An Ab Initio Study of 7-Norbornenyl and 7-Norbornadienyl Anions:

the absence of bis-Homoantiaromaticity

Ronald R. Sauers*

Department of Chemistry, Rutgers, The State University of New Jersey

New Brunswick, NJ 08903

Abstract: Ab initio calculations are reported for the 7-norbornyl, *syn*- and *anti*-7-norbornenyl, and the 7-norbornadienyl carbanions. Homodesmotic comparisons and gas phase proton affinity data reveal no evidence for bis-homoantiaromaticity in the *syn*-7-norbornenyl system. Each of the ions is stabilized, *inter alia*, by delocalization of the negative charge into anti-parallel C-C bonds of the molecular framework giving rise to lengthened sigma bonds. Each of these ions was found to be more stable than methyl carbanion as measured by proton affinity calculations. Electron affinity calculations for the corresponding radicals were more positive than that for methyl radical.
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In 1970 Breslow, Pagni and Washburn[1] studied H/D exchange rates of *anti*-7-cyanonorbornene (**1**) for comparison with 7-cyanonorbornane (**2**). These workers found an H-D exchange rate ratio of 1.4 ±0.2 for **1** vs **2** in t-butanol-O-D. On the basis of these results they concluded that there was no evidence for "bis-homoantiaromaticity", *i.e.* destabilization of the anionic charge in the carbanion **3** (R=CN) attributable to

**1**   **2**   **3**
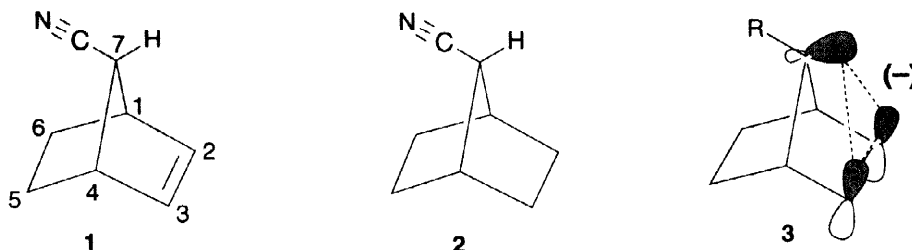
formation of a cyclic array of 4 π electrons. Although the presence of the cyano group was a necessary feature of the experimental methodology, it may have also inadvertently served to reduce any interaction between the π-system and the charge by delocalizing the charge. Ohorodnyk and Santry[2] studied the unsubstituted anion **3**, R=H computationally using CNDO/2-SCF methodology and concluded that its structure was "classical" with a highly localized sp³-like orbital on C7. A comparison of the energy of **3**, R=H with norbornene led to an estimated 1 kcal/mol of "nonclassical stabilization" energy for this ion. Dewar and Schoeller[3] using MINDO/2 methods attributed tilting of the anionic carbon in **3** (R=H) to repulsions between the double bond and the lone pair but did not comment on the overall relative stability of the ion or other aspects of the geometry.

It appeared that application of currently available ab initio methodology might provide not only more precise structural details about these structures but also quantitative data on their relative stability. Our immediate goals were to compute high level structures and energies for members of the 7-norbornyl anionic

