Supporting Information for

Quantum Chemistry Studies of Electronically Excited Nitrobenzene, TNA and TNT

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This document contains 1 figure (p. 2) and 9 tables containing the optimized Cartesian coordinates (in Å) for the S_0 and S_1 minima and S_0/S_1 conical intersections of nitrobenzene (NB, p. 3-5), 2,4,6-trinitroaniline (TNA, p. 6-8) and 2,4,6-trinitrotoluene (TNT, p. 9-11). MP2 was used to minimize on the ground state (S_0). State-averaged CASSCF (2 states in the average; 10 electons/8 orbitals in the active space) was used to optimize the excited state (S_1) minima and the S_0/S_1 conical intersections. All optimizations were performed with the Gaussian03 program.

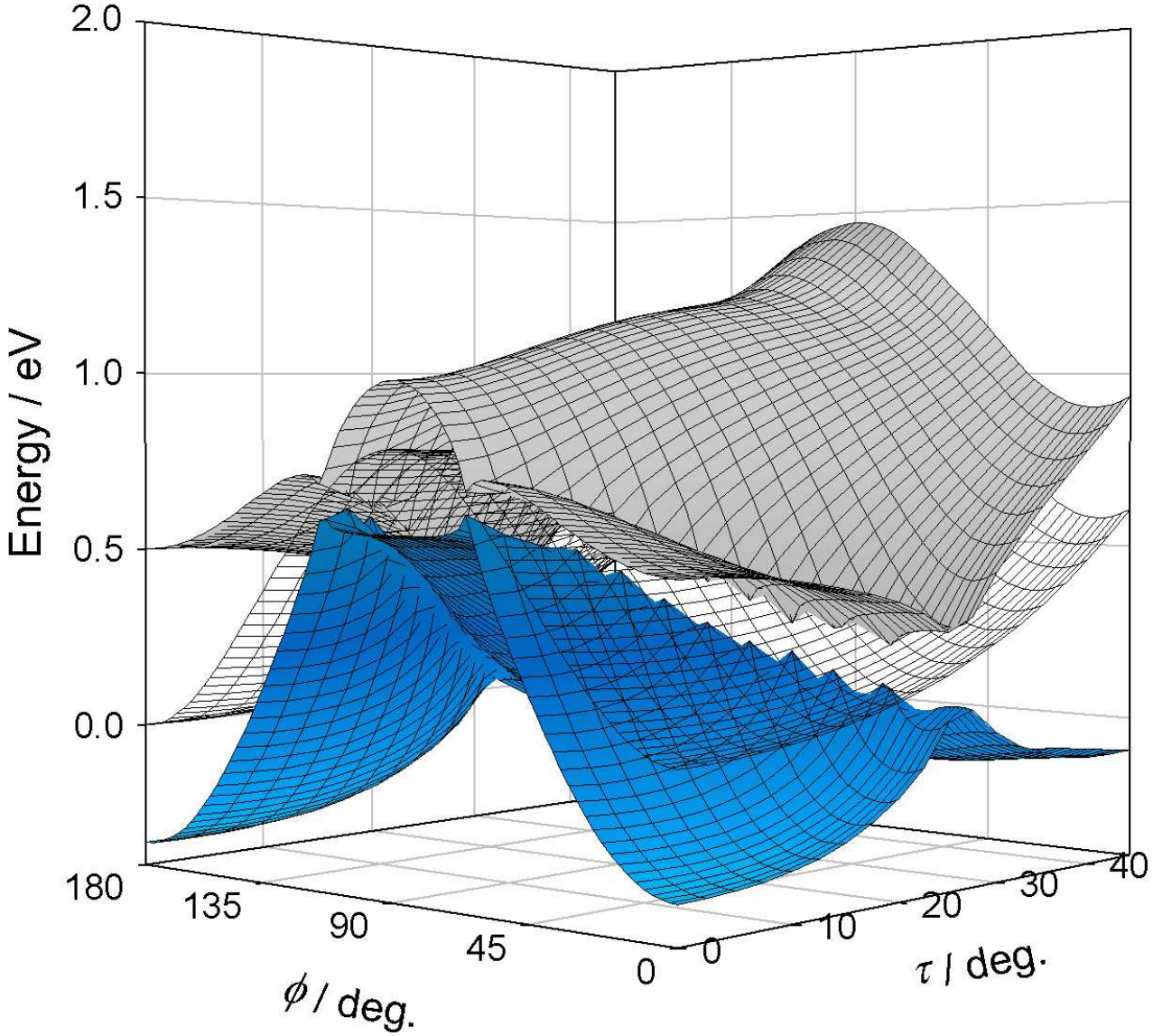


Figure S1 Reduced-space potential surfaces showing the 3-state ($T_2/S_0/S_1$) near-degeneracy of TNA, calculated with the TD-PBE0/cc-pVDZ method. The two coordinates that are varied are the out-of-plane rotation of the NO_2 group, ϕ, and its pyramidalization, τ. All other coordinates were fixed at the values of the **TNA-S_0Min** structure, except the C-N and N-O bond lengths and the O-N-O bond angle of one ortho-NO_2 group which were set to the values of **TNA-S_0S_1CI**.

Table S1 Cartesian coordinates of the **S_0 minimum of NB** optimized with MP2/cc-pVDZ.

C	0.00000000	0.00000000	0.00000000
C	1.40046856	0.00000000	0.00000000
C	-0.75355156	1.18045425	0.00000000
C	2.06553678	1.23641288	0.00000000
C	-0.06923371	2.40631788	0.00000000
C	1.33631589	2.43842683	0.00000000
H	1.94012993	-0.94900566	0.00000000
