

Theoretical Study of the Fragmentation Pathways of Norbornane in its Doubly Ionized Ground State

by

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SUPPORTING INFORMATION

Optimized Geometries (in Angstroms, Å) and total energies in Hartree

(Atomic Units, a.u.) Obtained using Gaussian98.

Figure 3: Relaxation of doubly ionized norbornane to five membered monocyclic intermediates (C5-min_x, x= 1, 2, 3)

Fig. 3a, S₂ (C_{2v}):

19 E(B3LYP/cc-pVDZ)= -273.1022707 a.u.

C	0.000000	0.000000	1.460308
C	0.000000	1.140556	0.445540
C	0.000000	-1.140556	0.445540
C	1.189396	0.728787	-0.592118
C	-1.189396	0.728787	-0.592118
C	1.189396	-0.728787	-0.592118
C	-1.189396	-0.728787	-0.592118
H	0.888023	0.000000	2.113036
H	-0.888023	0.000000	2.113036
H	0.000000	2.188466	0.769548
H	0.000000	-2.188466	0.769548
H	1.247513	1.268297	-1.545853
H	-1.247513	1.268297	-1.545853
H	1.247513	-1.268297	-1.545853
H	-1.247513	-1.268297	-1.545853
H	1.935129	1.180349	0.130189
H	-1.935129	1.180349	0.130189
H	1.935129	-1.180349	0.130189
H	-1.935129	-1.180349	0.130189

19 E(MPW1K/cc-pVDZ)= -273.039298833 a.u.

C	0.000000	0.000000	1.445479
C	0.000000	1.128143	0.439418
C	0.000000	-1.128143	0.439418
C	1.165279	0.721385	-0.587783
C	-1.165279	0.721385	-0.587783
C	1.165279	-0.721385	-0.587783
C	-1.165279	-0.721385	-0.587783
H	0.882873	0.000000	2.094583
H	-0.882873	0.000000	2.094583
H	0.000000	2.170356	0.762769
H	0.000000	-2.170356	0.762769
H	1.233814	1.264085	-1.531656
H	-1.233814	1.264085	-1.531656
H	1.233814	-1.264085	-1.531656
H	-1.233814	-1.264085	-1.531656
H	1.899352	1.163083	0.143206
H	-1.899352	1.163083	0.143206
H	1.899352	-1.163083	0.143206
H	-1.899352	-1.163083	0.143206

Fig. 3b, S₁ (C_s):

19 E(B3LYP/cc-pVDZ)= -273.130047670 a.u.

C	-1.099022	1.020707	0.000000
C	-0.688762	0.164097	1.149288
C	-0.688762	0.164097	-1.149288
C	-0.688762	-1.241178	0.766171
C	1.882888	0.592630	0.684065
C	-0.688762	-1.241178	-0.766171
C	1.882888	0.592630	-0.684065
H	-2.224857	1.085063	0.000000
H	-0.775003	2.072930	0.000000
H	-0.604753	0.528799	2.183153
H	-0.604753	0.528799	-2.183153
H	0.068885	-1.877060	1.261326
H	2.274301	-0.259440	1.250672
H	0.068885	-1.877060	-1.261326
H	2.274301	-0.259440	-1.250672
H	-1.637145	-1.634653	1.234333
H	1.663525	1.507944	1.249355
H	-1.637145	-1.634653	-1.234333
H	1.663525	1.507944	-1.249355

19 E(MPW1K/cc-pVDZ)= -273.058634480 a.u.

C	-1.088220	1.004063	0.000000
C	-0.638456	0.165524	1.135056
C	-0.638456	0.165524	-1.135056
C	-0.638456	-1.233107	0.758221
C	1.785017	0.590042	0.679146
C	-0.638456	-1.233107	-0.758221
C	1.785017	0.590042	-0.679146
H	-2.205571	1.010517	0.000000
H	-0.801687	2.059437	0.000000
H	-0.554710	0.529499	2.163408
H	-0.554710	0.529499	-2.163408
H	0.107746	-1.868074	1.253222
H	2.203449	-0.243904	1.242043
H	0.107746	-1.868074	-1.253222
H	2.203449	-0.243904	-1.242043
H	-1.590874	-1.599986	1.220883
H	1.554050	1.500546	1.237806
H	-1.590874	-1.599986	-1.220883
H	1.554050	1.500546	-1.237806

Fig. 3c, S₁ (C_s)

