

The Remarkably Stabilized Trilithiocyclopropenium Ion, $C_3Li_3^+$, and Its Relatives

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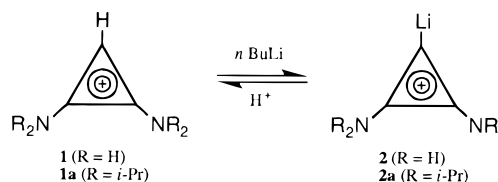
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Abstract: The structures and energies of lithiated cyclopropenyl cations and their acyclic isomers ($C_3H_{3-n}Li_n^+$, $n = 0-3$) have been calculated employing ab initio MO (HF/6-31G*) and density functional theory (DFT, Becke3LYP/6-311+G*) methods. The cyclic isomers (**4**, **6**, **10**, and **14**) are always favored, but when lithium is substituted sequentially along the $C_3H_3^+$, $C_3H_2Li^+$, $C_3HLi_2^+$, and $C_3Li_3^+$ series, the acyclic forms (**5**, **7**, **11**, **16**) become progressively less competitive energetically. A triply bridged $c-C_3(\mu-Li)_3^+$ geometry, **14**, was preferred over the classical form **3** by 8.7 kcal/mol. A single lithium substituent results in a very large (67 kcal/mol) stabilization of the cyclopropenyl cation. The favorable effects of further lithium substitution are attenuated but are still large: 48.2 and 40.5 kcal/mol for the second and third replacements, respectively. Comparison with polyamino-substituted cyclopropenyl cations suggest $c-C_3Li_3^+$ (**3** and **14**) to be a good candidate for the thermodynamically most stable carbenium ion. The stabilization of the cyclopropenyl cation afforded by the excellent π -donor substituent NH_2 (42.8, 33.4, and 23.7 kcal/mol for the first, second and third NH_2 groups, respectively) is uniformly lower than the corresponding values for Li substitution. The total stabilization due to two NH_2 groups, and a Li (128.2 kcal/mol) is higher than that due to three NH_2 groups (99.8 kcal/mol). All the lithiated cyclopropyl radicals are computed to have exceptionally low adiabatic ionization energies (3.2–4.3 eV) and even lower than the ionization energies of the alkali metal atoms Li–Cs (4.0–5.6 eV). The ionization energy of $C_3Li_3^+$ is the lowest (3.18 eV), followed by $C_3(\mu-Li)_3^+$ (3.35 eV). The 1H , 6Li , and ^{13}C NMR data of cyclopropenyl cation and its lithium derivatives indicate the carbon, lithium, and hydrogen chemical shifts to increase with increasing lithium substitution on the ring. The computed 1H chemical shifts and the magnetic susceptibility anisotropies as well as the nucleus independent chemical shifts (NICS, based on absolute magnetic shieldings) reveal enhanced aromaticity upon increasing lithium substitution. The B3LYP/6-311+G*-computed vibrational frequencies agree closely with experiment for cyclopropenyl cation and, hence, can be used for the structural characterization of the lithiated and amino species.

Introduction

Lithium substitution is remarkably effective in stabilizing carbenium ions (e.g., CLi_3^+),^{1–3} carbonium ions (e.g., CLi_5^+ , CLi_6^+),⁴ and hypermetalated carbocations with unusual stoichiometries (e.g., $C_2Li_8^+$, $C_3Li_{12}^+$, etc.).⁵ All of these lithiated carbocations and many more have been observed experimentally in the gas phase.^{2,4b,5,6} The considerable thermodynamic stability of these species as isolated entities suggests that they may also be observable in solution under suitable conditions. Indeed, an example has already been reported: the bis-dialkylamino-substituted cyclopropenium ion (**1a**) undergoes

H/Li exchange with butyllithium in CH_2Cl_2 solution to give the lithiated cyclopropenium ion **2a**. Protonation of **2a** regenerates **1a**.⁷



We showed earlier that the σ -electron donating ability of lithium stabilizes the methyl cation nearly as effectively as

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Table 1. Energies of Acyclic Isomers Relative to Substituted Cyclopropenyl Cations at Various Computational Levels

molecule	HF ^a	B3LYP ^b	MP2 ^c	MP4 ^d
		C ₃ H ₃ ⁺		
4	0.0	0.0	0.0	0.0
5	33.6	23.3	31.3	27.2
		C ₃ H ₂ Li ⁺		
6	0.0	0.0	0.0	0.0
7	21.9	13.1	21.8	16.3
8	36.3	27.4	37.3	33.2
9	44.1	32.1	42.8	37.4
		C ₃ HLi ₂ ⁺		
10	0.0	0.0	0.0	0.0
11	22.3	14.5	24.9	19.7
12	40.2	59.8	42.4	37.9
13	35.9	31.7	30.2	29.9
		C ₃ Li ₃ ⁺		
14	0.0	0.0	0.0	0.0
3	4.9	8.7	10.6	10.3
15	15.5	13.2	24.2	19.1
16	46.6	40.9	54.4	49.0
		C ₃ H ₂ (NH ₂) ⁺		
17	0.0	0.0	0.0	0.0
18	19.2	7.5	17.9	13.7

^a HF/6-31G* + 0.89ZPE. ^b B3LYP/6-311+G* + ZPE. ^c MP2(fc)/6-31G* + 0.89ZPE/HF/6-31G*. ^d MP4SDTQ(fc)/6-31G* + 0.89ZPE/HF/6-31G*.

π -donation from an amino group.^{3,8} This suggests that the trilithiocyclopropenium ion (**3**), might be an unusually stable species.^{5b} Experimentally, C₃Li₃⁺ has been observed as one of the most abundant peaks in the flash vaporization mass spectrum of C₃Li₄.^{5b,c} Using field desorption techniques, C₃Li₃⁺ is almost the only, and certainly the most abundant, peak in the mass spectrum of C₃Li₄.^{5b}

Of all the Hückel $4n + 2$ π -electron monocyclic species, the cyclopropenium ion (C₃H₃⁺, **4**) has, by far, the largest stabilization energy⁹ and has even been detected in the tail of Halley's comet!¹⁰ Were it not for the high degree of strain associated with the sp² centers in a three-membered ring, the cyclopropenium ion would also be remarkably stable in absolute sense. Lithium substitution may help here as well. As first pointed out by Dill et al.,^{11a,b} lithium substitution reduces the strain energies in small ring systems. Ab initio calculations on tetralithiotetrahydrene demonstrate this dramatically.¹¹ Lithium substitution of the cyclopropenium ion (**4**) should thus be favorable in two respects: the charge would be stabilized and the ring strain reduced.

The stabilizing effects of NH₂ and other π -donor substituents on C₃H₃⁺ isomers have been studied computationally by Hopkinson and Lien.¹² The π -conjugation of the amino group with the three-membered carbocyclic ring (as computed for c-C₃H₂NH₂⁺) affords greater stabilization (30.7 kcal/mol) as

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Table 2. Level Dependence of the Energies (kcal/mol) of Eqs 1–20

eq	HF ^a	B3LYP ^b	MP2 ^c	MP4 ^d
1	-82.8	-73.4	-80.0	-81.6
2	-76.3	-67.0	-75.8	-76.1
3	-88.0	-77.3	-85.3	-87.0
4	-56.1	-48.2	-56.6	-56.6
5	-55.7	-46.8	-53.5	-53.2
6	-42.9	-40.5	-50.6	-49.9
7	-49.7	-41.7	-51.3	-50.6
8	-175.3	-155.7	-183.1	-182.7
9	-157.9	-135.5	-157.2	-160.9
10	-225.4	-196.7	-222.4	-222.1
11a	-89.8	-94.8	-103.6	-103.3
11b	-82.8	-73.4	-80.0	-81.6
12a	-72.8	-72.9	-81.8	-80.1
12b	-99.8	-87.0	-96.7	-97.5
13	-56.7	-58.6	-62.2	-61.9
14	-42.3	-42.8	-48.8	-48.4
15	-34.7	-33.4	-39.1	-38.3
16	-26.4	-23.7	-29.5	-28.3
17	-103.4	-99.8	-117.4	-115.0
18	-62.5	-52.1	-61.4	-61.1
19	-139.5	-128.2	-149.4	-147.7
20	-161.7	-143.7	-167.5	-166.7

^a HF/6-31G* + 0.89ZPE. ^b B3LYP/6-311+G* + ZPE. ^c MP2(fc)/6-31G* + 0.89ZPE/HF/6-31G*. ^d MP4SDTQ(fc)/6-31G* + 0.89ZPE/HF/6-31G*.

compared to hydroxy (7.9 kcal/mol) or methyl (14.6 kcal/mol) substitution.^{12b} However, substituents such as F and -NC, which stabilize carbenium ions,¹³ destabilize the cyclopropenyl cation (**4**). In contrast, experimental results⁷ and computational studies on related molecules⁸ show that lithium substitution can be expected to be at least as effective as amino groups in stabilizing C₃H₃⁺.

