© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 1
-jo010379N

RECEIVED

AUG 24 2001

Journal of Organic Chemistry

Supplemental Material (45 pages)

Energy data used to create Table 4 — Page S3

Energy and C–2^{+} ^{13}C NMR data for the 2-methyl-2-norbornyl cation at fixed C2–C6 distances (MP2/6-31G* and NMR at B3LYP/6-31G*) — Page S4

Energy and C–2^{+} ^{13}C NMR data for the 2-methyl-2-norbornyl cation at fixed C2–C6 distances (B3LYP/6-31G*) — Page S5

Cartesian Coordinates:
(Energies in Hartrees; Frequencies in cm^{-1})

Cl^{-} — Page S6

HCl — Page S7

HCl_2^{-} — Page S8

3,7-Dichlorocycloheptatriene — Page S9
- B3LYP/6-31G*
- B3LYP/6-31G* (SCIPCM)
- B3LYP/6-311+G**
- B3LYP/6-311+G** (SCIPCM)

Chlorotropylium — Page S11
- B3LYP/6-31G*
- B3LYP/6-31G* (SCIPCM)
- B3LYP/6-311+G**
- B3LYP/6-311+G** (SCIPCM)

t-Butyl Chloride
- C1 Symmetry: — Page S13
  - B3LYP/6-31G*
  - B3LYP/6-311+G**
  - B3LYP/6-311+G** (SCIPCM)
- C3 Symmetry — Page S15
  - B3LYP/6-31G*
  - B3LYP/6-31G* (SCIPCM)

t-Butyl Cation
- C1 Symmetry — Page S16
  - B3LYP/6-31G*
  - B3LYP/6-31G* (SCIPCM)
  - B3LYP/6-311+G**
  - B3LYP/6-311+G** (SCIPCM)

Camphenyl Chloride Page S18
B3LYP/6-31G*
B3LYP/6-31G* (SCIPCM)
B3LYP/6-311+G**
B3LYP/6-311+G** (SCIPCM)

Camphenyl Cation Page S22
B3LYP/6-31G*
B3LYP/6-31G* (SCIPCM)
B3LYP/6-311+G**
B3LYP/6-311+G** (SCIPCM)
MP2/6-31G*
MP2/6-311+G**
MP3/6-31G*
MP4(SDQ)/6-31G*
QCISD/6-31G*

2-Methyl-2-norbornyl Chloride Page 31
B3LYP/6-31G*
B3LYP/6-31G* (SCIPCM)
B3LYP/6-311+G**
B3LYP/6-311+G** (SCIPCM)

2-Methyl-2-norbornyl Cation Page 35
B3LYP/6-31G*
B3LYP/6-31G* (SCIPCM)
B3LYP/6-311+G**
B3LYP/6-311+G** (SCIPCM)
MP2/6-31G*
MP2/6-311+G**
MP3/6-31G*
MP3(full)/6-31G*
MP4(SDQ)/6-31G*
MP4(SDQ,full)/6-31G*
QCISD/6-31G*

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 3

Primary Energy Data Used to Create Table 4

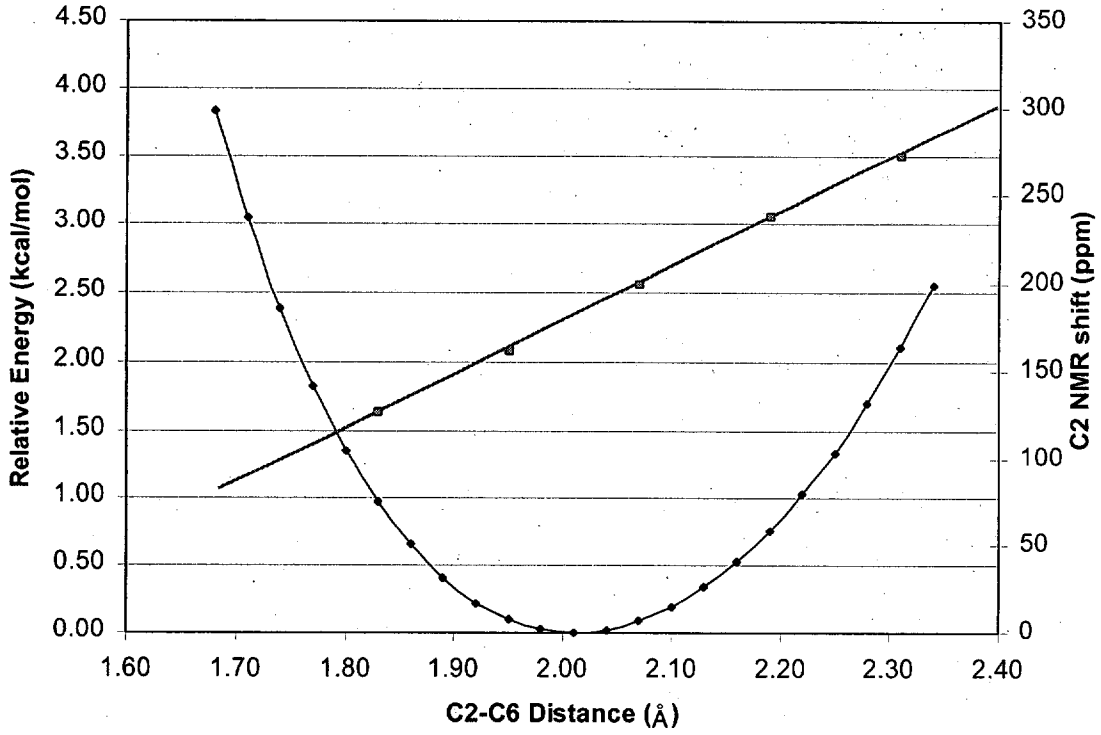
All values in Hartrees, All Structures Optimized, Energies for B3LYP/6–311+G**, ZPVE Value from B3LYP/6–31G* frequencies

Equation 1	$R^+_{(g)}$	–391.125015	ZPVE = 0.248976	
	$R^+_{(solv)}$	–391.197387		
	$R–Cl_{(g)}$	–851.629775	ZPVE = 0.253308	
	$R–Cl_{(solv)}$	–851.632206		
	$Cl^-_{(g)}$	–460.385835		
Equation 2	$R^+_{(g)}$	–312.475650	ZPVE = 0.192194	
	$R^+_{(solv)}$	–312.551619		
	$R–Cl_{(g)}$	–772.992014	ZPVE = 0.196590	
	$R–Cl_{(solv)}$	–772.994524		
Equation 3	$R^+_{(g)}$	–157.596698	ZPVE = 0.117112	(0.116076)*
	$R^+_{(solv)}$	–157.680932		
	$R–Cl_{(g)}$	–618.135605	ZPVE = 0.123232	(0.121823)*
	$R–Cl_{(solv)}$	–618.138290		
Equation 4	$R^+_{(g)}$	–730.356289	ZPVE = 0.109656	
	$R^+_{(solv)}$	–730.433460		
	$R–Cl_{(g)}$	–1190.832521	ZPVE = 0.109949	
	$R–Cl_{(solv)}$	–1190.837971		
Equation 5	$HCl_{(g)}$	–460.833852	ZPVE = 0.006673	
	$HCl_{(solv)}$	–460.836785		
	$HCl_2^-{}_{(g)}$	–921.177579	ZPVE = 0.006057	
	$HCl_{2(solv)}$	–921.244121		

