Supporting information for the manuscript

Isomerization Pathways from the Norbornadiene to the Cycloheptatriene Radical Cation by Opening A Bridgehead-Methylene bond: A Theoretical Investigation

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Content

All data presented in this supporting information refer to calculations which have been done in the unrestricted (restricted) formalism for the doublet (singlet) structures and in conjunction with the 6-311+G(d,p) basis set. Default convergence criterions for geometries and SCF-energies were used in all of the B3LYP, HF and MP2 calculations. For the CCSD(T) calculations we set the convergence criterion for the root mean square of the SCF-density matrix to 10^{-10}.

Table S1. $C_7H_8^{\bullet+}$ (and neutral singlet C_7H_8) potential energy surface: Total B3LYP SCF-energies for all compounds. Total CCSD(T)//B3LYP-energies, B3LYP-thermal corrections to Gibbs free energy at 1.0 atm and 100.0 K for the doublet structures, and imaginary frequencies of all B3LYP optimized transition states.

	Total B3LYP SCF-energy (Hartree)	Total CCSD(T)//B3LYP-energy (Hartree)	Thermal correction to Gibbs free energy (Hartree)	Imaginary frequency (cm^{-1})
N$^{\bullet+}$	-271.2531447	-270.507183	0.119617	---
NCD$^{\bullet+}$	-271.2880326	-270.5298797	0.118944	---
I1	-271.2408876	-270.4870594	0.116953	---
CHT$^{\bullet+}$	-271.2991802	-270.52987892	0.118932	---
TS1	-271.2105187	-270.4571324	0.115672	263.3770i
TS2	-271.273481	-270.5146679	0.117378	335.0880i
TS3	-271.2022972	-270.4538156	0.115933	410.3213i
TS4	-271.2133058	-270.4604828	0.115082	582.5404i
TS5	-271.1982401	-270.4439936	0.115598	449.6032i
Neutral N	-271.549986	---	---	---
Neutral NCD	-271.5716964	---	---	---
Neutral TS (N–NCD)	-271.4661321	---	---	467.2293i

Table S2. $C_7H_8^{\bullet+}$ potential energy surface: Total SCF-energies, total MP2 and PMP2-energies, imaginary frequencies of the MP2 (or HF) optimized transition states, and the $<S^2>$ values of the SCF reference wavefunctions used in the MP2 calculations.

	Total SCF-energy (Hartree)	Total MP2-energy (Hartree)	Total PMP2-energy (Hartree)	Imaginary frequency (cm^{-1})	$<S^2>$
N$^{\bullet+}$	-269.45194	-270.410851	-270.4125809	---	0.763313
NCD$^{\bullet+}$	-269.4856041	-270.4261862	-270.4325395	---	0.845831
I1	-269.4393415	-270.3825786	-270.3905398	---	0.874498
CHT$^{\bullet+}$ (bent minimum)	-269.5007958	-270.4121298	-270.4258993	---	1.02309
CHT$^{\bullet+}$ (planar TS)	-269.5012103	-270.4120576	-270.4256121	54.2386i	1.019592
TS1	-269.4112653	-270.3314568[a]	-270.3517013[a]	540.7073i	1.146738
TS2	-269.4744644	-270.403003	-270.4128396	398.0638i	0.904724
TS3	-269.4089961	-270.3394461[a]	-270.3525172[a]	251.4357i	0.985975
TS4	-269.4200212	-270.341804	-270.355419	533.9001i	0.944906
TS5	-269.3966705	-270.3325485	-270.3433832	628.7103i	0.986603

[a] Single point MP2 calculation on the HF geometry.

Table S3. Substituted potential energy surface: Total B3LYP SCF-energies for all compounds and imaginary frequencies of the transition structures.

	Total B3LYP SCF-energy (Hartree)	Imaginary frequency (cm^{-1})
N-2CH$_3$$^{\bullet+}$	-349.907190295	---
NCD-2CH$_3$$^{\bullet+}$	-349.950235050	---
CHT-2CH$_3$$^{\bullet+}$	-349.951772740	---
Q-2CH$_3$$^{\cdot+}$	-349.892904357	---
BHE-2CH$_3$$^{\cdot+}$	-349.883161045	---
MS-I1-2CH$_3$	-349.884248269	---
MS-I2-2CH$_3$	-349.883777059	---
TS1-2CH$_3$	-349.878111930	499.7342i
TS2-2CH$_3$	-349.928437624	364.2978i
MS-TS1-2CH$_3$	-349.873069902	1024.5095i
MS-TS2-2CH$_3$	-349.869279333	294.6717i
MS-TS6-2CH$_3$	-349.874662852	397.1612i
MS-TS7-2CH$_3$	-349.876678967	308.9719i
MS-TS9-2CH$_3$	-349.877562001	602.9750i