These considerations suggest that lithiated cyclopropenium ions, C₃Li₃⁺ in particular, might have exceptional stability due to the combination of highly favorable π -delocalization and σ -donation effects. The present investigation examines (and confirms) this possibility, as well as compares the effectiveness of various combinations of lithium and amino substituents in stabilizing isomeric C₃H₃⁺ cations. Do the unusual geometries often favored by lithiocarbons^{1-6,9,11} have counterparts in the lithiated cations? It is shown how the results fit into and extend the general patterns of behavior. Moreover, the computed vibrational frequencies, ¹H, ⁶Li, and ¹³C NMR chemical shifts, and adiabatic ionization energies for the lithiated cyclopropenium ions will aid experimental characterization of these species.

Computational Methods

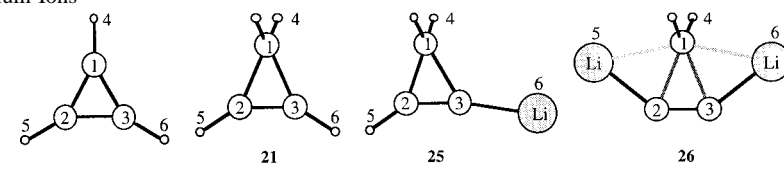
The potential energy surfaces (PES) were explored using *ab initio*⁸ (HF/6-31G*) and DFT methods (Becke3LYP/6-311+G* termed B3LYP here)¹⁴ employing Gaussian 94 program.¹⁵ Frequency analyses, which characterize stationary points on the PES and provide zero-point energies,¹⁶ were carried out both at the HF/6-31G* and B3LYP levels.

The first set of geometries examined were based on the structures of the two known C₃H₃⁺ isomers, the cyclopropenyl cation (**4**) and the

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Table 3. GIAO-Becke3LYP/6-311+G*/Becke3LYP/6-311+G*-Computed Ring ^1H (italic), ^6Li (underlined), and ^{13}C NMR Chemical Shifts^a for Substituted Cyclopropenium Ions^b


molecule	atom no.					
	1	2	3	4	5	6
4 , C_3H_3^+ ^c	178.0 (162.1)	178.0 (162.1)	178.0 (162.1)	10.5 (10.6)	10.5 (10.6)	10.5 (10.6)
6 , $\text{C}_3\text{H}_2\text{Li}^+$	232.9 (218.2)	196.3 (179.6)	196.3 (179.6)	4.3 (2.4)	11.0 (11.2)	11.0 (11.2)
10 , $\text{C}_3\text{H}\text{Li}_2^+$	217.4 (199.3)	251.6 (235.0)	251.6 (235.0)	11.8 (12.0)	5.9 (3.7)	5.9 (3.7)
3 , C_3Li_3^+	277.0 (257.7)	277.0 (257.7)	277.0 (257.7)	7.5 (5.0)	7.5 (5.0)	7.5 (5.0)
14 , C_3Li_3^+	288.4 (274.1)	288.4 (274.1)	288.4 (274.1)	10.1 (7.3)	10.1 (7.3)	10.1 (7.3)
17 , $\text{C}_3\text{H}_2(\text{NH}_2)^+$	154.0 (144.9)	144.8 (133.7)	144.8 (133.7)		9.0 (8.7)	9.0 (8.7)
1 , $\text{C}_3\text{H}(\text{NH}_2)_2^+$ ^c	102.8 (95.7)	138.5 (131.1)	138.5 (131.1)	6.8 (7.1)		
19 , $\text{C}_3(\text{NH}_2)_3^+$	113.5 (107.3)	113.5 (107.3)	113.5 (107.3)			
20 , $\text{C}_3\text{Li}_2(\text{NH}_2)^+$	193.6 (183.7)	210.2 (199.4)	210.2 (199.4)		5.9 (3.7)	5.9 (3.7)
2 , $\text{C}_3\text{Li}(\text{NH}_2)_2^+$	146.5 (142.5)	154.7 (146.7)	154.7 (146.7)	4.8 (2.8)		
21 , C_3H_4 (C_{2v})	3.9 (-0.3)	116.7 (110.8)	116.7 (110.8)	7.3 (7.3)	7.1 (7.6)	7.1 (7.6)
25 , $\text{C}_3\text{H}_3\text{Li}$ (C_s)	0.9 (-5.4)	131.7 (123.5)	138.1 (136.0)	0.4 (0.2)	7.5 (8.1)	8.9 (6.0)
26 , $\text{C}_3\text{H}_2\text{Li}_2$ (C_{2v}) ^d	-16.6 (-21.8)	148.3 (140.1)	148.3 (140.1)	-1.2 (-1.9)	14.0 (9.4)	14.0 (9.4)

^a The absolute shielding for the reference molecules, tetramethylsilane and Li^+ are $^{13}\text{C} = 184.0$, $^1\text{H} = 32.3$, and $^6\text{Li} = 95.3$. ^b GIAO-HF/6-31+G*/Becke3LYP/6-311+G*-computed chemical shifts are given in parentheses with $^{13}\text{C} = 200.8$, $^1\text{H} = 32.6$, and $^6\text{Li} = 95.4$ as the shielding values for the reference molecules, tetramethylsilane and Li^+ . ^c The experimental shifts are $^{13}\text{C} = 177$ and $^1\text{H} = 11.1$ for **4** and $^{13}\text{C}(1) = 99.0$ and $^{13}\text{C}(2,3) = 133.7$ for **1**. ^d Reference 43.

propargyl cation, **5**.¹⁷ The hydrogens were replaced systematically with lithium to give a set of monolithiated (**6–8**), dilithiated (**10–12**), and trilitiated (**3** and **16**) carbocations with classical structures. Since lithium is known to have a propensity for bridging,^{3,6b,8,18} additional structural possibilities (**9**, **13**, **14**, **15**) also were considered. We also computed the geometries, stabilization energies, and spectroscopic (IR, NMR) properties of **1**, **2**,⁷ and other cyclopropenium ions with combinations of Li and NH_2 groups (**17–20**) for comparison. The effects of electron correlation were probed by single-point calculations at MP4SDTQ(fc)/6-31G* (frozen core fourth-order Moller–Plesset theory with all single, double, triple, and quadruple substitutions) for all species,¹⁹ using the HF/6-31G* geometries.

