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A Computational Study of Proton and Electron Affinities

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Abstract: Proton and electron affinities were calculated for a series of 28 carbanions and radicals using MP2/6-31 and B3LYP methods. Structural and electronic factors that control anion and radical stabilization were examined by natural bond orbital analyses. New examples of hyperconjugation were found for lone pairs and radical centers and adjacent C-H* and C-C* orbitals. Correlations between %-s-character of C-H bonds and anions with proton affinity were poor.

Keywords: carbanions; radicals and radical reactions; theoretical studies; hydrocarbons

As quantum methods for the calculation of thermochemical data have made significant strides in recent years, experimental measurements have become more problematic due to the growing size of molecules of current interest and difficulties with kinetically unstable intermediates.[1] Although the importance of carbanions and radicals in both synthetic chemistry and mechanistic studies is unquestioned, fundamental data on their structure and properties are obtained with difficulty. Experimental measurements of electron affinities have produced much useful information on the stability of carbanions in the gas phase, but the scope of this methodology is limited, *inter alia*, by the intrinsic stability of carbanions relative to electron detachment and/or fragmentation. Carbanions with lifetimes of < 25 μsec cannot be detected in conventional flowing afterglow experiments, for example.[2] Electron spin resonance and infrared spectroscopic studies have yielded much useful information about radicals albeit in rigid matrices at low temperatures.[1a,3] Thermodynamic cycles coupled with measurements of redox properties of carbanion/radical couples in solution can be used to evaluate homolytic bond dissociation energies and pK_a's of hydrocarbons, but these calculations require knowledge of gas phase electron affinities to estimate solvation energies of carbanions.[4]

The present state of the art of computational chemistry can provide an accurate basis for comparison of the structure and properties of reactive intermediates. Although scattered reports of quantum calculations have been published, use of different basis sets and/or methodology makes comparison difficult. In this communication, we apply ab initio and density functional quantum methodology to the computation of proton[5] and electron[6] affinities of an extended series of 28 aliphatic and alicyclic systems. The results provide a comprehensive compilation of the structure, relative stability, proton affinity (PA), and electron affinity (EA) of these systems. Detailed analysis of the orbital structure of these intermediates provides insight into the electronic factors that govern their stability and structure. Of especial interest was a study of the relationship between calculated percent s-character of C-H bonds and proton affinity.

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Computational Methodology. All structures were fully optimized by analytical gradient methods at the R(U)HF/6-31+G(d) level using the Gaussian94 suite of programs.[7a] Energies for all systems were obtained *via* full geometry optimization at the R(U)MP2(FC)/6-31+G(d,p) and R(U)B3LYP/6-311++G(2d,p) levels[7b]. In addition, a subset of representative systems was examined at the R(U)B3LYP/6-31+G(d,p) and R(U)B3LYP/6-311++G(3df,2dp) levels. Reported energies were and corrected for thermal effects at 298.15 Kelvin and for zero-point energy differences computed at the R(U)HF/6-31+G(d) level (scaling factor= 0.9153 [8]). Select natural bond orbital analyses (NBO) and natural population analyses (NPA) were carried out using keywords: NLMO (natural localized molecular orbitals), BNDIDX (bond index), and RESONANCE.[9] The latter term lowers the occupancy threshold for acceptable Lewis structures in the search for delocalized structures. Results discussed below were obtained via density functional methodology unless otherwise noted.

The following systems were investigated as radicals, carbanions, and related hydrocarbons: **Primary**: methyl, ethyl, neopentyl, Cs,C1-cyclopropylcarbinyl, 3-butenyl. **Secondary**: 2-propyl, cyclopropyl, a,e-H-cyclobutyl, a,e-H-cyclopentyl, a,e-H-cyclohexyl, 2-*exo*,*endo*-H-norbornyl, 5-*exo*,*endo*-H-norbornenyl, 7-norbornanyl, 7-*anti*, *syn*-H-norbornenyl, 3-nortricyclyl. **Tertiary**: t-butyl, 1-bicyclo[1.1.1]pentyl, cubyl, 1-norbornyl, 4-nortricyclyl, 1-bicyclo[2.2.2]octyl.

Proton Affinity. Proton affinities have been used to compare "stabilities" of anions relative to the related hydrocarbons. Anions more stable than methyl anion are less basic and the corresponding hydrocarbons will have smaller PA values. For example, propene gives rise to the allyl anion with PA=391 kcal/mol compared to methane with PA=~417 kcal/mol. The energy difference between these two, –26 kcal/mol, represents the energy change for the equation shown (R = CH_2=CH).

$$CH_3^- + R\text{-}CH_3 \text{ -------> } CH_4 + R\text{-}CH_2^- \qquad \text{(eq. 1)}$$

The data in **Table 1** illustrate the effect of methodology and basis set on the calculation of proton affinities for a select set of molecules. The differences between MP2 and B3LYP methods (columns 2 and 3) varies from 2.7 kcal/mol to 3.7 kcal/mol and the range increases with more extended B3LYP basis sets. Although the amount of experimental data is limited, MP2 methodology gives slightly better agreement.

Table 1. Proton Affinity (kcal/mol): 298.15 K

System	MP2/ 6-31+G(d,p)	B3LYP/ 6-31+G(d,p)	B3LYP/ 6-311++G(2d,p)	B3LYP/6-311++G(3df,2dp)	Literature Values[a]
Methyl	419.0	415.4	414.5	414.5	416.6±1.6, 418±3.5
Ethyl	421.8	418.6	417.0	417.0	420.1
2-Propyl	419.6	415.9	413.3	413.4	419.4
t-Butyl	412.1	409.4	406.8	406.9	413.1
Cyclopropyl	415.5	412.7	411.1	411.3	410±1, 411.5,409±4.5

[a] See Table 2 for references.