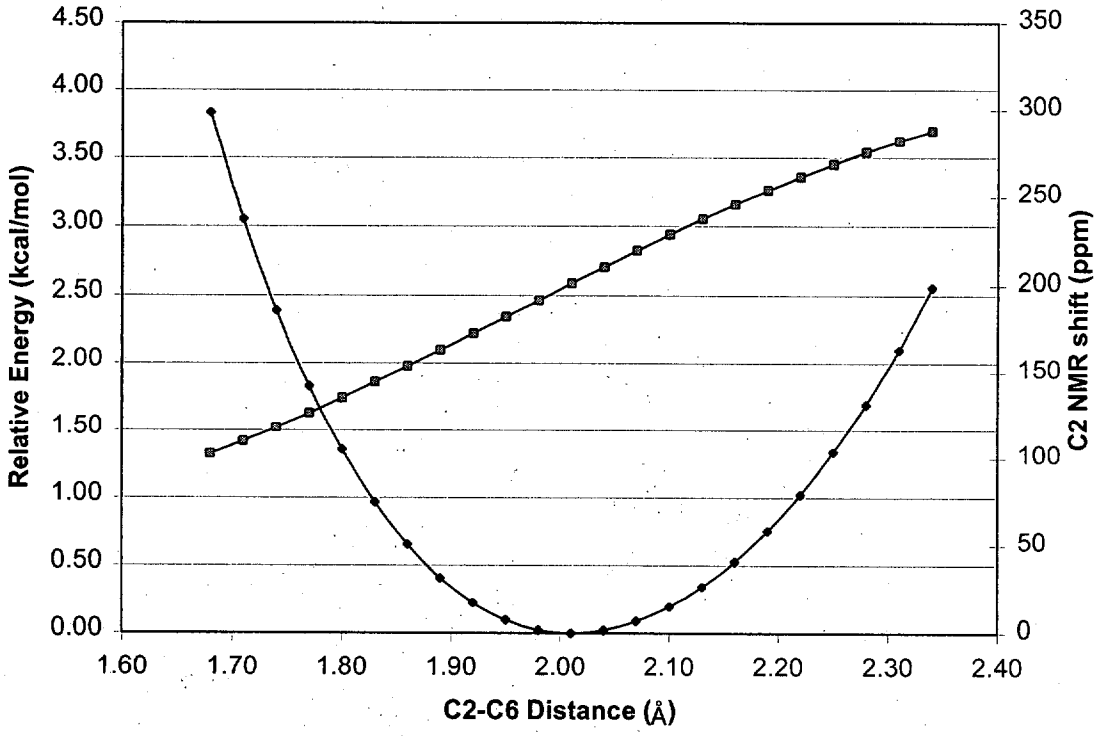
*B3LYP/6–311+G**

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 4

MP2/6-31G* opt // MP2/6-31G* nmr

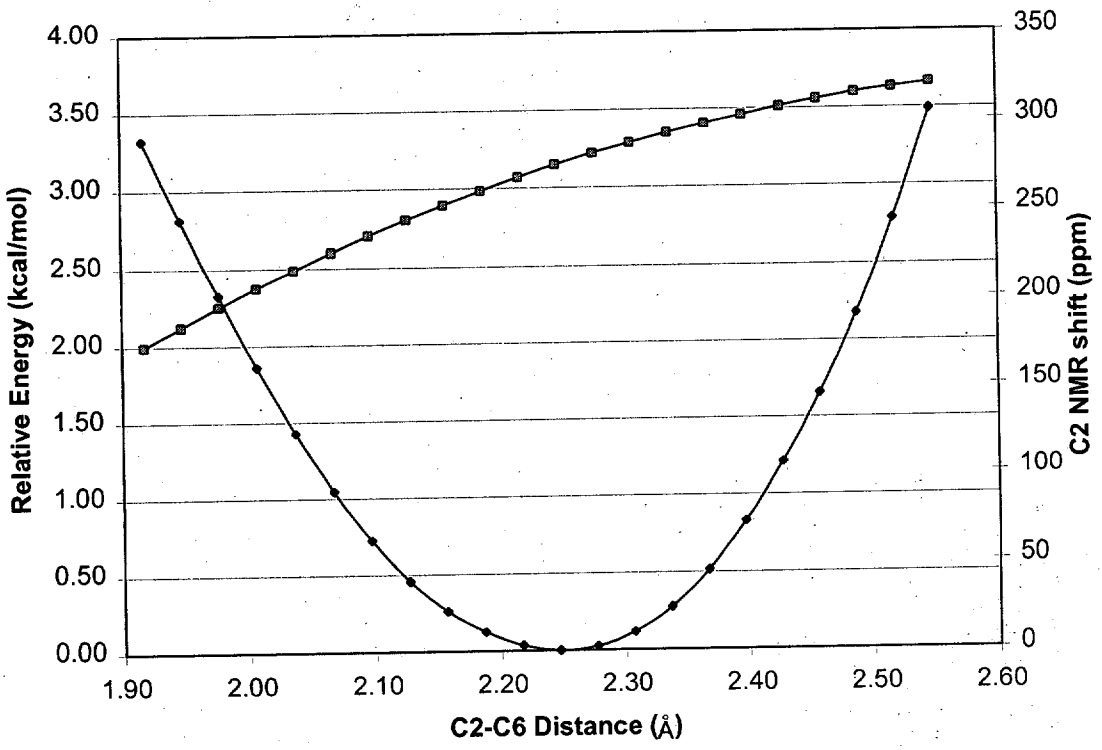


MP2/6-31G* opt // B3LYP/6-31G* nmr



© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 5

B3LYP/6-31G* opt // B3LYP/6-31G* nmr



© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 6

Cl-

$Cl^-_{(g)}$	6-31G*	E = -460.252233
$Cl^-_{(solv)}$	6-31G*	E = -460.345107
$Cl^-_{(g)}$	6-311+G*	E = -460.385835
$Cl^-_{(solv)}$	6-311+G*	E = -460.394012