Tables 1 and 2 show the relative energies of the lithiated species and the stabilization energies obtained from eqs 1–20, respectively, at various computational levels.²⁰ The computed ^1H , ^6Li , and ^{13}C NMR chemical shifts for the cyclic species, their aromaticity, and the vibrational frequencies for substituted cyclopropenyl cations are given in Tables 3–5. Table 6 includes the adiabatic ionization energy [IE = $E(\text{radical}) - E(\text{cation})$] of the lithiated cyclopropenyl radicals along with experimental values where available. Figure 1 provides the

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Table 4. Bond Length Alternation (Δr , Å),^a ^1H and ^6Li Chemical Shifts (δ , ppm),^b Magnetic Susceptibilities (χ , ppm cgs), Their Anisotropies (χ_{anis} , ppm cgs) and Exaltations (Λ , ppm cgs),^c Nucleus Independent Chemical Shifts, [NICS(0), NICS(1), ppm],^d and Stabilization Energies (SE, kcal/mol) from Eqs 21–24^e (Figure 2) for Lithiated Cyclopropenium Ions **4**, **6**, **10**, **3**, and **14**

property	4	6	10	3	14
Δr	0.0	0.063	0.074	0.0	0.0
δ (^1H)	10.5	11.0	11.8		
δ (^6Li)		4.3	5.9	7.5	10.1
χ	-13.4	-12.9	-12.1	-10.1	-13.3
χ_{anis}	-29.4	-35.2	-41.2	-48.4	-57.2
NICS(0)	-27.6	-24.6	-20.5	-14.8	-22.1
NICS(1)	-16.0	-18.2	-20.1	-21.6	-23.7
Λ^f	-10.2	-15.2	-12.6	-8.8	-12.0 ^g
SE	-59.0	-56.6	-84.1	-95.1	-104.2 ^h

^a Becke3LYP/6-311+G*-optimized geometries. ^b GIAO-Becke3LYP/6-311+G*/Becke3LYP/6-311+G*. ^c CSGT-Becke3LYP/6-311+G*/Becke3LYP/6-311+G*. ^d GIAO-HF/6-31+G*/Becke3LYP/6-311+G*. ^e Becke3LYP/6-311+G*/Becke3LYP/6-311+G*. ^f Calculated using eqs 21–24 at CSGT-Becke3LYP/6-311+G*/Becke3LYP/6-311+G*. ^g $\Lambda(\mathbf{3}) + [\chi(\mathbf{14}) - \chi(\mathbf{3})]$. ^h $\text{SE}(\mathbf{3}) + [E_{\text{B3LYP}}(\mathbf{14}) - E_{\text{B3LYP}}(\mathbf{3})]$.

B3LYP geometric parameters and the natural charges (in italics), obtained from natural population analysis (NPA).²¹ Unless otherwise stated, the discussion is based on B3LYP results.

Results and Discussion

C_3H_3^+ . Both the cyclopropenyl cation (**4**) and the propargyl cation (**5**) have been characterized experimentally.²² The extensively computed energy difference between **4** and the less stable **5** also calibrates the levels used here.^{9,17} Our best value of 23.3 kcal/mol (Table 1) at B3LYP (27.2 kcal/mol at MP4SDTQ/6-31G*) favoring **4** are within the error bounds of

(20) (a) The ΔH in eqs 1–20 includes the HF/6-31G* zero-point energies (scaled by a factor of 0.89 and applied to the HF, MP2, and MP4 total energies). For details, see: Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem. Symp.* **1979**, *13*, 225. (b) Krishnan, R.; Schlegel, H. B.; Binkley, J. S.; Whiteside, R. A.; Frisch, M. J.; Pople, J. A.; Hout, R. F., Jr.; Hehre, W. J. *Int. J. Quantum Chem. Symp.* **1981**, *15*, 269. (c) No scaling factor for the Becke3LYP/6-311+G* zero-point energies were used in eqs 1–20. See: Schleyer, P. v. R.; Jiao, H.; Glukhovtsev, M.; Chandrasekhar, J.; Kraka, E. *J. Am. Chem. Soc.* **1994**, *116*, 10129.

(21) Reed, A. E.; Weinhold, F.; Curtiss, L. A. *Chem. Rev.* **1988**, *88*, 899 and references therein.

Table 5. B3LYP/6-311+G*-Computed Vibrational Frequencies (ν , cm^{-1}) for Substituted Cyclopropenium Ions

freq	4	6	10	3	14
ν_1	764.4 (a_2'')	193.3 (b_2)	134.0 (a_1)	130.1 (e')	177.7 (a_2'')
ν_2	929.6 (e')	268.3 (b_1)	208.5 (b_2)	165.1 (a_2'')	212.9 (e')
ν_3	1009.7 (e'')	476.0 (a_1)	217.3 (b_1)	180.2 (a_2')	284.5 (e'')
ν_4	1028.4 (a_2')	829.3 (b_1)	306.6 (a_2)	294.2 (e'')	386.7 (a_2')
ν_5	1308.3 (e')	931.5 (a_1)	495.6 (a_1)	509.7 (a_1')	542.8 (a_1')
ν_6	1665.3 (a_1')	953.0 (b_2)	544.7 (b_2)	572.1 (e')	571.8 (e')
ν_7	3245.4 (e')	1007.7 (a_2)	902.8 (b_1)	1099.4 (e')	1098.7 (e')
ν_8	3295.6 (a_1')	1148.4 (b_2)	943.0 (b_2)	1595.3 (a_1')	1501.8 (a_1')
ν_9		1364.9 (a_1)	1051.0 (a_1)		
ν_{10}		1661.7 (a_1)	1327.9 (b_2)		
ν_{11}		3241.7 (b_2)	1635.6 (a_1)		
ν_{12}		3278.5 (a_1)	3225.8 (a_1)		

freq	17	1	19	20	2
ν_1	404.5 (b_2)	258.4 (a_1)	229.6 (a_2'')	138.7 (a_1)	150.7 (b_2)
ν_2	486.9 (b_1)	347.2 (b_1)	245.2 (e')	152.5 (b_2)	176.5 (b_1)
ν_3	635.4 (b_1)	494.7 (a_2)	320.2 (e'')	167.4 (b_1)	246.7 (a_1)
ν_4	648.2 (a_2)	508.0 (b_2)	359.0 (a_1'')	267.8 (a_2)	381.9 (a_2)
ν_5	819.2 (b_1)	526.0 (b_1)	371.3 (a_2'')	393.5 (b_2)	401.2 (b_1)
ν_6	870.2 (a_1)	539.3 (a_2)	500.1 (e'')	422.3 (b_1)	409.7 (b_1)
ν_7	960.8 (a_2)	618.3 (a_2)	586.4 (e'')	505.9 (a_1)	503.1 (a_2)
ν_8	983.6 (b_2)	630.6 (b_1)	608.6 (a_2')	548.5 (b_1)	509.3 (a_1)
ν_9	1031.6 (a_1)	805.0 (b_1)	799.5 (a_1')	562.4 (b_2)	512.4 (b_2)
ν_{10}	1125.3 (b_2)	843.6 (a_1)	903.7 (e')	608.9 (a_2)	608.5 (b_1)
ν_{11}	1333.3 (b_2)	896.6 (b_2)	1213.6 (a_2')	859.7 (a_1)	621.9 (a_2)
ν_{12}	1492.0 (a_1)	1086.3 (b_2)	1236.6 (e')	1098.0 (b_2)	864.6 (a_1)
ν_{13}	1680.3 (a_1)	1121.3 (a_1)	1564.1 (e')	1273.1 (a_1)	887.1 (b_2)
ν_{14}	1889.2 (a_1)	1229.1 (b_2)	1684.2 (a_1')	1380.8 (b_2)	1124.3 (a_1)
ν_{15}	3252.8 (b_2)	1396.6 (a_1)	1686.5 (e')	1678.4 (a_1)	1216.5 (b_2)
ν_{16}	3288.7 (a_1)	1596.1 (b_2)	2084.0 (a_1')	1807.6 (a_1)	1440.6 (a_1)
ν_{17}	3548.1 (a_1)	1683.4 (a_1)	3595.2 (e')	3563.8 (a_1)	1488.0 (b_2)
ν_{18}	3654.9 (b_2)	1697.5 (b_2)	3602.3 (a_1')	3669.5 (b_2)	1682.1 (a_1)
ν_{19}		1983.3 (a_1)	3706.7 (a_2')		1685.2 (b_2)
ν_{20}		3283.8 (a_1)	3708.1 (e')		1958.1 (a_1)
ν_{21}		3570.8 (b_2)			3584.2 (b_2)
ν_{22}		3575.0 (a_1)			3586.8 (a_1)
ν_{23}		3682.0 (b_2)			3695.5 (b_2)
ν_{24}		3683.0 (a_1)			3696.2 (a_1)

the experimental difference of 23 ± 4 kcal/mol based on appearance potential measurements.²³

C₃H₂Li⁺. Although experimental details on C₃H₂Li⁺ are lacking, an X-ray structure of a dimer of a highly substituted derivative of neutral lithiated cyclopropene (1-C₃H₃Li, **25**) has been reported very recently.²⁴ The influence of lithium substitution on C₃H₃⁺ also is dramatic. While the lithiocyclopropenium ion **6** remains the most stable C₃H₂Li⁺ energy minimum, the open form, **7** (Figure 1), which can be regarded as lithiated allenyl cation, is stabilized to a greater extent. The energy difference between **6** and **7** (13.1 kcal/mol) is decreased by over 10 kcal/mol from the corresponding **4** and **5** energy difference (Table 1). Although linear C₃H₃⁺ (**5**) can be thought of as a resonance hybrid of the propargyl and allenyl cations, substitution of lithium at the “-yne end”, as in **8**, is less effective: **7** is 14.3 kcal/mol more stable than **8**. Preference of Li for an acetylide position has also been noticed previously.^{6d} Structure **9** with a bridging lithium is 4.7 kcal/mol less stable than **8** and is the intermediate for lithium 1,3-shifts between the terminal carbon atoms in **8**.

