Society 135(25): 9629–9634, 2013

Carbocations generated under stable conditions by ionization of matrix-isolated radicals: the allyl and benzyl cations.

by Vladimir Mišić, Krzysztof Piech and Thomas Bally*

Supporting Information

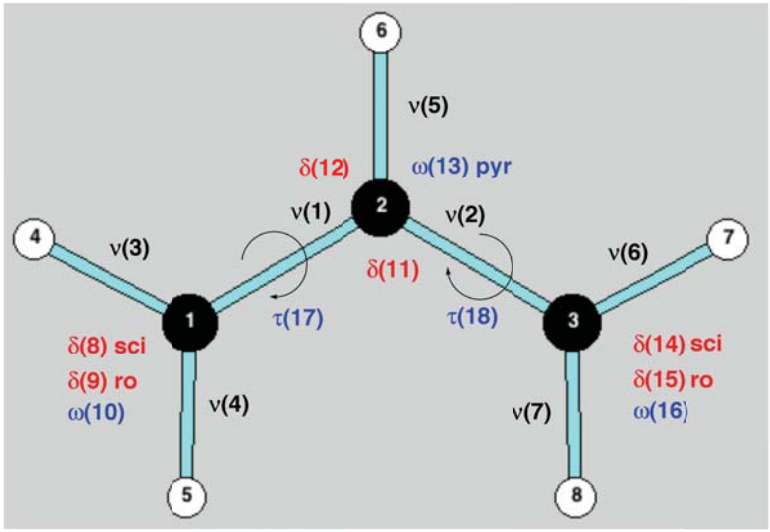
1. Figure and Table showing the definition of internal valence coordinates in the allyl radical and cation
2. Figure and Table showing the definition of internal valence coordinates in the benzyl radical and cation
3. Cartesian coordinates and energies of the species discussed in this work

In addition, there is a separate Excel spreadsheet which contains the full results of the scaled force field calculations (all calculated and observed frequencies, and full force constant matrix and potential energy distribution of all normal modes in terms of the valence coordinates)

Full quotation of Reference 28 (Gaussian program)

M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, 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, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian 09, Revision C.01, Gaussian, Inc., Wallingford CT, 2010.

Definition of internal coordinates in the allyl radical and cation



ν(2) stretch [C(2)-C(3)]
ν(3) stretch [C(1)-H(4)]
ν(5) stretch [C(1)-H(5)]
ν(6) stretch [C(3)-H(6)]
ν(7) stretch [C(3)-H(7)]

δ(8) CH_2 scissoring (in plane):
2[H(4)-C(1)-H(5)]
−[C(2)-C(1)-H(4)]
−[C(2)-C(1)-H(5)]

δ(9) CH_2 rocking (in plane):
+[C(2)-C(1)-H(4)]
−[C(2)-C(1)-H(5)]

ω(10) CH_2 pyramidalization
C(1) out of the plane [C(2)-H(4)-H(5)]

δ(11) C-C-C bend (in plane) [C(3)-C(2)-C(1)]

δ(12) C-H(6) bend (in plane)
+[H(6)-C(2)-C(3)]
−[H(6)-C(2)-C(1)]

ω(13) C-H(6) wag (out-of-plane)
C(2) out of the plane [C(1)-C(3)-H(6)]

δ(14) CH_2 scissoring (in plane):
2[H(7)-C(3)-H(8)]
−[C(2)-C(3)-H(7)]
−[C(2)-C(3)-H(8)]

δ(15) CH_2 rocking (in plane):
+[C(2)-C(3)-H(7)]
−[C(2)-C(1)-H(8)]