H	-1.84384411	1.12470209	0.00000000
H	3.15992722	1.25894866	0.00000000
H	-0.63909810	3.34090487	0.00000000
H	1.86237647	3.39834974	0.00000000
N	-0.71258222	-1.30027610	0.00000000
O	-1.94466299	-1.26952645	0.00000000
O	-0.02371639	-2.32225086	0.00000000
C	0.00000000	0.00000000	0.00000000
C	1.40046856	0.00000000	0.00000000
C	-0.75355156	1.18045425	0.00000000
C	2.06553678	1.23641288	0.00000000
C	-0.06923371	2.40631788	0.00000000
C	1.33631589	2.43842683	0.00000000
H	1.94012993	-0.94900566	0.00000000

Table S2 Cartesian coordinates of the **S_1 minimum of NB** optimized with SA-2-CAS(10/8)/ cc-pVDZ.

C	−0.01123039	0.0904215426	−0.0182959368
C	−0.0144664746	0.027919526	1.3762511452
C	1.2028054128	−0.0140148987	2.0508119676
C	2.3966497436	−0.0037690307	1.3566767866
C	2.3899570657	0.0484027569	−0.0385513757
C	1.1891365677	0.0933709792	−0.7377085588
H	−0.9433399696	0.0042108204	1.9249700906
H	1.1646083855	0.1387295732	−1.8145909224
N	−1.223621143	0.1056020061	−0.7276253227
H	1.2029832641	−0.0616494214	3.1312038754
H	3.3228749238	0.060047936	−0.5851681917
O	−1.3363840483	0.1589846523	−1.9411324411
O	−2.301167478	0.6212197516	−0.0294576333
H	3.3353951403	−0.0380181933	1.8917325172
C	−0.01123039	0.0904215426	−0.0182959368
C	−0.0144664746	0.027919526	1.3762511452
C	1.2028054128	−0.0140148987	2.0508119676
C	2.3966497436	−0.0037690307	1.3566767866
C	2.3899570657	0.0484027569	−0.0385513757
C	1.1891365677	0.0933709792	−0.7377085588
H	−0.9433399696	0.0042108204	1.9249700906

Table S3 Cartesian coordinates of the **S_0/S_1 conical intersection of NB** optimized with SA-2-CAS(10/8)/cc-pVDZ.