The stabilizing effects of lithium substitution can be evaluated in different ways, e.g., by isodesmic equations using CH₃Li as

(22) (a) Breslow, R.; Groves, J. T.; Ryan, G. *J. Am. Chem. Soc.* **1967**, *89*, 5048. (b) Farnum, D. G.; Mehta, G.; Silberman, R. G. *J. Am. Chem. Soc.* **1967**, *89*, 5048. (c) Breslow, R.; Groves, J. T. *J. Am. Chem. Soc.* **1970**, *92*, 984. (d) Lossing, F. P. *Can. J. Chem.* **1972**, *50*, 3973. (e) Ausloos, P. J.; Lias, S. G. *J. Am. Chem. Soc.* **1981**, *103*, 6505.

(23) Lias, S. G.; Bartmess, J. E.; Liebmann, J. F.; Holmes, J. C.; Levin, R. D.; Mallard, W. G. *J. Phys. Chem. Ref. Data* **1988**, *17*, Suppl. 1.

(24) Sorger, K.; Schleyer, P. v. R.; Stalke, D. *J. Am. Chem. Soc.* **1996**, *118*, 1086.

Table 6. Becke3LYP/6-311+G* Ionization Energies^a (IE, eV) of Substituted Cyclopropenium Ions and Related Reference Molecules

molecule	sym	total energy	mult	S ²	IE	expt ^b
C ₃ H ₃ ⁺ (4)	D _{3h}	-115.754 22	1	0.0		
C ₃ H ₃ [*]	C _s	-115.979 20	2	0.753	6.12	6.6
C ₃ H ₃ ⁺ (5)	C _{2v}	-115.714 80	1	0.0		
C ₃ H ₃ [*]	C _{2v}	-116.033 11	2	0.77	8.66	8.68
C ₃ H ₂ Li ⁺ (6)	C _{2v}	-122.749 32	1	0.0		
C ₃ H ₂ Li [*]	C _{2v}	-122.906 50	2	0.752	4.28	
C ₃ HLi ₂ ⁺ (10)	C _{2v}	-129.714 67	1	0.0		
C ₃ HLi ₂ [*]	C _s	-129.864 23	2	0.75	4.07	
C ₃ Li ₃ ⁺ (3)	D _{3h}	-136.653 78	1	0.0		
C ₃ Li ₃ [*]	C _{2v}	-136.770 72	2	0.75	3.18	
C ₃ Li ₃ ⁺ (14)	D _{3h}	-136.668 28	1	0.0		
C ₃ Li ₃ [*]	D _{3h}	-136.791 36	2	0.75	3.35	
CH ₃ ⁺	D _{3h}	-39.486 71	1	0.0		
CH ₃ [*]	D _{3h}	-39.849 67	2	0.754	9.88	9.8
CH ₂ Li ⁺	C _{2v}	-46.491 95	1	0.0		
CH ₂ Li [*]	C _{2v}	-46.753 61	2	0.753	7.12	
CHLi ₂ ⁺	C _{2v}	-53.379 50	1	0.0		
CHLi ₂ [*]	C _{2v}	-53.628 50	2	0.766	6.78	
CLi ₃ ⁺	C _{2v}	-60.391 53	3	2.009	4.37 ^c	4.6
CLi ₃ [*]	D _{3h}	-60.371 82	1	0.0		
CLi ₃ ⁺	D _{3h}	-60.552 11	2	0.781	4.91	
Li ⁺	Kh	-7.284 92	1	0.0		
Li [*]	Kh	-7.491 33	2	0.75	5.62	5.4
Na ⁺	Kh	-162.087 57	1	0.0		
Na [*]	Kh	-162.286 78	2	0.75	5.42	5.1
K ⁺	Kh	-27.970 63 ^d	1	0.0		
K [*]	Kh	-28.133 98 ^d	2	0.75	4.44	4.3
Rb ⁺	Kh	-23.705 78 ^d	1	0.0		
Rb [*]	Kh	-23.863 96 ^d	2	0.75	4.30	4.2
Cs ⁺	Kh	-19.731 52 ^d	1	0.0		
Cs [*]	Kh	-19.877 09 ^d	2	0.75	3.96	3.9

^a IE = $E(\text{radical}) - E(\text{cation})$. ^b Reference 32. ^c IE for ²CLi₃^{*} to ³CLi₃⁺, the IE to ¹CLi₃⁺ is 4.91 eV. ^d Total energy at Becke3LYP/LANL2DZ.

a standard. Thus, eq 1 shows that lithium stabilizes the methyl cation by 73.4 kcal/mol. Lithium substitution stabilizes the cyclopropenium ion (eq 2) slightly less (ca. 6 kcal/mol) than the methyl cation (eq 1). But the effect of lithium substitution is larger with the propargyl cation (eq 3), where the charge is more localized (Figure 1).

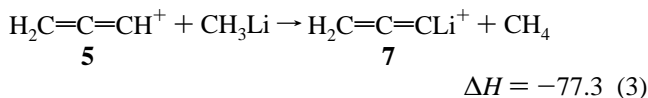
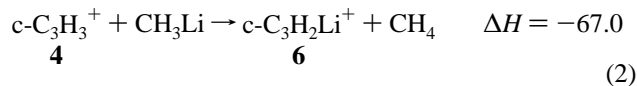
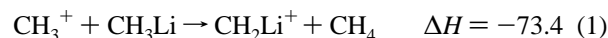
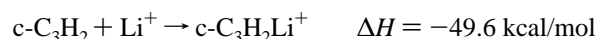


Table 2 summarizes the dependence of stabilization energies (ΔH in kcal/mol) for isodesmic eqs 1–20 at various theoretical levels. Inclusion of correlation, i.e., MP2 and MP4, for the HF/6-31G* optimized geometries gives similar values. This emphasizes the success of the isodesmic equations in canceling errors for these species.

As supported by the NBO analysis,²¹ species such as CH₂Li⁺ and C₃H₂Li⁺ (**6**) can also be regarded as lithium cation-complexes of the singlet carbenes (CH₂) and cyclopropenylidene (c-C₃H₂), respectively. The following B3LYP reaction energies show the interaction of Li⁺ with the larger system (c-C₃H₂) to be more favorable energetically.