HCl

$HCl_{(g)}$ B3LYP/6-31G*

	X	Y	Z
H	0	0	-1.217946
Cl	0	0	0.071644

E = -460.795694 ZPVE = 0.006673

$HCl_{(solv)}$ B3LYP/6-31G*

	X	Y	Z
H	0	0	-1.219071
Cl	0	0	0.071710

E = -460.798842

$HCl_{(g)}$ B3LYP/6-311+G**

	X	Y	Z
H	0	0	-1.217468
Cl	0	0	0.071616

E = -460.833848

$HCl_{(solv)}$ B3LYP/6-311+G**

	X	Y	Z
H	0	0	-1.217468
Cl	0	0	0.071616

E = -460.836785

HCl_2^-

$HCl_{2(g)}$ B3LYP/6-31G*

	X	Y	Z
Cl	0	0	1.585853
H	0	0	0
Cl	0	0	1.576513

E = -921.096489 ν = *318.6* *ZPVE = 0.006057*

$HCl_2^-{}_{(solv)}$ B3LYP/6-31G*

	X	Y	Z
Cl	0	0	1.576513
H	0	0	0
Cl	0	0	1.576513

E = -921.168706

$HCl_2^-{}_{(g)}$ B3LYP/6-311+G**

	X	Y	Z
Cl	0	0	-0.000043
H	0	0	-1.577507
Cl	0	0	-1.577504

E = -921.177579

$HCl_2^-{}_{(solv)}$ B3LYP/6-311+G**

	X	Y	Z
Cl	0	0	-0.000042
H	0	0	1.569337
Cl	0	0	-1.569335

E = -921.244121

3, 7-Dichlorocycloheptatriene

B3LYP/6-31G*

	X	Y	Z
C	0.650083	-0.807148	1.004008
Cl	2.947999	-0.440303	-0.369422
C	-0.672072	-0.837903	1.290818
H	1.287078	-1.529179	1.507699
C	0.905674	1.300074	-0.348841
H	1.602206	1.876807	-0.950162
C	1.325829	0.084499	0.097705
C	-0.334865	1.944360	-0.015979
C	-1.476904	1.396764	0.464939
H	-0.347500	3.018670	-0.191759
H	-2.307133	2.066836	0.675742
Cl	-2.264688	-0.848393	-0.997797
C	-1.760327	-0.046357	0.662866
H	-0.995903	-1.561787	2.035331
H	-2.679532	-0.169237	1.232773

E = -1190.703012 ν = *43.0* *ZPVE = 0.109949*

B3LYP/6-31G* (SCIPCM)

	X	Y	Z
C	0.656060	-0.815137	0.993195
Cl	2.959255	-0.451904	-0.373157
C	-0.666166	-0.832323	1.292421
H	1.284583	-1.553045	1.483697
C	0.923151	1.296773	-0.354964
H	1.625056	1.871955	-0.951074
C	1.334111	0.076518	0.092598
C	-0.313081	1.947921	-0.028267
C	-1.458188	1.411007	0.464812
H	-0.323528	3.018537	-0.221743
H	-2.285032	2.088526	0.662414
Cl	-2.313821	-0.849995	-0.992826
C	-1.745137	-0.016805	0.699893
H	-0.990756	-1.563782	2.028321
H	-2.667197	-0.137634	1.261986

E = -1190.708782

B3LYP/6-311+G**

	X	Y	Z
C	0.646813	-0.782623	1.027959
Cl	2.932539	-0.439410	-0.366866
C	-0.673622	-0.820755	1.307540
H	1.287364	-1.487441	1.546893
C	0.890174	1.297572	-0.358426
H	1.581606	1.866505	-0.969377
C	1.313703	0.093150	0.103518
C	-0.348593	1.943293	-0.028105
C	-1.488247	1.395425	0.449843
H	-0.364076	3.014161	-0.211059
H	-2.321410	2.059667	0.656088
Cl	-2.225716	-0.867755	-0.001158
C	-1.759738	-0.047234	0.657446
H	-0.997343	-1.528566	2.064307
H	-2.685064	-0.175482	1.210901

E = -1190.832521

B3LYP/6-311+G** (SCIPCM)

	X	Y	Z
C	0.650557	-0.786002	1.023200
Cl	2.939686	-0.447885	-0.368943
C	-0.670001	-0.813542	1.312366
H	1.285060	-1.500716	1.535322
C	0.900945	1.294762	-0.365158
H	1.595566	1.862261	-0.973295
C	1.317269	0.087974	0.100288
C	-0.334451	1.946059	-0.039973
C	-1.476053	1.406523	0.448295
H	-0.348163	3.013733	-0.237633
H	-2.306767	2.076032	0.644979
Cl	-2.256578	-0.872485	-0.998979
C	-1.749375	-0.024030	0.685788
H	-0.993909	-1.523699	2.066080
H	-2.677974	-0.151791	1.230396

E = -1190.837971

Chlorotropylium Cation

B3LYP/6-31G*

	X	Y	Z
C	2.295026	0.695851	-0.00316
C	1.189866	1.561717	0.000533
C	-0.169724	1.264045	0.00567
H	1.426338	2.623049	-0.000501
C	2.29505	-0.695818	-0.00441
H	3.270355	1.175948	-0.00954
C	1.189936	-1.561742	0.000059
H	3.270388	-1.175905	-0.00736
C	-0.169676	-1.263999	0.000212
H	1.426382	-2.623080	0.001041
H	-0.845134	-2.114966	0.001139
Cl	-2.514994	-0.000025	-0.000334
H	-0.845161	2.115019	-0.000446

E = -730-266643 ν_{lowest} *= 113.7 ZPVE = 0.109656*

B3LYP/6-31G* (SCIPCM)

	X	Y	Z
C	2.293581	0.696223	-0.000115
C	1.190916	1.561513	0.000088
C	-0.169183	1.263281	0.000222
H	1.425978	2.621523	-0.000104
C	2.293582	-0.696225	-0.000164
H	3.267848	1.175180	-0.000309
C	1.190913	-1.561510	-0.000010
H	3.267851	-1.175117	-0.000200
C	-0.169184	-1.263284	0.000163
H	1.425979	-2.621519	0.000211
H	-0.842026	-2.114517	0.000330
Cl	-2.518178	0.000001	-0.000157
H	-0.842029	2.114512	0.000038
C	-0.779721	-0.000001	0.000267

E = -730.343294

B3LYP/6-311+G**

	X	Y	Z
C	-2.290812	-0.694063	-0.000052
C	-1.187567	-1.558329	0.000250
C	0.168575	-1.261487	-0.000034
H	-1.423839	-2.617963	0.000464
C	-2.290784	0.694025	-0.000291
H	-3.264550	-1.173312	-0.000126
C	-1.187591	1.558356	0.000102
H	-3.264534	1.173275	-0.000682
C	0.168594	1.261517	0.000274
H	-1.423871	2.617980	0.000174
H	0.843127	2.111033	0.000472
Cl	2.511349	-0.000012	-0.000107
H	0.843131	-2.110986	-0.000218
C	0.785853	0.000011	0.000041

E = -730.356289

B3LYP/6-311+G** (SCIPCM)

	X	Y	Z
C	2.289428	0.694523	-0.000049
C	1.188772	1.558274	0.000120
C	-0.168029	1.260627	0.000034
H	1.423728	2.616786	0.000253
C	2.289432	-0.694524	-0.000159
H	3.262288	1.172834	-0.000101
C	1.188773	-1.558270	0.000059
H	3.262292	-1.172833	-0.000390
C	-0.1680226	-1.260627	0.000157
H	1.423731	-2.616783	0.000118
H	-0.840032	-2.110476	0.000262
Cl	-2.514781	-0.000001	-0.000075
H	-0.840035	2.110476	-0.000115
C	-0.777132	-0.0000001	0.000045