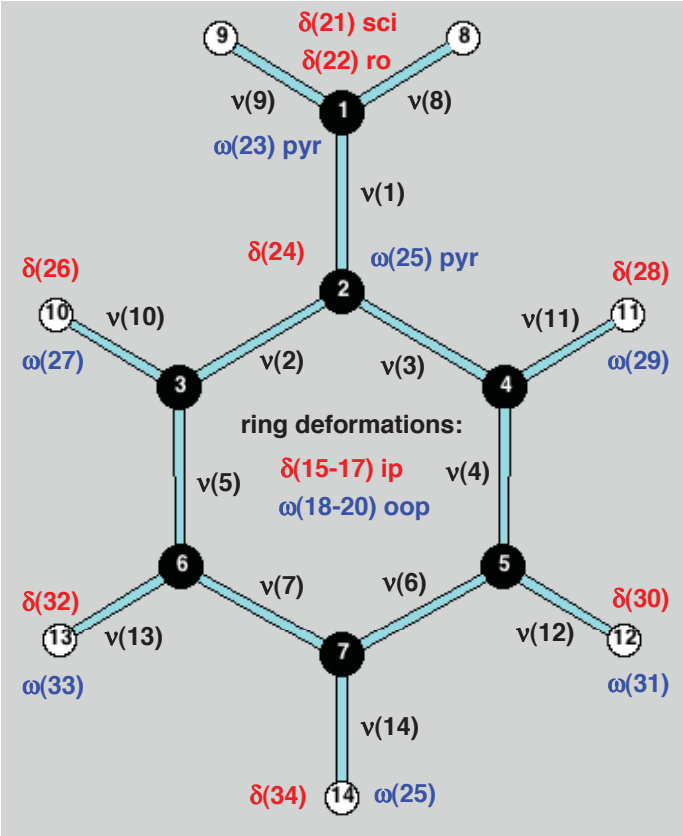
ω(16) CH_2 pyramidalization
C(3) out of the plane [C(2)-H(7)-H(8)]

τ(17) C-CH_2 torsion
twist [C(3)-C(2)-C(1)-H(4)]
+[C(6)-C(2)-C(1)-H(4)]
+[C(3)-C(2)-C(1)-H(5)]
+[C(6)-C(2)-C(1)-H(5)]

τ(18) C-CH_2 torsion
twist [C(1)-C(2)-C(3)-H(7)]
+[C(1)-C(2)-C(3)-H(8)]
+[H(6)-C(2)-C(3)-H(7)]
+[H(6)-C(2)-C(3)-H(8)]

Definition of internal coordinates in the benzyl radical and cation

ν(1) stretch [C(1)-C(2)]
ν(2) stretch [C(2)-C(3)]
ν(3) stretch [C(2)-C(4)]
ν(5) stretch [C(3)-C(6)]
ν(6) stretch [C(5)-C(7)]
ν(7) stretch [C(6)-C(7)]
ν(8) stretch [C(1)-H(8)]
ν(9) stretch [C(1)-H(9)]
ν(10) stretch [C(3)-H(10)]
ν(11) stretch [C(4)-H(11)]
ν(12) stretch [C(5)-H(12)]
ν(13) stretch [C(6)-H(13)]
ν(14) stretch [C(7)-H(14)]



δ(15) in-plane ring deformation:
bend [C(4)-C(2)-C(3)]
– 0.5[C(2)-C(3)-C(6)]
– 0.5[C(3)-C(6)-C(7)]
+ C(6)-C(5)-C(7)
– 0.5[C(7)-C(5)-C(4)]
– 0.5[C(5)-C(4)-C(2)]

δ(16) in-plane ring deformation (a= $\sqrt{3}/2$):
bend a[C(2)-C(3)-C(6)]
– a[C(3)-C(6)-C(7)]
+ a[C(7)-C(5)-C(4)]
– a[C(5)-C(4)-C(2)]

δ(17) in-plane ring deformation:
bend [C(4)-C(2)-C(3)]
– [C(2)-C(3)-C(6)]
+ [C(3)-C(6)-C(7)]
– [C(6)-C(5)-C(7)]
+ [C(7)-C(5)-C(4)]
– [C(5)-C(4)-C(2)]

ω(18) out-of-plane ring deformation(b=1.5):
twist b[C(4)-C(2)-C(3)-C(6)]
–b[C(3)-C(6)-C(7)-C(5)]
+b[C(6)-C(7)-C(5)-C(4)]
–b[C(5)-C(4)-C(2)-C(3)]

