Supporting Information

Photochemistry of Nitrophenol in Clusters: Intra- vs. Inter-molecular Hydrogen Bond Dynamics

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1. Cartesian coordinates of optimal structure of phenol, 2-nitrophenol and 4-nitrophenol

Below, we provide the Cartesian coordinates of phenol, 2-nitrophenol and 4-nitrophenol clusters. All these structures were obtained by energy minimization at the DFT/B97 level using Grimme's D3 correction with the aug-cc-pVDZ basis set. All coordinates are shown in Ångstrom units.

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 30
Dimer of 2-nitrophenol – stacking structure
 C     1.960822     0.187085    -1.105182
 C     0.670040     0.382040    -0.617716
 C     0.330365     0.012511     0.704321
 C     1.297193    -0.551437     1.529521
 C     2.610744    -0.751552     1.048574
 C     2.962496    -0.382804    -0.287769
 N     3.584527    -1.360524     1.937855
 O     4.755626    -1.553481     1.498916
 O     4.183442    -0.552343    -0.828269
 O     3.251672    -1.682421     3.082150
 H     4.749219    -0.966439    -0.120738
 H     2.228231     0.448879    -2.128900
 H    -0.089220     0.807968    -1.275653
 H    -0.685110     0.154137     1.074363
 H     1.063286    -0.859869     2.546541
 C     1.257008    -4.079337     1.388232
 C     2.584358    -4.324875     1.042903
 C     3.071411    -4.000559    -0.244505
 C     2.214964    -3.427915    -1.178586
 C     0.866381    -3.174753    -0.841521
 C     0.365245    -3.498093     0.458747
 N     0.011086    -2.556661    -1.840224
 O    -1.188170    -2.303589    -1.524662
 O    -0.899491    -3.278431     0.862951
 O     0.467274    -2.284663    -2.954103
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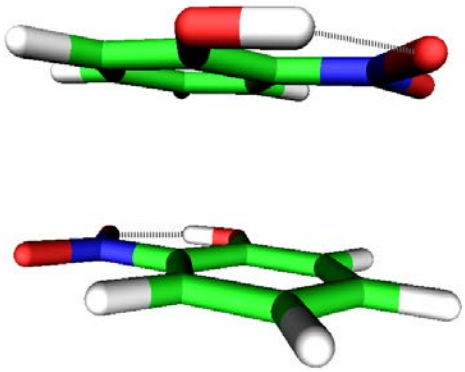

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 H     -1.370520     -2.855897      0.093126
 H      0.875682     -4.309936      2.383118
 H      3.257552     -4.756358      1.785450
 H      4.114690     -4.183133     -0.501968
 H      2.564667     -3.151725     -2.171314
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 30
Dimer of 2-nitrophenol – hydrogen bonded structure
 C      0.000000      0.000000      0.000000
 C      0.000000      0.000000      1.431663
 C      1.252762      0.000000      2.091220
 C      2.442256      0.000104      1.366204
 C      2.431315     -0.002796     -0.049085
 C      1.215094     -0.003783     -0.724110
 O     -1.096298     -0.003214      2.205931
 N     -1.244674      0.010015     -0.751245
 O     -1.216227     -0.013117     -1.985992
 O     -2.327760      0.039449     -0.103299
 N     -4.505717     -1.511988      1.145627
 O     -4.359336     -0.555124      1.962831
 C     -5.243873     -1.261644     -0.078443
 C     -5.743127      0.043674     -0.383037
 C     -6.437536      0.220636     -1.601958
 C     -6.626575     -0.848830     -2.474840
 C     -6.129556     -2.137308     -2.165220
 C     -5.439062     -2.337633     -0.974327
 O     -5.594689      1.119510      0.408533
 O     -4.035274     -2.632593      1.362213
 H     -5.079204      0.815478      1.204327
 H     -6.279920     -2.968618     -2.854731
 H     -6.810825      1.219252     -1.831081
 H     -7.163697     -0.684406     -3.411159
 H     -5.036556     -3.313729     -0.708924
 H     -1.894903     -0.019260      1.616269
 H      1.247987     -0.002869      3.181593
 H      3.393771      0.000584      1.901939
 H      3.366700     -0.003908     -0.609698
 H      1.168671     -0.004752     -1.811797
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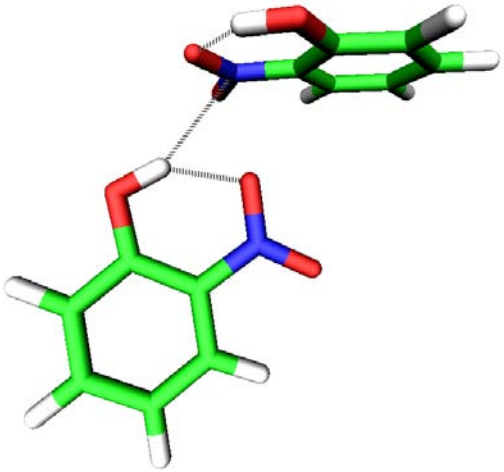