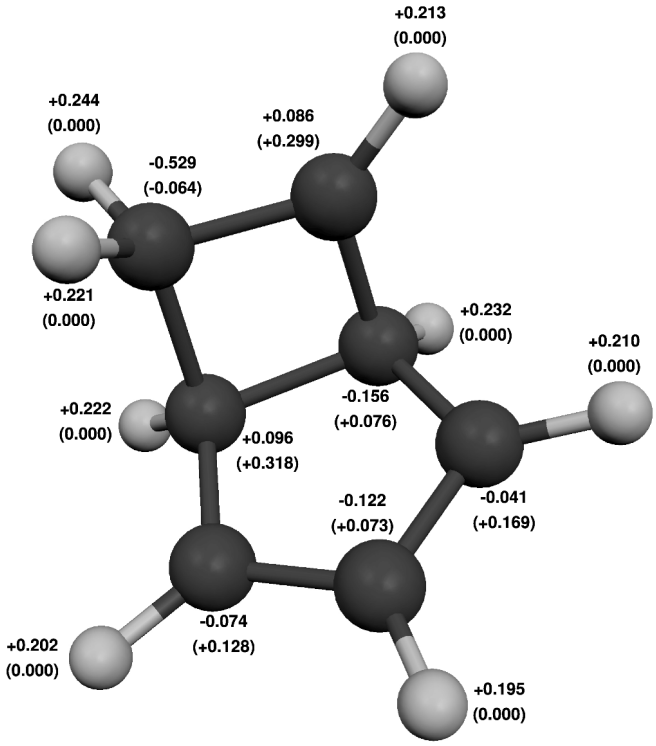

Figure S1. B3LYP/6-311+G(d,p) optimized Mulliken atomic charges for the radical cation intermediate, I1. Atomic charges with hydrogens summed into the carbon atoms are given within parentheses.

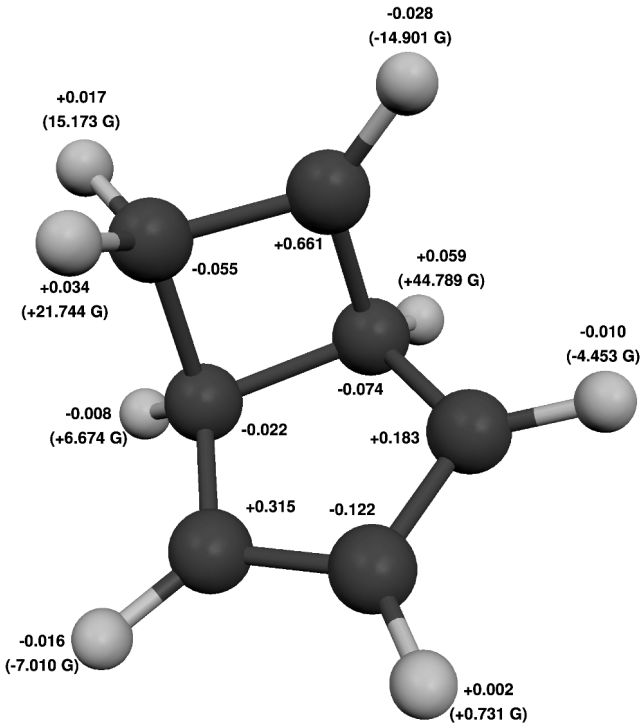

Figure S2. B3LYP/6-311+G(d,p) optimized Mulliken atomic spin densities (and ^{1}H hyperfine coupling constants) for the radical cation intermediate I1.

xyz-matrices for all stationary points on the $C_7H_8^{\bullet+}$ (and neutral singlet C_7H_8) potential energy surface

$N^{\bullet+}$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.910593	-0.558925	-0.908760
C	-1.048067	-0.075961	0.559906
C	0.137861	-0.784903	1.204873
C	-0.407569	1.304563	0.467038
C	0.585888	1.229051	-0.482577
C	0.596344	-0.201300	-1.010733
C	1.131857	-0.859998	0.255788
H	-1.102991	-1.627475	-1.024925
H	-1.530967	0.010689	-1.603727
H	-2.004543	-0.146793	1.066504
H	0.203244	-1.087236	2.242547
H	-0.642576	2.152361	1.098280
H	1.292244	2.004895	-0.750110
H	1.136126	-0.386226	-1.933198
H	2.138516	-1.233940	0.394581

MP2/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.001865	-0.002193	-0.002704
C	-0.006716	-0.007942	1.543209
C	1.483320	0.005862	1.839657
C	-0.232170	1.464980	1.839923
C	0.377833	2.183243	0.821781
C	0.996149	1.171720	-0.128361
C	2.093825	0.724744	0.822259
H	0.390034	-0.932766	-0.424277
H	-0.983364	0.234886	-0.424283
H	-0.616980	-0.725592	2.085468
H	1.955430	-0.388185	2.734698
H	-0.696737	1.867604	2.735097
H	0.487669	3.261782	0.758935
H	1.299806	1.528730	-1.109088
H	3.140592	1.006922	0.759653

