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Remarkable Stabilities, Geometries, and Electronic States of Lithium-Substituted Carbenium Ions, $CLi_{3-n}H_n^+$ (n = 0-3), and the Corresponding Radicals

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Abstract: The thermodynamic stability of the CLi_3^+ cation is extraordinary. The low experimental gas-phase ionization potential (IP) of CLi_3 (4.6 ± 0.3 eV) can be compared with the IP's of Li (5.3), Na (5.1), K (4.3), and $CH_2N(CH_3)_2$ (5.7 eV). Furthermore, the geometry and electronic structure of CLi_3^+ also are unusual: molecular orbital theory including electron correlation predicts CLi_3^+ to prefer a C_{2v} Jahn-Teller distorted geometry and a triplet ground state. This triplet preference is attributed to multicenter delocalization of the π electron; $CHLi_2^+$ is similar, but CH_2Li^+ and CH_3^+ are indicated to have singlet ground states. Parallel studies on the neutral CLi_nH_{3-n} species lead to a satisfactory reproduction of the experimentally observed lowering of the radical IP's (from 9.8 eV for CH_3 to 4.6 eV for CLi_3). Lithium is a remarkably effective stabilizing substituent for carbenium ions, comparable to NH_2 in this respect. Thus, the stabilization energies (relative to CH_3^+) of CLi_3^+ and the guanidinium ion, $C(NH_2)_3^+$, are comparable. The corresponding radicals are also stabilized by lithium substitution.

Introduction

When lithium vapor above 970 K is allowed to permeate through a graphite membrane, CLi_3 is produced.[1] Its ionization potential to give CLi_3^+ was determined to be remarkably low, 4.6 ± 0.3 eV.[2] As part of a continuing research program on the nature of compounds of carbon and lithium,[3] we have now investigated by means of theoretical calculations the nature of CLi_3, CLi_3^+, and their lower homologues where one or more lithium atoms have been replaced by hydrogens. Only a few of these species have been examined previously.[3d,e,j]

The electronic structures of the lithiated carbocations pose alternatives not normally considered. Take CH_3^+ as a model. The familiar molecular orbitals utilized are shown in Figure 1.[4] The HOMO is a doubly degenerate set of σ bonding MOs and the LUMO is a nonbonding π orbital concentrated on the central atom. Therefore, CH_3^+ prefers to be a ground state D_{3h} singlet. But what about CH_3^+ triplet excited states?[5] Jahn-Teller distortion away from D_{3h} symmetry is expected. Two C_{2v} forms are possible. In both, the π orbital is singly occupied, but the other singly occupied orbital is either σ_S (a_1) or σ_A (b_2). These $^3B_1$ and $^3A_2$ triplet methyl cations are not competitive with the singlet in energy.[5] However, the situation can be quite different when the hydrogens in CH_3^+ are replaced by lithium. Since the C-Li σ bond is relatively weak, the σ_S and σ_A orbitals of singlet CLi_3^+ lie high in energy. The π orbital, on the other hand, is stabilized through pπ-pπ interaction between carbon and lithium.[3] Both these effects might lead to a π occupancy and a preferential stabilization of the triplet form. Lithiomethyl cations could thus be prototypes of carbenium ions with triplet ground states. There are precedents for such unusual electronic structures; triplet forms of CH_2Li_2,[3a,6] $H_2C{=}CLi_2$,[3m,7] etc., are found calculationally to be the ground states of these species.

Computational Details

Ab initio calculations were carried out on the cation series, CH_3^+, CH_2Li^+, $CHLi_2^+$, and CLi_3^+, and on the corresponding radicals. Geometries were optimized at the restricted Hartree-Fock (RHF) level for singlet states and the unrestricted Hartree-Fock (UHF) level[8] for doublets and triplets. The highest level basis set used was 6-31G*[9] (split-valence including d functions on first-row atoms).[9] The larger systems, CLi_3^+ and CLi_3, were optimized only at the split-valence levels, 3-21G[10] or 4-31G (5-21G for lithium is implied).[11] Nonplanar structures were examined, but none were found to be local minima. (However, see Note Added in Proof.)