Table 2 lists the calculated values of PA for the complete series of carbanions. In the primary series: R-CH_2(-), ethyl anion (R=CH_3) was the only system that showed a significantly higher calculated PA than methane 417.0 vs 414.5. For example, the neopentyl system (eq.1, R = t-butyl-, PA = 406.8) gave rise to *ca.* 7.7 kcal/mole stability over the methyl anion. Each of the two minimum energy conformers of cyclopropylcarbinyl anion (eq.1, R=cyc-C_3H_5-) was found to have a relatively low PA (409.1 and 408.1) representing "stabilization energies" of 5.3-6.4 kcal/mol relative to the methyl system. The allyl substituent

Table 2: Equations 2 and 3, Proton Affinities, and Electron Affinities (kcal/mol): 298.15 K

Method/ Basis Set	Energy Change R(U)B3LYP/ 6-311++G(2d,p)		Affinity R(U)B3LYP/ 6-311++G(2d,p)		Affinity R(U)MP2/ 6-31+G(d,p)		Literature (Reference)	
System	Equation 2 Anions	Equation 3 Radicals†	PA	EA	PA	EA	PA	EA‡
Methyl			414.5	1.58	419.0	-8.75	418.8±3.5[2b],416.6±1.7[10]	1.8[11], +
Ethyl	2.53	-4.38	417.0	-5.11	421.8	-3.41	420.1[12],421.0[13]	-6.4[12], –
2-Propyl	-1.18	-7.82	413.3	-4.84	419.6	-3.03	419.4[12]	-9.5[12], –
Cyclopropyl	-3.35	3.04	411.1	8.18	415.5	11.62	409±4.5[2b],410.1±1[5e],411.5[13]	6.9,[13]8.4[12,5e],+
a-H-Cyclobutyl	-0.52	-6.42	414.0	-4.10	418.9	-0.073	417.4[12]	-7.5[12], –
e-H-Cyclobutyl	-2.96	-6.42	411.5	-1.66	415.3	3.56	417.4[12]	–
a-H-Cyclopentyl	-4.53	-10.02	410.0	-3.83	414.0	-0.11	416.1[12]	-7.0[12], –
e-H-Cyclopentyl	-5.37	-10.02	409.1	-2.99	414.3	0.26	416.1[12]	–
a-H-Cyclohexyl	-4.09	-7.44	410.4	-1.55	415.2	2.00		+
e-H-Cyclohexyl	-6.64	-7.44	407.8	1.00	412.6	4.60		+
Neopentyl	-4.49	-3.20	410.0	3.09	413.2	6.85	417±3.5[2b], 408.9[12]	4.8[12], +
3-Butenyl	-7.30	-3.92	407.2	5.18	412.4	6.84	412[12]	1.7[12], +
c-Propylcarbinyl (C_1)	-5.34	-7.51	409.1	-0.37	412.9	3.54	410.5[12]	3.2[12], +
c-Propylcarbinyl (C_s)	-6.39	-7.51	408.1	0.68	411.8	4.67		+
3-Nortricyclyl	-5.58	-4.80	408.9	2.58	410.7	9.02		x
x-H-2-Norbornanyl	-2.98	-7.54	411.5	-2.76	414.2	2.38		–
n-H-2-Norbornanyl	-2.89	-7.54	411.6	-2.86	414.8	1.85		–
x-H-5-Norbornenyl	-3.28	-7.39	411.2	-2.31	413.9	5.63		+
n-H-5-Norbornenyl	-8.89	-7.39	405.6	3.30	408.2	11.28		+
7-Norbornyl	-5.61	-1.27	408.9	6.14	411.4	11.58		x
s-H-7-Norbornenyl	-4.53	-1.43	410.0	4.90	412.1	10.54		x
a-H-7-Norbornenyl	-4.26	-0.37	410.2	5.69	412.8	11.03		x
t-Butyl	-7.64	-10.49	406.8	-1.05	412.1	3.02	413.1[12]	-5.9[12], –
1-Bicyclo[1.1.1]pentyl	-6.96	0.52	407.5	9.23	409.4	14.41	411±3.5[2b]	+
1-Norbornyl	-5.44	1.38	409.0	8.62	411.3	14.26		x
4-Nortricyclyl	-6.41	4.84	408.1	13.1	409.2	19.37		x
Cubyl	-7.96	-0.67	406.5	9.08	407.6	15.80	404±3[14]	11.5±2[14]
1-Bicyclo[2.2.2]octyl	-5.73	-4.48	408.7	3.15	410.2*	5.30*		x

† One isomer where identical values are listed. ‡ ref. 2a: anion detected = +; anion undetected = –; no results = x. * MP2/6-31+G(d)

confers 7.3 kcal/mol stabilization energy over the methyl system (eq.1, R = CH_2=CH-CH_2-, PA= 407.2), but the stabilizing interactions are less clear in this case. All secondary anions had lower or equal PA values to the isopropyl anion and all tertiary systems were within ± 2 kcal/mol of the value for t-butyl anion.

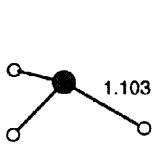
In general, the agreement between the calculated and experimental values of PA is fair. The absence of proton affinity data for several of the anions is likely to be a consequence of gas phase instability relative to electron detachment or fragmentation reactions.[2] Flowing afterglow experiments did not give rise to detectable anions for the following systems: ethyl, 2-propyl, cyclobutyl, 2-norbornyl, and cyclopentyl, but anions were detected for: methyl, 3-butenyl, cyclopropyl, 1-bicyclo[1.1.1]pentyl, 5-norbornenyl, and cyclopropylcarbinyl.[2]