NCD$^{\bullet+}$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	0.000255	0.000974	0.000494
C	0.000809	0.002206	1.543125
C	1.325508	0.002180	0.790080
C	-0.386710	1.236969	2.185028
C	0.328652	2.415164	2.002099
C	1.552412	2.415053	1.306641
C	2.075517	1.236902	0.785407
H	-0.270739	-0.931299	-0.476419
H	-0.289888	0.909738	-0.509383
H	-0.337554	-0.928434	1.983841
H	1.877130	-0.928502	0.724452
H	-1.264474	1.234742	2.823466
H	-0.029156	3.332811	2.453843
H	2.123578	3.332734	1.230388
H	3.073054	1.234769	0.357693

MP2/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	0.009239	0.047104	0.016264
C	0.001856	-0.009498	1.559325
C	1.338947	-0.009509	0.799215
C	-0.374964	1.213722	2.201545
C	0.301963	2.409726	1.956391
C	1.526655	2.409715	1.260180
C	2.083558	1.213700	0.803930
H	-0.278489	-0.866628	-0.489783
H	-0.252147	0.992786	-0.443424
H	-0.341557	-0.954629	1.965805
H	1.863877	-0.954647	0.712077
H	-1.224727	1.204590	2.881145
H	-0.068479	3.332521	2.392012
H	2.090473	3.332502	1.164693
H	3.102188	1.204553	0.421381

I1

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.490701	-0.053769	-0.058943
C	-0.441824	-0.264664	1.398050
C	1.427634	0.744790	2.047883
C	0.033159	1.126883	1.706841
C	0.132410	1.416151	0.173002
C	1.576606	1.393458	-0.120923
C	2.295812	0.941672	0.971129
H	0.021702	-0.753088	-0.724982
H	-1.527869	0.052652	-0.401115
H	-0.581951	-1.129395	2.035287
H	1.699124	0.319296	3.007130
H	-0.511544	1.768159	2.402690
H	-0.447214	2.221097	-0.271150
H	1.993583	1.599019	-1.100231
H	3.356966	0.732406	0.987287

MP2/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.437367	-0.050800	-0.053120
C	-0.383791	-0.250068	1.406614
C	1.387351	0.730599	2.034462
C	0.007614	1.167548	1.707605
C	0.121930	1.457540	0.186016
C	1.551673	1.397220	-0.115110
C	2.265152	0.903513	0.958610
H	0.099744	-0.722820	-0.728134
H	-1.481294	0.051222	-0.375834
H	-0.494158	-1.112448	2.056540
H	1.639176	0.291890	2.996734
H	-0.541954	1.793338	2.413521
H	-0.473608	2.234570	-0.288118
H	1.961089	1.589420	-1.104166
H	3.314335	0.633944	0.956333

CHT$^{\bullet+}$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-1.472707	0.000000	-0.639326
C	-1.472864	0.000000	0.728634
C	-0.362270	0.000000	1.610240
C	0.996507	0.000000	1.315867
C	1.642392	0.000000	0.053459
C	1.075821	0.000000	-1.191644
C	-0.348669	0.000000	-1.608562
H	-2.449878	0.000000	-1.115708
H	-2.446800	0.000000	1.206813
H	-0.610457	0.000000	2.667085
H	1.659718	0.000000	2.175320
H	2.726909	0.000000	0.085596
H	1.768227	0.000000	-2.029719
H	-0.498490	0.850662	-2.300699
H	-0.498490	-0.850662	-2.300699

MP2/6-311+G(d,p) – bent minimum

Atom	*x*	*y*	*z*
C	0.001853	0.088023	-0.005885
C	0.002471	0.069749	1.349483
C	1.123482	-0.077161	2.208504
C	2.485834	-0.048760	1.899278
C	3.119626	0.134698	0.641975
C	2.534629	0.140795	-0.580754
C	1.118451	-0.068579	-0.970125
H	-0.972105	0.182201	-0.484902
H	-0.964314	0.149889	1.838609
H	0.890369	-0.176391	3.266512
H	3.156417	-0.129149	2.752170
H	4.198822	0.257466	0.666769
H	3.201929	0.269143	-1.432312
H	0.903355	0.536074	-1.862249
H	1.049781	-1.106010	-1.368136

$CHT^{\bullet+}$ (continued)