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 45
Trimer of 2-nitrophenol – stacking structure
 C      0.000000      0.000000      0.000000
 C      0.000000      0.000000      1.413068
 C      1.197925      0.000000      2.124797
 C      2.441769     -0.001398      1.452562
 C      2.470047     -0.001672      0.062035
 C      1.262707      0.001039     -0.671465
 N      1.338847     -0.013675     -2.122742
 O      2.440655     -0.017126     -2.678141
 O     -1.193445     -0.011040     -0.621719
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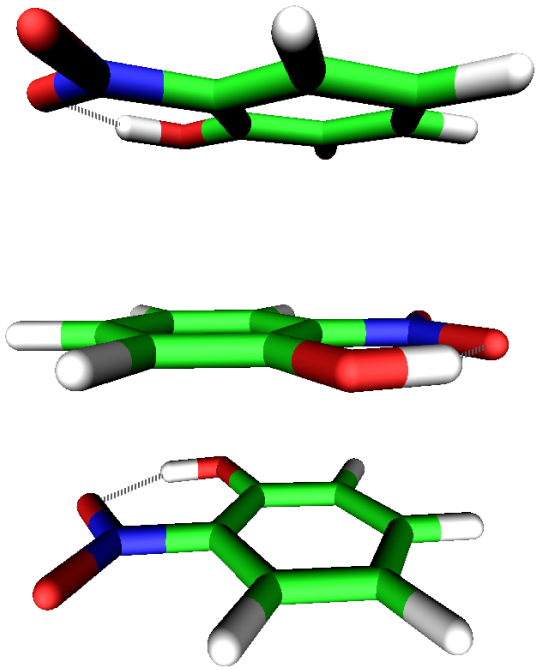
O	0.255663	-0.033851	-2.776139
C	1.354326	-3.237273	-2.108402
C	2.542147	-3.245546	-1.380659
C	2.521868	-3.246356	0.030690
C	1.250798	-3.238020	0.685967
C	0.054423	-3.231693	-0.064409
C	0.102158	-3.229327	-1.453316
N	1.155848	-3.237870	2.130787
O	0.047167	-3.241117	2.675346
O	3.705429	-3.259872	0.671369
O	2.229851	-3.232741	2.802790
C	2.365398	-6.474519	0.403040
C	1.954278	-6.484538	1.731706
C	0.573049	-6.506671	2.034330
C	-0.381313	-6.520409	1.019091
C	0.008722	-6.509362	-0.339198
C	1.407740	-6.486005	-0.635604
N	1.882166	-6.456997	-2.009358
O	3.094250	-6.432288	-2.237865
O	-0.966064	-6.515151	-1.266465
O	1.021776	-6.446288	-2.936628
H	3.493767	-3.252070	1.645132
H	3.511409	-3.254691	-1.878086
H	1.398074	-3.233543	-3.198048
H	-0.822467	-3.221947	-2.029726
H	-0.893954	-3.222923	0.467920
H	-0.511324	-6.491278	-2.152675
H	-1.448720	-6.526982	1.241138
H	0.244893	-6.498656	3.075005
H	2.694319	-6.460760	2.531646
H	3.420216	-6.441115	0.137418
H	-1.001098	-0.021239	-1.599269
H	-0.964044	-0.016340	1.921610
H	1.169689	-0.017568	3.215571
H	3.374661	-0.015327	2.016298
H	3.410656	-0.017821	-0.484943



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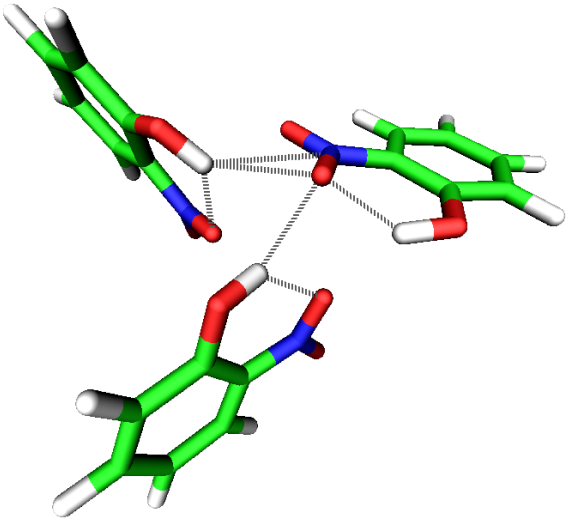
Trimer 2-nitrophenol – hydrogen bonded structure

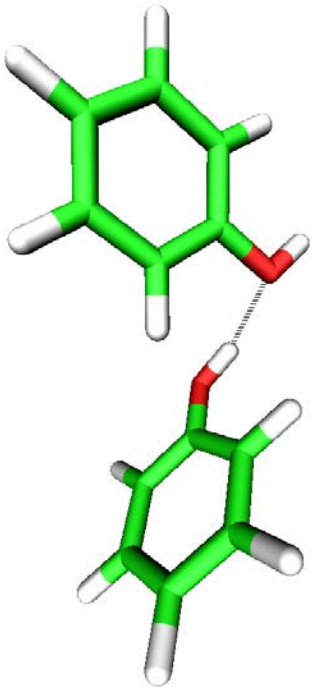
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.412247
C	1.227928	0.000000	2.143135
C	2.437206	0.000501	1.411318
C	2.424620	-0.007204	0.017454
C	1.204605	-0.007814	-0.697609
N	-1.284372	0.004537	2.102216
O	-2.335913	0.138557	1.446673
O	1.317894	0.009173	3.487029
O	-1.278401	-0.141474	3.366035
O	0.740971	-3.008373	3.949012
N	1.994501	-3.032054	3.826567

O	2.552592	-3.545153	2.850466
C	2.794220	-2.420310	4.873194
C	2.181878	-1.731666	5.966910
C	3.031004	-1.129304	6.925713
C	4.416495	-1.210394	6.807080
C	5.012568	-1.898000	5.723410
C	4.201674	-2.494461	4.763167
O	0.860490	-1.590171	6.158659
O	-1.911646	-2.900580	5.183032
N	-1.697701	-4.145662	5.181343
O	-1.234645	-4.734897	6.163495
C	-2.001667	-4.890657	3.972514
C	-2.430004	-4.221619	2.783507
C	-2.686552	-5.011220	1.637265
C	-2.525910	-6.394613	1.672235
C	-2.100419	-7.046738	2.853853
C	-1.836933	-6.294465	3.993871
O	-2.603142	-2.896044	2.662942
H	-2.395229	-2.479984	3.541263
H	-1.975676	-8.129965	2.874548
H	-3.010330	-4.496041	0.732350
H	-2.731869	-6.978914	0.772978
H	-1.501146	-6.762892	4.917381
H	0.379434	-2.111641	5.466405
H	2.558613	-0.603064	7.755718
H	5.045798	-0.737928	7.564156
H	6.097920	-1.962989	5.637731
H	4.627014	-3.027038	3.914242
H	3.370775	-0.002906	1.974834
H	3.372352	-0.016448	-0.524656
H	1.202624	-0.017603	-1.788102
H	-0.957283	-0.000929	-0.518681
H	0.390371	-0.062239	3.841065



