
O	3.48284016	-1.46752026	0.24180729
H	1.25267247	1.70665484	-0.01655033
H	1.29786265	-2.58796171	-0.03104132
H	-1.18557643	-2.63728788	-0.02571224
H	-3.35276651	-1.43329533	-0.02345277
H	-4.61192096	0.68986419	-0.02301920
H	-3.40212287	2.86601223	-0.02302381
H	-0.92830789	2.91620131	-0.02277336

1NN

$^{1}(gs)_{min}$

C -1.056021 0.224128 0.019209
C -1.433620 1.551018 0.044958
C -0.439418 2.549621 0.094182
C 0.897185 2.192845 0.089567
C 2.663592 0.476051 -0.009148
C 3.047055 -0.849540 -0.090323
C 2.067049 -1.866188 -0.139092
C 0.718765 -1.558104 -0.091805
C 1.292694 0.833598 0.030086
C 0.299535 -0.204294 0.002507
N -2.140486 -0.763090 0.013523
O -2.046747 -1.724520 0.785375
O -3.091442 -0.554660 -0.752320
H -2.486263 1.805470 0.035692
H -0.728957 3.593578 0.135730
H 1.666399 2.958700 0.125075
H 3.409457 1.264826 0.018990
H 4.099713 -1.108930 -0.121453
H 2.373039 -2.903786 -0.212210
H -0.015167 -2.351203 -0.118235

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

C -1.034544 0.186415 -0.026512
C -1.424877 1.494996 0.040415
C -0.439757 2.510539 0.090431
C 0.886611 2.178513 0.086098
C 2.676008 0.474937 0.003750
C 3.069048 -0.833091 -0.078009
C 2.095418 -1.859220 -0.152209
C 0.761260 -1.551254 -0.136196
C 1.299023 0.821302 0.018614
C 0.337574 -0.197039 -0.047286
N -2.018100 -0.858151 -0.082563
O -2.301527 -1.500646 0.952945
O -3.191424 -0.495434 -0.693144
H -2.465871 1.749038 0.055371
H -0.745086 3.538704 0.140713
H 1.637992 2.945448 0.130054
H 3.406605 1.261367 0.056451
H 4.113289 -1.084851 -0.088558
H 2.406395 -2.885106 -0.221086
H 0.028307 -2.330928 -0.188960

$(^{1}n_{A}\pi^{*}/gs)_{CI}$

O -1.91289 -1.91793 -0.0242638
N -1.9658 -0.603583 0.00881361
O -3.28153 -0.569087 0.0200437
C -1.14837 0.315553 0.0251903
C -1.6485 1.58275 0.060441
C -0.751741 2.67984 0.112268
C 0.580913 2.46246 0.100107
C 1.11539 1.1462 0.0356463
C 0.24942 0.032348 0.00712343
C 0.810712 -1.27481 -0.0801376
C 2.16696 -1.43803 -0.128344
C 3.03394 -0.313472 -0.0864694
C 2.52132 0.93313 -0.00709472
H 3.17114 1.78889 0.0209799
H 1.26398 3.29145 0.134457
H -1.14562 3.67744 0.159071
H -2.70835 1.74268 0.0574733
H 0.169309 -2.13123 -0.0973943
H 2.58261 -2.42614 -0.19394
H 4.09748 -0.461688 -0.119955

LIIC g4

C 0.49895870 -0.95692634 0.04855203
C 1.86424070 -0.95692634 0.04855203
C 2.55724228 0.27881158 0.04855203
C 1.86388478 1.44618001 0.02758786

C	-0.27682287	2.68235481	-0.02342883
C	-1.63494257	2.69395440	-0.04213142
C	-2.35464896	1.47149175	-0.02563695
C	-1.69220215	0.27506606	0.01119033
C	0.44268598	1.45705232	0.01103872
C	-0.26945629	0.24373956	0.03110585
N	-0.12732506	-2.11810382	0.06696344
O	-1.23104471	-2.45096085	-0.50768967
O	0.48646189	-3.27872653	0.34501619
H	2.40286650	-1.88340458	0.05307799
H	3.63081748	0.27922713	0.06015678
H	2.38551654	2.38564853	0.02211260
H	0.27638114	3.60379398	-0.03614933
H	-2.16865679	3.62589367	-0.06924573
H	-3.42850726	1.48653064	-0.03980167
H	-2.24411714	-0.64225050	0.03020330

2M1NN

$^{1}(gs)_{min}$

C -1.034544 0.186415 -0.026512
C -1.424877 1.494996 0.040415
C -0.439757 2.510539 0.090431
C 0.886611 2.178513 0.086098
C 2.676008 0.474937 0.003750
C 3.069048 -0.833091 -0.078009
C 2.095418 -1.859220 -0.152209
C 0.761260 -1.551254 -0.136196
C 1.299023 0.821302 0.018614
C 0.337574 -0.197039 -0.047286
N -2.018100 -0.858151 -0.082563
O -2.301527 -1.500646 0.952945
O -3.191424 -0.495434 -0.693144
H -2.465871 1.749038 0.055371
H -0.745086 3.538704 0.140713
H 1.637992 2.945448 0.130054
H 3.406605 1.261367 0.056451
H 4.113289 -1.084851 -0.088558
H 2.406395 -2.885106 -0.221086
H 0.028307 -2.330928 -0.188960