MP2/6-311+G(d,p) – planar TS

Atom	*x*	*y*	*z*
C	0.001958	0.057071	0.007824
C	-0.010862	0.067897	1.362584
C	1.105968	0.052222	2.241382
C	2.470302	0.036560	1.945576
C	3.123032	0.032406	0.683129
C	2.550147	0.028178	-0.544646
C	1.126769	0.023210	-0.955940
H	-0.972707	0.070534	-0.479398
H	-0.987286	0.089389	1.838413
H	0.862473	0.056796	3.301652
H	3.131037	0.030682	2.809796
H	4.209057	0.030513	0.711825
H	3.235604	0.022842	-1.391793
H	0.981222	0.855126	-1.670757
H	0.973849	-0.853428	-1.615400

TS1

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.019020	-0.029927	-0.000371
C	0.003088	0.004630	1.530483
C	1.499312	0.005316	1.804282
C	-0.637313	1.356649	1.804781
C	-0.002183	2.341888	1.129901
C	1.221434	1.931294	0.461965
C	2.117033	1.001461	1.129218
H	0.658169	-0.692072	-0.531001
H	-0.907072	0.299459	-0.530879
H	-0.529403	-0.837465	1.980480
H	1.994476	-0.791060	2.344485
H	-1.568774	1.462668	2.345475
H	-0.360023	3.360157	1.037527
H	1.606462	2.540155	-0.350942
H	3.190384	1.114477	1.036446

HF/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.015158	-0.023631	-0.008334
C	0.002528	0.003694	1.522068
C	1.491359	0.008684	1.813507
C	-0.630776	1.351003	1.814065
C	-0.006437	2.338561	1.125671
C	1.225659	1.937833	0.475835
C	2.115902	0.996113	1.125112
H	0.648300	-0.688186	-0.535142
H	-0.900092	0.291222	-0.534735
H	-0.527159	-0.833895	1.958641
H	1.985654	-0.767675	2.365066
H	-1.543843	1.464846	2.365995
H	-0.367735	3.343879	1.016298
H	1.609342	2.544749	-0.327565
H	3.179027	1.100437	1.015365

TS2

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	0.025317	-0.023288	0.013705
C	-0.085406	0.015157	1.541913
C	1.471220	0.017667	0.196903
C	0.095760	1.143402	2.282468
C	0.699211	2.361281	1.808701
C	1.705590	2.409745	0.845691
C	2.183939	1.259806	0.232479
H	-0.365243	-0.953771	-0.387366
H	-0.407578	0.853145	-0.465095
H	-0.377314	-0.911351	2.023228
H	2.026796	-0.914420	0.269942
H	-0.217851	1.126942	3.322473
H	0.447357	3.277391	2.333958
H	2.223945	3.346378	0.678634
H	3.152752	1.277652	-0.262564

MP2/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	0.048440	-0.021465	0.077576
C	-0.174630	0.035800	1.562311
C	1.532132	-0.001140	0.184970
C	0.085189	1.113819	2.301148
C	0.704483	2.310253	1.787447
C	1.681130	2.397668	0.794659
C	2.200442	1.267886	0.231039
H	-0.342444	-0.941221	-0.353201
H	-0.352055	0.851407	-0.443868
H	-0.555972	-0.855310	2.058702
H	2.110561	-0.919752	0.139288
H	-0.186788	1.131726	3.353593
H	0.473935	3.230310	2.325602
H	2.169624	3.355566	0.650833
H	3.184452	1.330188	-0.235030

TS3

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.181865	-0.182251	0.059604
C	-0.015190	0.018382	1.586548
C	1.488101	0.005688	1.845183
C	-0.488909	1.438807	1.482901
C	0.066865	1.819589	0.224198
C	1.369406	1.316422	-0.105578
C	2.182789	0.671943	0.903622
H	0.509291	-0.817280	-0.492536
H	-1.188541	-0.165269	-0.351690
H	-0.589749	-0.657279	2.218376
H	1.919957	-0.526868	2.682372
H	-1.280951	1.938254	2.022794
H	-0.389438	2.552058	-0.436578
H	1.765728	1.537681	-1.091263
H	3.262504	0.709110	0.841440

HF/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.161347	-0.135207	0.070271
C	-0.003746	0.027336	1.596085
C	1.494236	-0.011462	1.845036
C	-0.458283	1.465058	1.530100
C	0.078133	1.804406	0.220438
C	1.352986	1.313606	-0.098133
C	2.185091	0.660186	0.912165
H	0.491568	-0.785914	-0.488900
H	-1.156936	-0.084116	-0.341611
H	-0.584049	-0.655038	2.198555
H	1.929133	-0.547075	2.666937
H	-1.317506	1.913462	1.987666
H	-0.415324	2.462382	-0.474716
H	1.741881	1.510537	-1.082409
H	3.254162	0.720824	0.847910