26
Dimer of phenol

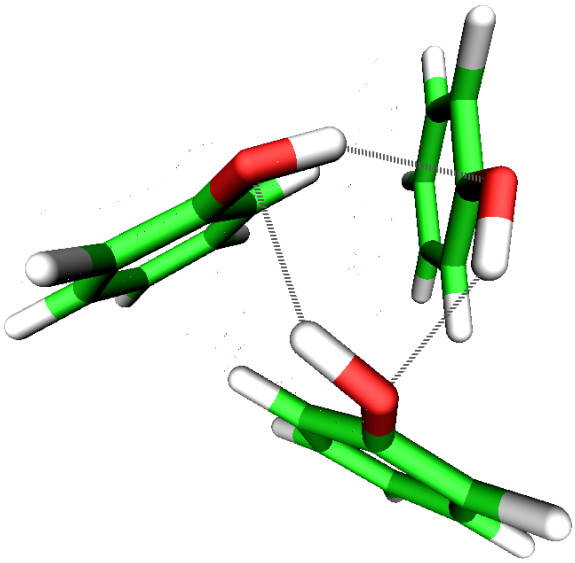
C	1.429741	0.652216	0.127414
C	0.850873	-0.018218	1.215109
C	0.487752	0.718443	2.350497
C	0.696291	2.106079	2.405820
C	1.275114	2.761053	1.308907
C	1.644855	2.038045	0.164604
O	1.786998	-0.111767	-0.978551
H	0.690712	-1.097316	1.170221
H	0.035332	0.198255	3.199779
H	0.409102	2.672272	3.295831
H	1.442424	3.841806	1.337645
H	2.097684	2.550284	-0.691630
H	2.133950	0.471505	-1.669669
C	0.476962	-3.429171	-0.634583
C	1.723086	-3.450279	0.023966



C	2.066277	-4.547747	0.828192
C	1.185262	-5.628946	0.978964
C	-0.051609	-5.602675	0.312286
C	-0.410694	-4.512222	-0.489413
O	0.076770	-2.386298	-1.429056
H	2.418067	-2.614997	-0.097804
H	3.035589	-4.555504	1.336558
H	1.458458	-6.482535	1.605379
H	-0.747770	-6.440690	0.418832
H	-1.372106	-4.481640	-1.008636
H	0.723215	-1.657278	-1.357085

39
Trimer of phenol

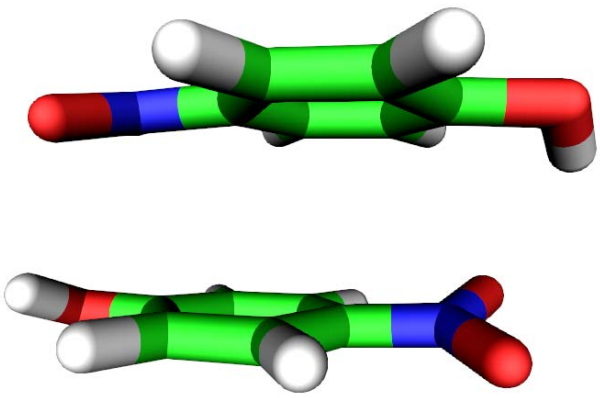
O	-0.179434	0.386855	-0.202267
O	-0.257577	0.430724	2.640591
O	2.339096	0.267896	1.394752
C	-0.519105	-0.857152	-0.707764
C	-0.621617	-0.739080	3.290244
C	2.843295	-1.014534	1.308102
C	-0.258731	-0.856553	4.650178
C	-0.551050	-2.046960	5.346856
C	-1.203187	-3.116544	4.698709
C	-1.566570	-2.983661	3.343212
C	-1.280511	-1.799544	2.631996
H	0.251297	-0.023404	5.140789
H	-0.265212	-2.136090	6.399604
H	-1.424985	-4.038901	5.242745
H	-2.069954	-3.805749	2.825210
H	-1.544840	-1.716955	1.575166
C	3.846740	-1.235434	0.348972
C	4.350522	-2.529489	0.161449
C	3.865072	-3.602474	0.926938
C	2.876698	-3.364433	1.893931
C	2.363182	-2.075236	2.093677
H	4.210685	-0.393268	-0.245041
H	5.127266	-2.698650	-0.590330
H	4.257597	-4.611431	0.774486
H	2.490933	-4.188707	2.500826
H	1.583559	-1.906274	2.838740
C	0.429222	-1.857320	-0.969375
C	-0.005529	-3.109010	-1.429035
C	-1.369545	-3.364335	-1.634766
C	-2.306049	-2.348457	-1.383195
C	-1.887254	-1.093504	-0.921266
H	1.491905	-1.675851	-0.797786
H	0.736385	-3.889828	-1.619293
H	-1.700371	-4.343916	-1.990077
H	-3.372451	-2.532015	-1.544264
H	-2.605593	-0.295580	-0.716536
H	1.638472	0.313411	2.078785



H	0.782670	0.447924	-0.042621
H	-0.557783	0.409701	1.706153

30
Dimer of 4-nitrophenol – stacking structure

C	0.252811	-2.345720	-0.968419
C	0.754459	-1.829344	0.237924
C	-0.098778	-1.301316	1.218138
C	-1.467006	-1.231596	0.961100
C	-1.978933	-1.708734	-0.264445
C	-1.117356	-2.303619	-1.211075
N	2.201398	-1.761995	0.442707
O	2.625325	-1.560848	1.584984
O	-3.295389	-1.623744	-0.593961
O	2.930902	-1.876696	-0.561573
O	3.310311	1.268532	-0.442528
C	1.976955	1.501176	-0.312954
C	1.023173	1.005917	-1.228735
C	-0.334447	1.227087	-1.008166
C	-0.736110	1.950326	0.125872
C	0.206196	2.489384	1.019018
C	1.563088	2.267240	0.797769
N	-2.161447	2.076432	0.431285
O	-2.496007	2.763535	1.404591
O	-2.967601	1.455673	-0.285960
H	0.942504	-2.756276	-1.706311
H	-1.538247	-2.690801	-2.141299
H	-2.140489	-0.780725	1.694914
H	0.321629	-0.910678	2.144827
H	-3.727045	-0.967825	-0.021675
H	3.456806	0.525903	-1.052721
H	2.317097	2.646857	1.490112
H	-0.138247	3.048822	1.889123
H	-1.085646	0.821448	-1.684505
H	1.350174	0.422370	-2.092867



