J. Am. Chem. Soc. **1982**, *104*, 4275–4276

Lithiated Carbocations. The Generation, Structure, and Stability of CLi_5^+

Eluvathingal D. Jemmis,[†] Jayaraman Chandrasekhar,
Ernst-Ulrich Würthwein, and Paul von Ragué Schleyer*

Institut für Organische Chemie
der Friedrich-Alexander-Universität Erlangen-Nürnberg
D-8520 Erlangen, Federal Republic of Germany

John W. Chinn, Jr., Frederick J. Landro, and
Richard J. Lagow*

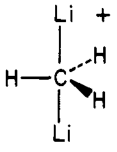
Department of Chemistry, University of Texas at Austin
Austin, Texas 78712

Brian Luke and John A. Pople*

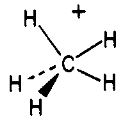
Department of Chemistry, Carnegie-Mellon University
Pittsburgh, Pennsylvania 15213

Received December 16, 1981

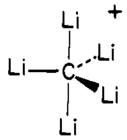
A search for unusual geometries and coordination at carbon led to the theoretical prediction that $CH_3Li_2^+$ (**1**) prefers D_{3h} symmetry and a linear three-center two-electron bond.[1] In contrast, the parent carbonium ion, CH_5^+, is indicated to have the C_s structure, **2**, with a closed three-center two-electron bond.[2] $CH_3Li_2^+$ was calculated to be quite stable toward all possible decomposition pathways.[1] Experimentally, $CH_3Li_2^+$ appears as the base peak in the mass spectrum of the pyrolysis products of $LiB(CH_3)_4$.[3] Ions with the composition RLi_2^+ generally are the base peaks in the mass spectra of alkyllithium compounds.[4] The flash vaporization mass spectrum of $(CH_3Li)_n$ is now found also to give $CH_3Li_2^+$ ions (81% intensity relative to the base peak, $(CH_3Li)_2^+$).[5] Encouraged by these results, we have extended our studies to CLi_5^+ (**3**), the subject of the present paper. We also consider the possible dication, CLi_6^{2+} (**4**).



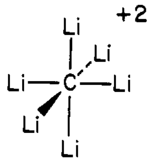
1 D_{3h}



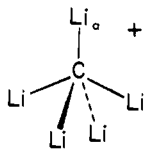
2 C_s



3 D_{3h}



4 O_h



3′ C_{4v}

Table I. STO-3G, 3-21G, and 4-31G Energies (au)[a]

species	STO-3G// STO-3G	3-21G// 3-21G	4-31G// 4-31G
H_2	−1.117 51	−1.122 96	−1.126 83
Li^+	−7.135 45	−7.187 09	−7.233 26
Li_2	−14.638 75	−14.769 25	−14.860 66
Li_3^+ (D_{3h})	−21.858 47	−22.02368	−22.163 29[b]
CH_3^+	−38.779 48	−39.009 13	−39.175 12
CLi_3^+ (D_{3h})[c]	−59.175 76	−59.586 03	−59.875 62
CH_4	−39.726 86	−39.976 88	−40.139 77
CH_5^+ (C_s)	−39.918 87	−40.160 56	−40.327 15
CLi_4 (T_d)	−66.666 68[d]	−67.131 54	−67.466 85[b]
CLi_5^+ (**3**, D_{3h})[b]	−73.938 22	−74.454 40	−74.833 37
(**3′**, C_{4v})[b]	−73.936 65	−74.453 13	−74.831 47
CLi_6^{2+} (**4**, O_h)[b]	−81.053 27	−81.63028	−82.052 39

[a] STO-3G and 3-21G energies may be found in Whiteside et al. (Whiteside, R. A.; Frisch, M. J.; Binkley, J. S.; DeFrees, D. J.; Schlegel, H. B.; Raghavachari, K.; Pople, J. A. "Carnegie-Mellon Chemistry Archive", Pittsburgh, PA, 2nd ed., 1981 (available from Pople, J. A.)). For 4-31G energies, see ref 1. [b] This work. [c] Energies for the $^1A_1'$ singlet are given, but the CLi_3^+ ground state probably is a triplet; see ref 11a. [d] Collins, J. B.; Dill, J. D.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, J. A. *J. Am. Chem. Soc.* 1976, *98*, 5419.

Two approaches were employed. The stability of CLi_5^+, first probed with the use of SCF-MO calculations in 1976, was indicated to be so favorable that experimental verification was sought. The ion has now been observed in the gas phase along with many other intriguing lithiated carbocations.