Table I lists the energies and Table II the geometries of the optimized structures. These geometries were used in subsequent single-point calculations with the 6-31G** basis set (which includes p functions on hydrogen).[9] The resulting energies are designated "HF" in Table III. Corrections for electron correlation were evaluated using Møller-Plesset perturbation theory[12] with the 4-31G (Table I) and 6-31G** (Table III)

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Table I. Hartree-Fock and MP2/4-31G Energies of Optimized CH_nLi_{3-n} Ions and Radicals[a]

species	state	3-21G//3-21G	4-31G//4-31G	6-31G*//6-31G*	MP2/4-31G/HF/4-31G
CH_3^+	$^1A_1'$ (D_{3h})	−39.00913 (0.0)	−39.17512 (0.0)	−39.23064 (0.0)	−39.24205 (0.0)
	$^3B_1$ (C_{2v})	−38.87299 (85.4)	−39.03684 (86.8)	−39.09016 (88.2)	−39.09237 (93.9)
	$^3A_2$ (C_{2v})	−38.86934 (87.7)	−39.03474 (88.1)	−39.09095 (87.8)	−39.09304 (93.5)
CH_3	$^2A_2$ (D_{3h})	−39.34261	−39.50497	−39.55899	*e*
CH_2Li^+	$^1A_1$ (C_{2v})	−45.91361 (2.9)	−46.11907 (3.1)	−46.17551 (1.7)	−46.18643 (0.0)
	$^3B_1$ (C_{2v})	−45.91830 (0.0)	−46.12401 (0.0)	−46.17782 (0.0)	−46.17971 (4.2)
CH_2Li	$^2B_1$ (C_{2v})	−46.13337	−46.33894	−46.39468	−46.42029
$CHLi_2^+$	$^1A_1$ (C_{2v})	−52.76156 (23.6)	−53.00844 (23.6)	−53.06196 (24.1)	−53.07837 (15.8)
	$^3A_2$ (C_{2v})	−52.79923 (0.0)	−53.04610 (0.0)	−53.10019 (0.0)	−53.10358 (0.0)
$CHLi_2$	$^2B_1$ (C_{2v})		−53.19459	−53.25101	−53.25323
CLi_3^+	$^1A_1'$ (D_{3h})	−59.58603 (22.5)	−59.87562 (22.2)	−59.92557[b] (23.5)	−59.95459 (13.3)
	$^3B_1$ (C_{2v})	−59.62178 (0.0)	−59.91093 (0.0)	−59.96309[b] (0.0)	−59.97571 (0.0)
	$^3A_2$ (C_{2v})	−59.62181 (0.0)	−59.91077 (0.1)	−59.96294[b] (0.1)	−59.97433 (0.9)
	$^3A_1'$ (D_{3h})		−59.87506 (22.5)	−59.92872[c] (21.5)	−59.93878 (23.2)
CLi_3	$^2A_2''$ (D_{3h})	−59.73198	−60.02089[d]	−60.07233[c]	−60.09668

[a] Energies in hartrees; relative energies (in parentheses) in kcal/mol. [b] 4-31G geometries; values using 3-21G geometries are 0.00005 ± 0.00002 hartrees higher. [c] 4-31G geometries. [d] A lower energy is obtained when the wave function has C_{2v} symmetry, but this appears to be an artifact; see text. [e] The MP2/6-31G*//MP2/6-31G* energies of CH_3 and CH_3^+, −39.66875 and −39.32514, respectively, give IP(CH_3) = 9.34 eV; a similar value (9.33 eV) is obtained at MP3 with the same basis set.

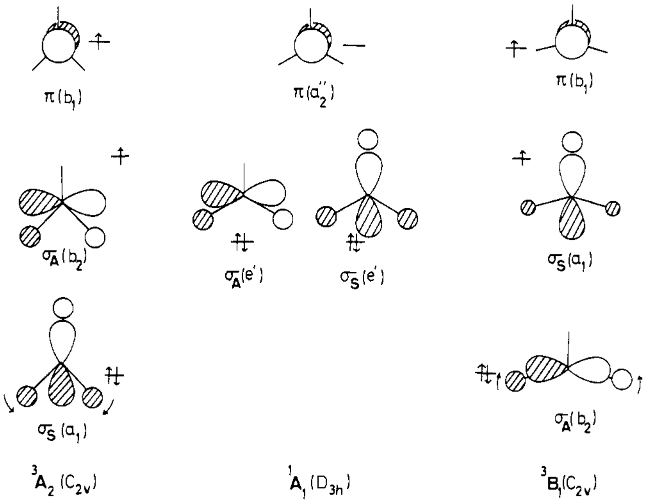

Figure 1. Structure-determining molecular orbitals of the singlet ($^1A_1$) and triplet ($^3A_2$ and $^3B_1$) methyl cations. Such orbitals are also involved in the lithiated methyl cations and radicals.

basis sets. The cation calculations were carried out to second (MP2), third (MP3), and partial fourth (limited to single, double, and quadrupole substitutions, MP4SDQ) orders (Table III).