Carbanion Structure/Energy. Structural information is summarized in **Figures 1** and **2** which list calculated bond distances and improper dihedral angles for radicals and carbanions. Whereas tetrahedral geometry leads to an improper dihedral angle of 120°, the anions examined assume geometries with values ranging from 132.8° for cyclohexyl anion (axial-H) to 123° for t-butyl anion to 83.5° for the 1-bicyclo[1.1.1]pentyl system. Several systems show extended lengths for C-H bonds oriented *anti*-parallel to lone pair orbitals of the anions: ethyl (Δ=0.032 Å), 2-propyl (Δ=0.037 Å), t-butyl (Δ=0.041 Å), C_s-cyclopropylcarbinyl *vs* C_1-cyclopropylcarbinyl (Δ=0.016 Å), and cyclohexyl anion with equatorial H (Δ=0.015 Å). *Anti*-parallel C-C lengthening is seen in the C_1-cyclopropylcarbinyl system (Δ=0.061 Å), and neopentyl (Δ=0.023 Å), 1-norbornyl (C2-C3=1.589Å *vs* C2-C3=1.564Å in norbornane), and the 7-norbornyl systems described in an earlier report.[15] These bond length changes can be attributed to bond weakening caused by perturbation interactions between the lone pair HOMO and LUMO's from *anti*-parallel neighboring C-H or C-C σ* bonds, *i.e.*, negative ion hyperconjugation.[16] Natural bond order (NBO) analysis showed significant 2nd-order perturbation stabilization energies associated with these lengthened bonds: ethyl (1 X 13.3 kcal/mol), 2-propyl (2 X 15.7 kcal/mol), t-butyl (3 X 15.3 kcal/mol), neopentyl (1 X 11.7 kcal/mol), 1-norbornyl (2 X 13.2 kcal/mol). NBO analyses of the two cyclopropylcarbinyl anions revealed significant stabilizing interactions between the lone pair and the anti-parallel C-C ring antibonding orbital in the conformer with C_1 symmetry (1 X 18.0 kcal/mol) and with the antibonding cyclopropyl C-H orbital in the C_s structure: (1 X 13 kcal/mol).

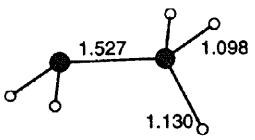
Similarly, the H-equatorial forms of cyclobutyl and cyclohexyl anions are stabilized by interaction of the filled p-like orbitals with the C-H* orbital of the adjacent anti-parallel C-H bonds, by 2 X 13.4 and 2 X 18.1 kcal/mole, values comparable to 2-propyl anion (see above). The H-axial form of cyclohexyl anion shows strong perturbation interactions with the anti-parallel C-C* orbitals (2 X 16.6 kcal/mol) giving rise to lengthened C-C bonds: 1.548 Å *vs* 1.535 Å. Cyclopentyl anion shows a similar pattern: 2 X 16.8 kcal/mol (H-equatorial) and 2 X 12.8 kcal/mol (H-axial).

The effects of sequential substitution of methyl groups for hydrogen is complex and involves competing inductive and/or polarizability effects and negative ion hyperconjugation.[1b] The calculated PA values for methyl, ethyl, isopropyl, and t-butyl anions were 414.5, 417.0, 413.3, 406.8 kcal/mol, respectively. Examination of the structures, charge distributions, and natural localized molecular orbital analysis of these three systems provides some insight into the differences in stability of these anions relative to methyl anion. The NPA calculated charges at the anionic centers: methyl (-1.394), ethyl (-0.997), isopropyl (-0.633), t-butyl (-0.411) are consistent with the PA results. Although the charge dispersal per methyl group decreases in the series ethyl (–0.243), 2-propyl (-0.233), t-butyl (–0.196), the *combined* effect of three methyl groups in the t-butyl system

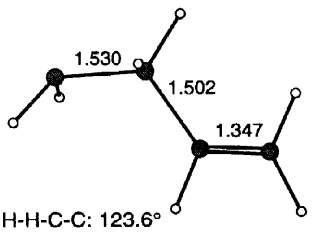
Figure 1a: Carbanions at RB3LYP/6-311++G(2d,p)