E = -730.433460

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 13

t-Butyl Chloride (C1)

B3LYP/6-31G*

	X	Y	Z
C	-0.197560	1.450910	0.010098
C	-0.000234	-0.001911	0.000015
C	1.357163	-0.556893	0.000859
C	-1.160624	-0.896521	-0.010940
H	0.708414	2.030297	0.193710
H	-1.005273	1.732593	0.700806
H	-0.597785	1.716425	-0.988201
H	-1.183723	-1.374374	0.989421
H	-1.010994	-1.735845	-0.703843
H	-2.115767	-0.396033	-0.178287
H	1.901940	-0.143392	-0.866505
H	1.401033	-1.646448	-0.014526
H	1.909685	-0.156728	0.867229

E = -157.554208 $\nu = 11.3 cm^{-1}$ *ZPVE = 0.117122*

B3LYP/6-311+G**

	X	Y	Z
C	0.817198	1.455451	-0.118125
C	0.372879	0.000044	-0.000006
C	0.817251	-0.625366	1.319429
C	0.817368	-0.829992	-1.201217
Cl	-1.493889	-0.000051	-0.000040
H	1.911630	1.500186	-0.124140
H	0.453995	2.047614	0.723738
H	0.450095	1.905449	-1.042254
H	0.452281	-1.855946	-1.127639
H	1.911809	-0.855736	-1.238108
H	0.452351	-0.398458	-2.134935
H	1.911669	-0.643061	1.360884
H	0.453530	-1.650295	1.411496
H	0.450582	-0.049713	2.171152

E = -618.135605

B3LYP/6-311+G** (SCIPCM)

	X	Y	Z
C	0.819602	-0.560627	1.348726
C	0.380765	0.000047	-0.000043
C	0.819310	-0.887701	-1.159997
C	0.819173	1.448493	-0.188870
Cl	-1.500722	-0.000106	0.000115
H	1.913601	-0.569195	1.391097
H	0.463841	-1.583188	1.486554
H	0.449934	0.053718	2.171612
H	0.448061	1.854129	-1.131714
H	1.913173	1.489800	-0.204346
H	0.464340	2.078915	0.628403
H	1.913345	-0.914529	-1.193156
H	0.457172	-0.499897	-2.113773
H	0.455709	-1.909221	-1.035526

E = -618.138283

t-Butyl Chloride (C3)

B3LYP/6-31G*

	X	Y	Z
C	0.000000	1.461908	-0.817391
C	0.000000	0.000000	-0.369127
C	1.266050	-0.730954	-0.817391
C	-1.266050	-0.730954	-0.817391
Cl	0.000000	0.000000	1.493018
H	0.000000	1.504567	-1.914021
H	0.887867	1.985859	-0.451908
H	-0.887867	1.985859	-0.451908
H	-1.275871	-1.761845	-0.451908
H	-1.302993	-0.752283	-1.914021
H	-2.163738	-0.224014	-0.451908
H	1.302993	-0.752283	-1.914021
H	1.275871	-1.761845	-0.451908
H	2.163738	-0.224014	-0.451908

E = -618.059589 ν_{low} *= 232.8* *ZPE = 0.123232*

B3LYP/6-31G* (SCIPCM)

	X	Y	Z
C	0.000000	1.462374	-0.819609
C	0.000000	0.000000	-0.379826
C	1.266453	-0.731187	-0.819609
C	-1.266453	-0.731187	-0.819609
Cl	0.000000	0.000000	1.501098
H	0.000000	1.505098	-1.915932
H	0.889153	1.985930	-0.456492
H	-0.889153	1.985930	-0.456492
H	-1.275290	-1.762994	-0.456492
H	-1.303453	-0.752549	-1.915932
H	-2.164442	-0.222936	-0.456492
H	1.303453	-0.752549	-1.915932
H	1.275290	-1.762994	-0.456492
H	2.164442	-0.222936	-0.456492

E = -618.062260

t-Butyl Cation

B3LYP/6-31G*

	X	Y	Z
C	-0.197560	1.450910	0.010098
C	-0.000234	-0.001911	0.000015
C	1.357163	-0.556893	0.000859
C	-1.160624	-0.896521	-0.010940
H	0.708414	2.030297	0.193710
H	-1.005273	1.732593	0.700806
H	-0.597785	1.716425	-0.988201
H	-1.183723	-1.374374	0.989421
H	-1.010994	-1.735845	-0.703843
H	-2.115767	-0.396033	-0.178287
H	1.901940	-0.143392	-0.866505
H	1.401033	-1.646448	-0.014526
H	1.909685	-0.156728	0.867229

E = -157.554208 $\nu = 11.3 cm^{-1}$ *ZPVE = 0.117122*

B3LYP/6-31G* (SCIPCM)

	X	Y	Z
C	-0.125951	1.456788	0.009918
C	-0.000580	-0.001956	0.000202
C	1.326467	-0.621608	0.000792
C	-1.201577	-0.837521	-0.010738
H	0.809216	1.985479	0.193084
H	-0.916500	1.772368	0.702916
H	-0.511023	1.734271	-0.988573
H	-1.243342	-1.308661	0.989683
H	-1.088096	-1.678916	-0.705170
H	-2.127462	-0.287511	-0.179326
H	1.883937	-0.233240	-0.867443
H	1.312049	-1.710738	-0.014596
H	1.891071	-0.247271	0.868378

E = -157.638311

B3LYP/6-311+G**

	X	Y	Z
C	0.257668	1.435246	0.016284
C	-0.002789	-0.001953	-0.009747
C	1.117751	-0.942556	-0.010745
C	-1.378905	-0.493684	-0.013360
H	1.273373	1.702977	0.304904
H	-0.498884	1.987039	0.581567
H	0.112229	1.758955	-1.034387
H	-1.548398	-0.882075	1.010714
H	-1.502225	-1.367162	-0.660624
H	-2.127426	0.273793	-0.205023
H	1.924801	-0.589922	-0.664520
H	0.843788	-1.972604	-0.228591
H	1.560393	-0.893323	1.001360

E = -157.596698

B3LYP/6-311+G** (SCIPCM)

	X	Y	Z
C	0.264661	1.431665	0.015764
C	-0.002897	-0.001949	-0.010208
C	1.111400	-0.946631	-0.010405
C	-1.379424	-0.485983	-0.013024
H	1.281235	1.688709	0.306639
H	-0.490545	1.981865	0.581524
H	0.121957	1.748478	-1.035209
H	-1.543511	-0.868666	1.011891
H	-1.502285	-1.357317	-0.660637
H	-2.119546	0.287683	-0.206023
H	1.916487	-0.593671	-0.663644
H	0.828195	-1.972590	-0.230491
H	1.545572	-0.897108	1.003190