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

C 0.286700 -0.175117 0.000549
C -1.087067 0.242109 0.056911
C -1.465672 1.559356 0.055433
C -0.434111 2.545326 0.007844
C 0.882546 2.194824 -0.040681
C 1.277828 0.825339 -0.046826
C 0.688919 -1.537130 -0.008863
C 2.018814 -1.864594 -0.061909

C 3.006921 -0.854872 -0.106560
C 2.643331 0.450646 -0.099253
N -2.120906 -0.753918 0.109360
O -2.307995 -1.407390 -1.090668
O -2.186655 -1.577397 1.039892
C -2.898550 2.026497 0.114928
H -0.714602 3.582796 0.011269
H 1.642383 2.954252 -0.075735
H 3.390227 1.223219 -0.133022
H 4.045419 -1.127528 -0.146337
H 2.314212 -2.897314 -0.068920
H -0.047291 -2.314136 0.025844
H -3.071897 2.576729 1.036367
H -3.105147 2.698848 -0.713301
H -3.601566 1.207400 0.073626

$(^1 n_A \pi^*/gs)_{CI}$

C 0.272073 -0.153281 -0.002602
C -1.091838 0.283566 0.074536
C -1.450195 1.608386 0.099357
C -0.405486 2.575952 0.063956
C 0.905953 2.203267 -0.002866
C 1.276559 0.828854 -0.039340
C 0.651080 -1.525781 -0.040970
C 1.956425 -1.873015 -0.110781
C 2.971576 -0.881855 -0.145883
C 2.639583 0.427606 -0.111242
N -2.024989 -0.587864 0.110505
O -3.338918 -0.504337 0.179565
O -2.034641 -1.905268 0.092417
C -2.879112 2.082644 0.198264
H -0.666982 3.618014 0.089807
H 1.677709 2.950451 -0.031059
H 3.401835 1.185199 -0.136989
H 4.002233 -1.179669 -0.199498
H 2.231498 -2.911192 -0.138976
H -0.101753 -2.287584 -0.011929
H -3.097418 2.402487 1.214302
H -3.035138 2.933908 -0.456874
H -3.589133 1.312571 -0.069741

LIIC g6

C -0.62166895 -0.15558473 -0.02109927
C 0.81343405 -0.15558473 -0.02109927
C 1.55867138 0.99632831 -0.02109927
C 0.85760063 2.23741176 -0.03797372
C -0.50607652 2.28311671 -0.04481189
C -1.28003510 1.08731743 -0.03509385
C -1.40216813 -1.34536661 -0.00948272

C	-2.75897085	-1.27605727	-0.01284850
C	-3.42030664	-0.02262267	-0.02920301
C	-2.70035712	1.12244068	-0.03984334
N	1.46314425	-1.31646044	-0.00987843
O	2.61463442	-1.58138834	0.61929939
O	1.04667928	-2.49486463	-0.34177425
C	3.06711277	1.01687750	-0.03346108
H	1.42576509	3.14961513	-0.04472935
H	-1.01375579	3.23023396	-0.05598206
H	-3.19439612	2.07715369	-0.05255974
H	-4.49400892	0.01145329	-0.03338252
H	-3.33937770	-2.18003260	-0.00407470
H	-0.91865898	-2.30126279	0.00023277
H	3.42808200	1.31917589	-1.01349275
H	3.43548435	1.73746677	0.69047731
H	3.49493369	0.05178531	0.19855433

NB

$(^1 n_A \pi^*/gs)_{CI}$

H	0.00000000	-2.19262950	0.06630733
C	0.00000000	-1.27354478	-0.47794242
C	0.00000000	-1.22635061	-1.83162392
C	0.00000000	0.00000000	-2.54000347
C	0.00000000	1.22635061	-1.83162392
C	0.00000000	1.27354478	-0.47794242
C	0.00000000	0.00000000	0.29115308
H	0.00000000	-2.14642158	-2.38821722
H	0.00000000	0.00000000	-3.61029533
H	0.00000000	2.14642158	-2.38821722
H	0.00000000	2.19262950	0.06630733
N	0.00000000	0.00000000	1.52566436
O	0.00000000	0.97241177	2.42307583
O	0.00000000	-0.97241177	2.42307583

LIIC g4

H	-1.91525130	1.03599467	-0.00033812
C	-0.84532830	1.03599467	-0.00033812
C	-0.11697513	2.19948306	-0.00033812
C	1.28901624	2.18192680	-0.00009087
C	1.97201502	0.95494116	0.00115964
C	1.29242938	-0.23954257	0.00309521
C	-0.14714920	-0.22381812	0.00183725
H	-0.63384869	3.14179875	-0.00106345
H	1.83825623	3.10285717	-0.00089866
H	3.04668877	0.94648889	0.00099002
H	1.81236650	-1.17544479	0.00410700
N	-0.83050804	-1.34690541	0.00469065
O	-0.29252500	-2.57821864	0.01754161
O	-2.08231291	-1.55643972	-0.02598926