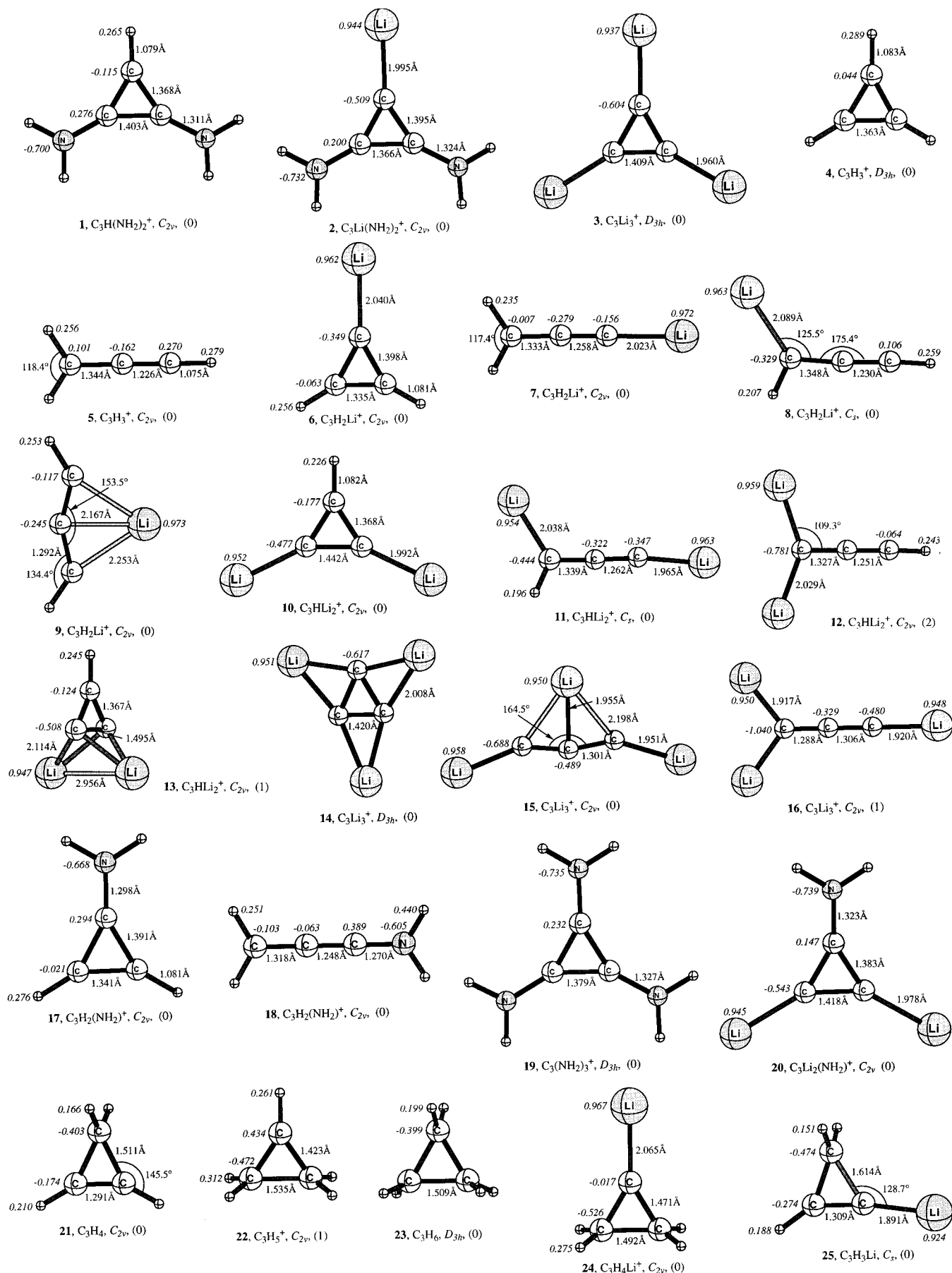
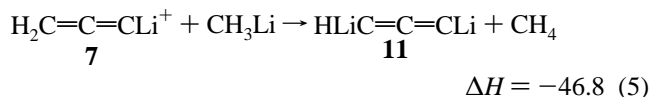
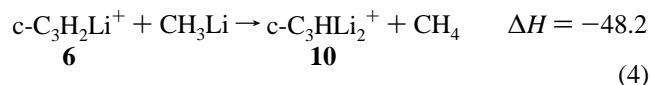


Figure 1. Becke3LYP/6-311+G*-optimized geometries (distances in angstroms and angles in degrees) and natural charges (italic) for 1–25. The number of imaginary frequencies is given in parentheses.

$C_3HLi_2^+$. The dilithiated cyclopropenium ion **10** as well as the 1,3-Li substituted acyclic isomer, **11**, are the two minima

located on the $C_3HLi_2^+$ PES. The symmetrical acyclic structure, **12**, is a second-order saddle point at B3LYP and a transition

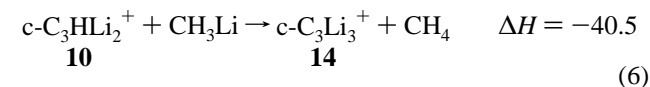
state at HF/6-31G* (see Supporting Information). A bridged structure similar to **9** optimized to the more stable **11**. The doubly bridged dilithiated cyclopropenium ion, **13**, is the transition state ($\nu_i = -158.8 \text{ cm}^{-1}$ at B3LYP) for lithium exchange in **10**.



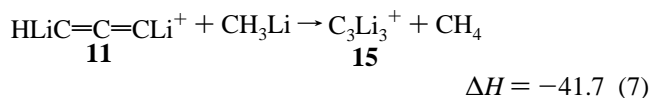
While the dilithiated cyclopropenium ion, **10**, is the most stable C_3HLi_2^+ isomer (Table 1), the additional stabilization afforded by the second lithium substitution (eq 4) is less than the gain afforded by the first replacement (eq 2). The same is true for **11**. The charges at the unsubstituted centers in **7** and **8** (CH_2 and CH , respectively; Figure 1) are less positive than in the propargyl cation, **5**. Consequently, the second lithium substitution is less stabilizing (compare eqs 3 and 5).

C_3Li_3^+ . The triply bridged trilithiocyclopropenium ion, **14**, is clearly the most stable C_3Li_3^+ isomer (Figure 1). Like **14**, **3** also has D_{3h} symmetry and is a minimum, but 8.7 kcal/mol higher in energy than **14** (Table 1). While the bridged structure **9** is less stable than the open form **8**, bridged **15** is 27.7 kcal/mol more stable than the classical species **16** (Table 1). The latter is the transition state for lithium exchange. Structures **14** and **15** bear an obvious relationship; they can be interconverted by formal opening or closing of a three-membered ring bond. However, this C_{2v} process is forbidden by orbital symmetry.

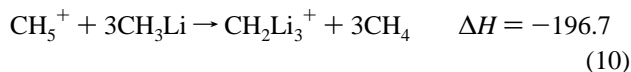
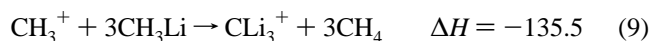
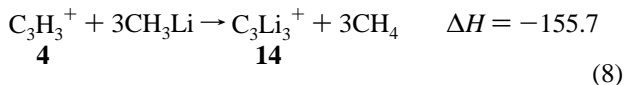
As was the case for the second substitution (eq 4), the third replacement of H by Li^+ (eq 6) still is quite stabilizing, albeit with a further attenuation, roughly 7.7 kcal/mol (eq 6 vs eq 4).



A smaller attenuation (5.1 kcal/mol) is found for the other

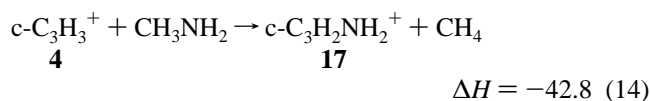
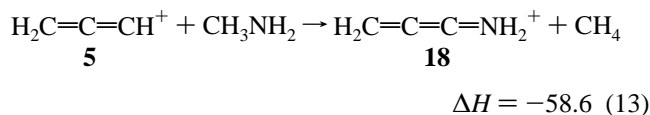
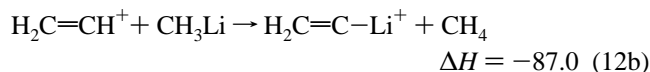
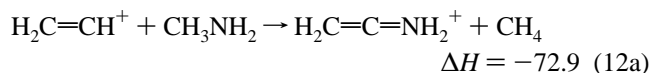
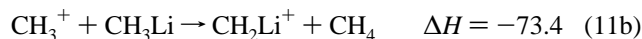
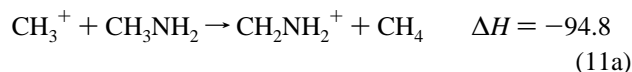


C_3Li_3^+ isomers (eq 7 vs eq 5). It is also of interest to compare the effects of triple lithium substitution of the cyclopropenium ion (eq 8) with that of the methyl cation (to give CLi_3^+ , eq 9) and of CH_5^+ (to give CH_2Li_3^+ , eq 10). The energies of all these three substitutions are remarkably large. Three lithiums stabilize $\text{c-C}_3\text{Li}_3^+$ (**14**, eq 8) even more than CLi_3^+ (eq 9).²⁴



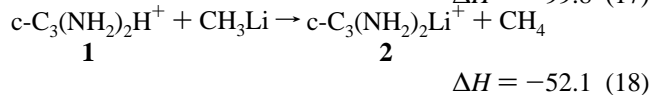
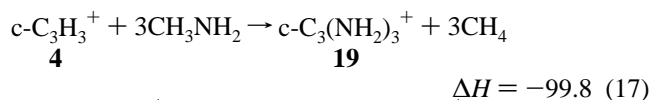
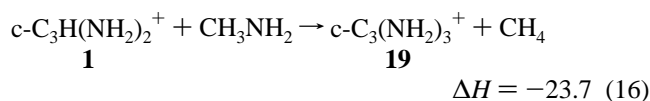
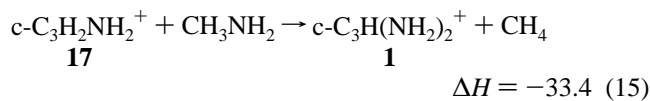
Lithium vs Amino Substitution. Because of its exceptionally strong π -donor ability, the amino group is the most effective methyl cation stabilizing substituent,²⁵ as evaluated by eq 11

(compare with eq 1). But the methyl cation is unusual. We had earlier shown²⁶ that lithium is even more effective than NH_2 in stabilizing the ethyl and vinyl cations (eq 12). The same is also true for the allenyl (compare eq 13 with eq 3) and the cyclopropenyl cations (compare eq 14 with eq 2).



