

Supporting Information

Full reference 40:

Gaussian 03, Revision B.04, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Figure A – Geometric parameter definitions a) Bond length definitions, b) Torsional angle definitions.

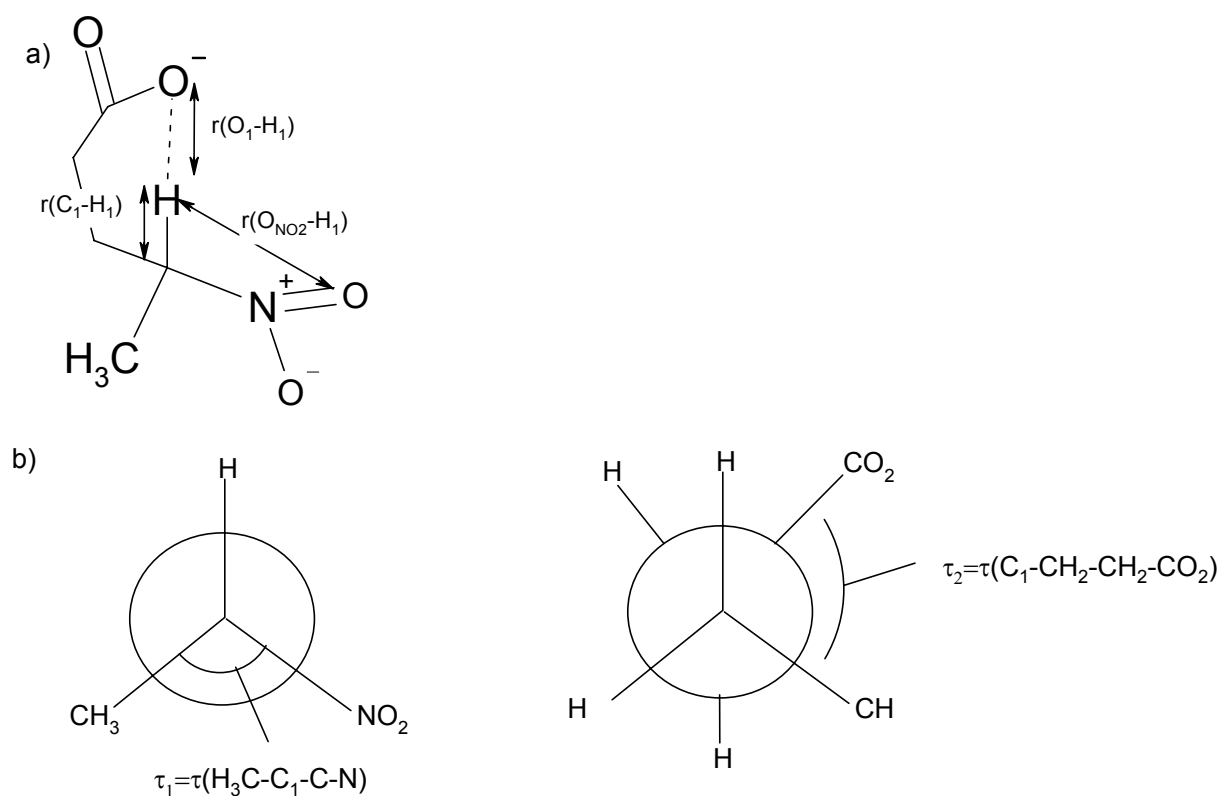


Table A – Gas phase B3LYP/6-31+G(d,p) model (optimised) geometric information.

	CH-CHA	CH-HEX	TS1	OH-HEX	TS2	OH-OCT-NO2	OH-CHA
$r(\text{O}_1\text{-H}_1)/\text{Å}$	4.51	2.17	1.18	1.03	0.98	1.11	-
$r(\text{C}_1\text{-H}_1)/\text{Å}$	1.09	1.09	1.44	1.75	2.17	2.61	-
rc	-3.41	-1.08	0.26	0.71	1.18	1.50	-
$r(\text{O}_{\text{NO}_2}\text{-H}_1)/\text{Å}$	2.36	2.10	2.94	2.51	2.38	1.33	-
$r(\text{C}_1\text{-O}_1)/\text{Å}$	4.51	2.89	2.58	2.73	3.03	3.35	-
$\tau 1/^\circ$	-122.0	-123.6	-136.0	-144.2	156.9	-175.5	-
$\tau 2/^\circ$	167.1	56.0	50.3	56.6	67.6	76.2	-

Table B – PCM B3LYP/6-31+G(d,p) model (optimised) geometric information.