ω(19) out-of-plane ring deformation(a= $\sqrt{3}/2$):

twist –a[C(4)-C(2)-C(3)-C(6)]
+2a[C(2)-C(3)-C(6)-C(7)]
–a[C(3)-C(6)-C(7)-C(5)]
–a[C(6)-C(7)-C(5)-C(4)]
+2a[C(7)-C(5)-C(4)-C(2)]
–a[C(5)-C(4)-C(2)-C(3)]

ω(20) out-of-plane ring deformation(c =2):

twist –c[C(4)-C(2)-C(3)-C(6)]
+c[C(2)-C(3)-C(6)-C(7)]
–c[C(3)-C(6)-C(7)-C(5)]
+c[C(6)-C(7)-C(5)-C(4)]
–c[C(7)-C(5)-C(4)-C(2)]
+c[C(5)-C(4)-C(2)-C(3)]

δ(21) CH_2 scissoring (in plane):

2[H(8)-C(1)-H(9)]
–[C(2)-C(1)-H(8)]
–[C(2)-C(1)-H(9)]

δ(21) CH_2 rocking (in plane):

+[C(2)-C(1)-H(8)]
–[C(2)-C(1)-H(9)]

ω(23) CH_2 pyramidalizationC(1) out of the plane [H(8)-C(2)-H(9)]

δ(24) R_2C-CH_2 bend (in plane)

+[C(3)-C(2)-C(1)]
–[C(4)-C(2)-C(1)]

ω(25) C-$(C)_3$ pyramidalization:C(2) out of the plane [C(3)-C(4)-C(1)]

δ(26) C-H(10) bend (in plane)

+[C(2)-C(3)-H(10)]
–[C(6)-C(3)-H(10)]

ω(27) C-H(10) wag (out-of-plane)C(3) out of the plane [C(2)-C(6)-H(10)]

δ(28) C-H(11) bend (in plane)

+[C(2)-C(4)-H(11)]
–[C(5)-C(4)-H(11)]

ω(29) C-H(11) wag (out-of-plane)C(4) out of the plane [C(2)-C(5)-H(11)]

δ(30) C-H(12) bend (in plane)

+[C(4)-C(5)-H(12)]
–[C(7)-C(5)-H(12)]

ω(31) C-H(12) wag (out-of-plane) C(5) out of the plane [C(4)-C(7)-H(12)]

δ(32) C-H(13) bend (in plane)

+[C(3)-C(6)-H(13)]

–[C(7)-C(6)-H(13)]

ω(33) C-H(13) wag (out-of-plane) C(6) out of the plane [C(3)-C(7)-H(13)]

δ(34) C-H(14) bend (in plane)
+[C(5)-C(7)-H(14)]
–[C(6)-C(7)-H(14)]

ω(35) C-H(14) wag (out-of-plane) C(7) out of the plane [C(5)-C(6)-H(14)]

τ(36) R_2C-CH_2 torsion
twist [C(3)-C(2)-C(1)-H(8)]
+[C(4)-C(2)-C(1)-H(8)]
+[C(3)-C(2)-C(1)-H(9)]
+[C(4)-C(2)-C(1)-H(9)]

Cartesian coordinates and energies of the allyl radical (B3LYP/6-31G*)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	1.229954	-0.195971
2	6	0.000000	0.000000	0.443054
3	6	0.000000	-1.229954	-0.195971
4	1	0.000000	2.161157	0.360597
5	1	0.000000	1.298889	-1.280787
6	1	0.000000	0.000000	1.533716
7	1	0.000000	-2.161157	0.360597
8	1	0.000000	-1.298889	-1.280787

Sum of electronic and zero-point Energies=	-117.194004
Sum of electronic and thermal Energies=	-117.190182
Sum of electronic and thermal Enthalpies=	-117.189237
Sum of electronic and thermal Free Energies=	-117.218498