E = -157.680932

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 18

Camphenyl Chloride

B3LYP/6-31G*

	X	Y	Z
C	1.753927	-1.383542	0.513308
C	2.411193	-0.058498	0.015658
H	2.737514	0.593375	0.830056
C	1.304994	0.555139	-0.871477
H	3.297275	-0.266871	-0.594678
H	1.667903	-1.438796	1.601862
H	2.334775	-2.257977	0.200325
C	0.382795	-1.398876	-0.216790
C	-0.574508	-0.355196	0.416625
H	-0.069339	-2.391577	-0.274620
C	0.753326	-0.717310	-1.549553
H	1.669225	1.339870	-1.542469
H	-0.104570	-0.549443	-2.203958
C	0.485728	1.915178	1.186006
H	1.519679	-1.266417	-2.108542
C	-0.867332	-0.549256	1.903504
Cl	-2.249948	-0.636298	-0.392099
C	0.077377	1.044956	-0.020447
C	-0.824931	1.929112	-0.905406
H	-1.754295	2.192462	-0.391336
H	-1.094614	1.448618	-1.848134
H	-0.292992	2.859458	-1.138662
H	1.100489	1.392763	1.922379
H	-0.398017	2.301046	1.706234
H	1.060928	2.779815	0.834140
H	-1.262967	-1.554069	2.079011
H	-1.610246	0.172311	2.254145
H	0.032957	-0.427753	2.511362

E = -851.497638

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 19

B3LYP/6-31G* (SCIPCM)

	X	Y	Z
C	1.751570	-1.386699	0.515556
C	2.412694	-0.065967	0.012210
H	2.742251	0.587330	0.823927
C	1.307236	0.548700	-0.874856
H	3.295958	-0.280086	-0.599935
H	1.666680	-1.438144	1.604152
H	2.326949	-2.264521	0.202765
C	0.378774	-1.400233	-0.213024
C	-0.568752	-0.351004	0.421729
H	-0.075022	-2.392497	-0.264462
C	0.750219	-0.723821	-1.548383
H	1.671999	1.330670	-1.548389
H	-0.106768	-0.553105	-2.203724
C	0.495012	1.917694	1.181082
H	1.514028	-1.277818	-2.105493
C	-0.866749	-0.539733	1.906962
H	-2.260414	-0.632877	-0.390462
C	0.082679	1.045039	-0.022548
C	-0.818318	1.929156	-0.908866
H	-1.745283	2.197910	-0.392861
H	-1.088660	1.447254	-1.850947
H	-0.283031	2.856641	-1.144415
H	1.109762	1.395473	1.917280
H	-0.386997	2.307482	1.701287
H	1.072199	2.778536	0.823727
H	-1.262802	-1.543554	2.087034
H	-1.605010	0.187331	2.255965
H	0.034594	-0.418784	2.512768

E = -851.499977

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 20

B3LYP/6-311+G**

	X	Y	Z
C	1.750279	-1.383037	0.513545
C	2.409681	-0.062169	0.009766
H	2.739513	0.589520	0.819225
C	1.302840	0.551513	-0.874408
H	3.290593	-0.274595	-0.602068
H	1.663883	-1.431606	1.599644
H	2.328000	-2.258194	0.206061
C	0.379045	-1.398829	-0.214620
C	-0.574233	-0.354442	0.418849
H	-0.073939	-2.388408	-0.269904
C	0.746272	-0.719681	-1.548774
H	1.664176	1.333224	-1.545968
H	-0.111436	-0.550779	-2.198264
C	0.494423	1.911316	1.184639
H	1.508168	-1.269632	-2.107612
C	-0.865440	-0.546348	1.903720
C	-2.249458	-0.631778	-0.391153
C	0.079478	1.044272	-0.020136
C	-0.822057	1.929314	-0.902552
H	-1.743979	2.201295	-0.384494
H	-1.101070	1.446672	-1.838492
H	-0.284719	2.851892	-1.142391
H	1.111042	1.388022	1.914816
H	-0.384845	2.296554	1.707640
H	1.066813	2.773721	0.830160
H	-1.257794	-1.549837	2.079926
H	-1.608556	0.172339	2.252433
H	0.033211	-0.421426	2.508711

E = -851.629775

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 21

B3LYP/6-311+G** (SCIPCM)

	X	Y	Z
C	1.749420	-1.388388	0.510452
C	2.409868	-0.066530	0.011230
H	2.735691	0.583289	0.823617
C	1.305530	0.549655	-0.874435
H	3.292115	-0.277603	-0.598908
H	1.665288	-1.442702	1.596226
H	2.323108	-2.262958	0.194506
C	0.376762	-1.399135	-0.216106
C	-0.567449	-0.351963	0.422757
H	-0.077654	-2.388095	-0.269274
C	0.745926	-0.719754	-1.549799
H	1.668994	1.331154	-1.544704
H	-0.110123	-0.546321	-2.200735
C	0.496394	1.915538	1.182052
H	1.506756	-1.271720	-2.107603
C	-0.859821	-0.542786	1.906211
Cl	-2.259123	-0.630973	-0.388199
C	0.082524	1.045025	-0.020825
C	-0.818524	1.928124	-0.906077
H	-1.740393	2.201161	-0.388209
H	-1.093550	1.444883	-1.843110
H	-0.280273	2.850153	-1.144766
H	1.111069	1.393612	1.914531
H	-0.383486	2.303811	1.701803
H	1.071025	2.774625	0.823607
H	-1.249823	-1.546605	2.085562
H	-1.598699	0.179196	2.256967
H	0.041261	-0.418056	2.507115

E = -851.632206

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 22

Camphenyl Cation

B3LYP/6-31G*

	X	Y	Z
C	1.590666	-0.770469	0.954039
C	1.672883	0.755126	0.729860
H	1.236362	-1.027753	1.953624
H	2.571738	-1.235184	0.823930
C	0.639681	-1.220366	-0.180479
H	1.244098	1.355744	1.537307
C	0.933224	0.969110	-0.735461
H	2.679971	1.140917	0.544447
C	-0.752867	-0.533457	0.059028
H	0.564141	-2.300190	-0.319559
C	1.204876	-0.411314	-1.364680
H	0.684953	-0.549334	-2.314972
H	1.245706	1.893064	-1.220317
C	-1.430203	-0.829327	1.411186
C	-1.764967	-0.913255	-1.084749
C	-0.392708	0.899835	-0.172143
H	2.271905	-0.579884	-1.530674
C	-1.229269	2.064347	0.165140
H	-0.665990	3.000553	0.179563
H	-1.795075	1.931564	1.091908
H	-1.976235	2.151427	-0.643998
H	-2.721695	-0.407539	-0.929514
H	-1.931908	-1.992837	-1.022621
H	-1.408659	-0.681517	-2.090285
H	-0.860058	-0.449409	2.263140
H	-1.532473	-1.912418	1.531347
H	-2.434684	-0.398582	1.456235

E = -391.028147

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 23

B3LYP/6-31G* (SCIPCM)