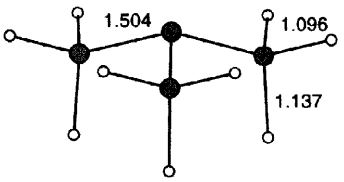
H-H-C-H: 118.4°
Methyl



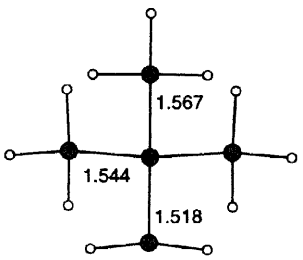
H-H-C-C: 121.4°
Ethyl



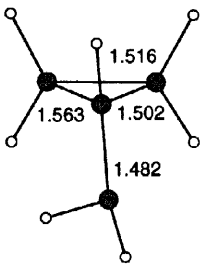
H-H-C-C: 123.6°
3-Butenyl



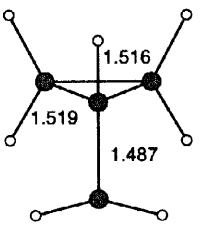
C-C-C-C: 123.0°
t-Butyl



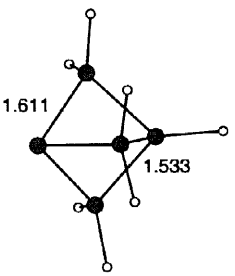
H-H-C-C: 123.8°
Neopentyl



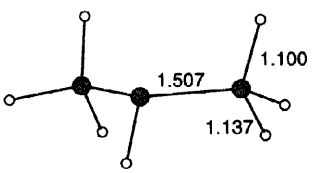
H-H-C-C: 129.0°
C_1-Cyclopropylcarbinyl



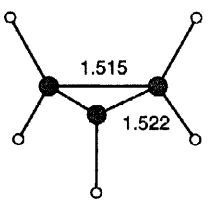
H-H-C-C: 127.2°
Cs-Cyclopropylcarbinyl



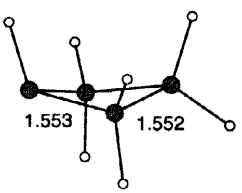
C-C-C-C: 83.5°
Bicyclo[1.1.1]pentyl



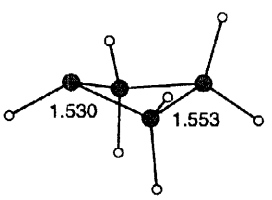
C-C-C-H: 122.2°
2-Propyl



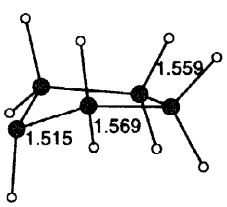
C-C-C-H: 102.5°
Cyclopropyl



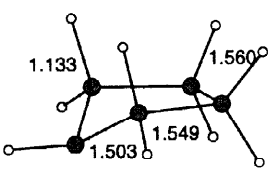
C-C-C-H: 110.5°
a-H-Cyclobutyl



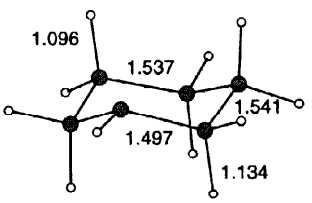
C-C-C-H: 122.6°
e-H-Cyclobutyl



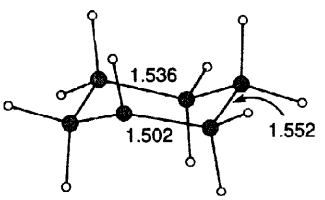
C-C-C-H: 119.3°
a-H-Cyclopentyl



C-C-C-H: 128.0°
e-H-Cyclopentyl

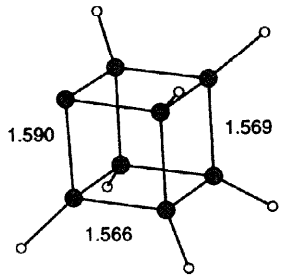


C-C-C-H: 131.4°
e-H-Cyclohexyl

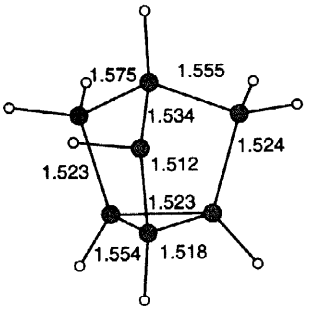


C-C-C-H: 132.8°
a-H-Cyclohexyl

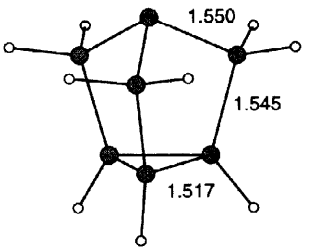
Figure 1b



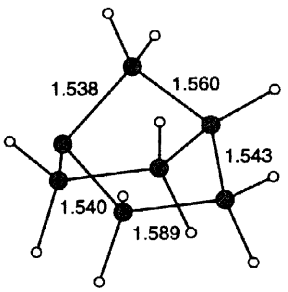
C-C-C-C: 88.0°
Cubyl



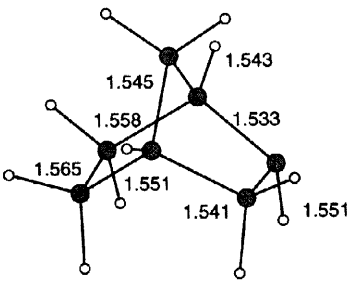
C-C-C-H:115.5°
3-Nortricyclyl



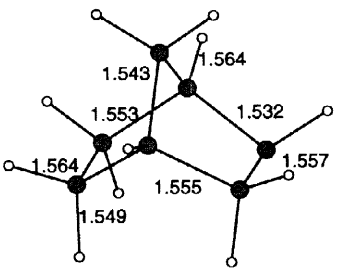
C-C-C-C: 100.8°
4-Nortricyclyl



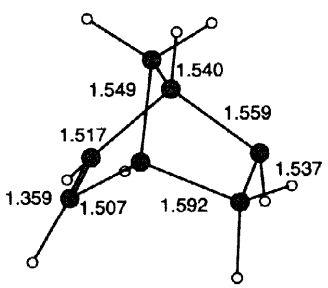
C-C-C-C: 102.9°
1-Norbornyl



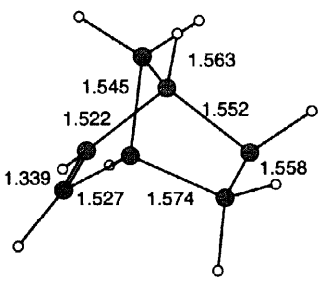
C-C-C-H: 120.6°
n-H-2-Norbornyl



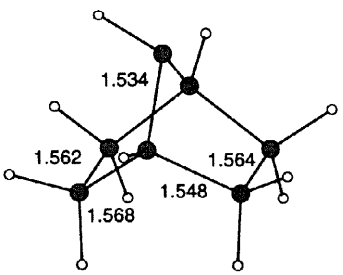
C-C-C-H: 115.9°
x-H-2-Norbornyl



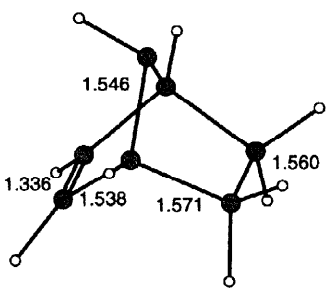
C-C-C-H: 118.6°
n-H-5-Norbornenyl



C-C-C-H: 114.6°
x-H-5-Norbornenyl

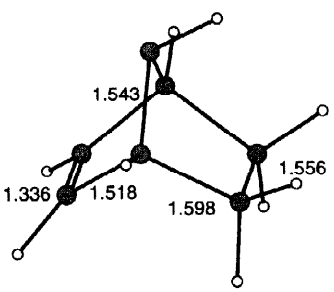


C-C-C-H: 114.6°
7-Norbornanyl



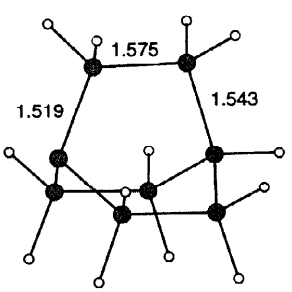
C_1-C_4-C_7-H_7: 111.1°
H-C_1-C_6-C_5: 171.3°

s-H-7-Norbornenyl



C_1-C_4-C_7-H_7: 112.1°
H-C_1-C_6-C_5: 173.0°

a-H-7-Norbornenyl



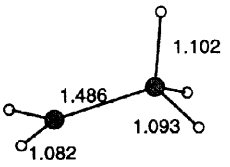
C-C-C-C: 118.6°

1-Bicyclo[2.2.2]octyl

Figure 2a: Radicals at UB3LYP/6-311++G(2d,p)