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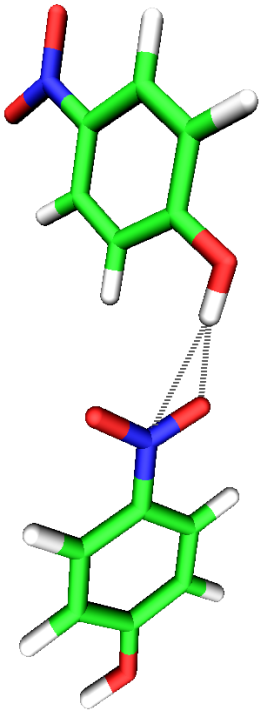
Dimer of 4-nitrophenol – hydrogen bonded structure

C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.410347
C	1.228477	0.000000	2.105584
C	2.443515	-0.004879	1.402729
C	2.414094	-0.010485	0.001982
C	1.207199	-0.007558	-0.712732
O	-1.216290	0.014328	2.026656
N	3.679513	-0.015969	-0.735598
O	4.729878	-0.015775	-0.074609
O	3.622785	-0.021387	-1.975146
O	-1.233535	0.009214	4.890724
N	-0.533904	-0.859768	5.451071

O	0.218722	-1.643197	4.855547
C	-0.633615	-0.963704	6.902017
C	-1.491267	-0.092951	7.591560
C	-1.578105	-0.200851	8.985708
C	-0.814644	-1.167330	9.669673
C	0.040340	-2.030497	8.955463
C	0.136684	-1.932713	7.559263
O	-0.955130	-1.210495	11.031025
H	-2.074683	0.648734	7.041227
H	-2.234847	0.457737	9.560453
H	0.632914	-2.781243	9.489430
H	0.793118	-2.591408	6.985489
H	-0.386427	-1.906976	11.387732
H	-1.122877	-0.006687	2.999347
H	-0.959709	0.004002	-0.524277
H	1.224232	-0.009558	-1.805159
H	3.403536	-0.004222	1.924452
H	1.230270	-0.002370	3.197543



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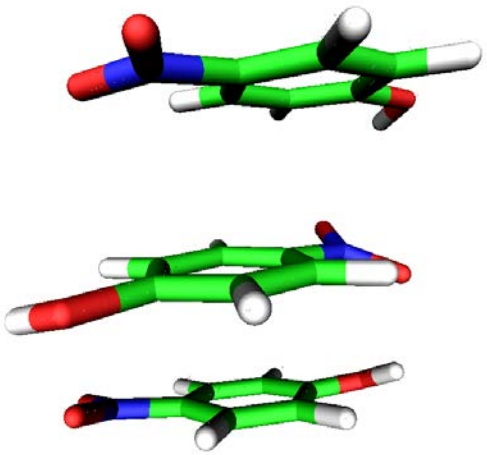
Trimer of 4-nitrophenol – stacking structure

C	-0.546346	-0.324833	0.567794
C	-0.115757	-0.342439	1.909998
C	1.250870	-0.184311	2.222029
C	2.172477	0.030533	1.199879
C	1.728058	0.072137	-0.131925
C	0.377849	-0.119438	-0.456093
O	-0.975770	-0.502954	2.954851
N	2.686721	0.367773	-1.203637
O	2.284912	0.316039	-2.373146
O	3.843674	0.671812	-0.877917
N	-1.242996	2.760998	1.695423
C	-0.324898	3.006718	0.594092
C	-0.815185	3.043472	-0.723106
C	0.052376	3.356365	-1.764672
C	1.412440	3.623509	-1.490875
C	1.906742	3.503005	-0.174613
C	1.034074	3.218858	0.870739
O	2.191014	4.007944	-2.530460
O	-0.876438	3.075030	2.842898
O	-2.349852	2.257364	1.443015
O	-1.548355	5.994923	1.867459
C	-0.261559	6.214168	1.481441
C	0.822235	6.167142	2.384025
C	2.123029	6.348297	1.915469
C	2.332786	6.544515	0.542358
C	1.258335	6.626377	-0.359225
C	-0.041700	6.484618	0.115417
N	3.703093	6.558422	0.030212
O	4.624890	6.786070	0.820098
O	3.869828	6.306439	-1.179199

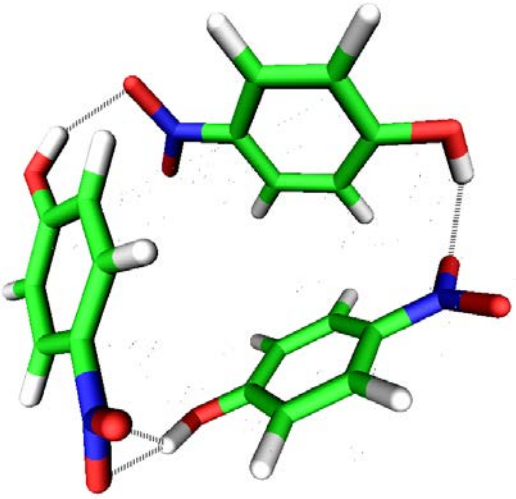


H	-1.873079	2.855345	-0.905921
H	-0.303868	3.429431	-2.793697
H	2.971581	3.642289	0.019377
H	1.391466	3.145364	1.895595
H	3.034021	4.361705	-2.194685
H	-1.607821	-0.439882	0.333442
H	0.065959	-0.080071	-1.499204
H	3.230204	0.182309	1.415666
H	1.562581	-0.209902	3.268055
H	-1.888842	-0.428796	2.634529
H	-0.896358	6.527314	-0.561495
H	1.456737	6.773142	-1.420722
H	2.978578	6.296213	2.589638
H	0.642682	5.960539	3.442439
H	-1.557853	5.622180	2.764419