Ab initio SCF-MO calculations were carried out with the GAUSSIAN 70, 76, and 80 series of programs[6] using STO-3G, 3-21G, and 4-31G (5-21G for Li) basis sets[7] with full geometry optimization. An additional detailed potential energy search used the MNDO method, with parameters for Li developed by Thiel and Clark.[8] With the minimal STO-3G basis, only one minimum on the CLi_5^+ potential-energy surface, corresponding to **3**, was found. Several C_s and C_{3v} structures collapsed to the D_{3h} structure (**3**) on geometry optimization. The MNDO search also indicated **3** to be the global energy minimum. Calculation of the harmonic frequencies of CLi_5^+ (3-21G//3-21G) confirms the D_{3h} structure (**3**) to be a minimum.[9] General experience indicates that the frequencies calculated at this level (in cm^{-1}: 102 (e′), 304 (e′), 326 (a_2''), 337 (e″), 496 (a_1'), 536 (a_1'), 664 (a_2''), and 675 (e′)) are expected to be ca. 12% higher than experimental values.[9]

The geometric parameters of **3** (D_{3h}) at STO-3G [3-21G] (4-31G) are $C–Li_e$ = 1.953 [1.999] (1.981) Å, $C–Li_a$ = 1.979 [2.022] (2.010) Å. This follows the general trend that axial bonds in D_{3h} pentacoordinate species are longer than equatorial bonds.[10] The STO-3G charges on the axial lithiums, 0.21, are slightly larger than those, 0.20, on the equatorial ones. The carbon (−0.02) is

---

[†] Present address: School of Chemistry, University of Hyderabad, Hyderabad 500134, India.

(1) Jemmis, E. D.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1979**. *101*, 527.

(2) (a) Dyczmons, V.; Kutzelnigg, W. *Theor. Chim. Acta* **1974**, *33*, 239. (b) Radom, L.; Poppinger, D.; Haddon, R. C. "Carbonium Ions"; Olah, G. A., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1976; Vol. V, Chapter 38. (c) Smith, R. D.; Futrell, J. H. *Chem. Phys. Lett.* **1975**, *36*, 545. (d) Collins, J. B.; Schleyer, P. v. R.; Pople, J. A.; Radom, L. *J. Am. Chem. Soc.* **1976**, *98*, 3436. (e) Krishnan, R.; Whiteside, R. A.; Pople, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1981**, *103*, 5649.

(3) Stucky, G., private communication. See: Rhine, W. E.; Stucky, G.; Petersen, S. W. *J. Am. Chem. Soc.* **1975**, *97*, 6401.

(4) (a) Berkowitz, J.; Bafus, D. A.; Brown, T. L. *J. Phys. Chem.* **1961**, *65*, 1380. (b) Brown, T. L. *Ann. N.Y. Acad. Sci.* **1966**, *136*, 98.

(5) Chinn, J. W., Jr.; Gurak, J. A.; Lagow, R. J., unpublished observations.

(6) (a) Hehre, W. J.; Lathan, W. A.; Newton, M. D.; Ditchfield, R.; Pople, J. A. *QCPE* **1973**, *11*, 236. (b) Binkley, J. S.; Whiteside, R. A.; Hariharan, P. C.; Seeger, R.; Pople, J. A.; Hehre, W. J.; Newton, M. D. *Ibid.* **1978**, *11*, 368. (c) Binkley, J. S.; Whiteside, R.; Krishnan, R.; Seeger, R.; Schlegel, H. B.; DeFrees, D. J.; Topiol, S.; Kahn, L. R.; Pople, J. A. *Ibid.* **1981**, *11*, 406.

(7) (a) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1959**, *51*, 2657. (b) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *Ibid.* **1971**, *54*, 724. (c) Hehre, W. J.; Pople, J. A. *Ibid.* **1972**, *56*, 4233. Dill, J. D.; Pople, J. A. *Ibid.* **1975**, *62*, 2921; (d) Binkley, J. S.; Pople, J. A.; Hehre, W. J. *J. Am. Chem. Soc.* **1980**, *100*, 939.

(8) (a) Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*, 4899. (b) Lithium parameterization: Thiel, W.; Clark, T., to be submitted for publication.

(9) Pople, J. A.; Krishnan, R.; Schlegel, H. B.; Binkley, J. S. *Int. J. Quantum Chem.* **1979**, *S13*, 325.