19 E(B3LYP/cc-pVDZ)= -273.109639214 a.u.

C	1.382658	0.516478	0.000000
C	0.937673	-0.912082	0.000000
C	0.000000	1.219105	0.000000
C	-0.442337	-0.897338	0.931905
C	-0.442337	-0.897338	-0.931905
C	-0.721100	0.565811	1.200822
C	-0.721100	0.565811	-1.200822
H	2.012731	0.715530	0.887227
H	2.012731	0.715530	-0.887227
H	1.572090	-1.810663	0.000000
H	0.028611	2.314244	0.000000
H	-1.161440	-1.722124	1.091837
H	-1.161440	-1.722124	-1.091837
H	-1.799713	0.771501	1.242918
H	-1.799713	0.771501	-1.242918
H	0.440301	-1.350317	1.523287
H	0.440301	-1.350317	-1.523287
H	-0.272602	0.852277	2.170505
H	-0.272602	0.852277	-2.170505

19 E(MPW1K/cc-pVDZ)= -273.073671919 a.u.

C	1.407993	0.574751	0.000000
C	1.155789	-0.893966	0.000000
C	0.000000	1.187378	0.000000
C	-0.673915	-0.888028	0.746705
C	-0.673915	-0.888028	-0.746705
C	-0.706465	0.525953	1.186903
C	-0.706465	0.525953	-1.186903
H	1.994025	0.847325	0.885297
H	1.994025	0.847325	-0.885297
H	1.939281	-1.685486	0.000000
H	-0.011743	2.276831	0.000000
H	-0.990616	-1.768123	1.319845
H	-0.990616	-1.768123	-1.319845
H	-1.774390	0.804006	1.232828
H	-1.774390	0.804006	-1.232828
H	0.689494	-1.309693	1.012001
H	0.689494	-1.309693	-1.012001
H	-0.291347	0.698772	2.184053
H	-0.291347	0.698772	-2.184053

Fig. 3d, C5-Min₁:

19 E(B3LYP/cc-pVDZ)= -273.199676924 a.u.

C	-0.307096	-1.158406	-0.033854
C	-1.831138	-0.928472	0.000136
C	0.272314	0.244622	0.314910
C	-2.065890	0.484032	-0.131235
C	2.752607	-0.342961	-0.115221
C	-0.841315	1.269264	-0.062632
C	1.665039	0.578610	0.038701
H	0.012354	-1.946759	0.659324
H	-0.008388	-1.460273	-1.050674
H	-2.487272	-1.577774	-0.612082
H	0.400866	0.311622	1.441360
H	-3.061149	0.935420	-0.263731
H	3.136232	-0.123654	-1.152668
H	-0.743766	1.645265	-1.117213
H	1.919604	1.651745	0.009077
H	-2.278266	-1.090305	1.031249
H	2.531737	-1.410750	-0.010146
H	-0.929089	2.198389	0.531200
H	3.640016	-0.013064	0.469476

19 E(MPW1K/cc-pVDZ)= -273.140503230 a.u.

C	-0.298890	-1.141427	-0.051243
C	-1.806741	-0.925197	0.014819
C	0.264929	0.244352	0.303436
C	-2.049883	0.473716	-0.126229
C	2.726085	-0.340308	-0.105941
C	-0.833328	1.254871	-0.073633
C	1.650097	0.579022	0.053431
H	0.037760	-1.935899	0.616208
H	-0.021081	-1.421519	-1.073354
H	-2.476099	-1.595648	-0.539695
H	0.395976	0.308023	1.423451
H	-3.042472	0.917849	-0.249514
H	3.017934	-0.143527	-1.170450
H	-0.753384	1.589498	-1.135706
H	1.906324	1.645321	0.042135
H	-2.205041	-1.019890	1.067916
H	2.502548	-1.398335	0.020261
H	-0.911742	2.191007	0.494075
H	3.635663	-0.007057	0.416837

Fig. 3e, C5-Min₂:

19 E(B3LYP/cc-pVDZ)= -273.193230690 a.u.

C	-1.830087	-0.961323	-0.040030
C	-2.116450	0.445977	0.030745
C	-0.892000	1.247677	0.078240
C	0.249762	0.268481	-0.019548
C	-0.298279	-1.103973	-0.003267
C	1.635697	0.635193	-0.145373
C	2.736121	-0.395089	0.115482
H	-0.871602	1.807641	1.054360
H	-0.877520	2.109252	-0.629778
H	-3.129292	0.877371	0.051771
H	0.140161	-1.733204	-0.803733
H	3.702715	0.028253	-0.189026
H	-2.331926	-1.342244	-0.973394
H	1.606002	0.877361	-1.259868
H	0.075878	-1.600697	0.922691
H	2.791026	-0.623676	1.192296
H	-2.427713	-1.535063	0.710623
H	1.828147	1.642906	0.271746
H	2.585533	-1.329553	-0.445181