*E-mail: sauers@rutchem.rutgers.edu

series **4 - 7** and to evaluate the structural and energetic effects resulting from the proximity of the double bonds and the anionic charge. The energies and structures of the hydrocarbons **8 - 10**, methane, and the methyl carbanion were also determined for use in homodesmotic comparisons and proton affinity calculations.
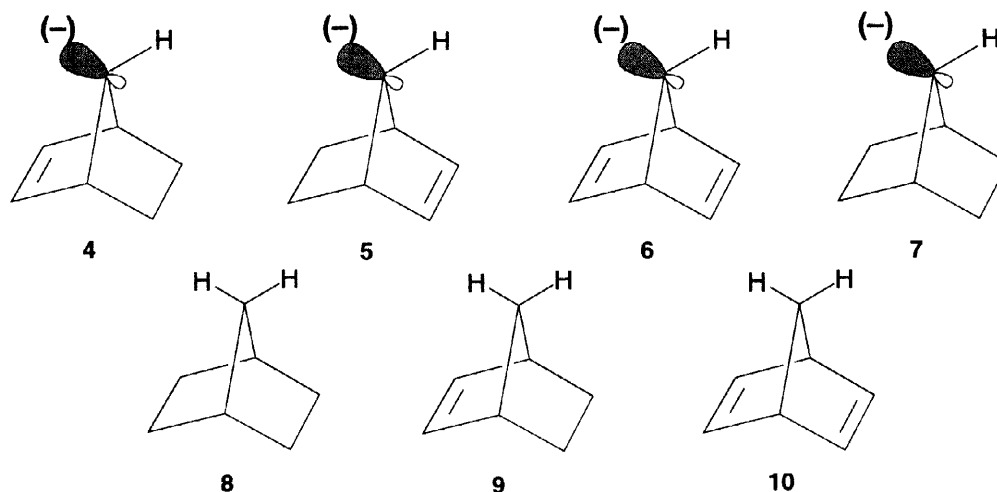

Computational Methodology. The Gaussian94 suite of programs was used throughout.[4] All structures were optimized by analytical gradient methods at the HF/6-31+G(d) level followed by normal coordinate analyses (unscaled) to establish that the structures were energy minima (no negative frequencies). Energy, structural and natural population analyses (NBO)[5] were carried out on fully optimized structures at the B3LYP/6-31++G(d)[6] and MP2(FC)/6-31+G(d,p) levels. NBO keywords used were NLMO (natural localized molecular orbitals) and RESONANCE. The latter term lowers the occupancy threshold for acceptable Lewis structures in the search for delocalized structures. Diffuse functions were invoked to accommodate the properties of anions.[7]

Results. The total energies [HF/6-31+G*, B3LYP/6-31++G(d), MP2/6-31+G(d,p)] and zero-point energies [HF/6-31+G(d)] for compounds **4-10** and methane/methyl anion are given in **Table 1**. A simple comparison of interest reveals that the ZPE-corrected energy differences between **4** and **5** are minor: -1.13, -0.324, and -0.633 kcal/mol at the HF, B3LYP and MP2 levels, respectively. An alternative comparison involves the

Table 1: Total Energy and Zero-point Energy (hartrees)

Structure	HF/6-31+G(d)	ZPE at HF/6-31+G(d)	B3LYP/6-31++G(d)	MP2/6-31+G(d,p)
4	-270.1736984	0.146167	-272.0637769	-271.1857153
5	-270.1758371	0.146495	-272.0646218	-271.1870526
6	-268.9655450	0.120474	-270.8128699	-269.9545545
7	-271.3731982	0.171670	-273.3052102	-272.4082270
8	-272.0612001	0.190008	-273.9754565	-273.0815243
9	-270.8618412	0.164527	-272.7362679	-271.8611977
10	-269.6596670	0.138388	-271.4880404	-270.6320234
CH4	-40.1956678	0.047641	-40.5206311	-40.3659532
CH3–	-39.5041504	0.030299	-39.8414523	-39.6813980