TS4

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	0.000724	0.004130	0.001623
C	0.001918	-0.003335	1.488235
C	2.529325	0.005071	1.440439
C	1.214820	0.672145	1.790819
C	0.866862	1.282832	0.173204
C	2.230176	1.316392	-0.404027
C	3.092869	0.459076	0.268705
H	0.509645	-0.818841	-0.506041
H	-0.986483	0.150756	-0.437796
H	-0.878351	-0.048361	2.128357
H	2.929522	-0.753596	2.101993
H	1.259533	1.304116	2.681127
H	0.286494	2.201671	0.165602
H	2.495137	1.992970	-1.208532
H	4.084515	0.189056	-0.071525

MP2/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	0.016636	0.071579	-0.000930
C	0.050773	-0.052594	1.468243
C	2.487200	0.030527	1.457511
C	1.176684	0.778132	1.751229
C	0.901817	1.345452	0.232547
C	2.242286	1.297602	-0.424211
C	3.059403	0.434641	0.273714
H	0.516894	-0.713116	-0.580580
H	-0.999311	0.213641	-0.385795
H	-0.752297	-0.376877	2.137674
H	2.863865	-0.686837	2.175724
H	1.210474	1.372507	2.668015
H	0.328681	2.272046	0.205898
H	2.489075	1.854607	-1.320247
H	4.044530	0.112770	-0.046610

TS5

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	0.002051	0.009118	0.001080
C	0.000595	0.008912	1.497850
C	1.464727	0.006998	2.177799
C	0.674575	1.238327	1.840108
C	1.198571	0.926062	-0.278873
C	2.487128	0.497365	0.097749
C	2.602508	-0.162120	1.313822
H	0.109919	-0.959576	-0.498348
H	-0.919696	0.475593	-0.350335
H	-0.771018	-0.460219	2.101610
H	1.494883	-0.328640	3.208070
H	0.541954	2.198697	2.326582
H	1.106006	1.680207	-1.054828
H	3.356294	0.742222	-0.504719
H	3.504763	-0.669091	1.636742

MP2/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.001218	-0.002431	-0.000665
C	0.015409	0.025261	1.491852
C	1.444989	-0.033419	2.165320
C	0.703411	1.257397	1.837448
C	1.198450	0.879685	-0.309397
C	2.477856	0.502529	0.093210
C	2.587974	-0.168076	1.302365
H	0.112413	-0.977834	-0.488772
H	-0.919594	0.472065	-0.352409
H	-0.790893	-0.385308	2.096599
H	1.477081	-0.369155	3.196778
H	0.581771	2.179399	2.400564
H	1.102555	1.634172	-1.091092
H	3.348970	0.805943	-0.480640
H	3.514083	-0.616375	1.653145

Neutral singlet N

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.869932	-0.533978	-0.868294
C	-0.976846	-0.040369	0.608391
C	0.164878	-0.886548	1.210395
C	-0.429172	1.388615	0.406840
C	0.533672	1.315292	-0.513112
C	0.644562	-0.163781	-0.940196
C	1.127947	-0.959934	0.290736
H	-1.057846	-1.604045	-0.979892
H	-1.487820	0.041571	-1.560935
H	-1.943199	-0.117667	1.104025
H	0.172122	-1.280873	2.217503
H	-0.751446	2.255025	0.968359
H	1.175391	2.108233	-0.872666
H	1.173110	-0.355089	-1.872649
H	2.099351	-1.427672	0.376976

Neutral singlet NCD

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.004296	-0.039057	-0.007240
C	-0.053821	0.019292	1.496992
C	1.313729	0.019545	0.719460
C	-0.402725	1.271829	2.182171
C	0.302302	2.408489	2.001215
C	1.565339	2.408478	1.283454
C	2.081282	1.271869	0.770058
H	-0.266152	-0.983215	-0.468774
H	-0.314432	0.844879	-0.551523
H	-0.338711	-0.900697	1.996457
H	1.888541	-0.900485	0.729739
H	-1.239320	1.251377	2.873450
H	-0.007757	3.321303	2.498239
H	2.151108	3.321247	1.271926
H	3.103306	1.251153	0.405130

Neutral singlet TS (N – NCD)

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.141268	-0.106403	-0.053766
C	0.149941	-0.062301	1.450184
C	1.624449	0.039754	1.779060
C	-0.576007	1.235907	1.728039
C	0.027779	2.298578	1.107886
C	1.264836	2.002700	0.469288
C	2.181187	1.088323	1.167644
H	-0.233576	-1.094999	-0.514570
H	-0.744141	0.657963	-0.512561
H	-0.317512	-0.921113	1.944254
H	2.126187	-0.640946	2.454675
H	-1.546689	1.259154	2.204664
H	-0.454953	3.261474	0.983072
H	1.673446	2.703744	-0.251259
H	3.232890	1.345798	1.235240

xyz-matrices for all stationary points optimized on the substituted potential energy surface