C	-0.071423	0.076025	0.110118
C	-0.003650	-0.095213	1.474626
C	1.254480	-0.128538	2.085706
C	2.397946	0.021779	1.337918
C	2.320128	0.201951	-0.052937
C	1.080718	0.203438	-0.678580
H	-0.911758	-0.215210	2.044772
H	0.997233	0.309411	-1.750769
N	-1.392014	0.109412	-0.440799
H	1.318219	-0.289012	3.153177
H	3.224896	0.319963	-0.631799
O	-1.532378	-0.570932	-1.563542
O	-1.673083	1.299226	-1.071977
H	3.364891	-0.010843	1.823203
C	-0.071423	0.076025	0.110118
C	-0.003650	-0.095213	1.474626
C	1.254480	-0.128538	2.085706
C	2.397946	0.021779	1.337918
C	2.320128	0.201951	-0.052937
C	1.080718	0.203438	-0.678580
H	-0.911758	-0.215210	2.044772

Table S4 Cartesian coordinates of the **S_0 minimum of TNA** optimized with MP2/cc-pVDZ.

C	-1.1373160023	-0.0291192229	-0.6556909261
C	-1.0603495323	0.002723898	0.7792985482
C	0.1425295493	0.0341394415	1.4813536658
C	1.3405249412	0.0343482814	0.7728487439
C	1.3539646625	0.0042156014	-0.6185837292
C	0.1436543795	-0.0261808241	-1.3077947396
H	0.1348806923	0.0497145213	2.5714822444
H	2.2936760759	0.0125132085	-1.1713538585
N	-2.3051480595	-0.0590316377	-1.3289759966
H	-3.1610529413	0.0018477471	-0.7890820177
H	-2.2640485594	-0.1407817024	-2.3386257339
N	2.6197460796	0.0671142958	1.5103533627
O	3.6526364056	0.045361285	0.8398425317
O	2.5557188712	0.113685224	2.7394391105
N	-2.2821060381	-0.0099146584	1.6169147962
O	-2.1427686673	-0.1624647406	2.827722568
O	-3.3779810337	0.1392887292	1.0559232408
N	0.2564067569	-0.0419527899	-2.7847808225
O	1.3675861495	0.1426188283	-3.2746341839
O	-0.7714079626	-0.2455483775	-3.4481513751

Table S5 Cartesian coordinates of the **S_1 minimum of TNA** optimized with SA-2-CAS(10/8)/ cc-pVDZ.

C	−1.1203670166	−0.2390178182	−0.6916598241
C	−1.0873140267	−0.1288352332	0.7194001609
C	0.074538767	0.0286679808	1.4325927973
C	1.2823028615	0.0951138631	0.7575100399
C	1.3126951847	−0.0001495447	−0.6155089166
C	0.140354467	−0.1669614699	−1.3318617852
H	0.03888686	0.1208333894	2.5061801725
H	2.2495935556	0.057666315	−1.1411846575
N	−2.2959041558	−0.4157705018	−1.3091135452
H	−3.1272571069	−0.4157284335	−0.761690835
H	−2.3443279616	−0.4546090839	−2.3010035093
N	2.5164257874	0.2850523131	1.4983005265
O	3.5421024592	0.313694462	0.8783137495
O	2.434866169	0.4050014744	2.6890054047
N	−2.340712946	−0.1493924574	1.4144288889
O	−2.6414230594	−1.1468541441	2.114487857
O	−2.4934795444	1.0367019886	2.1376596316
N	0.2705604043	−0.2535876082	−2.7822205828
O	1.3672641461	−0.1659620073	−3.2511713752
O	−0.7225969943	−0.4089025643	−3.4437040679
C	−1.1203670166	−0.2390178182	−0.6916598241

Table S6 Cartesian coordinates of the **S_0/S_1 conical intersection of TNA** optimized with SA-2-CAS(10/8)/cc-pVDZ.

C	-1.127399	-0.14972	-0.743482
C	-1.115181	-0.058258	0.675829
C	0.034044	0.06933	1.395419
C	1.26761	0.099075	0.74706
C	1.323037	0.011133	-0.61408
C	0.149943	-0.106087	-1.358619
H	0.002955	0.141074	2.463919
H	2.258956	0.029223	-1.12889
N	-2.294556	-0.260896	-1.390301
H	-3.137	-0.284343	-0.868751
H	-2.320791	-0.321014	-2.379034
N	2.474037	0.213833	1.521636
O	3.565542	0.228588	0.927725
O	2.374224	0.320719	2.757809
N	-2.394971	-0.110295	1.296632
O	-2.451024	-1.113371	2.296177
O	-2.680259	0.946911	2.3104
N	0.312915	-0.192566	-2.774143
O	1.45199	-0.168669	-3.23874
O	-0.689085	-0.314838	-3.494911

Table S7 Cartesian coordinates of the **S_0 minimum of TNT** optimized with MP2/cc-pVDZ.