	CH-CHA	CH-HEX	TS1	OH-HEX	TS2	N-OCT-NO2	OH-CHA
$r(\text{O}_1\text{-H}_1)/\text{Å}$	4.43	2.67	1.32	0.99	0.98	1.43	0.97
$r(\text{C}_1\text{-H}_1)/\text{Å}$	1.09	1.09	1.34	1.97	2.18	2.47	4.87
rc	-3.34	-1.58	0.02	0.97	1.20	1.04	3.90
$r(\text{O}_{\text{NO}_2}\text{-H}_1)/\text{Å}$	2.37	2.37	2.81	2.90	2.44	1.06	5.10
$r(\text{C}_1\text{-O}_1)/\text{Å}$	-122.07	3.26	2.60	2.88	3.05	3.27	4.96
$\tau 1/^\circ$	-122.8	-121.3	-135.3	-163.3	-170.7	-178.1	-179.1
$\tau 2/^\circ$	164.8	65.7	52.1	63.3	69.6	73.5	179.8

Table C – QM/MM B3LYP/6-31+G(d,p) (geometric) information.

	CH-CHA	CH-HEX	TS1	OH-HEX	TS2	OH-OCT-NO2	OH-CHA
$r(\text{O}_1\text{-H}_1)/\text{Å}$	4.59	2.36	1.19	1.00	0.98	1.08	0.97
$r(\text{C}_1\text{-H}_1)/\text{Å}$	1.09	1.09	1.41	1.93	2.61	2.58	4.91
rc	-3.50	-1.27	0.22	0.92	1.62	1.50	3.94
$r(\text{O}_{\text{NO}_2}\text{-H}_1)/\text{Å}$	2.39	2.40	2.21	2.38	2.30	1.39	5.03
$r(\text{C}_1\text{-O}_1)/\text{Å}$	4.28	2.78	2.56	2.84	2.97	3.30	4.99
$\tau 1/^\circ$	-122.7	-121.4	-139.6	-156.4	-165.2	-177.3	-175.6
$\tau 2/^\circ$	170.2	58.9	49.6	64.6	67.5	71.2	167.1

Table D – Gas phase AM1-SRP model (optimised) geometric information.

	CH-CHA	CH-HEX	TS1	OH- HEX	TS2	OH-OCT- NO2	OH- CHA
$r(\text{O}_1\text{-H}_1)/\text{\AA}$	4.50	2.63	1.30	-	0.98	0.97	-
$r(\text{C}_1\text{-H}_1)/\text{\AA}$	1.10	1.10	1.35	-	2.06	3.31	-
rc	-3.40	-1.53	0.05	-	1.08	2.34	-
$r(\text{O}_{\text{NO}_2^-}\text{-H}_1)/\text{\AA}$	2.41	2.66	2.71	-	3.24	2.09	-
$r(\text{C}_1\text{-O}_1)/\text{\AA}$	4.24	2.66	2.60	-	2.92	3.98	-
$\tau 1/^\circ$	-119.1	-118.2	-136.1	-	158.1	-178.2	-
$\tau 2/^\circ$	170.6	53.6	52.0	-	65.1	135.4	-

Table E – QM/MM AM1-SRP (optimised) geometric information.

	CH-CHA	CH-HEX	TS1	OH- HEX	TS2	OH-OCT- NO2	OH- CHA
$r(\text{O}_1\text{-H}_1)/\text{\AA}$	4.51	2.38	1.28	1.40	1.04	0.97	0.97
$r(\text{C}_1\text{-H}_1)/\text{\AA}$	1.10	1.10	1.31	1.96	2.79	2.91	4.82
rc	-3.42	-1.28	0.02	0.56	1.74	1.94	3.85
$r(\text{O}_{\text{NO}_2^-}\text{-H}_1)/\text{\AA}$	2.50	2.54	2.83	3.05	2.28	2.04	5.17
$r(\text{C}_1\text{-O}_1)/\text{\AA}$	4.23	2.98	2.50	3.06	3.45	3.49	4.94
$\tau 1/^\circ$	-118.6	-118.7	-125.0	-177.4	-179.0	-179.7	-179.8
$\tau 2/^\circ$	170.1	61.7	52.1	72.3	85.8	78.2	176.5

Table F Total charge and total spin are followed by the Cartesian co-ordinates (Å) of the B3LYP/6-31+G(d,p) *in vacuo* optimised stationary points.