N-2CH$_3^{\bullet+}$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.000732	-0.001324	0.006268
C	0.029089	0.034866	1.588104
C	1.522270	0.045079	1.867782
C	-0.200579	1.510617	1.867214
C	0.399159	2.216095	0.849914
C	1.021903	1.202032	-0.094407
C	2.122355	0.750997	0.851104
C	0.529082	-1.307100	-0.588092
C	-1.375314	0.311176	-0.587307
H	-0.574708	-0.674724	2.146108
H	2.002617	-0.365490	2.746910
H	-0.683159	1.918689	2.746293
H	0.483944	3.292165	0.765899
H	1.325930	1.558917	-1.074021
H	3.170535	1.009024	0.768024
H	0.601983	-1.221485	-1.674952
H	1.514188	-1.592458	-0.210293
H	-0.160757	-2.125736	-0.369358
H	-1.303390	0.400763	-1.673944
H	-2.071189	-0.503077	-0.371151
H	-1.816145	1.235642	-0.205942

NCD-2CH$_3$$^{\bullet+}$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.041314	0.035019	-0.040064
C	0.053759	0.065554	1.559070
C	1.330732	0.074771	0.769031
C	-0.299239	1.268650	2.265973
C	0.463852	2.416671	2.170520
C	1.670299	2.425556	1.428554
C	2.110171	1.287798	0.781325
C	-0.385554	-1.317467	-0.606564
C	-0.541381	1.207554	-0.834800
H	-0.302741	-0.872929	1.968879
H	1.869742	-0.857165	0.637215
H	-1.176488	1.254888	2.903921
H	0.164463	3.307383	2.710315
H	2.277622	3.322921	1.411361
H	3.073014	1.287934	0.281724
H	0.021793	-1.410590	-1.618617
H	-0.002213	-2.141766	-0.003817
H	-1.472339	-1.422548	-0.686669
H	-0.128425	1.158294	-1.846830
H	-1.629501	1.143428	-0.927261
H	-0.292465	2.178835	-0.413935

CHT-2$CH_3^{\bullet+}$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	0.019354	0.000000	0.007155
C	0.007180	0.000000	1.377863
C	1.101770	0.000000	2.273270
C	2.462493	0.000000	1.986284
C	3.102363	0.000000	0.725093
C	2.537867	0.000000	-0.524018
C	1.122981	0.000000	-0.996146
C	0.930568	1.268012	-1.907114
C	0.930568	-1.268012	-1.907114
H	-0.962317	0.000000	-0.461524
H	-0.972970	0.000000	1.843875
H	0.842837	0.000000	3.327579
H	3.125222	0.000000	2.846172
H	4.187237	0.000000	0.755586
H	3.246754	0.000000	-1.349048
H	1.664623	-1.254448	-2.715100
H	1.050385	-2.188868	-1.335032
H	-0.066965	-1.253310	-2.350577
H	1.664623	1.254448	-2.715100
H	-0.066965	1.253310	-2.350577
H	1.050385	2.188868	-1.335032

Q-2CH$_3$$^{\bullet+}$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.002959	0.000000	0.001642
C	0.029133	0.000000	1.548821
C	1.530720	0.000000	-0.202577
C	1.185768	0.840767	1.996508
C	2.149309	0.841115	0.872439
C	1.185768	-0.840767	1.996508
C	2.149309	-0.841115	0.872439
C	-0.656799	1.267110	-0.556743
C	-0.656799	-1.267110	-0.556743
H	-0.872367	0.000000	2.149796
H	1.987774	0.000000	-1.184921
H	1.279141	1.386771	2.924603
H	3.080941	1.386884	0.822817
H	1.279141	-1.386771	2.924603
H	3.080941	-1.386884	0.822817
H	-0.576390	-1.290334	-1.645977
H	-0.195608	-2.176561	-0.162627
H	-1.719948	-1.289582	-0.306330
H	-0.576390	1.290334	-1.645977
H	-1.719948	1.289582	-0.306330
H	-0.195608	2.176561	-0.162627

BHE-2CH$_3^{\bullet+}$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.005975	-0.022158	-0.007791
C	0.022992	-0.034455	1.492634
C	1.507003	-0.028076	-0.356023
C	1.405455	0.032504	2.009911
C	2.292418	0.506971	0.840730
C	2.350898	-1.055465	1.584613
C	2.384460	-1.098618	0.188095
C	-0.638743	1.287624	-0.538601
C	-0.721441	-1.245536	-0.615983
H	-0.844805	-0.058929	2.135595
H	1.791620	0.306725	-1.348194
H	1.600930	0.415993	3.005537
H	3.179942	1.123517	0.864793
H	3.142514	-1.451271	2.211794
H	3.208664	-1.540528	-0.361195
H	-0.613555	1.311588	-1.631535
H	-1.682056	1.349528	-0.223992
H	-0.121183	2.172090	-0.158439
H	-0.650970	-1.232702	-1.707035
H	-0.300312	-2.185231	-0.250803
H	-1.780714	-1.228374	-0.352503