The correlation calculations for the radicals were limited to MP2 using the 4-31G (Table I) and the 6-31G** (Table III) basis sets. The wave functions and energies of the radicals, CLi_3, $CHLi_2$, and CH_2Li, were calculated using the UHF conserved-state technique[13] in conjunction with a second-order variation procedure.[14] This procedure assures that the converged Hartree-Fock energy represents a minimum with respect to small changes of the wave functions and is particularly important in cases where classical SCF methods fail to converge. Such failure may indicate that several Hartree-Fock states have similar energies. The conserved-state technique allows one particular state to be selected; thus, it is necessary to ensure that this state corresponds to the required energy minimum.

The relative Møller-Plesset energies (given in parentheses in Tables I (MP2/4-31G) and III) only change modestly with increase in size of the basis set or with the MP order. As expected, the electron correlation corrections increase the stability of the singlet relative to the triplet forms by about 10 kcal/mol.

Results and Discussion

Several characteristics of the lithium-substituted carbenium ions are notable. Before considering reasons for the remarkable stability of these species, it is appropriate to discuss their electronic structures and geometries. The same applies to the related lithiated radicals.

Table II. Geometries of CH_nLi_{3-n} Ions and Radicals[a]

species	state	geometry
CH_3^+	$^1A_1'$ (D_{3h})	CH = 1.078
	$^3B_1$ (C_{2v})	CH_1 = 1.305;[b] CH_2 = 1.084; H_2CH_2 = 161.5
	$^3A_2$ (C_{2v})	CH_1 = 1.074;[b] CH_2 = 1.157; H_2CH_2 = 76.0
CH_3	$^2A_2'$ (D_{3h})	CH = 1.073
CH_2Li^+	$^1A_1$ (C_{2v})	CLi = 2.162; CH = 1.085; HCH = 107.6
	$^3B_1$ (C_{2v})	CLi = 2.357; CH = 1.072; HCH = 136.6
CH_2Li	$^2B_1$ (C_{2v})	CLi = 1.943; CH = 1.091; HCH = 106.8
$CHLi_2^+$	$^1A_1$ (C_{2v})	CLi = 2.097; CH = 1.095; LiCLi = 140.0
	$^3A_2$ (C_{2v})	CLi = 2.038; CH = 1.088; LiCLi = 111.4
$CHLi_2$	$^2B_1$ (C_{2v})	CLi = 2.062; CH = 1.088; LiCLi = 74.6
CLi_3^+	$^1A_1'$ (D_{3h})	CLi = 2.032 (2.050)
	$^3B_1$ (C_{2v})	CLi_1 = 1.934 (1.946);[c] CLi_2 = 2.044 (2.059); Li_2CLi_2 = 142.2 (143.2)
	$^3A_2$ (C_{2v})	CLi_1 = 2.019 (2.045);[c] CLi_2 = 2.020 (2.039); Li_2CLi_2 = 96.0 (96.6)
	$^3A_1'$ (D_{3h})	CLi = 1.947
CLi_3	$^2A_2''$ (D_{3h})	CLi = 1.988

[a] HF/6-31G* geometries in all cases except CLi_3^+ and CLi_3 where HF/4-31G values are given (HF/3-21G in parentheses): bond lengths in ångstrøms; angles in degrees. [b] H_1 is the unique hydrogen. [c] Li_1 is the unique lithium.

Singlet–Triplet Energy Differences for the Cations. The D_{3h} singlet is clearly the preferred form for the unsubstituted methyl cation.[5] The two triplet states lie more than 92 kcal/mol (MP4SDQ value; 85 kcal/mol at the UHF level) higher in energy. Of the two Jahn–Teller forms (Figure 1), the $^3A_2$ state is more stable than the alternative $^3B_1$ state (Table III). The energy difference between these two triplets is small and is rather sensitive to the inclusion of polarization functions on hydrogen.

Substitution by a single lithium results in a drastic reduction in the singlet–triplet energy difference. The $^3B_1$ state of CH_2Li^+, corresponding to a promotion of an electron from the C–Li σ_S bonding MO to the π MO, becomes competetive in energy. At the HF level, this state is slightly more stable than the singlet, but inclusion of electron correlation reverses the order of stability (Tables I and III).

Substitution by a second lithium favors the triplet preferentially. Hartree–Fock as well as all correlated energies of the singlet state of $CHLi_2^+$ are significantly higher than those of a $^3A_2$ triplet state. In this triplet, the b_2 (σ_A) orbital, predominantly C–Li bonding in character, and the b_1 (π) orbital are singly occupied.