(10) Gimarc, B. M. "Molecular Structure and Bonding, The Qualitative Molecular Orbital Approach"; Academic Press: New York, 1979; p 96.

(11) See: Hiraoka, K.; Kebarle, P. *J. Am. Chem. Soc.* **1976**, *98*, 6119.

0002-7863/82/1504-4275$01.25/0

Table II. Selected Ions from the Flash Vaporization Mass Spectrum of the Product Mixture from the Reaction of Lithium Vapor and CCl_4

positive ion	*m/e*	positive ion	*m/e*
CLi	19	C_2Li_8	80
CLi_2	26	C_3Li_{11}	113
CLi_3	33	C_3L_{12}	120
CLi_4	40	C_3Li_3	69
CLi_5	47	C_4Li_4	76
C_2Li	31	C_6Li_5	107
C_2Li_2	38	C_6Li_6	114
C_2Li_7	73		

indicated to be nearly electroneutral at this level. Absolute energies of **3** along with those of the species used in eq 1–7 are given in Table I.

By imposition of C_{4v} symmetry, an additional CLi_5^+ isomer, **3′**, could be calculated. The unique C–Li$_a$ bond distance is 1.959 (1.998) Å at STO-3G(3-21G); C–Li$_b$ = 1.965 (2.012 Å) and Li$_a$CLi$_b$ = 101.5° (101.2°). The energies of **3′** (C_{4v}) are only 1.0 (0.8) kcal/mol, STO-3G(3-21G), above those of **3** (D_{3h}). Hence, the energy surface of CLi_5^+ should be extremely flat, with almost no activation required for scrambling (pseudorotation).

The large exothermicity of eq 1 and 2 indicates the stability

	energies, kcal/mol				
	STO-3G	3-21G	4-31G	exptl	
$CLi_4 + Li^+ \rightarrow CLi_5^+$	−85.4	−85.2	−83.6	-	(1)
$CLi_3^+ + Li_2 \rightarrow CLi_5^+$	−77.6	−62.2	−60.9	-	(2)
$CH_4 + H^+ \rightarrow CH_5^+$	−120.5	−115.3	−117.6	−127[11]	(3)
$CH_3^+ + H_2 \rightarrow CH_5^+$	−13.7	−17.9	−15.8	−40[11]	(4)

of CLi_5^+ toward the most likely modes of dissociation. The enormous stabilization of both carbonium ions[1] and carbenium ions[12] by Li substitution has been noted earlier. Both CLi_3^+ and, possibly, CLi_4^+ have been reported experimentally.[13] These ions, CLi_5^+, and many other lithiated carbocations are found in the present study (Table II). Even though the H^+ affinity of CH_4 (eq 3) is considerably higher than the Li^+ affinity of CLi_4 (eq 1), CH_5^+ has a more favorable decomposition pathway (eq 4) compared to CLi_5^+ (eq 2). Since the basis sets employed here underestimate the stability of CH_5^+, errors in CLi_5^+ are likely to be in the same direction. The theoretical prediction that CLi_5^+ should be very stable thermodynamically has now been confirmed experimentally.

Tetralithiomethane, $(CLi_4)_n$, was prepared by the Lagow procedure by reacting lithium vapor with carbon tetrachloride.[14] A sample of the solid $(CLi_4)_n$, which must be handled under argon, was then studied with a specially designed flash vaporization mass spectrometric probe, capable of nonequilibrium vaporization of the sample at 1500 °C.[15] A selection of peaks observed mass spectrally are given in Table II. The elemental composition of CLi_5^+ (47.0800 amu) was established by exact mass measurements. Besides the observation of CLi_5^+ for the first time, the results establish that CLi_4 was produced;[14] its dimer, C_2Li_8, and trimer, C_3Li_{12}, are also indicated to be present. CLi_3^+ and its CLi_4 complex, $C_2Li_7^+$, also are found, as are $(C_2Li_2)_n^+$ (n = 1–3) and corresponding ions in which one lithium atom has been lost.