MS-I1-2CH$_3$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.016276	0.004339	-0.003059
C	0.020150	-0.002330	1.486705
C	1.439058	-0.006517	-0.521575
C	1.194265	-0.106481	2.185456
C	2.525087	0.600346	0.285910
C	2.428001	-0.472136	1.506583
C	2.465502	-0.902887	0.113233
C	-0.686808	1.323755	-0.481743
C	-0.813993	-1.212690	-0.519708
H	-0.920314	0.072061	2.026344
H	1.529238	0.132846	-1.595870
H	1.238786	0.091814	3.251306
H	3.282649	1.361526	0.173407
H	3.313292	-0.637603	2.109720
H	3.240604	-1.512043	-0.330253
H	-0.844617	-1.195317	-1.612504
H	-0.363015	-2.155123	-0.202413
H	-1.844811	-1.184378	-0.159646
H	-0.721727	1.334621	-1.573392
H	-1.711003	1.388202	-0.109681
H	-0.136682	2.202740	-0.140144

MS-I2-2CH$_3$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.012907	0.017722	-0.005539
C	0.026425	0.019996	1.492159
C	1.390205	0.012442	-0.590567
C	1.066492	-0.435740	2.250854
C	2.413200	0.829648	-0.079656
C	2.259468	-0.934569	1.664806
C	2.699214	-0.564350	0.390280
C	-0.744744	1.295712	-0.516780
C	-0.795662	-1.243195	-0.464372
H	-0.885510	0.331542	1.994070
H	1.534734	-0.494853	-1.542234
H	0.932421	-0.549070	3.320932
H	2.368536	1.699642	0.564815
H	2.846891	-1.655439	2.229060
H	3.447962	-1.146230	-0.135786
H	-0.874500	-1.239782	-1.554748
H	-0.296246	-2.161312	-0.149363
H	-1.806330	-1.241723	-0.052666
H	-0.797121	1.286498	-1.606422
H	-1.764283	1.311468	-0.126871
H	-0.237500	2.208700	-0.200190

TS1-2CH$_3$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.028589	0.001429	-0.038200
C	-0.010881	-0.019757	1.528867
C	1.479948	-0.023199	1.882558
C	-0.521503	1.372375	1.815361
C	0.089547	2.244480	0.915696
C	1.156747	1.605760	0.201953
C	2.110658	0.851034	1.103965
C	0.793519	-0.998914	-0.806821
C	-1.349724	0.278256	-0.720737
H	-0.593408	-0.827178	1.974349
H	1.907265	-0.659398	2.644047
H	-1.286921	1.635638	2.534882
H	-0.261678	3.247783	0.699711
H	1.540964	2.069984	-0.700777
H	3.167863	1.081028	1.088462
H	0.818235	-0.747845	-1.868426
H	1.802805	-1.141795	-0.433113
H	0.268544	-1.961973	-0.717344
H	-1.197054	0.663853	-1.731331
H	-1.871873	-0.679962	-0.831111
H	-2.006074	0.958831	-0.181081

TS2-2CH$_3$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.018602	0.037531	-0.028220
C	-0.017933	0.092869	1.529680
C	1.447314	0.084991	0.029504
C	0.302955	1.154772	2.319297
C	1.029499	2.324307	1.931113
C	1.956501	2.375534	0.881901
C	2.237749	1.275089	0.097860
C	-0.559429	-1.314307	-0.508275
C	-0.772545	1.204554	-0.683968
H	-0.396089	-0.810965	1.998081
H	1.981406	-0.864346	-0.006936
H	0.006536	1.100384	3.363042
H	0.953580	3.190354	2.581089
H	2.575206	3.259258	0.781386
H	3.150071	1.269299	-0.496089
H	-0.660728	1.135628	-1.768617
H	-1.834036	1.121080	-0.446952
H	-0.426560	2.184817	-0.363828
H	-0.451058	-1.396168	-1.591620
H	-0.034620	-2.153911	-0.046117
H	-1.621360	-1.398515	-0.269962