CH-CHA:

-1 1
8 2.627170 -0.877913 -1.215868
6 2.741439 -0.370918 -0.070338
8 3.778665 -0.081754 0.579529
6 1.395674 -0.084661 0.702243
6 0.178411 0.067105 -0.215138
6 -1.154148 0.027012 0.556008
1 -1.250597 -0.927867 1.077400
7 -2.299531 -0.011316 -0.447670
8 -2.852794 -1.096437 -0.645988
8 -2.599642 1.031773 -1.031903
6 -1.376151 1.198556 1.509848
1 -2.362027 1.149663 1.985553
1 -0.612651 1.161050 2.290724
1 -1.287897 2.150842 0.980696
1 0.236234 1.008493 -0.774423
1 0.211990 -0.744068 -0.949289
1 1.550726 0.799266 1.329916
1 1.246652 -0.935870 1.384664

CH-HEX:

-1 1
8 2.179348 0.151200 0.619186
6 1.750162 -0.593223 1.547536
8 2.405573 -1.269389 2.378110
6 0.193684 -0.723684 1.692610
6 -0.680794 0.182516 0.809935
6 -0.390510 0.042565 -0.698781
1 0.612007 0.452279 -0.856211
7 -1.338706 0.978602 -1.437461
8 -2.214937 0.500355 -2.166653
8 -1.192275 2.189664 -1.260331
6 -0.501167 -1.370728 -1.248162
1 -0.382277 -1.383683 -2.335047
1 0.303064 -1.965337 -0.808289
1 -1.463043 -1.832613 -1.003790
1 -1.743574 -0.044164 0.988204
1 -0.513534 1.229598 1.078566
1 -0.050068 -0.518676 2.742639
1 -0.062612 -1.779816 1.536700

TS1:

-1 1

8	1.867387	-0.019174	0.181947
6	1.652970	-0.405963	1.418418
8	2.532145	-0.482680	2.276951
6	0.207072	-0.825616	1.746303
6	-0.885334	-0.111266	0.922648
6	-0.591127	-0.164675	-0.574848
1	0.824584	0.003442	-0.369537
7	-1.076477	0.940924	-1.316807
8	-1.279036	0.802894	-2.552936
8	-1.245843	2.055764	-0.756713
6	-0.818936	-1.498690	-1.259475
1	-0.372148	-1.522232	-2.255854
1	-0.363565	-2.297419	-0.662477
1	-1.890855	-1.733094	-1.373542
1	-1.866341	-0.563168	1.155974
1	-0.936925	0.938078	1.221060
1	0.056421	-0.669534	2.818679
1	0.159873	-1.912270	1.583833

OH-HEX:

-1 1

8	1.916338	0.029837	0.213026
6	1.654469	-0.374130	1.456630
8	2.523047	-0.416226	2.316248
6	0.218652	-0.828926	1.725122
6	-0.879631	-0.103772	0.915293
6	-0.685298	-0.185170	-0.586277
1	1.029375	0.034983	-0.319767
7	-1.092237	0.914966	-1.321428
8	-1.293934	0.783744	-2.570315
8	-1.230266	2.052713	-0.768755
6	-0.878188	-1.520618	-1.263522
1	-0.408546	-1.545995	-2.250056
1	-0.438727	-2.320782	-0.654534
1	-1.945735	-1.766521	-1.412851
1	-1.853604	-0.536893	1.216105
1	-0.906448	0.951323	1.196742
1	0.047718	-0.725744	2.801021
1	0.196878	-1.907469	1.510942

TS2:

-1 1

8	1.794571	0.437049	0.359772
6	1.553760	-0.287918	1.461456
8	2.443396	-0.484327	2.272642
6	0.156479	-0.877772	1.636967
6	-1.015827	-0.180390	0.907729
6	-0.989466	-0.279052	-0.594954
1	0.979968	0.523481	-0.186171
7	-1.042525	0.852649	-1.337436
8	-1.315175	0.777008	-2.587112
8	-0.781204	2.001324	-0.804587
6	-1.354824	-1.568137	-1.271153
1	-0.817372	-1.697121	-2.216236
1	-1.119554	-2.419781	-0.618862
1	-2.430581	-1.626455	-1.517918
1	-1.940364	-0.648239	1.296228
1	-1.053462	0.876497	1.185760
1	-0.018945	-0.914537	2.718082
1	0.229382	-1.923624	1.305820

OH-OCT-NO₂:

-1 1

8	1.632116	1.010758	0.699958
6	1.576747	-0.040259	1.477157
8	2.529000	-0.401789	2.171488
6	0.280895	-0.871088	1.551083
6	-1.010297	-0.330269	0.895555
6	-1.100578	-0.424623	-0.602396
1	0.772189	1.266525	0.048551
7	-0.750463	0.602583	-1.360605
8	-0.937386	0.620597	-2.623683
8	-0.180890	1.672996	-0.791397
6	-1.674575	-1.625773	-1.291951
1	-1.059930	-1.920405	-2.150915
1	-1.740445	-2.469508	-0.595127
1	-2.682481	-1.432154	-1.692939
1	-1.844218	-0.913932	1.313939
1	-1.166860	0.710027	1.203148
1	0.109656	-1.035602	2.622567
1	0.525776	-1.857430	1.135595

OH-CHA:

-1 1

8	3.188257	-0.795942	1.002479
6	2.106619	-0.637640	0.432745
8	1.508639	-1.600280	-0.221053
6	1.458480	0.758789	0.502662
6	0.236417	1.077855	-0.388485
6	-1.084815	0.503875	0.042546
1	0.509326	-1.430209	-0.670245
7	-1.511398	-0.645017	-0.458151
8	-2.681215	-1.103153	-0.229553
8	-0.694376	-1.362215	-1.240640
6	-2.009885	1.239440	0.964971
1	-2.426086	0.568276	1.725642
1	-1.478175	2.057755	1.464446
1	-2.874556	1.666852	0.432145
1	0.132396	2.173389	-0.399961
1	0.446567	0.769430	-1.419042
1	2.271679	1.461005	0.278940
1	1.204999	0.925870	1.557802

Table G Total charge and total spin followed by the cartesian co-ordinates (Å) of the B3LYP/6-31+G(d,p) PCM optimised stationary points.

CH-CHA:

-1 1

8	2.714197	-0.426979	-1.317886
6	2.727868	-0.300307	-0.059985
8	3.764935	-0.297757	0.671401
6	1.383337	-0.147206	0.688438
6	0.156363	0.008253	-0.214399
6	-1.158233	0.032803	0.591219
1	-1.268989	-0.891645	1.160675
7	-2.295578	-0.045670	-0.422243
8	-2.815081	-1.146278	-0.620791
8	-2.620027	0.978638	-1.023600
6	-1.352721	1.256277	1.480170
1	-2.346875	1.259128	1.935472
1	-0.615942	1.223990	2.286255
1	-1.214667	2.182303	0.917141
1	0.230951	0.930093	-0.800795
1	0.124760	-0.826477	-0.920815
1	1.485536	0.706163	1.366811
1	1.271690	-1.032371	1.328899

CH-HEX:

-1 1

8	2.038088	0.807423	1.323030
6	1.724441	-0.359906	1.697074
8	2.531207	-1.238373	2.130147
6	0.231939	-0.760479	1.673968
6	-0.686210	0.088732	0.786654
6	-0.362122	-0.041940	-0.714337
1	0.656243	0.296350	-0.904398
7	-1.218841	0.985397	-1.445879
8	-2.421823	0.757050	-1.579807
8	-0.672708	2.014490	-1.849111
6	-0.618586	-1.421699	-1.314343
1	-0.470509	-1.413698	-2.397801
1	0.095358	-2.129583	-0.886745
1	-1.630458	-1.770312	-1.093786
1	-1.728306	-0.209530	0.947081
1	-0.586697	1.139632	1.075067
1	-0.127971	-0.674797	2.707788
1	0.157296	-1.823292	1.424159

TS1:

-1 1

6	-0.880675	-1.515182	-1.274918
6	-0.630330	-0.196991	-0.568617
6	-0.907644	-0.154261	0.936144
6	0.222420	-0.824928	1.747153
6	1.627856	-0.338744	1.394562
8	1.823059	0.018056	0.145007
7	-1.016277	0.937293	-1.294856
8	-1.217435	0.841033	-2.541602
8	-1.089257	2.072744	-0.736066
8	2.535614	-0.320159	2.235195
1	0.753276	-0.025263	-0.398038
1	-0.373009	-1.569340	-2.240485
1	-0.507717	-2.334463	-0.652662
1	-1.952492	-1.688310	-1.446657
1	-1.856140	-0.660658	1.164593
1	-1.006942	0.885535	1.251456
1	0.069172	-0.677557	2.818713
1	0.221934	-1.910424	1.578750

OH-HEX:

-1 1

8	1.900993	0.161340	0.190829
6	1.637218	-0.258300	1.442714
8	2.509713	-0.180264	2.294199
6	0.262234	-0.846960	1.692806
6	-0.910587	-0.159470	0.952174
6	-0.849930	-0.235361	-0.556364
1	1.081415	0.079934	-0.361966
7	-0.999401	0.881036	-1.281198
8	-1.132804	0.803899	-2.571835
8	-1.004957	2.065184	-0.739678
6	-0.998908	-1.556233	-1.261451
1	-0.303993	-1.664181	-2.100252
1	-0.819123	-2.377517	-0.561799
1	-2.012070	-1.680680	-1.670263
1	-1.830256	-0.653128	1.299792
1	-0.971922	0.885871	1.256967
1	0.092551	-0.823970	2.771517
1	0.323690	-1.905879	1.407431

TS2:

-1 1

8	1.772807	0.411913	0.284732
6	1.537096	-0.266658	1.424169
8	2.441538	-0.379504	2.236681
6	0.167499	-0.890534	1.615656
6	-1.034881	-0.184782	0.943497
6	-1.074438	-0.259776	-0.563020
1	0.966622	0.454501	-0.268813
7	-1.049835	0.849456	-1.296072
8	-1.234053	0.790906	-2.586146
8	-0.824855	2.030035	-0.766007
6	-1.350095	-1.563720	-1.253959
1	-0.644774	-1.756564	-2.069660
1	-1.283295	-2.389509	-0.539679
1	-2.356543	-1.581413	-1.694688
1	-1.934528	-0.680201	1.335404
1	-1.079027	0.858303	1.260811
1	0.007143	-0.958101	2.694702
1	0.251872	-1.923698	1.252427

OH-OCT-NO₂:

-1 1

8	1.585809	0.957587	0.726007
6	1.564493	-0.129367	1.411694
8	2.572711	-0.603578	1.986438
6	0.244680	-0.901694	1.565531
6	-1.018943	-0.294138	0.920837
6	-1.086005	-0.392076	-0.580031
1	0.521094	1.423369	-0.103715
7	-0.749658	0.610186	-1.348892
8	-0.869662	0.650897	-2.625424
8	-0.219540	1.760905	-0.777763
6	-1.582927	-1.634478	-1.254191
1	-0.931780	-1.920659	-2.086068
1	-1.632941	-2.456768	-0.537105
1	-2.587403	-1.480745	-1.669773
1	-1.882691	-0.845741	1.309772
1	-1.136345	0.744557	1.240432
1	0.071318	-1.010059	2.642401
1	0.416043	-1.917543	1.189881

OH-CHA:

-1 1

8	2.810818	0.479310	-1.235998
6	2.437487	-0.162917	-0.271449
8	3.351646	-0.911814	0.395292
6	1.024049	-0.212467	0.262658
6	0.045024	0.727434	-0.462880
6	-1.348422	0.655253	0.098834
1	2.948554	-1.381584	1.144120
7	-2.109814	-0.371132	-0.227668
8	-3.338953	-0.475081	0.226830
8	-1.668323	-1.324390	-1.019374
6	-1.895205	1.696538	1.031410
1	-2.206141	1.265556	1.992066
1	-1.136381	2.458761	1.228774
1	-2.780461	2.195967	0.615702
1	0.407408	1.756893	-0.381102
1	0.035646	0.464477	-1.525805
1	1.057762	0.013778	1.336000
1	0.668174	-1.246506	0.169841