45

Trimer of 4-nitrophenol – hydrogen bonded structure

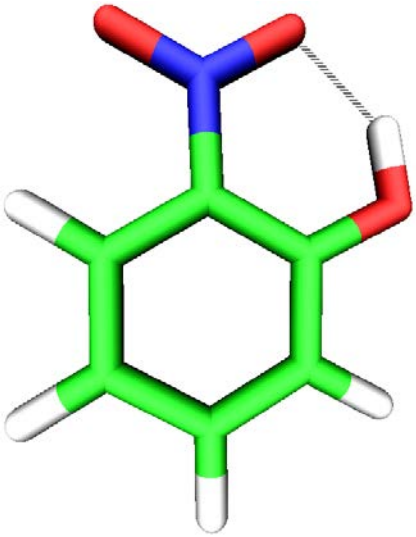
C	-1.667989	2.198460	1.122903
C	-0.917745	2.956385	0.205068
C	-1.311831	3.069124	-1.142952
C	-2.455905	2.407392	-1.575962
C	-3.203777	1.617863	-0.669388
C	-2.807128	1.531916	0.687266
N	0.295988	3.602060	0.661911
O	0.587519	3.560278	1.860695
O	-4.287512	0.976279	-1.154262
O	1.028293	4.158006	-0.198518
O	3.435010	2.926422	0.543612
C	3.253690	1.678406	0.070571
C	2.370732	1.376827	-0.997547
C	2.248851	0.067494	-1.451376
C	2.984586	-0.952849	-0.821228
C	3.856612	-0.670778	0.248685
C	4.002316	0.641822	0.679962
N	2.832548	-2.316753	-1.281506
O	2.339629	-2.526936	-2.393941
O	3.191899	-3.246665	-0.511194
O	1.634811	-2.803056	1.759473
C	0.379036	-2.646905	1.289604
C	-0.032140	-3.129051	0.022624
C	-1.334312	-2.909448	-0.415009
C	-2.235929	-2.214865	0.412080
C	-1.848679	-1.758162	1.687171
C	-0.546953	-1.975836	2.124331
N	-3.573878	-1.944216	-0.081031
O	-3.913042	-2.394088	-1.178897
O	-4.329400	-1.227336	0.624842
H	-0.717911	3.671860	-1.830415
H	-2.786259	2.473466	-2.614603
H	-3.396749	0.931888	1.381164



H	-1.341082	2.135987	2.161020
H	-4.604869	0.310338	-0.503798
H	2.725859	3.528526	0.215148
H	4.682349	0.894623	1.495872
H	4.418051	-1.479834	0.716331
H	1.582717	-0.181762	-2.278129
H	1.795546	2.177385	-1.465782
H	2.230899	-3.115120	1.037357
H	-0.216570	-1.628477	3.105306
H	-2.571753	-1.242025	2.317773
H	-1.663937	-3.264833	-1.391544
H	0.668677	-3.676776	-0.609691

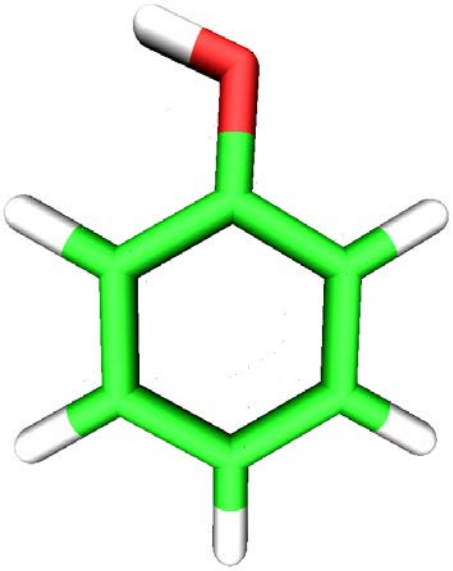
15
2-Nitrophenol

N	-1.066030	1.327240	0.000000
O	-0.789149	2.525406	0.000000
O	-2.257807	0.908815	0.000000
C	0.001951	0.343571	0.000000
C	-0.297939	-1.051599	0.000000
C	0.784443	-1.959847	0.000000
C	2.097382	-1.496207	0.000000
C	2.382301	-0.111930	0.000000
C	1.335572	0.802894	0.000000
O	-1.545324	-1.544609	0.000000
H	0.553990	-3.027555	0.000000
H	2.918886	-2.218794	0.000000
H	3.416522	0.239705	0.000000
H	1.512774	1.878965	0.000000
H	-2.140918	-0.743948	0.000000

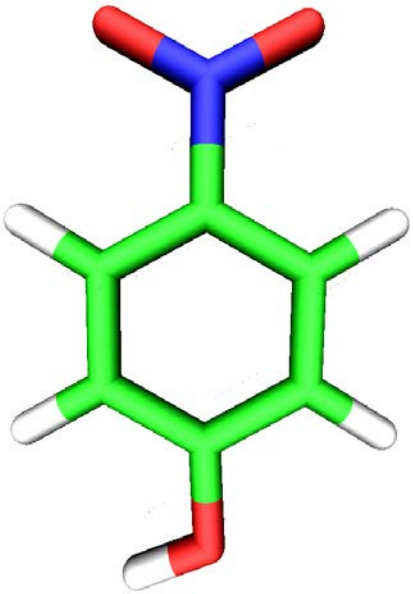


13
Phenol

C	-0.001080	0.000000	-0.000708
C	-0.001661	0.000000	1.402070
C	1.206741	0.000000	2.114967
C	2.427191	0.000000	1.416557
C	2.438456	0.000000	0.010930
C	1.224475	0.000000	-0.687697
O	3.647819	0.000000	2.057500
H	1.201466	0.000000	3.211118
H	3.397144	0.000000	-0.514137
H	1.237834	0.000000	-1.782086
H	-0.944690	0.000000	-0.553056
H	-0.948054	0.000000	1.951699
H	3.495345	0.000000	3.014409