No additional change in the singlet–triplet energy difference is calculated on going from $CHLi_2^+$ to CLi_3^+. The two Jahn–Teller distorted triplets of CLi_3^+, $^3A_2$ and $^3B_1$, have practically the same energy and are 24 kcal/mol more stable than the singlet

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Table III. Correlated Energies of CH_nLi_{3-n} Ions and Radicals (6-31G**)[a]

		HF	MP2	MP3	MP4SDQ
CH_2	$^1A_1$	−38.87630 (30.9)	−38.98705 (20.2)	−39.00609 (17.7)	−39.01004 (16.7)
	$^3B_1$	−38.92548 (0.0)	−39.01928 (0.0)	−39.03422 (0.0)	−39.03659 (0.0)
CH_3^+	$^1A_1'$	−39.23629 (0.0)	−39.34653 (0.0)	−39.36450 (0.0)	−39.36737 (0.0)
	$^3A_2$	−39.10138 (84.7)	−39.20107 (84.7)	−39.21741 (92.3)	−39.22009 (92.4)
	$^3B_1$	−39.09848 (86.5)	−39.19447 (95.4)	−39.21049 (96.6)	−39.21348 (96.6)
CH_2Li^+	$^1A_1$	−46.17917 (1.7)	−46.29036 (0.0)	−46.30844 (0.0)	−46.31170 (0.0)
	$^3B_1$	−46.18195 (0.0)	−46.27823 (7.6)	−46.29342 (9.4)	−46.29580 (10.0)
CH_2Li	$^2B_1$	−46.39842	−46.52968		
$CHLi_2^+$	$^1A_1$	−53.06419 (23.7)	−53.17731 (14.9)	−53.19437 (13.5)	−53.19761 (12.9)
	$^3A_2$	−53.10202 (0.0)	−53.20107 (0.0)	−53.21581 (0.0)	−53.21813 (0.0)
CLi_3^+	$^1A_1'$	−59.92552 (23.6)	−60.04671 (14.1)	−60.06168 (12.9)	−60.06490 (12.3)
	$^3A_2$	−59.96306 (0.0)	−60.06779 (0.8)	−60.08105 (0.7)	−60.08359 (0.6)
	$^3B_1$	−59.96287 (0.1)	−60.06910 (0.0)	−60.08223 (0.0)	−60.08448 (0.0)
CLi_3	$^2A_2''$	−60.07218	−60.19011		

[a] HF/6-31G* geometries, except CLi_3^+ (HF/3-21G) and CLi_3 (HF/4-31G). Energies in hartrees; relative energies (in parentheses) in kcal/mol.

at the HF level. The energy difference is reduced to 12 kcal/mol, still in favor of the triplets, at the MP4SDQ level.

Which of the lithomethyl cations are likely to be ground-state triplets? The problems associated with reliable theoretical prediction of singlet–triplet energy separations are well known.[15] In the present case, the best corrected estimates can be obtained by comparing the results with those for singlet vs. triplet methylene (Table III). The energies for eq 1 (in kcal/mol) at

$$CH_nLi_{3-n}^+ \text{ (triplet)} + CH_2 \text{ (singlet)} \rightarrow CH_nLi_{3-n}^+ \text{ (singlet)} + CH_2 \text{ (triplet)} \quad (1)$$

MP4SDQ/6-31G** are: CH_3^+, −109.1; CH_2Li^+, −26.6; $CHLi_2^+$, −3.8.

If we assume a value of 11 kcal/mol[16] for the singlet–triplet difference of CH_2 (instead of the MP4SDQ value of 16.7 kcal/mol in Table III), addition gives the following corrected energies, E(singlet) − E(triplet): CH_3^+, −98; CH_2Li^+, −16; $CHLi_2^+$, +7 kcal/mol. Using the same procedure, the triplet forms of CLi_3^+ are estimated to be 6 to 7 kcal/mol more stable than the singlet (the use of only the HF/3-21G geometries in this case is not likely to introduce large errors). We conclude that CH_3^+ (obviously!)[5] and CH_2Li^+ have singlet ground states, while $CHLi_2^+$ and CLi_3^+ probably are triplets in their ground states.