Cartesian coordinates and energies of the allyl cation (B3LYP/6-31G*)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	1.191313	-0.211446
2	6	0.000000	0.000000	0.494155
3	6	0.000000	-1.191313	-0.211446
4	1	0.000000	2.154478	0.296432
5	1	0.000000	1.205841	-1.300609
6	1	0.000000	0.000000	1.580767
7	1	0.000000	-2.154478	0.296432
8	1	0.000000	-1.205841	-1.300609

Sum of electronic and zero-point Energies=	-116.903503
Sum of electronic and thermal Energies=	-116.899677
Sum of electronic and thermal Enthalpies=	-116.898733
Sum of electronic and thermal Free Energies=	-116.927428

Cartesian coordinates and energies of the benzyl radical (B3LYP/6-31G*)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	0.000000	2.401909
2	6	0.000000	0.000000	0.995337
3	6	0.000000	1.218085	0.252007
4	6	0.000000	-1.218085	0.252007
5	6	0.000000	-1.211931	-1.133843
6	6	0.000000	1.211931	-1.133843
7	6	0.000000	0.000000	-1.839817
8	1	0.000000	-0.927974	2.964501
9	1	0.000000	0.927974	2.964501
10	1	0.000000	2.160759	0.793914
11	1	0.000000	-2.160759	0.793914
12	1	0.000000	-2.153799	-1.676632
13	1	0.000000	2.153799	-1.676632
14	1	0.000000	0.000000	-2.926103

Sum of electronic and zero-point Energies= -270.800192
Sum of electronic and thermal Energies= -270.794522
Sum of electronic and thermal Enthalpies= -270.793578
Sum of electronic and thermal Free Energies= -270.829207

Cartesian coordinates and energies of the benzyl cation (B3LYP/6-31G*)

Center Number	Atomic Number	Coordinates (Angstroms) X	Y	Z
1	6	0.000000	0.000000	2.353372
2	6	0.000000	0.000000	0.982938
3	6	0.000000	1.246332	0.254329
4	6	0.000000	-1.246332	0.254329
5	6	0.000000	-1.235822	-1.121517
6	6	0.000000	1.235822	-1.121517
7	6	0.000000	0.000000	-1.802580
8	1	0.000000	-0.926454	2.923151
9	1	0.000000	0.926454	2.923151
10	1	0.000000	2.180935	0.807818
11	1	0.000000	-2.180935	0.807818
12	1	0.000000	-2.163211	-1.684216
13	1	0.000000	2.163211	-1.684216
14	1	0.000000	0.000000	-2.889628

Sum of electronic and zero-point Energies= -270.544652
Sum of electronic and thermal Energies= -270.539018
Sum of electronic and thermal Enthalpies= -270.538074
Sum of electronic and thermal Free Energies= -270.573134

G4 results for the planar and 90 degree rotated benzyl radical and cation (only energies are given, the geometries differ insignificantly from those listed above.

Benzyl radical, planar:

```
G4 Energy=               -270.728922
G4(0 K)=                 -270.734680
G4 Enthalpy=             -270.727978
G4 Free Energy=          -270.763737
```

Benzyl radical, 90º twisted

```
G4 Energy=               -270.711480
G4(0 K)=                 -270.717168
G4 Enthalpy=             -270.710536
G4 Free Energy=          -270.746242

Low frequencies --- -386.5103   -0.0005   -0.0004    0.0006    6.6346
                     14.1965   20.0393  209.4551  304.9457

(the mode with the negative frequency corresponds to C–CH2 twisting)
```

Benzyl cation, planar:

```
G4 Energy=               -270.460553
G4(0 K)=                 -270.466265
G4 Enthalpy=             -270.459608
G4 Free Energy=          -270.494786
```

Benzyl cation, 90º twisted

```
G4 Energy=                  -270.711480
G4(0 K)=                 -270.717168
G4 Enthalpy=             -270.710536
G4 Free Energy=             -270.746242

Low frequencies --- -386.5103   -0.0005   -0.0004    0.0006    6.6346
                     14.1965   20.0393  209.4551  304.9457

(the mode with the negative frequency corresponds to C–CH2 twisting)
```