MS-TS1-2CH$_3$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	0.001117	-0.002387	0.006660
C	0.025039	0.029816	1.573760
C	1.500177	0.022723	1.933028
C	0.046299	1.489408	1.905223
C	0.734660	2.181611	0.887665
C	1.065488	1.117982	-0.168221
C	2.034347	0.963187	0.929137
C	0.483478	-1.336344	-0.566068
C	-1.368152	0.378855	-0.559302
H	-0.643789	-0.612287	2.136508
H	1.949350	-0.219394	2.884561
H	-0.302663	1.922862	2.837909
H	0.999845	3.227083	0.868645
H	1.394861	1.466632	-1.140111
H	3.029910	1.389862	0.932742
H	0.564133	-1.275620	-1.654077
H	1.458559	-1.632052	-0.170191
H	-0.230792	-2.129816	-0.334164
H	-1.323113	0.459953	-1.647752
H	-2.105546	-0.390298	-0.318377
H	-1.736912	1.331549	-0.167596

MS-TS2-2CH$_3$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.010138	-0.004032	0.003008
C	0.012784	0.003137	1.495302
C	1.503794	-0.011871	-0.301908
C	1.370165	0.263378	2.024169
C	2.250788	0.585659	0.792010
C	1.801944	-1.162475	1.829854
C	2.272268	-1.090580	0.501949
C	-0.616720	1.338484	-0.499777
C	-0.762098	-1.198548	-0.605173
H	-0.835246	-0.220780	2.130905
H	1.856963	0.103098	-1.320479
H	1.518789	0.739123	2.988491
H	3.170926	1.153419	0.785954
H	1.932771	-1.947274	2.566701
H	2.995885	-1.737624	0.025878
H	-0.554845	1.376631	-1.590198
H	-1.668744	1.408417	-0.219339
H	-0.092486	2.205166	-0.091448
H	-0.722076	-1.155582	-1.695949
H	-0.335307	-2.149886	-0.280463
H	-1.813314	-1.178962	-0.310372

MS-TS6-2CH$_3$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.011691	-0.015345	-0.004754
C	0.019914	-0.025853	1.491692
C	1.482186	-0.020548	-0.401592
C	1.282104	-0.218575	2.099075
C	2.442106	0.388763	0.702830
C	2.338826	-1.021048	1.520822
C	2.396510	-1.075617	0.090298
C	-0.661666	1.301087	-0.494559
C	-0.750112	-1.233039	-0.599658
H	-0.832655	0.274803	2.088343
H	1.716242	0.349383	-1.395104
H	1.459035	0.108653	3.118934
H	3.292163	1.051413	0.768964
H	3.165487	-1.372855	2.126828
H	3.225067	-1.518617	-0.444719
H	-0.659284	1.337308	-1.586668
H	-1.698932	1.357419	-0.158893
H	-0.132835	2.179722	-0.117210
H	-0.700347	-1.207307	-1.691682
H	-0.319014	-2.175743	-0.255944
H	-1.803685	-1.216165	-0.314379

MS-TS7-2CH$_3$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.015134	0.003961	-0.004544
C	0.020348	0.002106	1.486641
C	1.419321	-0.000530	-0.562378
C	1.159767	-0.195863	2.223631
C	2.513411	0.766018	-0.017738
C	2.383647	-0.565995	1.616638
C	2.565060	-0.701438	0.193035
C	-0.753751	1.275459	-0.498104
C	-0.766962	-1.263816	-0.483496
H	-0.917969	0.182356	2.003926
H	1.479984	-0.135743	-1.643090
H	1.130766	-0.120811	3.304289
H	3.001360	1.691649	0.242419
H	3.245356	-0.752338	2.252881
H	3.311342	-1.352305	-0.248658
H	-0.791843	1.278888	-1.589594
H	-1.779991	1.289030	-0.125438
H	-0.253857	2.187945	-0.166661
H	-0.827168	-1.258436	-1.575257
H	-0.260179	-2.177807	-0.167441
H	-1.786435	-1.281988	-0.092956

MS-TS9-2CH$_3$

B3LYP/6-311+G(d,p)

Atom	*x*	*y*	*z*
C	-0.011061	0.018607	-0.004961
C	0.021078	0.010940	1.485134
C	1.386409	0.002774	-0.614124
C	1.064254	-0.439011	2.243252
C	2.439743	0.812166	-0.157385
C	2.240695	-0.926091	1.634551
C	2.662121	-0.582034	0.336982
C	-0.727143	1.313209	-0.502193
C	-0.822225	-1.224780	-0.465172
H	-0.899790	0.298664	1.985923
H	1.455385	-0.442282	-1.608907
H	0.939297	-0.564219	3.312602
H	2.978651	1.743417	-0.124859
H	2.845727	-1.638422	2.192793
H	3.432600	-1.178373	-0.142940
H	-0.772574	1.315955	-1.592223
H	-1.748845	1.338571	-0.118506
H	-0.204966	2.212430	-0.171547
H	-0.909937	-1.207626	-1.554730
H	-0.333794	-2.154021	-0.165748
H	-1.829516	-1.212022	-0.045440