	X	Y	Z
C	1.591705	-0.782039	0.937773
C	1.669326	0.745037	0.736176
H	1.240230	-1.053820	1.931644
H	2.570656	-1.242134	0.795662
C	0.638417	-1.216778	-0.197914
H	1.238672	1.329259	1.550156
C	0.929230	0.979131	-0.722117
H	2.672021	1.134997	0.554820
C	-0.751623	-0.533873	0.055271
H	0.562023	-2.291694	-0.351431
C	1.195870	-0.390490	-1.371576
H	0.669016	-0.514068	-2.316456
H	1.239746	1.906660	-1.192743
C	-1.414591	-0.842319	1.409638
C	-1.767608	-0.905434	-1.081993
C	-0.393478	0.903038	-0.159782
H	2.259680	-0.556317	-1.542982
C	-1.229910	2.056997	0.180808
H	-0.656430	2.980518	0.257233
H	-1.853435	1.896627	1.060181
H	-1.913855	2.181461	-0.675858
H	-2.719530	-0.399534	-0.917177
H	-1.931677	-1.983290	-1.026475
H	-1.415432	-0.662674	-2.083316
H	-0.842582	-0.460222	2.255660
H	-1.503672	-1.925234	1.521800
H	-2.419460	-0.420160	1.461586

E = -391.197387

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 24

B3LYP/6-311+G**

	X	Y	Z
C	1.593379	-0.774367	0.943675
C	1.669137	0.751671	0.734501
H	1.242297	-1.042342	1.938661
H	2.573236	-1.234044	0.807607
C	0.641880	-1.216527	-0.191507
H	1.237807	1.340975	1.545519
C	0.927163	0.976631	-0.728784
H	2.671437	1.144143	0.552678
C	-0.750354	-0.534597	0.057631
H	0.568924	-2.292554	-0.339473
C	1.199880	-0.396612	-1.369614
H	0.676895	-0.528500	-2.315803
H	1.237176	1.902993	-1.204475
C	-1.418269	-0.840693	1.410288
C	-1.764319	-0.908467	-1.084204
C	-0.394723	0.899887	-0.164025
H	0.264070	-0.561278	-1.540228
C	-1.233778	2.056287	0.176049
H	-0.669789	2.988210	0.222988
H	-1.830061	1.906548	1.077201
H	-1.949083	2.161501	-0.657320
H	-2.720182	-0.409172	-0.920543
H	-1.925953	-1.986838	-1.031344
H	-1.413372	-0.665830	-2.086397
H	-0.849190	-0.459250	2.259051
H	-1.509736	-1.922812	1.526935
H	-2.424450	-0.421024	1.460889

E = -391.125015

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 25

B3LYP/6-311+G** (SCIPCM)

	X	Y	Z
C	1.591705	-0.782039	0.937773
C	1.669326	0.745037	0.736176
H	1.240230	-1.053820	1.931644
H	2.570656	-1.242134	0.795662
C	0.638417	-1.216778	-0.197914
H	1.238672	1.329259	1.550156
C	0.929230	0.979131	-0.722117
H	2.672021	1.134997	0.554820
C	-0.751623	-0.533873	0.055271
H	0.562023	-2.291694	-0.351431
C	1.195870	-0.390490	-1.371576
H	0.669016	-0.514068	-2.316456
H	1.239746	1.906660	-1.192743
C	-1.414591	-0.842319	1.409638
C	-1.767608	-0.905434	-1.081993
C	-0.393478	0.903038	-0.159782
H	2.259680	-0.556317	-1.542982
C	-1.229910	2.056997	0.180808
H	-0.656430	2.980518	0.257233
H	-1.853435	1.896627	1.060181
H	-1.913855	2.181461	-0.675858
H	-2.719530	-0.399534	-0.917177
H	-1.931677	-1.983290	-1.026475
H	-1.415432	-0.662674	-2.083316
H	-0.842582	-0.460222	2.255660
H	-1.503672	-1.925234	1.521800
H	-2.419460	-0.420160	1.461586

E = -391.197387

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 26

MP2/6-31G*

	X	Y	Z
C	1.561164	-0.659010	1.023639
C	1.430822	0.844931	0.783978
H	1.232464	-0.945416	2.023803
H	2.598095	-0.984232	0.904691
C	0.685160	-1.215788	-0.109326
H	0.822304	1.368463	1.530501
C	0.907210	0.930796	-0.841124
H	2.350304	1.430129	0.677459
C	-0.713518	-0.558736	0.053477
H	0.654340	-2.305828	-0.184020
C	1.274596	-0.467931	-1.312817
H	0.803264	-0.694500	-2.272391
H	1.256666	1.841834	-1.324315
C	-1.402507	-0.815719	1.393898
C	-1.674187	-0.980723	-1.089649
C	-0.354565	0.875229	-0.208806
H	2.353825	-0.606797	-1.419677
C	-1.230200	2.035115	0.074192
H	-0.706905	2.987649	-0.028591
H	-1.711784	1.966095	1.052272
H	-2.027464	2.006429	-0.682489
H	-2.645653	-0.494987	-0.966921
H	-1.824256	-2.061781	-1.020312
H	-1.298491	-0.750361	-2.088520
H	-0.850962	-0.402810	2.242104
H	-1.500726	-1.894393	1.547636
H	-2.408872	-0.388484	1.403998

E = -389.6225474

MP2/6-311+G**

	X	Y	Z
C	1.553439	-0.634387	1.045781
C	1.393234	0.865566	0.791779
H	1.213535	-0.915917	2.043120
H	2.598016	-0.936554	0.937215
C	0.697325	-1.217910	-0.092354
H	0.762528	1.384538	1.522742
C	0.903327	0.925178	-0.865813
H	2.297809	1.471387	0.676220
C	-0.706725	-0.566164	0.052466
H	0.674543	-2.307726	-0.154897
C	1.294511	-0.479407	-1.301178
H	0.831123	-0.727198	-2.259079
H	1.259841	1.835443	-1.342071
C	-1.401061	-0.806929	1.394951
C	-1.657259	-1.004028	-1.093153
C	-0.351723	0.871108	-0.220470
H	2.376511	-0.605049	-1.389368
C	-1.238069	2.029647	0.052681
H	-0.720569	2.983915	-0.064395
H	-1.712575	1.964348	1.034699
H	-2.037622	1.982625	-0.700923
H	-2.626742	-0.508559	-0.990236
H	-1.815926	-2.083224	-1.006500
H	-1.264747	-0.791477	-2.090335
H	-0.863738	-0.360189	2.236186
H	-1.478250	-1.884029	1.573937
H	-2.415731	-0.398379	1.385556

E = -389.8864522

MP3/6-31G*

	X	Y	Z
C	1.579046	-0.715064	0.983854
C	1.551660	0.807036	0.749896
H	1.244527	-0.986056	1.986110
H	2.589509	-1.110162	0.854077
C	0.659617	-1.219732	-0.144767
H	1.014931	1.364054	1.525201
C	0.921826	0.950768	-0.784633
H	2.524081	1.293211	0.636026
C	-0.733758	-0.548993	0.056617
H	0.605803	-2.305063	-0.249999
C	1.235523	-0.442500	-1.341649
H	0.740087	-0.623803	-2.297236
H	1.244692	1.865352	-1.278456
C	-1.407332	-0.818561	1.407556
C	-1.721771	-0.944985	-1.081825
C	-0.376975	0.885706	-0.196286
H	2.308336	-0.600154	-1.475576
C	-1.232514	2.046730	0.120163
H	-0.691650	2.992793	0.060890
H	-1.737661	1.943352	1.083545
H	-2.016185	2.057334	-0.653818
H	-2.689313	-0.459350	-0.931421
H	-1.870462	-2.026838	-1.027163
H	-1.363089	-0.700703	-2.083683
H	-0.841924	-0.413191	2.250426
H	-1.499113	-1.899134	1.551010
H	-2.414503	-0.394072	1.436513