homodesmotic equation shown in eq. 1. After correction for zero-point energy differences ΔH was found to be 1.44 (B3LYP) and 1.36 (MP2) kcal/mol, an indication of slight destablization attributable to the concurrence of
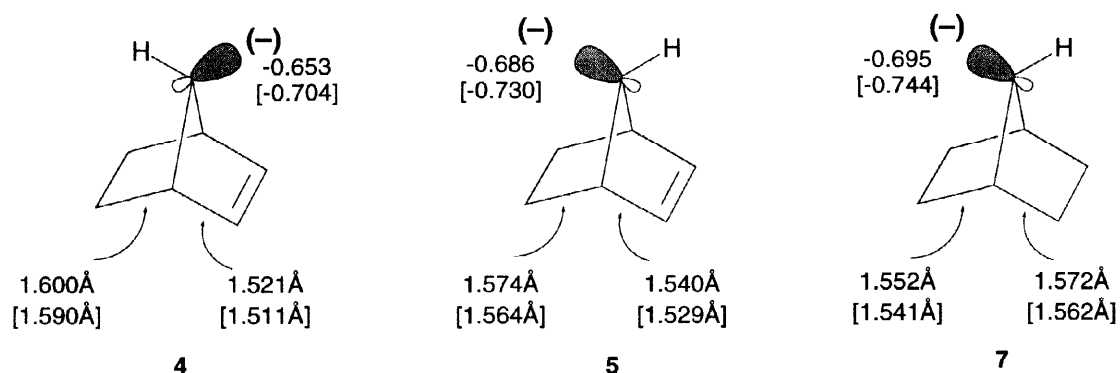

(eq. 1)

4
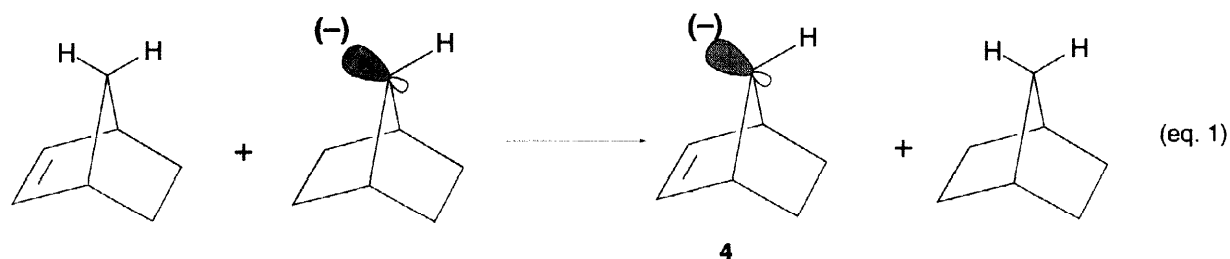
the double bond and the anionic center in **4**. For comparison, the same calculation for the isomeric anion **5** gave rise to a similar small destabilization energy of 1.11 (B3LYP) and 0.724 (MP2) kcal/mol. Examination of the energy of the 7-norbornadienyl anion by the same route (eq. 2) produced somewhat greater destabilization energies: 3.36 (B3LYP) and 2.88 (MP2) kcal/mol for **6**.


(eq. 2)

6
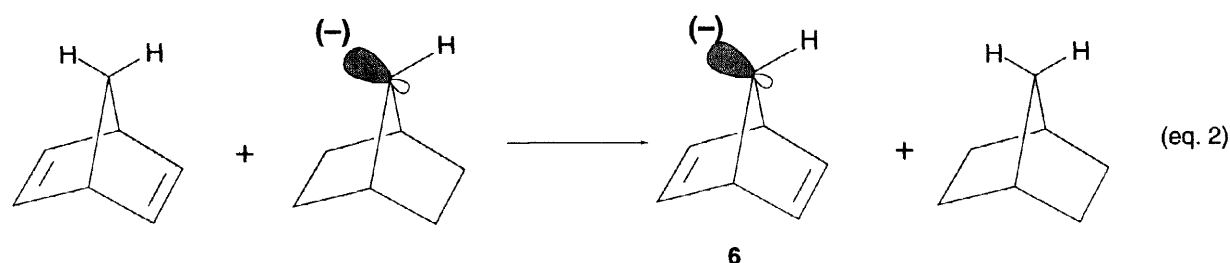
The geometry and charge distribution [Natural population (NPA)][5] of these systems were also examined to determine whether any unusual properties were associated with the *syn*-isomer **4**. In the event, relatively small differences in charge densities were found at C7 in systems **4, 5**, and **7** (**Figure 1**). Of greater interest are the unusual C-C bond lengths in **4**, and to a lesser extent in **5** and **7**. Most striking are the elongated 1,6/4,5 sigma bonds in **4** (1.590-1.600 Å). Presumably, the reduced electron density in the lone pair of **4** gives rise to increased electron density in the antibonding orbitals of the C-C bonds with consequent bond lengthening.[8]