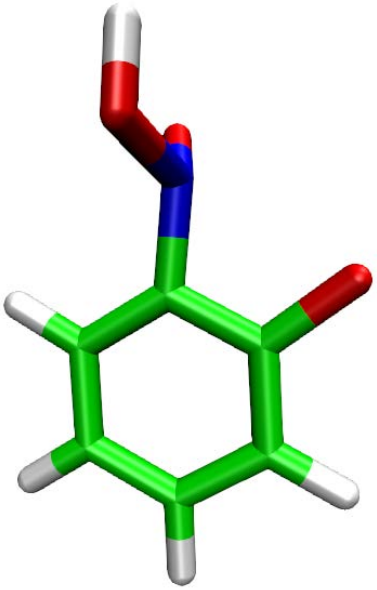


```
 15
4-Nitrophenol
 N     -1.066030      1.327240      0.000000
 O     -0.789149      2.525406      0.000000
 O     -2.257807      0.908815      0.000000
 C      0.001951      0.343571      0.000000
 C     -0.297939     -1.051599      0.000000
 C      0.784443     -1.959847      0.000000
 C      2.097382     -1.496207      0.000000
 C      2.382301     -0.111930      0.000000
 C      1.335572      0.802894      0.000000
 O     -1.545324     -1.544609      0.000000
 H      0.553990     -3.027555      0.000000
 H      2.918886     -2.218794      0.000000
 H      3.416522      0.239705      0.000000
 H      1.512774      1.878965      0.000000
 H     -2.140918     -0.743948      0.000000
```



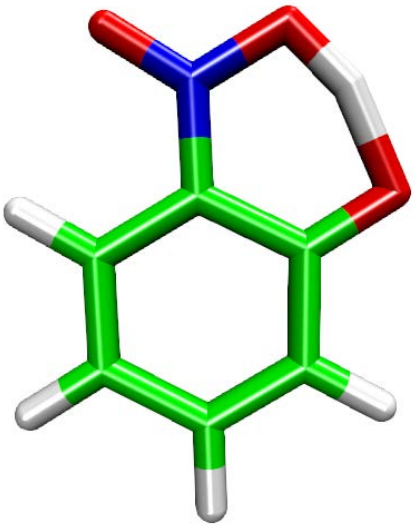
We also provide the Cartesian coordinates of 2-nitrophenol at various important points on PES: S_1/S_0 conical intersection (CI), structure upon hydrogen transfer in S_0 state (HT) and minimum in the S_1 state (S1MIN). All these structures were obtained at the SA3-CASSCF (4 electrons / 4orbitals) level with 6-31+g* basis set. The Coordinates are provided in Ångstrom units.

```
 15
CI of 2-nitrophenol
 C      0.000000      0.000000      0.000000
 C      0.000000      0.000000      1.395987
 C      1.204354      0.000000      2.075104
 C      2.371396     -0.008288      1.335292
 C      2.368456     -0.007205     -0.028843
 C      1.171953      0.010964     -0.735629
 N      3.710581      0.005221      1.877829
 O      4.201315      1.005577      2.385028
 O      3.581531     -0.039392     -0.611783
 O      4.025437     -1.191357      2.459122
 H      4.872600     -1.046193      2.873613
 H      1.163350      0.026555     -1.809173
 H     -0.936973      0.006312     -0.527215
 H     -0.928345      0.012892      1.935052
 H      1.245545      0.029442      3.148182
```



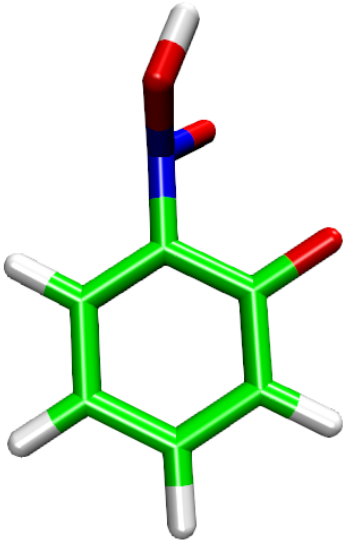
```
 15
HT of 2-nitrophenol
 C      0.000000      0.000000      0.000000
 C      0.000000      0.000000      1.442737
 C      1.196376      0.000000      2.136559
 C      2.412826     -0.001032      1.387286
 C      2.453293      0.000382     -0.065951
```

C	1.169449	0.000876	-0.726382
N	3.609479	-0.002735	2.083952
O	3.700106	-0.000072	3.306290
O	3.556026	0.010335	-0.714797
O	4.746915	-0.016687	1.386108
H	4.423404	-0.034748	0.383353
H	1.159920	0.003308	-1.814154
H	-0.946086	0.000710	-0.539813
H	-0.939243	0.000397	1.992532
H	1.239846	-0.000144	3.221247



15
S1MIN of 2-nitrophenol

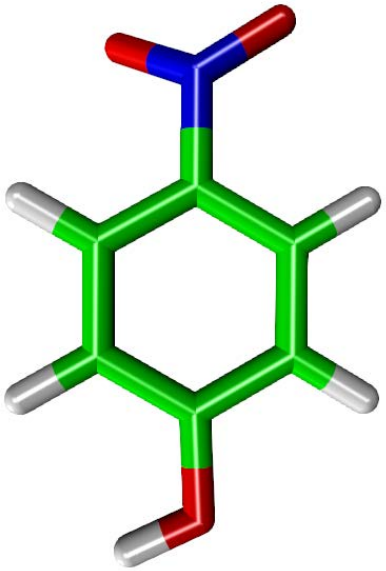
C	-0.107570	-1.265236	-2.108783
C	-0.209008	-1.449192	-0.736989
C	-0.100854	-0.367718	0.109129
C	0.058949	0.923161	-0.393412
C	0.136743	1.110316	-1.767472
C	0.075992	0.013255	-2.612665
N	-0.187170	-0.532920	1.525486
O	1.049409	-0.735586	2.085777
O	0.132438	1.968702	0.428609
O	-0.959560	0.182554	2.161361
H	0.947243	-0.464182	2.994997
H	0.252241	2.105077	-2.155066
H	0.148462	0.166111	-3.674167
H	-0.178765	-2.107474	-2.771285
H	-0.359849	-2.426956	-0.318717



Additionally,we show S1/S_0 conical intersection of 4-nitrophenol with a twisted NO2 grooup.