E = -389.6962121

MP4/6-31G*

	X	Y	Z
C	1.584271	-0.725914	0.971559
C	1.573901	0.798342	0.745044
H	1.250367	-1.001375	1.975216
H	2.592193	-1.132602	0.837145
C	0.657993	-1.216131	-0.157770
H	1.051302	1.358831	1.531211
C	0.924678	0.960194	-0.765230
H	2.556931	1.269581	0.631951
C	-0.734816	-0.548775	0.056201
H	0.602281	-2.302843	-0.275031
C	1.228489	-0.425630	-1.347954
H	0.727801	-0.593210	-2.305754
H	1.239001	1.881062	-1.258675
C	-1.405074	-0.832471	1.406323
C	-1.726545	-0.935868	-1.084396
C	-0.385495	0.886939	-0.187017
H	2.302348	-0.584583	-1.491057
C	-1.243253	2.044149	0.135787
H	-0.697906	2.991207	0.104946
H	-1.771022	1.924953	1.086965
H	-2.011115	2.074481	-0.656470
H	-2.696687	-0.453651	-0.925397
H	-1.871435	-2.020841	-1.039482
H	-1.372455	-0.680465	-2.087214
H	-0.838281	-0.431188	2.252787
H	-1.492425	-1.916550	1.541254
H	-2.415790	-0.411820	1.442322

E = -389.7155462

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 30

QCISD/6-31G*

	X	Y	Z
C	1.587264	-0.737524	0.962286
C	1.597424	0.788874	0.740590
H	1.251003	-1.012961	1.965490
H	2.589754	-1.157294	0.824826
C	0.654106	-1.215045	-0.167948
H	1.091960	1.354520	1.534668
C	0.927898	0.966856	-0.750764
H	2.589314	1.239725	0.620886
C	-0.737757	-0.547301	0.055645
H	0.594909	-2.300588	-0.294493
C	1.221627	-0.414608	-1.353488
H	0.715839	-0.570514	-2.310815
H	1.236595	1.890982	-1.242809
C	-1.404851	-0.837368	1.407029
C	-1.734260	-0.930469	-1.083701
C	-0.390617	0.889186	-0.180987
H	2.294621	-0.575776	-1.502802
C	-1.248122	2.045477	0.146037
H	-0.697095	2.990330	0.137414
H	-1.791769	1.914977	1.087139
H	-2.003023	2.092628	-0.658568
H	-2.703205	-0.446258	-0.920265
H	-1.880321	-2.015653	-1.040047
H	-1.382616	-0.673340	-2.087327
H	-0.837951	-0.435089	2.253363
H	-1.486460	-1.922662	1.539185
H	-2.417824	-0.421501	1.445963

E = -389.7195432

2-Methyl-2-norbornyl Chloride

B3LYP/6-31G*

	X	Y	Z
C	-1.612963	0.866770	-0.907995
C	-2.316918	0.263704	0.350669
H	-2.453041	0.998064	1.152746
C	-1.358014	-0.877581	0.765458
H	-3.308639	-0.128243	0.099180
H	-1.425040	1.940521	-0.827102
H	-2.221925	0.719743	-1.806566
C	-0.320491	0.017391	-1.038087
C	0.646060	0.366230	0.124456
H	0.155935	0.085904	-2.018548
C	-0.847742	-1.369909	-0.607009
H	-1.815266	-1.631650	1.412385
H	-0.065394	-2.130888	-0.540985
H	-0.298484	0.520672	2.113277
H	-1.649083	-1.737819	-1.257969
C	1.037478	1.831684	0.278327
Cl	2.248189	-0.548770	-0.184565
C	-0.076332	-0.250418	1.365842
H	0.549878	-1.004904	1.847829
H	1.470579	2.227664	-0.645593
H	1.773360	1.947353	1.079406
H	0.161436	2.435455	0.539581

E = -772.880979 ν *= 100.3* *ZPE = 0.196591*

B3LYP/6-31G* (SCIPCM)

	X	Y	Z
C	-1.615637	0.864052	-0.908775
C	-2.319708	0.260475	0.349298
H	-2.456932	0.995001	1.150719
C	-1.359114	-0.878706	0.765499
H	-3.309675	-0.134386	0.096172
H	-1.429451	1.937962	-0.829009
H	-2.221625	0.712980	-1.808413
C	-0.320989	0.016389	-1.038172
C	0.638599	0.371688	0.125862
H	0.154598	0.088168	-2.018743
C	-0.847056	-1.371254	-0.606196
H	-1.813903	-1.633193	1.413271
H	-0.065136	-2.132906	-0.537543
H	-0.300401	0.521641	2.114024
H	-1.647139	-1.739476	-1.258022
C	1.034035	1.835041	0.277098
Cl	2.256699	-0.548683	-0.183852
C	-0.078596	-0.248674	1.366292
H	0.547824	-1.003368	1.847658
H	1.464735	2.231041	-0.647861
H	1.767055	1.953104	1.080411
H	0.156960	2.436989	0.537385

E = -772.883423

B3LYP/6-311+G**

	X	Y	Z
C	-1.612404	0.867872	-0.905148
C	-2.316315	0.260504	0.350919
H	-2.453222	0.990748	1.153013
C	-1.356141	-0.879469	0.763596
H	-3.304703	-0.131621	0.098039
H	-1.424566	1.938411	-0.819475
H	-2.219612	0.724502	-1.802223
C	-0.320082	0.020026	-1.037389
C	0.644170	0.367868	0.125216
H	0.156275	0.090573	-2.014805
C	-0.845211	-1.368260	-0.609164
H	-1.810658	-1.633908	1.407133
H	-0.063797	-2.126221	-0.544321
H	-0.299548	0.516996	2.110014
H	-1.644426	-1.734162	-1.259184
C	1.035893	1.830860	0.278932
Cl	2.246528	-0.548481	-0.184174
C	-0.076136	-0.251121	1.363952
H	0.550336	-1.003774	1.842591
H	1.469457	2.224517	-0.643010
H	1.769448	1.945277	1.079142
H	0.161392	2.433147	0.538567

E = -772.992014

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 34

B3LYP/6-311+G** (SCIPCM)