C	-0.0134537448	0.0148373734	-0.0068505748
C	-0.0156863886	0.0488832912	1.387103165
C	1.2239774885	0.0443220509	2.033909676
C	2.471405309	0.0351741825	1.3749762065
C	2.3731901318	0.0059536256	-0.0320939671
C	1.169919468	0.0093862972	-0.7443255856
H	-0.9480813615	0.0795278849	1.952510113
H	1.1587958563	0.0094543121	-1.8351337941
N	-1.3114163535	0.005165817	-0.7286557157
N	1.1709109996	0.0464297119	3.5112945436
N	3.60010829	-0.0347652076	-0.8557959187
O	-1.2630428731	-0.0150167369	-1.958214646
O	-2.3305952387	0.0172984314	-0.0389521858
O	1.9443809135	-0.7165988304	4.0948438814
O	0.3401075916	0.790666786	4.0348842918
O	4.4915786454	-0.8020191926	-0.4848494592
O	3.618482847	0.6813333407	-1.8583608798
C	3.790807632	0.0910188852	2.1078546208
H	3.6837193608	0.6257958362	3.061205787
H	4.1513348143	-0.9255939084	2.3276991583
H	4.5527126127	0.5961850498	1.4990612833

Table S8 Cartesian coordinates of the **S_1 minimum of TNT** optimized with SA-2-CAS(10/8)/ cc-pVDZ.

C	−0.0055150079	0.0030286455	0.0027428031
C	−0.0054362473	0.0012118223	1.4150218963
C	1.1619303941	0.0028588851	2.1647557134
C	2.3776651975	0.0206887051	1.4926168225
C	2.4544271299	−0.0032332315	0.1278028551
C	1.2619087307	−0.0390155241	−0.5869994195
H	1.1443106136	−0.007814939	3.2395451089
H	3.4026384577	0.0057490115	−0.3801244751
N	3.6139908816	0.0601420956	2.2764083952
O	4.6363519624	0.0466096292	1.6774581537
O	3.5030172193	0.1074899997	3.4563809604
N	−1.261714134	0.0116874826	2.1008986172
O	−2.1099113213	−0.8674408034	1.880886241
O	−1.1324968876	0.2714514778	3.4594104486
N	1.4118768232	−0.1210474013	−2.0446275646
O	2.3455037809	0.4346372857	−2.5199622127
O	0.6106027153	−0.7588256943	−2.642126658
C	−1.2956814645	0.0790772445	−0.7837021305
H	−1.1623848915	0.6632180855	−1.6886681024
H	−1.6224746101	−0.9172256549	−1.0742603556
H	−2.0734414874	0.5359932498	−0.1814851386

Table S9 Cartesian coordinates of the **S_0/S_1 conical intersection of TNT** optimized with SA-2-CAS(10/8)/cc-pVDZ.

C	-0.016130	-0.013944	-0.029543
C	-0.034979	-0.064930	1.366928
C	1.119475	-0.108124	2.131606
C	2.339698	-0.094365	1.495071
C	2.423508	-0.029570	0.117246
C	1.254937	-0.002736	-0.615667
H	1.063567	-0.159533	3.205671
H	3.379676	-0.003678	-0.376079
N	3.568324	-0.144430	2.287517
O	4.609801	-0.133679	1.691964
O	3.456620	-0.134155	3.481944
N	-1.321920	-0.074202	2.021753
O	-1.348421	-0.923044	3.081921
O	-1.452617	1.000845	2.852026
N	1.415320	0.035478	-2.072210
O	2.263713	0.763628	-2.512644
O	0.653456	-0.611130	-2.739800
C	-1.291690	0.048830	-0.840396
H	-1.201469	0.776850	-1.644307
H	-1.493036	-0.918209	-1.297334
H	-2.132664	0.319336	-0.213697