Cation Geometries. In the singlet state of CH_3^+, there is optimum C–H σ bonding. The C–H distance of 1.078 Å is typical for an sp^2 hybridized carbon; a similar value (1.073 Å) is found for CH_3 (Table II). In the $^3B_1$ state of CH_3^+ the σ_S (a_1) orbital is only singly occupied. As a result, one C–H bond elongates to 1.305 Å. The other hydrogens move apart to increase the overlap in the doubly occupied σ_A (b_2) orbital. The resulting unique HCH angle is very large, 161.5 Å. The angular distortion in the $^3A_2$ state is just the opposite. Two hydrogens bend toward one another so as to increase the overlap in the doubly occupied σ_S (a_1) orbital. The unique HCH angle is now only 76°. Owing to the single occupancy of the σ_A (b_2) orbital, two of the C–H bonds lengthen to 1.157 Å. The single electron in the b_1 (π) orbital of the planar triplets has no first-order geometrical consequence as the orbital is purely nonbonding. Figure 1 illustrates these Jahn–Teller distortions.

The geometries of singlet and triplet CH_2Li^+ are also easy to understand. Since in the $^3B_1$ state a bonding σ electron has been removed essentially from the σ_S (a_1) C-Li bonding orbital, the C-Li distance (2.357 Å) increases from 2.162 Å in the singlet. The HCH angle widening from 107.6° ($^1A_1$) to 136.3° ($^3B_1$) is also similar to that found in the $^1A_1$, and $^3B_1$ methyl cations.[5] The $^1A_1$ and $^3B_1$ CH_2Li^+ ions can be considered to be complexes between Li^+ and singlet and triplet CH_2, respectively. The CH bond lengths and HCH angles in corresponding cations and carbenes are similar, showing only a weak geometrical alteration due to Li^+ complexation. The corrected singlet–triplet energy differences for CH_2 (−11 kcal/mol)[16] and for CH_2Li^+ (−16 kcal/mol) suggest that the Li^+ lithiation energy of singlet CH_2 is 27 kcal/mol greater than that of triplet CH_2. The protonation energy difference is much larger, 103 kcal/mol, also favoring singlet CH_2.

The geometry of triplet ($^3A_2$) $CHLi_2^+$ shows an unusual feature. As expected, the LiCLi angle decreases from 140.0 to 111.4° on going from the singlet to the $^3A_2$ state. However, the C–Li bond lengths *decrease* from 2.097 Å in the singlet to 2.038 Å in the triplet. This is rather surprising, since an electron has been removed from the C-Li σ_A bonding MO and this should weaken both C-Li bonds. A simple explanation invokes the effect of the singly occupied π orbital.[17] While this MO is nonbonding in CH_3^+, appreciable bonding interaction develops after lithium substitution. Thus, the considerable three-center π bonding in triplet $CHLi_2^+$ more than compensates for the weakness of the C–Li σ bond. The shorter C–Li bond length results. In triplet CH_2Li^+, this π C–Li bonding is insufficient to overcome the larger weakening of the σ C–Li bond.

Similar geometrical changes are also calculated for CLi_3^+. The unique LiCLi angle is smaller (96.0°) in the $^3A_2$ state, and is larger (142.2°) in the $^3B_1$ state. As in the case of $CHLi_2^+$, both types of C–Li bonds are shorter in the $^3A_2$ state relative to the C–Li length in the singlet. In the $^3B_1$ state, the unique C–Li bond is shortened (1.934 vs. 2.032 Å in the singlet) even though the corresponding σ MO is singly occupied. C–Li π bonding accounts for the observed bond-length changes.

We also considered the possibility of π^2 states. Thus, the D_{3h} triplet CLi_3^+ cation ($^3A_1'$) has a doubly occupied π (a_2'') orbital and two singly occupied σ_A and σ_S degenerate (e') orbitals. At the MP2/4-31G//HF/4-31G level (Table I) this state is about 23 kcal/mol less stable than the $^3A_2$ and $^3B_1$ forms and 13 kcal/mol less stable than the $^1A_1'$ state. The transfer of two σ electrons to the π orbital results in a pronounced shortening of the CLi bond in CLi_3^+, from 2.032 Å ($^1A_1'$) to 1.947 Å ($^3A_1'$). Doubly occupied π states in $CHLi_2^+$ and CH_2Li^+ were much less competitive in energy.