Figure 1. Bond Distance and NPA Charge Densities B3LYP [MP2]

1.600Å	1.521Å	1.574Å	1.540Å	1.552Å	1.572Å
[1.590Å]	[1.511Å]	[1.564Å]	[1.529Å]	[1.541Å]	[1.562Å]
4		**5**		**7**	

This idea was explored by means of Natural bond order analyses (NBO)[5] of these ions. This methodology provides quantitative evaluation of the perturbation interactions involving the "lone pairs" and the adjacent

LUMOs associated with anti-parallel bonds. Stabilization energies of 21.7 (**4**), 20.6 (**5**), and 22.6 (**7**) kcal/ mole were found by this method [MP2/6-31+G(d,p)]. Electron density maps constructed at the RHF/6-31+G(d) level for the HOMO's of ions **4**, **5**, and **7** illustrate graphically the contours of the electron density and the phasing associated with the perturbation interactions.[9]

Anion **4**   Anion **5**   Anion **7**
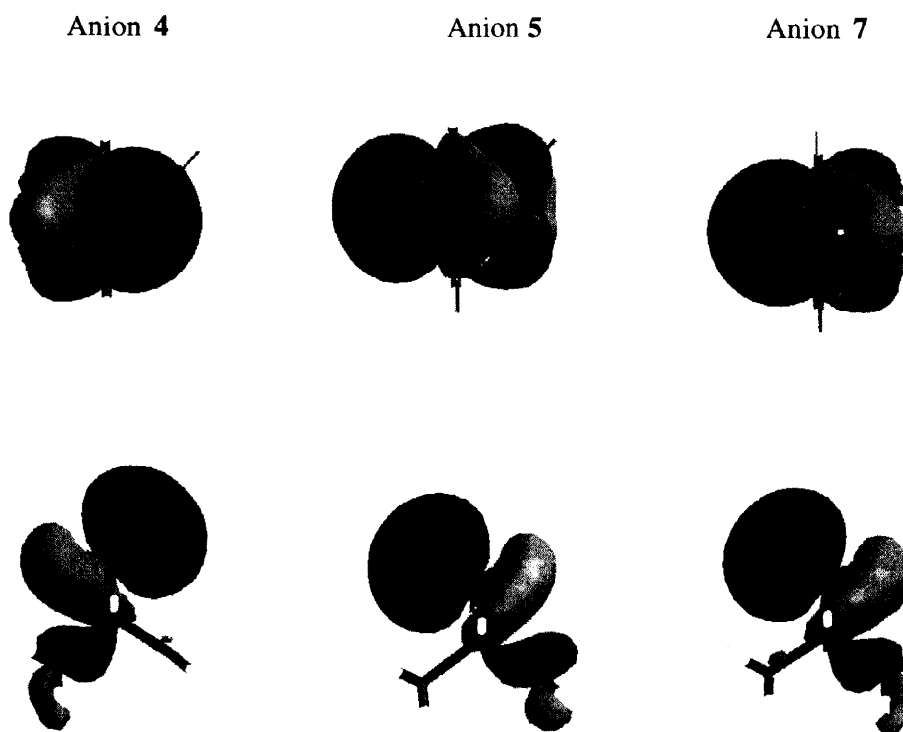
The ability of NBO analyses to calculate the sp^λ character of the lone pairs was also exploited. It was expected that the degree of p-character in these lone pair orbitals would deviate from pure sp^3 as a consequence of the compression of the C1-C7-C4 angles. The following hybridizations vs bond angles were obtained: $sp^{3.33}$@92.1° (**4**), $sp^{3.16}$@91.8° (**5**), $sp^{3.79}$@93.1° (**7**), and $sp^{2.59}$@89.2° (**6**). For comparison, hybridization of the lone pair orbital in methyl carbanion is calculated to be $sp^{6.15}$ (H-C-H angles = 110.4°) at the same level. The greater degree of s-character in the lone pair orbitals of the bicyclic carbanions relative to the methyl carbanion implies that these ions are stabilized relative to the latter. This idea was tested by evaluation of proton affinities of these anions. Simple, non-delocalized anions, e.g. methyl anion, typically are very strong bases with proton affinity of ~417 kcal/mol.[7,10,11] Resonance stabilized anions like allyl anion are much weaker bases: PA = 391 kcal/mol. Calculated proton affinities for anions **4-7** shown in **Table 2** confirm that each of the bicyclic anions is *stabilized* relative to the methyl anion. In every case the calculated basicity of the bicyclic anion was less than that of the methyl anion. The same concept can also be appreciated with homodesmotic comparisons described by eq. 3.
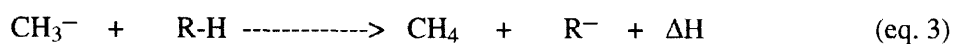
$$CH_3^- + R\text{-}H \longrightarrow CH_4 + R^- + \Delta H \qquad (eq. 3)$$