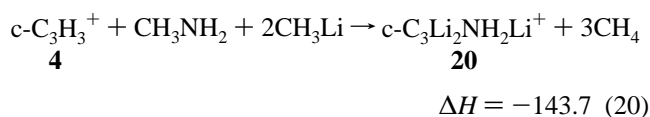
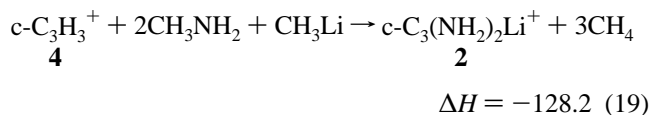
Hopkinson and Lien,¹² in their investigation of the effect of π -donor substituents on the stabilization of cyclopropenium cations, also called attention to the decreasing ability of amino groups to influence the more stable carbocations. The reason is apparent. The greater the number of π -donor (including hyperconjugating) substituents, the less effective each additional replacement can be. As the aromatic cyclopropenium ion has a highly stable π -system, the additional π -stabilization afforded by amino groups is relatively small. In contrast, lithium stabilizes in a complementary fashion, by σ -donation. Hence, lithium substitution enhances the stability of π -stabilized carbocations nearly as much (eq 2) or even more (eq 3) than the methyl cation (eq 1).

Similar isodesmic reactions can be employed to evaluate the stabilization due to further substitution of amino groups. The reaction energies of eqs 14–20 (also given in Table 2) show the effects of sequential amino substitutions. These should be compared with the corresponding eqs 2, 4, 6, and 8 for sequential lithium substitution.



(25) (a) Bernardi, F.; Bottoni, A.; Venturini, A. *J. Am. Chem. Soc.* **1986**, *108*, 5395. (b) Kapp, J.; Schade, C.; El-Nahasa, A. M.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 2236 and references therein.

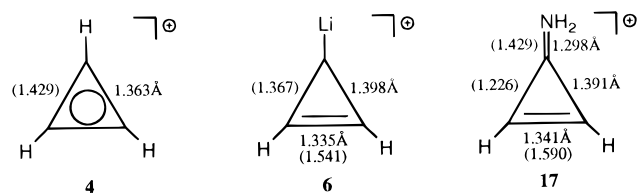
(26) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 5901.



The stabilization energies for the first, second, and third NH₂ substitution, 42.8, 33.4, and 23.7 kcal/mol, respectively, (eqs 14–16) are uniformly lower than the corresponding values for sequential Li substitution (67.0, 48.2, and 40.5 kcal/mol; Table 2, eqs 2, 4, and 6). The combined stabilization of 155.7 kcal/mol (eq 8) due to three Li substituents is larger than the total effect of three NH₂ groups (99.8 kcal/mol, eq 17). The stabilization energy per additional group attenuates with increasing number of substituents both for Li and for NH₂ replacements. The same is true when σ -donor (Li) and a π -donor (NH₂) are combined. This is probed in eq 18 which is a model for the experimentally observed conversion of **1** into **2**.⁷ While the additional stabilization afforded by Li substitution of *c*-C₃H-(NH₂)₂ is 14.9 kcal/mol less than that of the parent cyclopropenium ion (eq 2), the effect is still very large. Assuming an additivity of the individual stabilization energies [67.0 kcal/mol for the first Li (eq 2), 42.8 and 33.4 kcal/mol for the first and second NH₂ groups (eqs 14 and 15)], 143.2 kcal/mol can be estimated for eq 19. The calculated value (128.2 kcal/mol), although 15.0 kcal/mol lower due to attenuation, is still larger than the stabilization afforded by three NH₂ substituents (eq 17). Simple stabilization energy additivity indicates that two Li and one NH₂ substituents would be the ideal combination for the cyclopropenium ion [67.0 and 48.2 kcal/mol for the first and second Li (eqs 2 and 4) and 42.8 kcal/mol for the NH₂ (eq 14) gives an estimate of 158.0 kcal/mol]. The calculated value, 143.7 kcal/mol (eq 20), although 14.3 kcal/mol less than the estimated value due to attenuation, is still better than the combination of one Li and two NH₂'s.⁷ However, the largest stabilization is predicted for three Li substituents (eq 8).

Structural Comparisons of Lithium- and Amino-Substituted Cyclopropenium Ions. The B3LYP-optimized geometries for **1**–**20** are given in Figure 1 along with the “natural” charges (in italics) obtained from natural population analysis.²¹ The propargyl cation **5** has bond lengths expected for triple and double bonds, but when the hydrogens are substituted for lithiums along the **7**, **11**, **16** series, the difference between the two C–C bond lengths is reduced considerably. The C–C distances in **16** resemble those in substituted allenes. When the CH₂ terminus is lithiated, as in **8** and **12**, bond equalization occurs to a lesser extent. The trilithiated structures **3** and **14** have rather long C–C distances (1.409 and 1.420 Å, respectively). The bridged isomer of **3** is lower in energy because the lithium cations prefer higher coordination to the negatively charged centers. The natural charges in Figure 1 demonstrate that the bonding in the lithiated systems is almost completely ionic. Although the hydrogen charges decrease along the C₃H₃⁺ (**4**) > C₃H₂Li⁺ (**6**) > C₃HLi₂⁺ (**10**); C₃H₃⁺ (**4**) > C₃H₂(NH₂)⁺ (**17**) > C₃H(NH₂)₂⁺ (**2**) series (Figure 1), the ionic character of the C–H bonds (as obtained from the difference between the carbon and hydrogen charges) increases. This also explains the H/Li exchange in amino substituted cyclopropenium ions observed experimentally.⁷

The structural consequences of the two different substituents (Li and NH₂) on the C₃ skeleton are somewhat similar. A single Li or NH₂ substituent elongates the adjacent C–C and shortens the distal bonds (**4**, **6**, and **17**). The magnitude of the changes is larger with Li than with NH₂. With two Li or NH₂



substituents, the C–C bond between both substituents is lengthened considerably (1.442 Å in the dilithio derivative **10**, 1.495 Å in the doubly bridged structure **13**, and 1.403 Å in the diamino derivative, **1**). Triple substitution restores the 3-fold symmetry with intermediate C–C distances (1.409 Å in **3** and 1.379 Å in **19**).