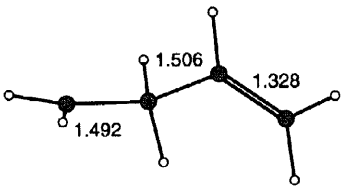
H-H-C-H: 180.0°

Methyl



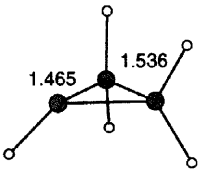
H-H-C-C: 172.3°

Ethyl



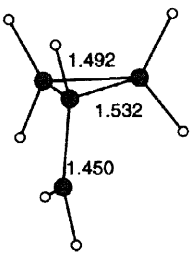
H-H-C-C: 172.7°

3-Butenyl



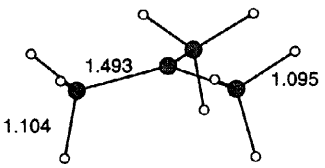
C-C-C-H: 124.4°

Cyclopropyl



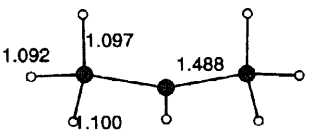
H-H-C-C: 180.0°

Cyclopropylcarbinyl



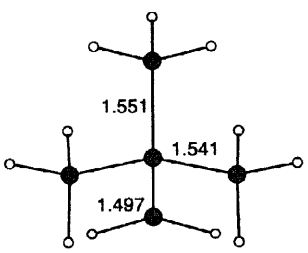
C-C-C-C: 157.8°

t-Butyl



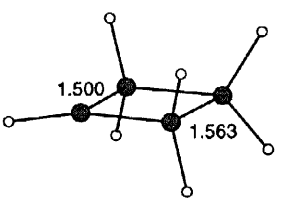
C-C-C-H: 167.7°

2-Propyl



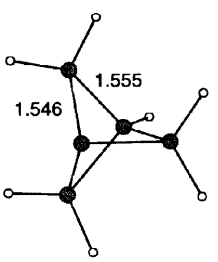
H-H-C-C: 169.7°

Neopentyl



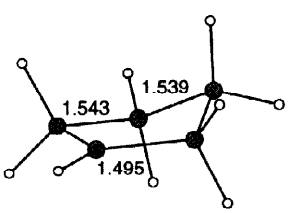
C-C-C-H: 179.7°

Cyclobutyl



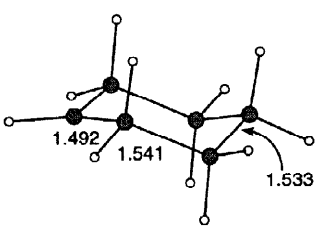
C-C-C-C: 90.0°

Bicyclo[111]pentyl



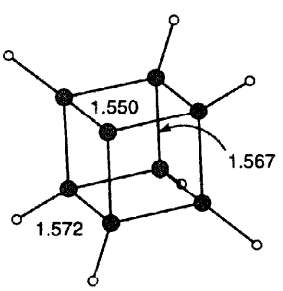
C-C-C-H: 180.0°

Cyclopentyl



C-C-C-H: 165.4°

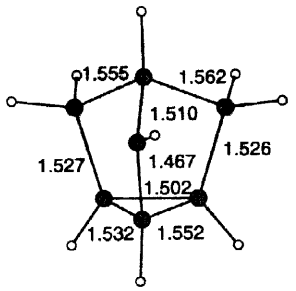
Cyclohexyl



C-C-C-C: 92.9°

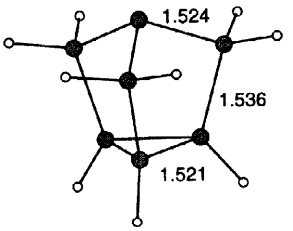
Cubyl

Figure 2b



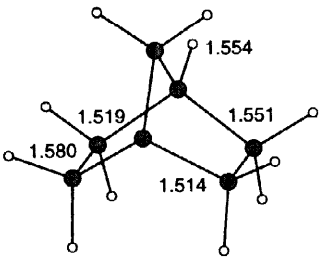
C-C-C-H:153.8°

3-Nortricyclyl



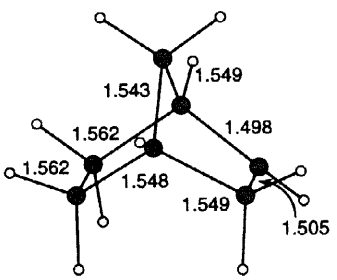
C-C-C-C: 109.5°

4-Nortricyclyl



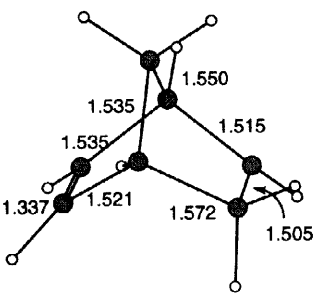
C-C-C-C: 112.7°

1-Norbornyl



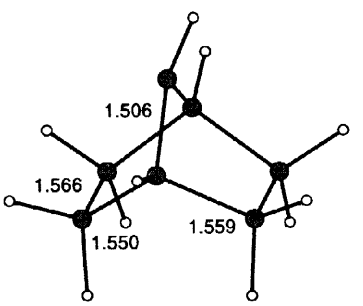
C-C-C-H: 163.5°

2-Norbornyl



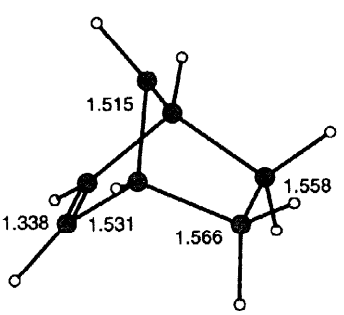
C-C-C-H: 159.0°

5-Norbornenyl



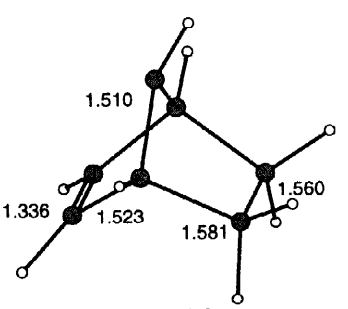
C-C-C-H: 146.7°

7-Norbornanyl



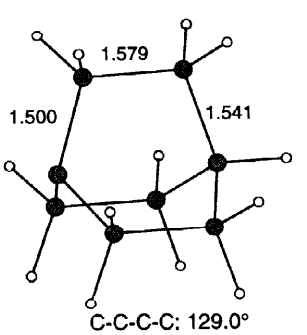
C-C-C-H: 137.7°

s-H-7-Norbornenyl



C-C-C-H: 143.3°

a-H-7-Norbornenyl

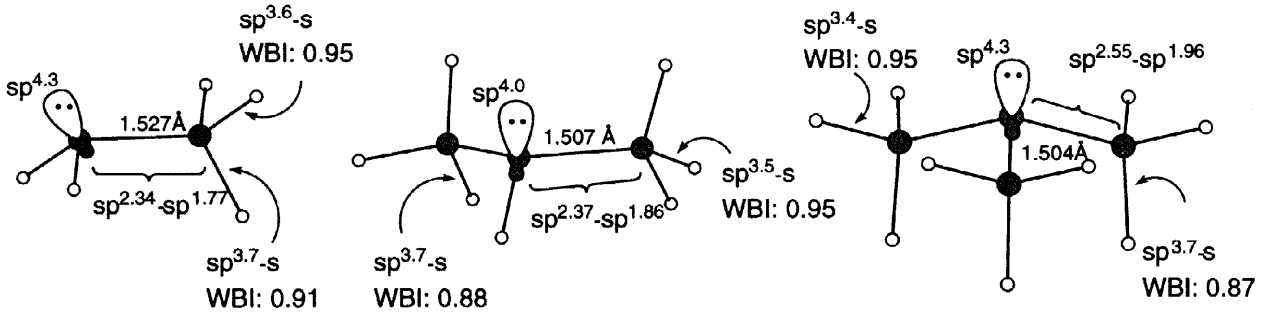


C-C-C-C: 129.0°

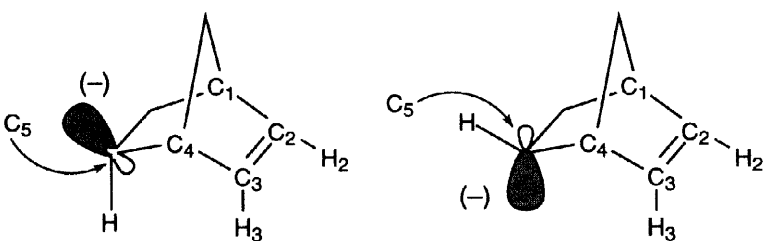
1-Bicyclo[2.2.2]octyl

results in greater total charge dispersal than that of the methyl groups of the isopropyl or ethyl systems: -0.588 *vs* –0.466 *vs* –0.243. Differences in hybridization between the attached methyl groups and the anionic carbon may also contribute to the dispersal of negative charge, but no clear trend can be seen.