19 E(MPW1K/cc-pVDZ)= -273.133051010 a.u.

C	-1.813191	-0.952085	-0.055810
C	-2.096192	0.445096	0.027114
C	-0.878516	1.237441	0.089374
C	0.247464	0.262513	-0.009682
C	-0.299508	-1.098273	0.023974
C	1.618279	0.624122	-0.160210
C	2.715181	-0.382991	0.111067
H	-0.865067	1.737664	1.089817
H	-0.850415	2.119277	-0.576067
H	-3.102752	0.875596	0.040662
H	0.158059	-1.751884	-0.732503
H	3.662626	0.012594	-0.258557
H	-2.260112	-1.252786	-1.038477
H	1.522715	0.788812	-1.281107
H	0.040358	-1.546336	0.978939
H	2.817585	-0.541076	1.189180
H	-2.442879	-1.558376	0.621991
H	1.818740	1.645457	0.189805
H	2.540035	-1.343878	-0.378647

Fig. 3f, C5-Min₃:

19 E(B3LYP/cc-pVDZ)= -273.172922719 a.u.

C	0.465433	1.259970	-0.313891
C	-0.455870	0.006840	-0.418071
C	1.734619	0.755925	0.191028
C	0.505074	-1.225906	-0.418052
C	-2.449295	-0.004883	-0.143315
C	1.780335	-0.680962	0.257209
C	-1.487875	-0.038966	0.894550
H	0.766112	1.630209	-1.334167
H	0.094630	2.176909	0.178336
H	-0.976826	0.035660	-1.403154
H	2.567613	1.414182	0.483097
H	0.097198	-2.113636	0.081439
H	-2.822094	-0.928957	-0.607042
H	1.811098	-0.834494	1.379256
H	-1.365249	-0.981073	1.437516
H	0.738051	-1.511916	-1.455348
H	-2.839603	0.944920	-0.534329
H	2.755551	-1.126211	-0.029188

H -1.381008 0.862307 1.506834

Figure 4: Transition states for proton transfer on the PES leading to C5-rings.

Fig. 4a, TS₁^{PT}:

19 E(B3LYP/cc-pVDZ)= -273.190087252 a.u.

C	0.321469	-1.139502	0.116202
C	1.837587	-0.940919	-0.085321
C	2.098866	0.471267	-0.026971
C	0.873777	1.257601	0.100996
C	-0.268428	0.248713	0.029139
C	-1.628567	0.595634	-0.080708
C	-2.791760	-0.344683	0.025936
H	0.826532	2.168433	-0.529720
H	0.921844	1.701226	1.135244
H	3.103312	0.920170	-0.067907
H	0.105032	-1.526815	1.132046
H	-3.572942	-0.076079	-0.701157
H	2.536916	-1.543996	0.536317
H	-1.851536	1.672654	-0.049902
H	-0.134869	-1.861379	-0.578164
H	-2.524671	-1.403841	-0.081689
H	2.216976	-1.229172	-1.110520
H	-1.050713	0.478948	-1.189173
H	-3.233541	-0.188822	1.028979

19 E(MPW1K/cc-pVDZ)= -273.132016305 a.u.

C	0.314940	-1.120413	0.122968
C	1.813305	-0.940234	-0.095569
C	2.084923	0.458924	-0.023889
C	0.869366	1.242464	0.108792
C	-0.259608	0.250076	0.042732
C	-1.607278	0.597646	-0.111038
C	-2.758611	-0.345534	0.035012
H	0.813733	2.156552	-0.502208
H	0.919670	1.660780	1.145634
H	3.086201	0.899415	-0.066886
H	0.102160	-1.489538	1.140997
H	-3.566338	-0.060841	-0.642488
H	2.517526	-1.571910	0.470976
H	-1.828173	1.666232	-0.034725
H	-0.164183	-1.840565	-0.547667

H	-2.494725	-1.390527	-0.134259
H	2.147781	-1.163719	-1.145663
H	-1.133106	0.515902	-1.214924
H	-3.142769	-0.239356	1.057161