Even though Li and NH₂ groups stabilize cyclopropenium ions, both substituents lengthen the adjacent C–C bonds. This is due to different reasons.²⁷ The Li effect arises from σ -electron donation (as shown above for **6** with the Wiberg bond indices given in parentheses), whereas the C=N character involving the π -donor substituent, NH₂, decreases the bond order of the adjacent C–C bond (see **17** above). The calculated C–C (1.379 Å) and C–N (1.327 Å) distances in the triamino cyclopropenyl cation **19** (Figure 1) are comparable to those found in the X-ray structure (C–C = 1.363 Å; C–N = 1.333 Å) of the substituted derivative, *c*-C₃(NMe₂)₃⁺.^{28b}

NMR Chemical Shifts of Lithium- and Amino-Substituted Cyclopropenium Ions. The ¹H, ⁶Li, and ¹³C NMR chemical shifts of the cyclopropenium cation and its lithium derivatives calculated both at GIAO-Becke3LYP/6-311+G* and GIAO-HF/6-31+G*²⁹ using the B3LYP-optimized geometries have quite unusual features (Table 3). The Becke3LYP-computed chemical shifts are discussed (these agree more satisfactorily with experimental values than the HF values, given in parentheses in Table 3). The ¹³C and ¹H chemical shifts of 178.0 and 10.5 of the cyclopropenium ion (**4**) compare well with the experimental values (177 and 11.1, respectively).^{22c,30} Monolithiation increases the chemical shifts, but more so for the carbons adjacent to lithium, e.g., for **6**: 232.9 for C(Li) and 196.3 for C(H). The ¹H chemical shifts are at very low field, 10.5 in C₃H₃⁺ and 11.0 in *c*-C₃H₂Li⁺. Dilithiation continues this trend; for **10**, the C(Li) chemical shift is 251.6 and C(H) is 217.4. There is a 11.4 ppm difference between the ¹³C chemical shifts calculated for the two trilithium isomers (**3**, 277.0; **14**, 288.4). These data should help characterize these species, should they be made experimentally.

The ⁶Li chemical shifts also show a larger spread. The δ values, 4.3 for *c*-C₃H₂Li⁺ (**6**), 5.9 for *c*-C₃HLi₂⁺ (**10**), 7.5 for *c*-C₃Li₃⁺ (**3**), and 10.1 for *c*-C₃(μ -Li)₃⁺ (**14**), are more shielded than computed for the nonaromatic cyclic analogues, C₃H₃Li (**25**) and C₃H₂Li₂ (**26**, Table 3). Experimental NMR data is available only on highly substituted amino derivative of **17** (¹³C(1) = 99.0; ¹³C(2,3) = 133.7). The observed values are in excellent agreement with the computed values (¹³C(1) = 102.8; ¹³C(2,3) = 138.5) for the diamino cyclopropenyl cation **1** (Table 3).

Aromaticity of Lithiated Cyclopropenium Ions. The aromaticity of lithiated cyclopropenium ions are demonstrated

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by the geometric (bond length alternation, Δr),^{31d-h,j} magnetic [¹H NMR chemical shifts,^{31a} magnetic susceptibility anisotropy (χ_{anis}),^{31c} exaltations (Λ),^{31b} and the nucleus independent chemical shifts (NICS)],³¹ⁱ and energetic (stabilization energies, SE) criteria.^{31d-g} Because of their D_{3h} symmetry, **3**, **4**, and **14** ($\Delta r = 0.0 \text{ \AA}$) might be more delocalized (Table 4) than **6** ($\Delta r = 0.063 \text{ \AA}$) and **10** ($\Delta r = 0.074 \text{ \AA}$). However, the change in Δr is attributed to the consequences of the σ -electron donating Li substituent rather than to decreased π -delocalization. This is shown by the ¹H NMR chemical shifts in Table 4. The protons in C_3H_3^+ (**4**) are shifted 3.4 ppm downfield compared to the olefinic protons in cyclopropene (**21**, Table 3) due to the cyclic π -delocalization and aromaticity in **4**. A single lithium substitution, as in **6**, leads to a further downfield ¹H shift (0.5 ppm relative to **4** and 3.5 ppm relative to the olefinic hydrogens in **25**). Double Li substitution (**10**) results in a 1.3 ppm downfield shift (Table 3) compared to **4**, suggesting an increase in the diatropic ring current in cyclic $\text{C}_3\text{H}_3-n\text{Li}_n$ ($n = 0-3$) series.

The magnetic susceptibility exaltation, which is a primary manifestation of aromaticity,^{31b,h,i,32} reveals all the lithiated cyclopropenium ions (**3**, **6**, **10**, and **14**) to be significantly aromatic, since the Λ values computed using eqs 21–24 (Figure 2) are highly negative and vary between -8.8 to -15.2 ppm cgs (Table 4). In addition, the computed magnetic susceptibility anisotropies (χ_{anis} , ppm cgs)^{31c,32} show the aromaticity to increase upon lithiation [-29.4 (**4**) < -35.2 (**6**) < -41.2 (**10**) < -48.4 (**3**) < -57.2 (**14**)] in accord to the increasing downfield ¹H chemical shifts. Further evidence for ring current effects are revealed from the computed NICS values.^{31i,33} Since the NICS values in the molecular plane [NICS(0)] are influenced by local contributions³² (for example, the C–C, C–H, and C–Li σ -bonds) of the three-membered ring, we consider the NICS(1) values³³ (where such bond contributions are minimized) to be better indicators of aromaticity trends in lithiated cyclopropenium ions (Table 4). Indeed, the NICS(1) values are all negative and range from -16.0 to -23.7 ppm, again showing enhanced aromaticity upon increasing lithium substitution. In addition, the most stable C_3Li_3^+ isomer, **14**, has a larger NICS(1) value (-23.7 ppm) than the classical alternative, **3** [NICS(1) = -21.6 ppm].

The SE's for **3**, **4**, **6**, and **14** were also evaluated from eqs 21–24 (Figure 2). The B3LYP-computed SE's for the cyclopropenyl cation (**4**, -59.0 kcal/mol, eq 21, Table 4) are in excellent agreement with the recent G2 value (-59.1 kcal/mol).^{9c} The SE of **6** (56.6 kcal/mol, eq 22, Table 4) is less than that of **4** due to the influence of lithium in the reference compound **24** (eq 25; also note eq 26). Increasing lithium substitution clearly results in a greater stabilization: **6** $<$ **10** (SE = -84.1 kcal/mol) $<$ **3** (SE = -95.1 kcal/mol). The SE of bridged C_3Li_3^+ (**14**) is even larger, -104.2 kcal/mol.

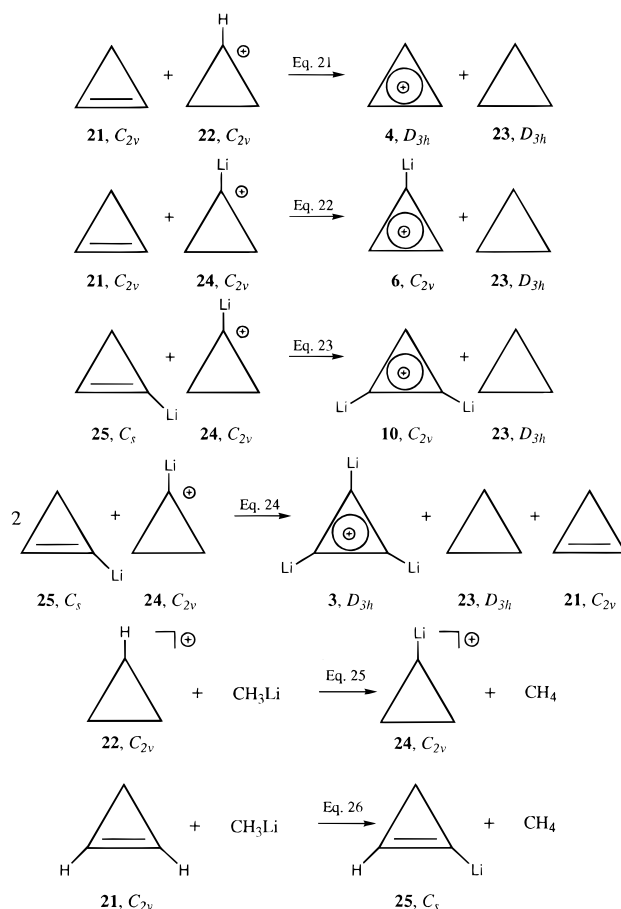


Figure 2. Schematic representation of the reactions (eqs 21–26) used to evaluate the stabilization energies (SE, kcal/mol) and magnetic susceptibility exaltations (Λ , ppm cgs for eqs 21–24) given in Table 5.