15
CI of 4-nitrophenol

C	-0.040441	-1.202281	0.036346
C	-0.118407	-1.198645	1.414553
C	-0.025420	-0.001936	2.115956
C	0.149895	1.190747	1.431181
C	0.233551	1.189629	0.047012
C	0.127002	-0.003539	-0.642431
O	-0.113267	-0.064339	3.460390
N	0.212981	-0.006331	-2.068421
O	0.126118	-1.032322	-2.739824
O	-0.455476	1.071366	-2.642677
H	0.225289	2.120906	1.967345
H	0.369439	2.117526	-0.477383
H	-0.117636	-2.119561	-0.513574
H	-0.254101	-2.113880	1.959476
H	-0.043599	0.794617	3.854768



2. Linear interpolations between important points on potential energy surface

We provide here additional mapping of the potential energy surface of nitrophenol molecules. The energies along the photodynamically relevant pathways are calculated with a single reference ADC(2) method; the part of PES near the conical intersection with the ground state clearly suffers from qualitative deficiencies. The curves were also recalculated with the CASSCF method. However, these results are sensitive on the choice of the active space and also the quantitative agreement is affected by the lack of dynamical correlation.

The interpolation coordinate connecting the global ground state minimum of 2-nitrophenol (here designated as FC structure) with the ground state minimum of the aci-nitro form of 2-nitrophenol (designated as HT in the graph) is shown in Figure S1. This graph shows that the hydrogen transfer is energetically feasible upon low-lying excitations. The presented data are the same as those shown in Fig. 1 (bottom panel) in the main text.

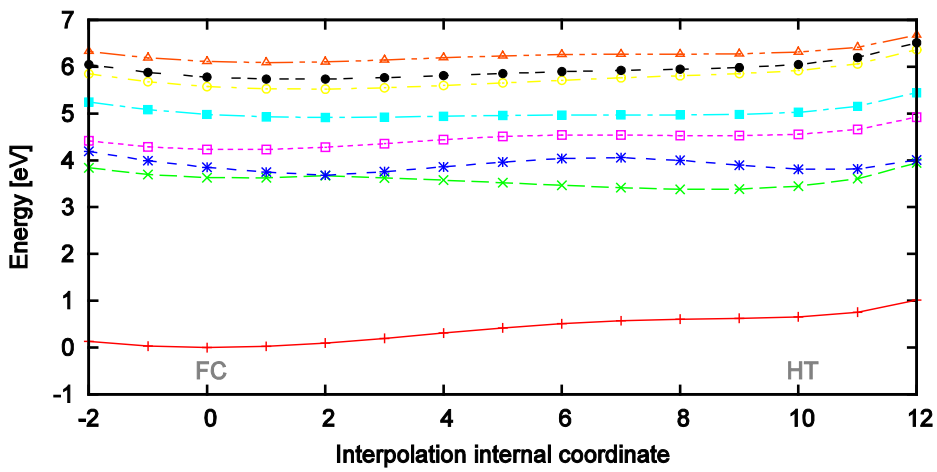


Figure S1: Linear interpolation along internal coordinates connecting ground state optimal structure of 2-nitrophenol (FC) and aci-nitro form of 2-nitrophenol (HT). Energies were calculated at the ADC(2) level with aug-cc-pVDZ basis set.

Looking at the interpolation between the global minimum on the S_0 state (FC) and minimum on the S_1 state (again with a transferred hydrogen, S1MIN), we observe a barrier on low lying excited states, see Fig. S2. This suggests that the proton transfer takes place in the planar geometry and only then the pyramidalization follows. It also indicates that the population might get trapped to a certain extent in the structure with hydroxyl group. Note that the S_1 minimum is close to the conical intersection with the ground state; the ADC(2) method there obviously fails. The general picture is confirmed by the CASSCF calculations (Figure S3).

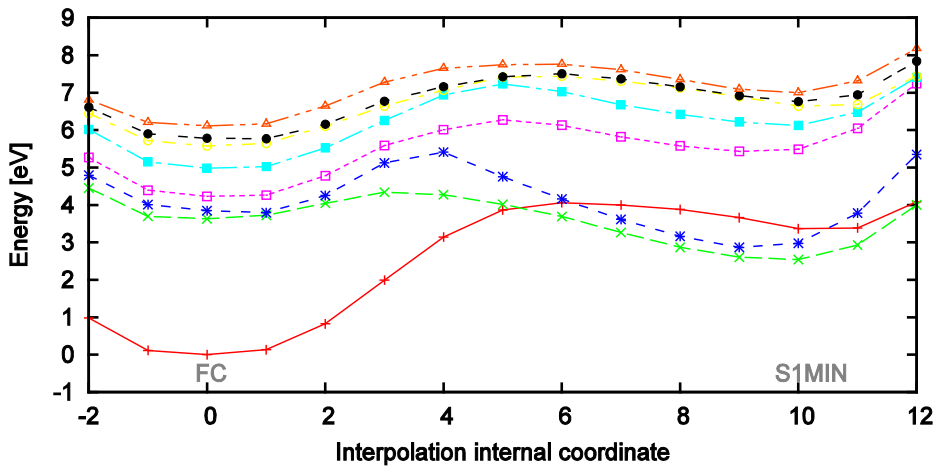


Figure S2: Linear interpolation along internal coordinates connecting ground state optimal structure of 2-nitrophenol (FC) and the global S_1 minimum (S1MIN). Energies were calculated at the ADC(2) level with aug-cc-pVDZ basis set.

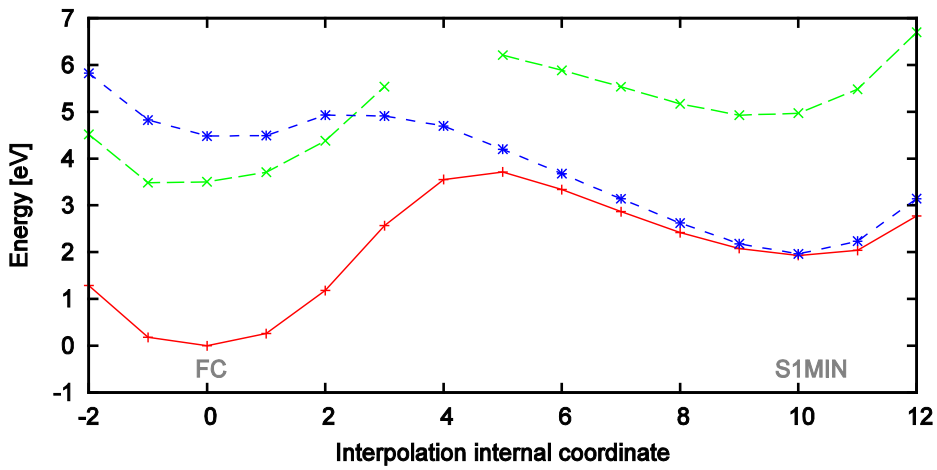


Figure S3: Linear interpolation along internal coordinates connecting ground state optimal structure of 2-nitrophenol (FC) and the global S_1 minimum (S1MIN). Energies were calculated at the SA3-CASSCF (4 electrons / 4 orbitals) level with 6-31+g* basis set.