	X	Y	Z
C	-1.615021	0.865197	-0.905805
C	-2.319119	0.257128	0.349525
H	-2.457423	0.987550	1.150935
C	-1.357069	-0.880490	0.763745
H	-3.305484	-0.138417	0.094603
H	-1.428938	1.935885	-0.820757
H	-2.219353	0.717875	-1.803956
C	-0.320486	0.019078	-1.037479
C	0.636977	0.373358	0.126512
H	0.154511	0.093066	-2.015208
C	-0.844501	-1.369547	-0.608300
H	-1.809086	-1.635214	1.408337
H	-0.063538	-2.128154	-0.540827
H	-0.301884	0.518924	2.110276
H	-1.642769	-1.735529	-1.258961
C	1.032972	1.834126	0.277387
Cl	2.254626	-0.548730	-0.183382
C	-0.078398	-0.248794	1.364389
H	0.548121	-1.001414	1.842989
H	1.464514	2.227558	-0.645509
H	1.763132	1.951036	1.080299
H	0.157423	2.434908	0.535423

E = -772.994524

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 35

2-Methyl-2-norbornyl Cation

B3LYP/6-31G*

	X	Y	Z
C	-1.490827	0.409257	-0.956202
C	-0.489446	1.414115	-0.350335
H	0.247455	1.811666	-1.053203
C	0.171713	0.593388	0.939327
H	-0.948273	2.269742	0.154824
H	-1.353946	0.284259	-2.033460
H	-2.520985	0.732778	-0.784168
C	-1.186622	-0.882353	-0.162796
C	0.274786	-1.270683	-0.511312
H	-1.902538	-1.693697	-0.294640
H	-0.716535	-1.121263	1.997309
C	-1.002405	-0.351353	1.272831
H	0.596256	1.272896	1.676348
C	2.471167	0.140824	-0.181252
H	0.511839	-1.467703	-1.562356
H	0.558182	-2.177608	0.055483
C	1.056178	-0.157392	0.090659
H	-1.870960	0.189654	1.656535
H	2.762139	1.149939	0.120634
H	2.755392	-0.062665	-1.218587
H	3.054705	-0.562814	0.439757

E = -312.399386 ν = *112.5* *ZPE = 0.192194*

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 36

B3LYP/6-31G* (SCIPCM)

	X	Y	Z
C	-1.500597	0.381585	-0.954915
C	-0.512459	1.409792	-0.363312
H	0.214053	1.807391	-1.075435
C	0.168909	0.617770	0.917898
H	-0.988290	2.262167	0.129381
H	-1.360430	0.242646	-2.029898
H	-2.534833	0.692452	-0.784102
C	-1.176410	-0.894786	-0.145464
C	0.284989	-1.274518	-0.496600
H	-1.884301	-1.715498	-0.259464
H	-0.683158	-1.092873	2.011329
C	-0.988028	-0.338266	1.279447
H	0.594751	1.306801	1.643608
C	2.471164	0.147824	-0.185492
H	0.519615	-1.480223	-1.545535
H	0.582897	-2.169109	0.080230
C	1.059536	-0.149354	0.085344
H	-1.859652	0.199804	1.659800
H	2.746525	1.171950	0.074833
H	2.766782	-0.104335	-1.207377
H	3.043414	-0.521452	0.481196

E = -312.474832

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 37

B3LYP/6-311+G**

	X	Y	Z
C	-1.495647	0.406269	-0.950044
C	-0.495456	1.412880	-0.350107
H	0.236883	1.807871	-1.055221
C	0.173369	0.593884	0.936093
H	-0.951642	2.267025	0.154073
H	-1.365188	0.281594	-2.025526
H	-2.523933	0.724262	-0.772889
C	-1.182942	-0.884598	-0.160019
C	0.277376	-1.264568	-0.515296
H	-1.895141	-1.695751	-0.289582
H	-0.702516	-1.123247	1.993622
C	-0.994372	-0.354790	1.273967
H	0.597059	1.272713	1.670175
C	2.467204	0.143210	-0.182212
H	0.511336	-1.459489	-1.564736
H	0.566989	-2.169074	0.048509
C	1.055531	-0.153443	0.085966
H	-1.861708	0.180088	1.661301
H	2.759788	1.148256	0.121851
H	2.756010	-0.065283	-1.214514
H	3.041685	-0.562029	0.442848

E = -312.475650

B3LYP/6-311+G** (SCIPCM)

	X	Y	Z
C	-1.507278	0.375173	-0.948243
C	-0.521403	1.407907	-0.364888
H	0.198928	1.803173	-1.080932
C	0.170754	0.621174	0.911811
H	-0.996431	2.258789	0.125682
H	-1.373247	0.234612	-2.021399
H	-2.540130	0.679247	-0.772191
C	-1.172014	-0.898248	-0.140063
C	0.288086	-1.268854	-0.499170
H	-1.875433	-1.720013	-0.249149
H	-0.664807	-1.091170	2.009868
C	-0.977861	-0.339706	1.281873
H	0.596856	1.311049	1.632908
C	2.467660	0.150373	-0.187483
H	0.519202	-1.473567	-1.546626
H	0.594495	-2.159961	0.075432
C	1.059566	-0.144681	0.079333
H	-1.848373	0.192297	1.666033
H	2.740909	1.175540	0.060670
H	2.773785	-0.122425	-1.198078
H	3.029191	-0.506397	0.498754

E = -312.551619

MP2/6-31G*

	X	Y	Z
C	0.222891	1.386303	-0.210774
C	1.410123	0.685928	-0.867625
H	1.348472	0.722776	-1.958064
H	0.914852	-1.398065	1.768159
H	2.354981	1.140709	-0.559275
H	-0.578371	1.683496	-0.895386
H	0.430481	2.262054	0.413004
C	-0.183986	0.335684	1.102220
C	-0.987502	-0.197811	0.077254
H	-0.610224	0.894067	1.933084
C	1.093946	-0.482572	1.192332
H	-2.953630	-0.841920	0.250863
C	-2.434082	0.046607	-0.133781
C	-0.158342	-1.169086	-0.706092
C	1.264242	-0.737096	-0.311086
H	-0.376881	-1.175654	-1.778442
H	-0.387948	-2.170003	-0.305199
H	2.052734	-1.436321	-0.594069
H	1.924702	0.064297	1.645681
H	-2.685368	0.131861	-1.193796
H	-2.797541	0.914965	0.418764

E = -311.2817726

© 2001 American Chemical Society, J. Org. Chem., Brunelle jo010379n Supporting Info Page 40

MP2/6-311+G**

	X	Y	Z
C	0.190543	1.386363	-0.174186
C	1.396248	0.732688	-0.848991
H	1.330835	0.800963	-1.937268
H	0.943779	-1.451081	1.715839
H	2.328305	1.197876	-0.519451
H	-0.618216	1.686823	-0.847983
H	0.375646	2.236310	0.490535
H	-0.186168	0.283005	1.127121
C	-0.980717	-0.206570	0.072051
H	-0.614573	0.818514	1.970140
C	1.109217	-0.511466	1.176364
H	-2.943484	-0.873406	0.210619
C	-2.432018	0.037360	-0.130584
C	-0.142381	-1.147407	-0.745500
C	1.277781	-0.713104	-0.338096
H	-0.360780	-1.116352	-1.816556
H	-0.363989	-2.158852	-0.369115
H	2.074519	-1.390142	-0.645792
H	1.930846	0.036446	1.643442
H	-2.678857	0.171061	-1.186676
H	-2.799070	0.876623	0.463194

E = -311.4841088