Lithiomethyl Radicals. In the unsubstituted methyl radical, the singly occupied MO (a_2'') is essentially nonbonding. However, in the lithiomethyl radicals, the π acceptor ability of lithium makes this orbital bonding. This is reflected in the calculated geometries of these species. Thus, the lithiated radicals are all planar and

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Table IV. Experimental Ionization Potentials (eV)

radical	ionization potential	ref
methyl	9.8	*a*
ethyl	8.5	*a*
2-propyl	7.7	*a*
tert-butyl	6.9	*a*
allyl	8.1	*b*
benzyl	7.4	*b*
diphenylmethyl	7.3	*c*
tropyl	6.2	18
CH_2OH	7.6	20
CH_2NH_2	6.2	20
CH_2NMe_2	5.7	20
Li	5.4	18
Na	5.1	18
K	4.3	18
Rb	4.2	18
Cs	3.9	18
CLi_3	4.6	1

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Table V. Methyl Stabilization Energies, Equations 2 and 3 (in kcal/mol)

	4-31G	6-31G*	expt[a]
CH_2Li^+	−77.6	−78.1	
$CHLi_2^+$	−124.0[b]	−123.7[b]	
CLi_3^+	−145.3[b]		
$CH_2CH_3^+$	−29.6	−29.5	−40
$CH(CH_3)_2^+$	−50.0	−51.2	−64
$C(CH_3)_3^+$	−67.8		−81
$CH_2NH_2^+$	−89,[c] −93.3[d]	−86.5	−98
$CH(NH_2)_2^+$	−128[c]		
$C(NH_2)_3^+$	−147[c]		
CH_2Li	−8.6	−9.6	
$CHLi_2$	−33.9	−36.5	
CLi_3	−29.5		
CH_2CH_3	−2.9[e]	−2.9[f]	−6.0
$CH(CH_3)_2$	−5.8[e]		−9.5
$C(CH_3)_3$	−8.9[e]		−12.9
CH_2NH_2	−10.2[g]		−10[h]

[a] Calculated from data in ref 18. For more recent literature and cation results calculated at higher levels, see ref 5. [b] Singlet cation data employed. The triplet cation value should be slightly lower (see text). [c] Reference 19a. [d] Reference 3e. [e] For data, see Yoshime, M.; Pacansky, J. *J. Chem. Phys.*, in press, and references cited therein. Values in Leroy, G.; Peeters, D.; Wilante, C.; Khaki, M. *Nouv. J. Chim.* 1980, *4*, 403, are not fully optimized. [f] "Carnegie-Mellon Quantum Chemistry Archive": Whiteside, R. A.; Frisch, M. J., Binkley, J. S.; Raghauachari, K.; DeFrees, D. J.; Schlegel, H. B., Pople, J. A., 2nd ed., 1981, available from Pople, J. A. [g] Crans, D.; Clark, T.; Schleyer, P. v. R. *Tetrahedron Lett.* 1980, *21*, 3681. [h] Reference 20.

the C–Li bond lengths are shorter than in the corresponding singlet cations (without occupied π-type orbitals): 1.943 (CH_2Li) vs. 2.162 Å (CH_2Li^+), 2.062 ($CHLi_2$) vs. 2.097 Å ($CHLi_2^+$), and 1.988 (CLi_3) vs. 2.032 Å (CLi_3^+) (Table II). The bond angles preferred by the radicals and by the corresponding singlet cations also reveal significant differences. While the HCH angle of 106.8° found for CH_2Li deviates only slightly from the angle of 107.6° found for CH_2Li^+, the LiCLi angles adopted by $CHLi_2$ and $CHLi_2^+$ are 74.6 and 140.0°, respectively. This small angle in $CHLi_2$ has a more complex origin. A three-center, one-electron π bond is present; the corresponding MO is unoccupied in singlet $CHLi_2^+$. In addition, the ground state of $CHLi_2$ does not have the expected σ occupancy. The $2b_2$ orbital is occupied in α but not in β spinspace. In β spinspace, a higher ($5a_1$) orbital (not shown in Figure 1) is occupied instead, and a smaller LiCLi angle results.

In the case of the CLi_3 radical we approach the limits of single determinant theory. The wave function obtained for the D_{3h} structure indicates, by means of our second-order energy variation procedure, that lowering of the symmetry to C_{2v} would lead to lower energy. Consequently, we reoptimized the geometry and obtained two different C_{2v} structures with lower energy. Inclusion of electron correlation at the MP2 level, however, results in the convergence of the energies of these C_{2v} structures; thus, further geometry optimization using more sophisticated CI methods are likely to yield a unique doublet wave function with D_{3h} symmetry. We believe this should be preferred for CLi_3. Further work on CLi_3 and $CHLi_2$ is planned.

As in the case of the lithiomethyl cations, we also considered the possibility of doubly π-occupied states of the CLi_3 and $CHLi_2$ radicals. For CLi_3 the occupation of a π-type orbital in both α and β spinspaces leads to broken symmetry for the two configurations of lowest energy. In the lower energy 2π $CHLi_2$ state, the $2b_2$ orbital is singly occupied. While this enhances the populations of the CLi bonds, the energy is unfavorable. In fact, all doubly π occupied states we considered are higher in energy than the singly π occupied ground states.