Table 2. Proton Affinities and Reaction Energies: kcal/mol

Reaction	Proton Affinity		Reaction	Energy	
	B3LYP[a]	MP2[b]		B3LYP[a]	MP2[b]
7 + H⁺ ---> 8	409.1	411.0	CH₃⁻ + 8 ---> CH₄ + 7	-6.23	-7.69
4 + H⁺ ---> 9	410.5	412.4	CH₃⁻ + 9 ---> CH₄ + 4	-4.83	-6.33
5 + H⁺ ---> 9	410.1	411.7	CH₃⁻ + 9 ---> CH₄ + 5	-5.16	-6.96
6 + H⁺ ---> 10	412.4	413.9	CH₃⁻ + 10 ---> CH₄ + 6	-2.87	-4.80
CH₃⁻+ H⁺ ---> CH₄	415.3	418.7[c]	-	-	-

[a] B3LYP/6-31++G(d). [b] MP2/6-31+G(d,p). [c] Lit.: 416.6 ± 0.8^{12}; 418 ± 3.5^{13}.

The increased delocalization of these ions relative to methyl anion raised the possibility that they might be sufficiently stable to be detectable in the gas phase.[12b,13] In general, simple secondary and tertiary carbanions have lifetimes < 25 μsec and are not detectable in flowing afterglow experiments.[13] Because the principle decay mechanism involves loss of an electron to form an alkyl radical, the relative stabilities of the bicyclic radicals became an important component of this analysis. Evaluation of the ΔH for equation **4** corrected with the experimentally determined value of 1.8 ± 0.7 kcal/mol for EA(CH₃)[14] can be used to estimate the thermodynamic stabilities of the bicyclic radicals.

$$R^- + CH_3\cdot \quad \text{------>} \quad R\cdot + CH_3^- \qquad \text{(eq. 4)}$$
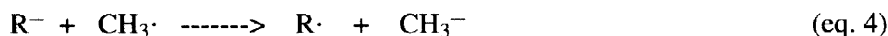
It was important to first determine an optimum methodology/basis set for these comparisons in given the need to compare correlation effects between the neutral and the ion in a balanced manner.[15,16] The necessary criteria were to reproduce the experimental EA value for methyl and also be able to handle large molecules at the same level. This goal was accomplished using DFT and an extended basis set B3LYP/6-311++(2d,p) which combination led to a calculated EA(CH₃) = 1.47 kcal/mol.[17] Electron affinities for the norbornyl systems **11-14** were obtained in the same way, and relevant data are listed in **Table 3**. Attempts to optimize the
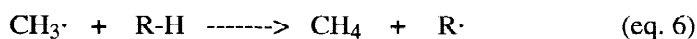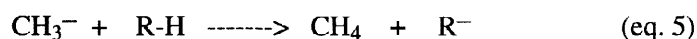