More important is the finding that the bond between the methyl carbon and the anionic center varies from $sp^{1.77}$-$sp^{2.34}$ to $sp^{2.55}$ -$sp^{1.96}$ concurrent with shortened bond lengths. This finding of increasing double bond character between the methyl groups and the anionic carbon is consistent with intervention of negative ion hyperconjugation.[16] Consistent with this idea, C-H bonds anti-parallel to the axis of the hybrid orbital at the anionic center are lengthened and have diminished Wiberg bond indices[17] (WBI) and increased p-character relative to C-H bonds in other orientations. These effects combine to increase the stability of the t-butyl anions relative to ethyl and isopropyl anions and, presumably, are important factors in other systems studied.



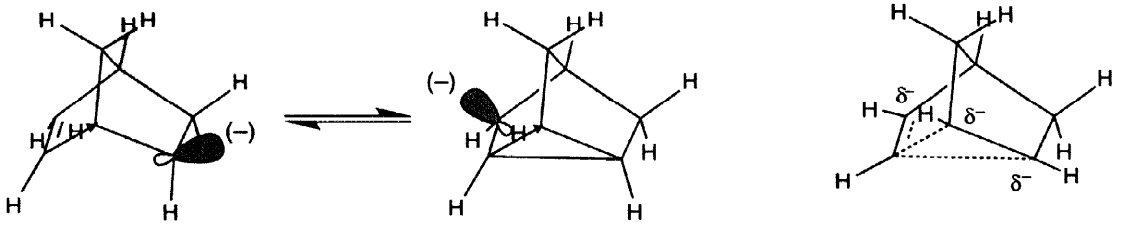
The four norbornenyl anionic systems display significantly different responses to the presence of the pi-systems. Whereas the *syn*- and *anti*-7-norbornenyl anionic systems have about the same calculated PA's (410.0 *vs* 410.2) the two 5-norbornenyl isomers differ by 5.5 kcal/mol: 411.1 (*exo*-H) vs 405.6 (*endo*-H). The greater acidity of the *endo*-H system is attributed to partial bonding to the double bond as described by NBO analysis. For example, the Wiberg bond index[17] between carbons 3 and 5 was found to be 0.114 compared to 0.030 for the exo-H isomer. In addition, the C=C double bond distances were 1.339 (*exo*-H); 1.359 (*endo*-H) an indication of increased single bond character of the latter. More surprising was the high degree of non-planarity of the double bonds of the *exo*-H and endo-H systems. In both cases the alkene hydrogens were bent below (*endo*) the normal plane of the pi-system. The H_2-C_2=C_3-C_4 dihedral angles illustrates this point: *endo*-H: 160.2°; *exo*-H: 167.8 °; norbornene: 172.5°. Even more pronounced is the puckering about C_2 as measured