The ionization potentials (in eV) for the radicals calculated at the MP2/6-31G** level are: 6.5 (CH_2Li) and 3.3 (CLi_3). Similar IP's are obtained at MP2/4-31G (Table I): 6.4 (CH_2Li), 4.1 ($CHLi_2$), and 3.3 (CLi_3). The higher theoretical level underestimates the experimental IP of CH_3 (9.84)[2] by 0.5 eV. If the calculated IP for CLi_3 is corrected by this amount, the experimental value, 4.6 ± 0.3 eV,[1] is still somewhat larger.

Thermodynamic Stability of Lithiomethyl Radicals and Cations. In addition to their unusual electronic structure, the lithiomethyl radicals and cations are remarkable in another respect: they are indicated to possess exceptional thermodynamic stability. The stability can be assessed in a variety of ways. A comparison with selected experimental ionization potentials (Table IV) provides an indication. Although the stability of the radicals is also involved, the IP's tend toward lower values as the stability of the cation formed increases. Thus the IP's of the allyl, benzyl, tropyl, and the *tert*-butyl radicals are significantly lower than that of the methyl radical. Recently, Griller and Lossing have reported that $Me_2NCH_2\cdot$ has an IP of only 5.7 eV, "the lowest thus far reported for any organic species".[20] However, $CLi_3\cdot$ has an even lower IP, 4.6 eV.[1] On the basis of IP's, CLi_3^+ is the most stable substituted methyl cation known to date.

Quantitative estimates of the stabilization of the lithiomethyl radicals and cations by substituents can be obtained from the energies of the isodesmic reactions:

$$R_nH_{n-3}C\cdot + CH_4 \rightarrow R_nH_{n-3}CH + CH_3\cdot \qquad (2)$$

$$R_nH_{n-3}C^+ + CH_4 \rightarrow R_nH_{n-3}CH + CH_3^+ \qquad (3)$$

Although our computations have been carried out at a higher theoretical level (MP4SDQ/6-31G**//6-31G*), most of the results available for comparison are at the 4-31G//4-31G level. For the sake of consistency, we have computed the energies of reactions 2 and 3 (R = CH_3, NH_2, and Li) at the 4-31G//4-31G level for the lithiomethyl radicals and cations. These results (Table V) again establish the remarkable stability associated with the lithium substitution. Previous comparison of CH_2Li^+ and $CH_2NH_2^+$ indicated lithium to be nearly as effective as an amino group in stabilizing a carbenium ion.[3e] The present results show that the cumulative effect of double and triple substitution is also similar for the two groups. Similar attenuation or "saturation" is noted both for Li and NH_2; the extra stabilization due to the second substituent is less than the first, and the third is less than the second.

The calculated stabilization energy of singlet CLi_3^+ (145 kcal/mol) is practically the same as that for $C(NH_2)_3^+$ (147 kcal/mol). The stabilization energy for triplet CLi_3^+ is even larger. In comparison to Li, the methyl group is only half as effective. Thus the stabilization energy of CH_2Li^+ is about as large as that of the *tert*-butyl cation. It should thus be possible to observe lithiated carbocations in condensed phases, provided media can be found to prevent side reactions.

Lithium is also quite effective in stabilizing free radicals. Reference data for methyl and amino substituents, provided in

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(20) Griller, D.; Lossing, F. P. *J. Am. Chem. Soc.* **1981**, *103*, 1586.

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Table V, reveal just how well lithium functions in this respect. Since both the CLi_3 radical and the CLi_3^+ cation are highly stabilized, the remarkably low experimental ionization potential of the former, 4.6 ± 0.3 eV, is not a full measure of the carbenium ion stability. Were not the CLi_3 radical so stable, its IP would be even lower.

What is the origin of the remarkable stability of these lithiated species? A carbenium ion is stabilized by a group which increases the electron density at the central carbon atom. Conventionally, only π donors have been considered to be stabilizing because of the formally vacant carbenium ion p orbital. However, σ donors can be just as effective. Increasing the electron density at the charged atom through donation is an efficient mode of stabilization. Interestingly, several α-metallocarbenium ions have been implicated as intermediates in catalytic isomerization reactions.[21] The unusual structures reported for carbenoids have also be rationalized on the basis of ion pairs involving metallocarbenium ions.[22] The stabilization of a radical by lithium can be attributed both to its π acceptor and σ donor abilities.