11   **12**   **13**   **14**
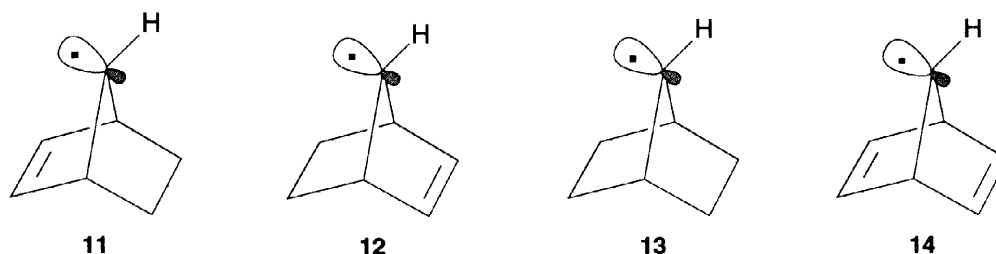
Table 3. Electron Affinities: kcal/mol

Total energy: Radicals		ZPE	Total energy: Anions		ΔH (eq. 4)	EA[d]
R =	hartrees[a]	hartrees[b]	R =	hartrees[c]		
11	-272.1282974	0.149269	4	-272.1341031	+4.12	5.9
12	-272.1301859	0.149517	5	-272.1348182	+3.33	5.1
13	-273.3706094	0.174875	7	-273.3769736	+4.53	6.3
14	-270.8809846	0.114686[e]	6	-270.8818973[f]	+1.27	3.1
CH₃	-39.8561318	0.031125	CH₃	-39.8576426	-	-

[a] UB3LYP/6-311++G(2d,p). [b] UHF/6-31+G(d). [c] RB3LYP/6-311++G(2d,p). [d] eq.4 + 1.8. [e] UB3LYP/6-31++G(d,p). [f] ZPE at UB3LYP/6-31++G(d,p) = 0.111238 h.

norbornadienyl radical **14** at the UHF/6-31+G(d) level led to a first-order saddle point [NImag=1 ; ν_i = -577.9 cm^{-1})]. A true minimum energy structure was found at the UB3LYP/6-31++G(d) level (NImag=0).

Each of the norbornyl radicals **11-14** has a greater electron affinity than the methyl radical.[11-13] Ultimately, this is a consequence of greater stabilization of the bicyclic anions relative to methyl carbanion vs. stabilization of the bicyclic radicals relative to the methyl radical. To illustrate this, equation **4** can be derived from the equations **5** and **6**:

$$CH_3^- + R\text{-}H \longrightarrow CH_4 + R^- \qquad \text{(eq. 5)}$$

$$CH_3\cdot + R\text{-}H \longrightarrow CH_4 + R\cdot \qquad \text{(eq. 6)}$$

Calculation of ΔH values for R = 7-norbornyl gives the following values for eq. **5** and eq. **6**: -5.65 and -1.11 kcal/mol, respectively.[18] Future studies with simpler systems will deal with the effect of substitution on radical vs. carbanion stability.