endo-5H-norbornenyl anion *exo*-5H-norbornenyl anion

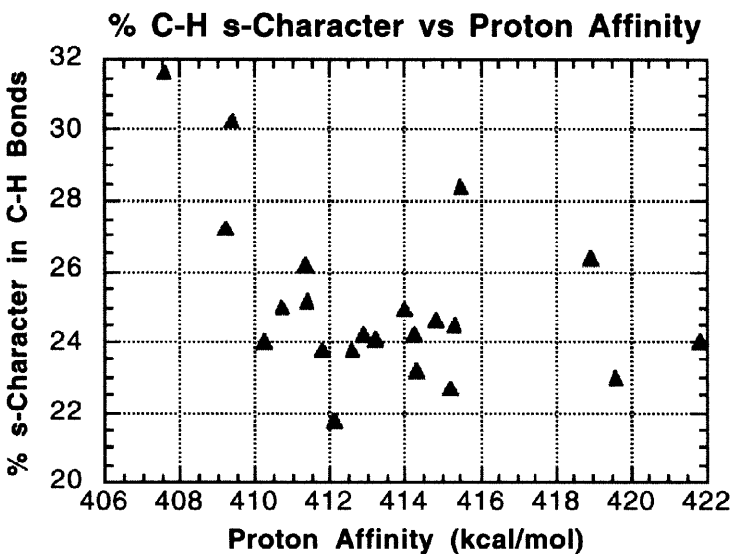
by dihedral angle H_2-C_1-C_2-C_3: endo-H: 157.5°; exo-H: 167.3°; norbornene: 172.7°. This distortion is attributed to electron:pi-repulsion with consequent re-hybridization of carbon atoms of the pi-bond leading to more s-character and concomitant pyramidalization.[18] These carbanions have been linked experimentally with

the 3-nortricyclyl anion either as a set of rapidly equilibrating structures or a symmetrical non-classical intermediate. Reaction of either *exo*-2-chloronorbornene or 3-nortricyclyl chloride with sodium resulted in a mixture of norbornene and nortricyclene.[19] The results of our calculations support the concept of equilibrating



anionic structures at least in the gas phase since we found discrete minimum energy structures for both the tricyclic and bicyclic forms. Since the energy difference between the two anions is small, the 3-nortricyclyl anion is more stable by 3.3 kcal/mol, it likely that the interconversion barrier between these intermediates is also small. By the same token it should be noted that both conformers of the cyclopropylcarbinyl anion are slightly less stable than the 3-butenyl anion 1.9 and 0.90 kcal/mol. These results are consistent with the known behavior of organometallic derivatives of cyclopropylcarbinyl and 3-butenyl systems.[20]

PA Correlation with %-s-Character. A recent study reports a good relationship between calculated ΔH_{acid} and % C-H s-character for six compounds: ethane, cubane, cyclopropane, ethene, cyclopropene and ethyne.[5b,21] NBO analysis affords a convenient opportunity to evaluate the dependency of proton affinity on calculated % s-character (cf. Supplementary Table) for an extended series of molecules. The plot below shows the PA data for all saturated 2° and 3° systems calculated at the MP2/6-31+G(d,p) level. [21,22]



The absence of a clear correlation likely is a reflection of the dependency of proton affinity on the both the % s-character of the C-H bonds as well as the carbanionic centers. It is likely that long range effects are also important (see below).

Electron Affinity. Evaluation of electron affinities as a function of structure involves comparisons between the relative energy of carbanions and the related radicals. This was accomplished by computing the energy changes for the isodesmic relationships described by equations 2 and 3. Combining these equations

CH_3^- + R-H -------> CH_4 + R^- (eq. 2)

$CH_3\cdot$ + R-H -------> CH_4 + R· (eq. 3)

defines electron affinity as normalized by the experimental EA value[11] (1.8±0.7 kcal/mol) for methyl radical (equation 4). Positive values of EA denote electron bound systems.

R^- + $CH_3\cdot$ -------> R· + CH_3^- + 1.8 kcal/mol (eq. 4)

A comparison of several methods and basis sets is given in **Table 3**. Serious discrepancies are seen for MP2 results with methyl and t-butyl radicals. More extensive data on these reactions is given in **Table 2** for

Table 3. Electron Affinity (kcal/mol): 298.15 K

System	MP2/ 6-31+G(d,p)	B3LYP/ 6-31+G(d,p)	B3LYP/ 6-311++G(2d,p)	B3LYP/6-311++G(3df,2dp)	Literature Values[a]
Methyl	-8.75	0.66	1.58	1.79	1.8
Ethyl	-3.41	-5.75	-5.11	-5.21	-6.4
2-Propyl	-3.03	-6.51	-4.84	-5.10	-9.5
t-Butyl	3.03	-2.71	-1.05	-1.28	-5.9
Cyclopropyl	11.63	7.24	8.18	7.89	6.9, 8.4

[a] See Table 2 for references.