The HT structure is on the S_1 state energetically close to the S_1/S_0 conical intersection and to the S_1 minimum as described below both at the ADC(2) (Fig. S4) and CASSCF (Fig. S5) levels.

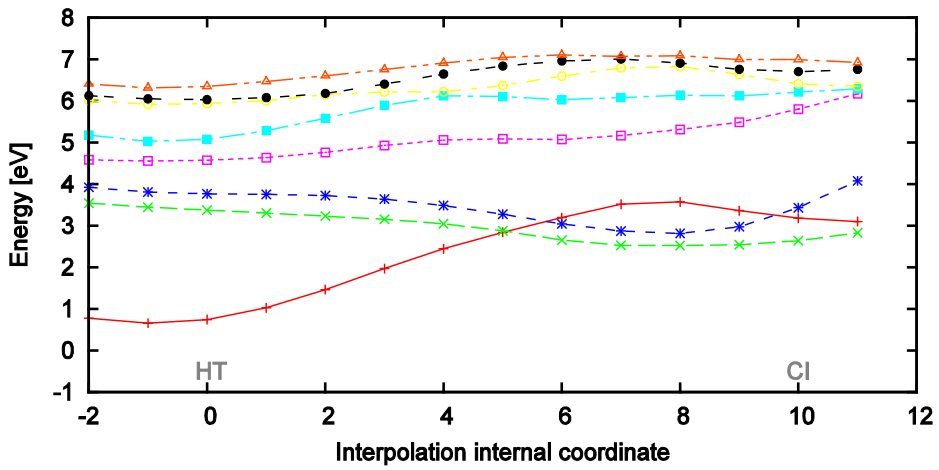


Figure S4: Linear interpolation along internal coordinates connecting aci-nitro form of 2-nitrophenol (HT) and S_1/S_0 conical intersection (CI). Energies were calculated at the ADC(2) level with aug-cc-pVDZ basis set.

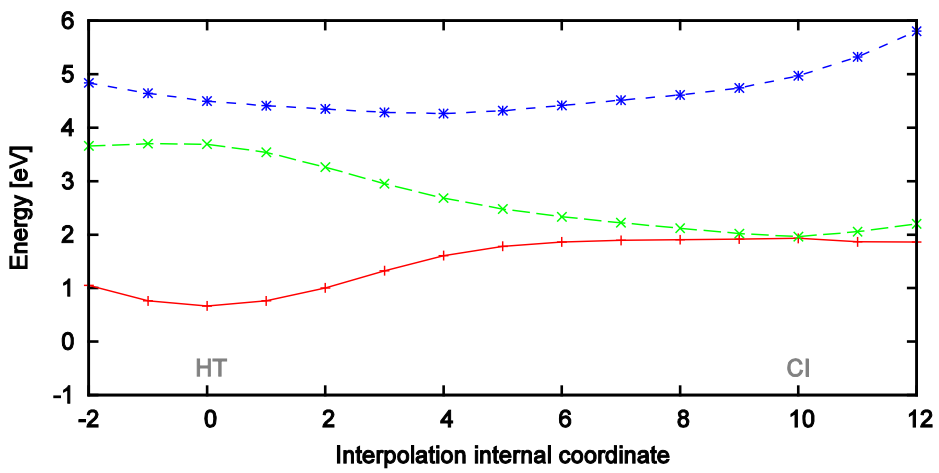


Figure S5: Linear interpolation along internal coordinates connecting aci-nitro formo of 2-nitrophenol (HT) and S_1/S_0 conical intersection (CI). Energies were calculated at the SA3- CASSCF (4 electrons / 4 orbitals) level with 6-31+g* basis set.

Finally, we show that for 4-nitrophenol, the molecule can relax into the ground state without transfer of hydrogen (see Fig. S6).

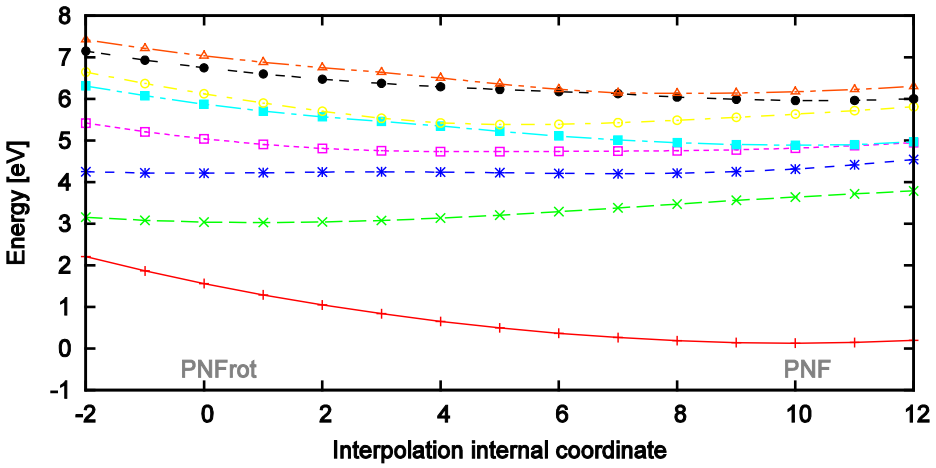


Figure S6: Linear interpolation (and extrapolation) along internal coordinates of 4-nitrophenol structures between Franck-Condon point of 4-nitrophenol (PNF) and S_1/S_0 conical intersection with a twisted nitro group (PNFrot). Energies were calculated on ADC(2) level with aug-cc-pVDZ basis set, the PNFrot point was optimized at the SA3-CASSCF CASSCF(4 electrons / 4 orbitals) level with 6-31+g* basis set.