The homodesmotic comparison shown in eq. **7** was designed to reveal any special consequences,

11   (eq. 7)
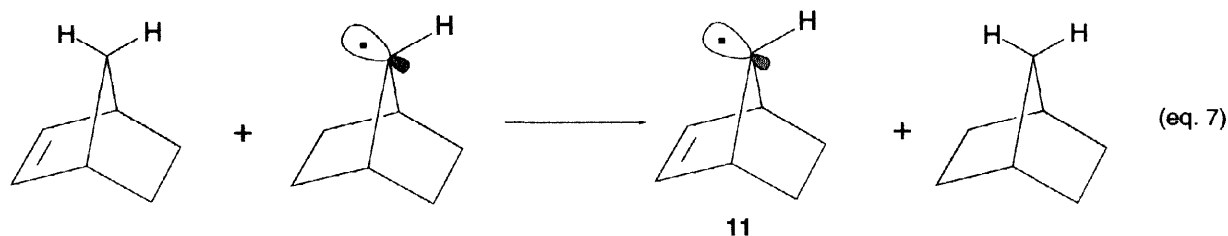
if any, of the interaction between the radical center and the double bond.[19] In fact, a small destabilization was found at the UB3LYP/6-311++G(2d,p) level: ΔH = 0.91 kcal/mol. Similarly, the anti-radical **12** is stabilized to the extent of -0.11 kcal/mol.

Another geometric feature of interest in these systems are the deviations from planarity about the lone pair and the radical center. The anions were uniformly more puckered at this site with the following C_1-C_7-C_4-H angles:**4** (112.1°); **5** (111.1°); **6** (107.7°); **7** (114.5°). The corresponding values for the radicals were: **11** (143.3°); **12** (137.7°); **13** (146.7°); **14** (134.7°).

Finally, we evaluated the role of counterions in the anionic structures by incorporating Li$^+$ into **4** and **5**.[20] The calculated structure [MP2/6-31+G(d,p)] for anti-anion **15** had a C_7-Li bond distance of 2.04 Å, typical for

15   **16**
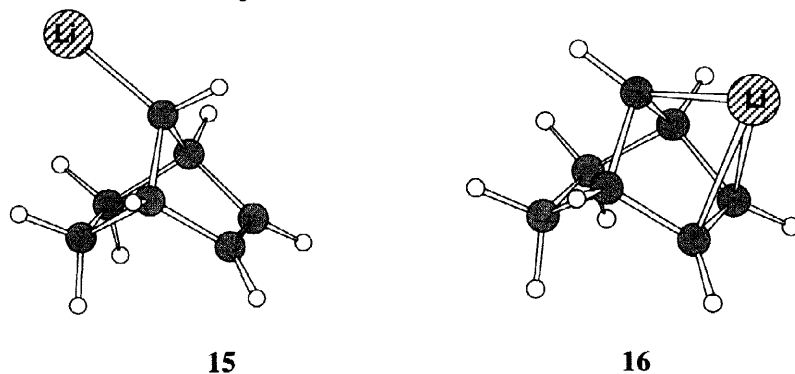
a monomeric alkyl lithium compound.[20] In the *syn*-structure the C7-Li bond distance was 2.00 Å and was accompanied by coordination of Li to the double bond at C-Li distances=2.49 Å. Coordination stabilizes the *syn*--form **16** by 5.59 kcal/mol relative to the *anti*-form **15**. These results could be significant in interpretations of experimental data where relative stabilities have been determined in solution in the presence of a counterion, *i.e.*, the exchange reaction conditions studied by Breslow, *et al.*[1]

Conclusions: These studies have shown that there is no computational evidence for bis-homoantiaromaticity in the *syn*-7-norbornenyl anion **4** in the gas phase. In view of these results, it is unlikely that solution phase experiments in the presence of counterions will reveal evidence for bis-homoantiaromaticity. Far from being "classical" carbanions the ions **4-7** are significantly delocalized by perturbation interaction with geometrically accessible LUMOs from C-C bonds. This results in bond lengthening on the one hand and decreased basicity relative to the methyl anion on the other hand. The latter result was unexpected to some extent[11] and we are examining the proton affinities and electron affinities of simpler carbanions in this context.[21] Since the calculated electron affinities for radicals **11-14** are signifcantly greater than that for methyl radical it is likely that ions **4-7** will be detectable in the gas phase in contrast to simpler secondary anions.[13]

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