Vibrational Frequencies of Lithium and Amino-Substituted Cyclopropenium Ions. The lithiated cyclopropenium ions may also be characterized by vibrational spectroscopy. Experimental frequencies (cm^{-1}) are known for the cyclopropenyl cation (**4**)³⁴ [3183, 1626 (a_1'); 1031 (a_2'); 3138, 1290, 927 (e'); and 990 (e'')], but such IR data are not available for the lithiated derivatives (**6**, **10**, **3**, and **14**). Apart from the symmetric (3295.6 cm^{-1}) and asymmetric (3245.4 cm^{-1}) C–H stretching vibrations of **4** (which are overestimated somewhat compared to experimental values), all of the B3LYP/6-311+G* computed normal modes (Table 5) are in excellent agreement with experiment.^{34a} This calibrates our computational results for the unknown compounds. As evident from Table 5, the C–H symmetrical stretch (a_1' or a_1) decreases from 3296 (**4**) to 3279 (**6**) and to 3226 cm^{-1} (**10**) as a function of lithium substitution. The symmetrical C–C stretching frequencies (a_1' or a_1) also follow similar trends (1665.3 (**4**) $>$ 1661.7 (**6**) $>$ 1635.6 (**10**) $>$ 1595.3 (**3**) $>$ 1501.8 (**14**) cm^{-1}); the C_3Li_3^+ isomer (**3**, **14**) data are the lowest in the series. The asymmetric e' stretch involving the $\text{C}^1\text{--C}^2$ and $\text{C}^1\text{--C}^3$ bonds (see Table 3 for atom numbering) in **4** (1308.3 cm^{-1}), **3** (1099.4 cm^{-1}), and **14** (1098.7 cm^{-1}) splits into the a_1 (1364.9 cm^{-1} in **6**; 1051.0 cm^{-1} in **10**) and b_2 (1148.4 cm^{-1} in **6**; 1327.9 cm^{-1} in **10**) normal modes in the corresponding C_{2v} structures. The computed normal modes given in Table 5 also should help in characterizing the lithiated and amino-substituted cyclopropenium ions.

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Adiabatic Ionization Energies of Lithiated Cyclopropenium Ions. The energies of the radicals, also fully optimized at B3LYP (using the unrestricted formalism) and characterized as energy minima, were used to compute the adiabatic ionization energies [IE = $E(\text{radical}) - E(\text{cation})$]. The IE of CLi_3^* has been measured experimentally;² the very low value of 4.6 eV lies in the middle of the IE range of the alkali metals (Table 6).³⁵ With B3LYP, the singlet state of CLi_3^+ is 12.4 kcal/mol above the triplet ground state. The computed adiabatic IE [$E(^2\text{CLi}_3^*) - E(^3\text{CLi}_3^+)$] of 4.37 eV agrees well with the experimental value and is far closer than the ab initio value (3.8 eV) reported earlier.⁶ Similarly, the computed IE (6.12 eV) of the cyclopropenyl and propargyl radicals (8.66 eV) compare well with the experimental values of 6.6 and 8.68 eV, respectively.³⁵ The difference between the computed and experimental IE's is the largest for cyclopropenyl radical. However, our B3LYP estimate (6.12 eV) is better than the G2 results (IE = 6.06 eV) by Glukhovtsev et al.^{9c} Also note the agreement between the computed and experimental IE's for the alkali metals given in Table 6.

The adiabatic IE's decrease with increasing lithium substitution along the **6**, **10**, **3**, and **14** series; the trend is similar to the corresponding $\text{CH}_n\text{Li}_{3-n}$ ($n = 0-3$) species (Table 6). The computed IE (3.18 eV) for the classical trilitiated species, C_3Li_3^* , is even lower than that for a cesium atom (3.96 eV)! Although, the IE for $\text{C}_3(\mu\text{-Li})_3^*$ is slightly higher (3.35 eV) than its classical C_3Li_3^* alternative, this IE still is very low in comparison to the values given in Table 6. The thermodynamic stability of C_3Li_3^+ is remarkable.

Conclusions

Benefitting from large "aromatic" stabilization, the cyclic $\text{C}_3\text{H}_n\text{Li}_{3-n}^+$ ($n = 0-3$) structures are always favored over their acyclic alternatives. The downfield ¹H NMR chemical shifts and the magnetic susceptibility anisotropies (> -29.4 ppm cgs) as well as the NICS(1) values (> -16.0 ppm) demonstrate increasing aromaticity of cyclopropenium ions (**3**, **4**, **6**, **10**, and **14**) upon successive lithium substitution.

Lithium substitution stabilizes carbenium ions considerably inductively (e.g., over 70 kcal/mol both in CH_2Li^+ and in $\text{c-C}_3\text{H}_2\text{Li}^+$). Successive lithiation along the $\text{C}_3\text{H}_2\text{Li}^+$, $\text{C}_3\text{H}\text{Li}_2^+$, C_3Li_3^+ series results in attenuation (the stabilizations for **6**, **10**, and **14** are 67.0, 48.2, and 40.5 kcal/mol, respectively). However, the falloff in these lithium-substituted cyclopropenium ions is somewhat less than the attenuation along the CH_2Li^+ , CHLi_2^+ , and CLi_3^+ series. Sequential NH_2 substitution shows similar behavior, but the magnitudes of the stabilization are reduced. A combination of NH_2 and Li substituents is more stabilizing than three NH_2 groups, but three Li substituents are even better. Both the Li and the NH_2 substituents elongate the adjacent C-C bonds; former through hyperconjugation and the latter by π -localization. The B3LYP-computed ¹³C, ¹H, and ⁶Li chemical shifts increase with increasing lithium substitution. The agreement between the B3LYP-computed and observed chemical shifts and vibrational frequencies for **4** should aid in identifying the unknown $\text{C}_3\text{H}_n\text{Li}_{3-n}$ ($n = 0-3$) cations.

The adiabatic IE's of cyclic $\text{C}_3\text{H}_n\text{Li}_{3-n}$ ($n = 0-3$) radicals decrease with increasing lithium substitution. They are considerably lower than the IE's of their $\text{CH}_n\text{Li}_{3-n}$ ($n = 0-3$)

counterparts and are comparable to those of alkali metal atoms. The computed IE of $\text{c-C}_3\text{Li}_3^*$ (3.18 eV) is even lower than the cesium atom (3.96 eV).

The great stability of C_3Li_3^+ suggests that it might be persistent in solution, provided suitable conditions can be found. The trichlorocyclopropenium ion resembles carbenoids in some of its reaction;³⁶ metal-halogen exchange might lead to C_3Li_3^+ in solution. Although trialkylsilyl groups are destabilizing (compared to the alkyl groups) when attached to a carbenium ion center,³⁷ the tris(trimethylsilyl)cyclopropenylum cation³⁸ has been synthesized recently and characterized by X-ray diffraction. This cation also might be a good starting material for the preparation of lithiated cyclopropenium ions experimentally. Attention also is called to the X-ray structure of [$\{\text{Fe}(\text{CO})_2\text{Cp}\}_3(\mu_3\text{-C}_3)\text{][SbF}_6\text{]}^{39}$ and its relation to **4** and **19**,⁴⁰ as well as to the Schmidbaur et al.'s highly substituted aurocarbocations⁴¹ which are related to the lithiocarbocations, e.g., CLi_5^+ and CLi_6^{2+} .⁴ A monolithiated cyclopropenium ion has been characterized experimentally⁷ with two stabilizing dialkyl amino substituents (**2**, see introduction) as has the analogous bis-(diisopropylamino)cyclopropenium perchlorate⁴² (a substituted derivative of **1**). Our results (eq 19 vs eq 20) show that one NH_2 and two Li substituents should be more stabilizing than two NH_2 and one Li substituents, so that further experimental explorations of lithiocyclopropenium ion chemistry should be rewarding.

Acknowledgment. We dedicate this paper to Prof. John A. Pople in commemoration of our joint research on lithium chemistry. We also thank Dr. Peter S. Gregory and Dr. M. N. Glukhovtsev for their contributions to this project and Prof. R. Weiss for suggestions. Financial support from the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie and at Hyderabad, by the Department of Science and Technology, New Delhi, is acknowledged as well as the Alexander von Humboldt Foundation for a postdoctoral fellowship to G.S.

Supporting Information Available: HF, MP2, MP4, and Becke3LYP total (hartrees) and zero-point energies (kcal/mol) and the number of imaginary frequencies for **1-20** along with those for reference compounds needed to evaluate the thermochemical equations (2 pages). See any current masthead page for ordering and Internet access instructions.

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