calculations at the MP2/6-31+G(d,p) and B3LYP/6-311++G(2d,p) levels. In general, there is a good qualitative agreement of B3LYP EA values with results from flowing afterglow experiments.[2] For those carbanions that have not been detected experimentally, *e.g.* ethyl, propyl, cyclobutyl, cyclopentyl, cyclohexyl, we find negative electron affinities. Seven systems for which we calculate positive values of EA have been detected (B3LYP, MP2): cyclopropyl (8.2, 11.6), neopentyl (3.1, 6.8), bicyclo[1.1.1]pentyl (9.2, 14.4), cyclopropylcarbinyl (0.7, 4.7), 5-norbornenyl (3.3, 11.3), cubyl (9.1, 15.8), and 3-butenyl (5.2, 6.8). In those cases where B3LYP density functional methods and MP2 methods led to opposite conclusions, e-H-cyclobutyl (-1.7 *vs* 3.6), e-H-cyclopentyl (-3.0 *vs* 0.26), a-H-cyclohexyl (-1.6 *vs* 2.0), 2-*endo*-H-norbornyl (-2.9 *vs* 1.8), 5-*exo*-H-2-norbornenyl (-2.3 *vs* 5.6), and t-butyl (-1.1 *vs* 3.0), the experimental evidence is in better agreement with density functional results.[6,23] For example, the 2-norbornanyl anion has not been detected in the gas phase.[2] Both epimers were found to have negative electron affinities by the B3LYP method, but both had positive EAs using MP2 methods. In the case of the t-butyl anion, MP2 methodology gave a positive electron affinity in opposition with experimental results.

Radical Structure/Energy. Planarity of the radicals varies from 180° for the methyl radical to 157.8° for t-butyl radical to 90.0° for the 1-bicyclo[1.1.1]pentyl radical.[3,24] Radical stability for simple alkyl systems follows the expected order: methyl < ethyl < isopropyl < t-butyl (equation 3, **Table 2**).[1a] Each of the substituted methyl radicals is more stable than methyl but the factors that control the relative order are not clear: methyl < neopentyl < 3-butenyl < ethyl < cyclopropylcarbinyl (Cs).[25] Although the cyclopropyl group confers a significant stabilization (6.4 kcal/mol) on the primary center[26] (ethyl *vs* cyclopropylcarbinyl), the cyclopropyl

ring in the 4-nortricyclyl radical is destabilizing relative to the 1-norbornyl radical. Evidence for hyperconjugation can be deduced from a comparison of the equivalent C-C bond lengths in this structure with those of the perpendicular Cs form of this radical (transition state for CH_2 rotation). Increases in bond length of ~0.021 Å were found. Similarly, t-butyl radical displays two different C-H bond lengths, for example: 1.104Å (parallel) and 1.095Å (angled) and the neopentyl radical shows two short angled C-C bonds at 1.541 Å and one longer parallel one at 1.551 Å (**Figure 2**).

In a qualitative way the relative stability of tertiary systems reflects the influence of strain: t-butyl > 1-bicyclo[2.2.2]octyl > cubyl > bicyclo[1.1.1]pentyl > 1-norbornyl > 4-nortricyclyl.[27] The relative positions of cubyl *vs* 1-norbornyl radicals was unexpected and may be the result of favorable interactions involving cross ring hyperconjugative effects in the former.[28] The EA's for many of the secondary systems is clearly influenced by hybridization changes induced by bond angle compression, but not in a simple fashion.

In summary, these results extend earlier computational studies and provide a consistent basis for comparison of the structural and energetic properties of a series of aliphatic and alicyclic systems. Structural analyses of several systems provided a detailed picture of the importance of C-H and C-C hyperconjugation effects in both anions and radicals. With few exceptions, agreement between calculated PA and EA values and experimental results was generally satisfactory. Some of the discrepancies may be caused by experimental problems associated with PA and EA measurements as shown by the variations in published results (cf. Table 2).[2,12] Use of larger basis sets may also narrow some of the differences. No correlation was found between % s-character of ionizing C-H bonds and proton affinity. Several of the radicals investigated are predicted to have positive electron affinities and may be sufficiently stable to be observable species in conventional gas phase flowing afterglow or Fourier transform ion cyclotron resonance experiments.

Acknowledgements. We wish to acknowledge helpful discussions with Profs. K. Krogh-Jespersen, J. K. Lee, and S. T. Graul. This work was supported partially by the National Center for Supercomputing Applications under grant number CHE980007N and utilized the SGI Power Challenge Array at National Center for Supercomputing Applications, University of Illinois at Urbana-Champaign.

References and Notes

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Supplementary Table: NBO Calculated %s-Character [MP2/6-31+G(d,p)]

System	C-H	Anion	System	C-H	Anion
Methyl	25.0	14.0	3-Nortricyclyl	25.0	20.4
Ethyl	24.0	16.4	x-H-2-Norbornanyl	24.2	19.3
2-Propyl	23.0	18.9	n-H-2-Norbornanyl	24.6	16.5
Cyclopropyl	28.4	34.1	x-H-5-Norbornenyl	25.1	21.0
a-H-Cyclobutyl	26.4	24.3	n-H-5-Norbornenyl	24.2	18.2
e-H-Cyclobutyl	24.5	21.6	7-Norbornyl	25.2	20.9
a-H-Cyclopentyl	23.2	16.7	s-H-7-Norbornenyl	25.2	24.0
e-H-Cyclopentyl	24.9	18.3	a-H-7-Norbornenyl	25.5	23.1
a-H-Cyclohexyl	22.7	12.0	t-Butyl	21.8	19.9
e-H-Cyclohexyl	23.8	16.0	1-Bicyclo[1.1.1]pentyl	30.3	41.7
Neopentyl	24.1	15.0	1-Norbornyl	26.2	22.6
3-Butenyl	24.3	13.4	4-Nortricyclyl	27.2	25.1
c-Propylcarbinyl (C_1)	24.2	13.0	Cubyl	31.6	36.9
c-Propylcarbinyl (C_s)	23.8	14.0	1-Bicyclo[2.2.2]octyl	24.0	16.7