Fig. 4b, TS₂^{PT}:

19 E(B3LYP/cc-pVDZ)= -273.170365406 a.u.

C	1.834000	-0.673838	0.141414
C	1.770941	0.760152	0.067722
C	0.428967	1.264107	-0.200999
C	-0.467513	-0.004069	-0.136922
C	0.464846	-1.243067	-0.286555
C	-1.595502	-0.029596	0.905097
C	-2.269875	-0.004994	-0.408714
H	0.525860	1.714699	-1.224302
H	0.142173	2.128001	0.429253
H	-1.092358	0.012794	-1.193627
H	2.637328	1.424314	0.212625
H	0.141223	-2.089473	0.332432
H	-2.636056	-0.940108	-0.853540
H	2.047522	-0.797985	1.249449
H	-1.679431	-0.960468	1.473576
H	0.526774	-1.589937	-1.329406
H	-2.660453	0.939241	-0.810684
H	2.751861	-1.126468	-0.286827
H	-1.699626	0.873226	1.514789

Fig. 4c, TS₃^{PT}:

19 E(B3LYP/cc-pVDZ)= -273.168879746 a.u.

C	-1.901640	-0.476795	-0.399575
C	-1.629565	0.932235	-0.310684
C	-0.369044	1.209720	0.362760
C	0.330308	-0.157109	0.591702
C	-0.812545	-1.202099	0.412373
C	1.540616	-0.485232	-0.468156
C	2.727370	0.245283	-0.161927
H	-0.748122	1.613822	1.345745
H	0.188003	2.076099	-0.036866
H	0.766056	-0.227040	1.594679
H	-2.297231	1.717978	-0.695640
H	-0.496248	-2.150126	-0.041811

H	3.665387	-0.253189	0.134833
H	-1.844808	-0.643667	-1.517101
H	1.703353	-1.569304	-0.497930
H	-1.206229	-1.450230	1.412243
H	2.754880	1.346072	-0.188746
H	-2.963083	-0.750951	-0.222180
H	1.165046	-0.105483	-1.446180

Figure 5: Charge fragmentation of five membered monocyclic intermediates

Fig. 5a, TS^{Dis}:

19 E(B3LYP/cc-pVDZ)= -273.133628743 a.u.

C	2.323816	-0.756746	-0.116901
C	2.319444	0.678921	-0.239578
C	0.979740	1.230352	-0.122593
C	0.079908	0.056503	0.229600
C	0.850050	-1.212481	-0.082635
C	-1.132980	0.160902	0.820462
C	-4.588660	-0.070532	-0.417172
H	0.805244	1.580314	-1.182853
H	0.900619	2.170163	0.454582
H	3.220467	1.289736	-0.393924
H	0.663453	-2.022060	0.636810
H	-4.825443	0.067532	0.648045
H	2.814894	-0.833228	0.903142
H	-1.652102	-0.735560	1.170143
H	0.568284	-1.601091	-1.079656
H	-4.514351	0.802813	-1.081262
H	3.053537	-1.292669	-0.751259
H	-1.554183	1.136612	1.075721
H	-4.468323	-1.084083	-0.826582

19 E(MPW1K/cc-pVDZ)= -273.061173684 a.u.

C	2.272612	-0.750328	-0.064646
C	2.277670	0.672726	-0.197301
C	0.942273	1.217720	-0.152198
C	0.048824	0.053935	0.194717
C	0.815665	-1.199253	-0.133235
C	-1.136290	0.153684	0.801696
C	-4.426231	-0.065704	-0.392310
H	0.836739	1.492213	-1.235628
H	0.827454	2.172269	0.373160

H	3.181131	1.278107	-0.306407
H	0.592737	-2.033504	0.533693
H	-4.670400	0.047471	0.668704
H	2.644758	-0.753997	1.002007
H	-1.644555	-0.742264	1.151434
H	0.595342	-1.531156	-1.156823
H	-4.343452	0.818398	-1.031816
H	3.054331	-1.302482	-0.597259
H	-1.543283	1.122771	1.079326
H	-4.297946	-1.064506	-0.820735

Fig. 5b, C₅H₇⁺=CH₂:

15 E(B3LYP/cc-pVDZ)= -233.725215390 a.u.

C	0.016988	1.211197	0.150227
C	-0.852778	-0.025057	0.057545
C	0.079440	-1.214810	0.244736
C	1.457533	-0.663531	-0.185842
C	1.369501	0.781748	-0.095674
C	-2.163369	-0.020248	-0.186554
H	-0.221371	-2.100458	-0.328793
H	0.130195	-1.509896	1.308022
H	2.379107	-1.120554	0.208905
H	-2.723931	-0.952968	-0.278631
H	2.224716	1.463212	-0.194575
H	0.207315	1.449366	1.252408
H	-2.721862	0.911360	-0.301445
H	1.586468	-0.735061	-1.307701
H	-0.304528	2.179210	-0.264819

15 E(MPW1K/cc-pVDZ)= -233.670837701 a.u.

C	0.021415	1.203128	0.163319
C	-0.842189	-0.021951	0.063982
C	0.077278	-1.201090	0.256999
C	1.434100	-0.663952	-0.194873
C	1.357630	0.769059	-0.102272
C	-2.139084	-0.017093	-0.196724
H	-0.231274	-2.089310	-0.294806
H	0.139510	-1.476167	1.317789
H	2.359094	-1.129730	0.156172
H	-2.695259	-0.944668	-0.290335
H	2.210906	1.440737	-0.215374
H	0.237589	1.413963	1.257184
H	-2.691294	0.909285	-0.321903

H	1.514889	-0.701834	-1.316226
H	-0.299061	2.169120	-0.235082

Figure 7: The third order saddle point enabling a relaxation of doubly ionized norbornane to a six membered monocyclic species

Fig. 7, S₃ (C_s):

19 E(B3LYP/cc-pVDZ)= -273.052977631 a.u.

C	0.000000	1.175168	0.000000
C	-0.375647	-1.158605	0.000000
C	0.563630	0.701265	1.323734
C	0.563630	0.701265	-1.323734
C	0.302122	-0.851072	1.285151
C	0.302122	-0.851072	-1.285151
H	-0.006190	2.284805	0.000000
H	-1.107788	-1.990173	0.000000
H	0.058171	1.051953	2.254980
H	0.058171	1.051953	-2.254980
H	1.579533	1.145465	1.438602
H	1.579533	1.145465	-1.438602
H	-0.222761	-1.233602	2.169130
H	-0.222761	-1.233602	-2.169130
H	1.368868	-1.218029	1.322632
H	1.368868	-1.218029	-1.322632
C	-1.419044	0.223712	0.000000
H	-2.037265	0.284919	-0.908832
H	-2.037265	0.284919	0.908832

Figure 8: Relaxation of doubly ionized norbornane to a six membered monocyclic species

Fig. 8, C₆-Min₄ (C_s):

19 E(B3LYP/cc-pVDZ)= -273.218596958 a.u.

C	-0.019653	-1.899845	0.000000
C	0.000000	1.021466	0.000000
C	-0.006357	-1.226345	1.274679
C	-0.006357	-1.226345	-1.274679
C	0.148537	0.304554	1.282164
C	0.148537	0.304554	-1.282164

H	-0.098110	-2.998799	0.000000
H	-1.341932	2.548160	0.000000
H	0.715898	-1.753232	1.941702
H	0.715898	-1.753232	-1.941702
H	-0.955583	-1.571203	1.767383
H	-0.955583	-1.571203	-1.767383
H	1.186065	0.586638	1.590539
H	1.186065	0.586638	-1.590539
H	-0.463646	0.784016	2.066742
H	-0.463646	0.784016	-2.066742
C	-0.222145	2.459398	0.000000
H	0.109603	2.966790	-0.919164
H	0.109603	2.966790	0.919164

19 E(MPW1K/cc-pVDZ)= -273.159256268 a.u.

C	-0.002473	-1.882986	0.000000
C	0.000000	1.009942	0.000000
C	-0.013958	-1.212546	1.265631
C	-0.013958	-1.212546	-1.265631
C	0.150926	0.299947	1.271107
C	0.150926	0.299947	-1.271107
H	-0.062248	-2.976689	0.000000
H	-1.330352	2.509146	0.000000
H	0.665038	-1.740831	1.959301
H	0.665038	-1.740831	-1.959301
H	-0.989586	-1.542377	1.697378
H	-0.989586	-1.542377	-1.697378
H	1.190194	0.574507	1.552803
H	1.190194	0.574507	-1.552803
H	-0.441049	0.784665	2.057175
H	-0.441049	0.784665	-2.057175
C	-0.218012	2.437403	0.000000
H	0.111347	2.940330	-0.913258
H	0.111347	2.940330	0.913258