Our results refer only to the thermodynamic stability of the various species. A discussion of kinetic stability is beyond the scope of the present work. We emphasize that solvation and association are important for these and other lithium compounds. However, the experimental observation in the gas phase of monomeric $CLi_3\cdot$ as well as the cations, CH_2Li^+, and CLi_3^+,[1] is a stimulus for further experimental and theoretical study of organolithium compounds.[23]

Conclusions

The principal conclusions to be drawn from this study are the following:

1. Substitution of hydrogen by lithium in the methyl cation lowers the energy of triplet states more than singlets. CH_2Li^+ is still a ground-state singlet, but with a much reduced singlet–triplet separation compared with CH_3^+. $CHLi_2^+$ and CLi_3^+ are predicted to have triplet ground states.
2. The ionization potential of CLi_3 is predicted to be 6 eV less than that of CH_3, in reasonable agreement with experiment.
3. Lithium is a strong stabilizing substituent for carbenium ions, comparable to π donors such as NH_2. CLi_3^+ is one of the most stable carbenium ions known.

Note Added in Proof. After writing this paper, additional work has revealed the triplet methyl cation (but not its lithiated counterparts) to be nonplanar. This will be discussed in a future publication.

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Registry No. CH_3^+, 14531-53-4; $CH_3\cdot$, 2229-07-4; CH_2Li^+, 62581-43-5; $CH_2Li\cdot$, 81506-43-6; $CHLi_2^+$, 81506-44-7; $CHLi_2\cdot$, 81506-45-8; CLi_3^+, 81506-46-9; $CH_2CH_3^+$, 14936-94-8; $CH(CH_3)_2^+$, 19252-53-0; $C(CH_3)_3^+$, 14804-25-2; $CH_2NH_2^+$, 54088-53-8; $CH(NH_2)_2^+$, 50676-76-1; $C(NH_2)_3^+$, 43531-41-5; $CH_2\cdot$, 2465-56-7; $CH_2OH\cdot$, 2597-43-5; $CH_2NH_2\cdot$, 10507-29-6; $CH_2NMe_2\cdot$, 30208-47-0; Li, 7439-93-2; Na, 7440-23-5; Rb, 7440-17-7; Cs, 7440-46-2; $CLi_3\cdot$, 81506-48-1; ethyl, 2025-56-1; 2-propyl, 2025-55-0; *tert*-butyl, 1605-73-8; allyl, 1981-80-2; benzyl, 2154-56-5; diphenylmethyl, 4471-17-4; tropyl, 3551-27-7.

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Heats of Formation of Some Simple Alkyl Radicals[1]

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Abstract: Equilibrium constants, K, for the system $\mathrm{Me}\cdot + \mathrm{RI} \rightleftarrows \mathrm{MeI} + \mathrm{R}\cdot$ were measured in solution by using electron paramagnetic resonance spectroscopy. Given the entropies of the components of the equilibrium and the heats of formation of the iodides, the relative heats of formation of the alkyl radicals were obtained. With $\Delta H_{f,300}(\mathrm{Me}\cdot) = 34.4$ kcal mol^{-1} chosen as a standard, the following heats of formation for other alkyl radicals were obtained: Et·, 28.0; *n*-Pr·, 22.8; *i*-Pr·, 19.2; *s*-Bu·, 13.9; c-$C_5H_9\cdot$, 25.1; *t*-Bu·, 9.4 kcal mol^{-1}. These data lead to the following C–H bond dissociation energies for simple alkanes: primary C–H, ~100; secondary C–H, ~96; tertiary C–H, ~94 kcal mol^{-1}.

The C–H bond dissociation energies, BDE, in simple alkanes form a vital part of our understanding of the influence of thermodynamic properties on chemical reactivity. Differences in these energies, while small in percentage terms, obviously have a profound influence on the pathways of chemical reactions. They are, nevertheless, notoriously difficult to quantify, as are the related heats of formation of alkyl radicals, $\Delta H_f(\mathrm{R}\cdot)$, eq 1. For example,

$$\mathrm{BDE(R-H)} = \Delta H_f(\mathrm{R}\cdot) + \Delta H_f(\mathrm{H}\cdot) - \Delta H_f(\mathrm{R-H}) \qquad (1)$$

estimates of the bond dissociation energy for the simplest tertiary C–H bond, i.e., that in isobutane,[2-8] cover the range 91.2–97.4 kcal mol^{-1}. The spread in these values is due entirely to discrepancies in the measured values of $\Delta H_f(t\text{-}\mathrm{Bu}\cdot)$.[2-7]

In a preliminary report of this work,[9] we demonstrated that a "radical buffer"[10] system could be used to measure the *relative*

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