We considered CLi_6^{2+} next. Would the stabilizing influence of the six lithiums overcome the electrostatic repulsion inherent in dications? We probed only the most likely octahedral symmetry, **4**. The optimized C–Li distances were 2.063 Å at STO-3G, 2.094 Å at 3-21G, and 2.090 Å at 4-31G. Like **3**, the STO-3G charges, C = −0.05 and Li = 0.34, indicate CLi_6^{2+} to have an essentially neutral central carbon bonded to a "sphere" of partially positively charged lithium atoms. The stability toward decompositions was examined by using reactions 5–7. Equations 5 and 6 are exothermic. The only favorable decomposition mode is indicated by eq 7 which, as written, is somewhat endothermic; however, this may change at higher theoretical levels.

	energies, kcal/mol			
	STO-3G	3-21G	4-31G	
$CLi_4 + 2Li^+ \rightarrow CLi_6^{2+}$	−72.6	−78.2	−74.7	(5)
$CLi_3^+ + Li_3^+ \rightarrow CLi_6^{2+}$	−12.0	−12.9	−8.5	(6)
$CLi_5^+ + Li^+ \rightarrow CLi_6^{2+}$	+12.8	+7.0	+8.9	(7)

Further calculations not feasible at present will be needed before the existence of CLi_6^{2+} can be predicted theoretically. However, the STO-3G//STO-3G frequencies indicate octahedral CLi_6^{2+} to be a local minimum; thus, eq 7 should be associated with a kinetic barrier. The electronic structures of these high-symmetry systems, CLi_5^+ and CLi_6^{2+}, follow the general pattern of D_{3h} and O_h molecular orbitals discussed by Gimarc.[10] Since only octets of valence electrons are present, these ions are hypercoordinate but not hypervalent. However, the present results also imply the existence of neutral hypervalent carbon–lithium compounds, e.g., CLi_5 and C_2Li_8. In addition to these species, our calculations (to be reported subsequently) indicate CLi_6^+, CLi_6, and CLi_8 to be stable thermodynamically.[16]

Acknowledgment. This work was supported at Erlangen by the Fonds der Chemischen Industrie and was facilitated by a NATO Grant. Work at the University of Texas was supported by the National Science Foundation and the Robert A. Welch Foundation. Work performed at Carnegie-Mellon University was partially supported by NSF Grant CHE 80-01061-01.

Registry No. H_2, 1333-74-0; Li^+, 17341-24-1; Li_2, 14452-59-6; Li_3^+, 12596-48-4; CH_3^+, 14531-53-4; CLi_3^+, 81506-46-9; CH_4, 74-82-8; CH_5^+, 15135-49-6; CLi_4, 38827-79-1; CLi_5^+, 81616-33-3; CLi_6^{2+}, 81616-34-4.

---

[12] (a) Chandrasekhar, J.; Pople, J. A.; Seeger, R.; Seeger, U.; Schleyer, P. v. R. submitted for publication in *J. Am. Chem. Soc.* (b) Apeloig, Y.; Schleyer, P. v. R.; Pople, J. A. *Ibid.* **1977**, *99*, 1291.

[13] Wu, C. H.; Ihle, H. R. *Chem. Phys. Lett.* **1979**, *61*, 54.

[14] Chung, C.; Lagow, R. J. *J. Chem. Soc., Chem. Commun.* **1972**, 1078.

[15] (a) Shimp, L. A.; Morrison, J. A.; Gurak, J. A.; Chinn, J. W., Jr.; Lagow, R. J. *J. Am. Chem. Soc.* **1981**, *103*, 5951. (b) Guark, J. A.; Chinn, J. W., Jr.; Lagow, R. J. *J. Am. Chem. Soc.* **1982**, *104*, 2637.

[16] Schleyer, P. v. R.; Würthwein, E.-U.; Pople, J. A., unpublished observations.

Inherently Dissymmetric Chromophores and Vibrational Circular Dichroism. The CH_2–CH_2–C*H Fragment

Leo Laux, Vaughan Pultz, S. Abbate, Henry A. Havel,
John Overend, and Albert Moscowitz*

Chemistry Department, University of Minnesota
Minneapolis, Minnesota 55455

David A. Lightner*

Chemistry Department, University of Nevada-Reno
Reno, Nevada 89557

Received April 12, 1982

The concept of the "inherently dissymmetric chromophore"[1] has proved quite useful for the stereochemical interpretation of circular dichroism (CD) spectra of electronic origin.[2] In the present communication we point out that the same concept can be used to marked advantage in the case of vibrational circular dichroism (VCD) spectra.[3,4] We illustrate the point by way of the inherently dissymmetric CH_2–CH_2–C*H fragment ubiquitous in six-membered ring compounds that approximate the chair conformation.

An inherently dissymmetric chromophore is one whose local (inherent) symmetry is sufficiently low that, even in isolation, its associated transitions are both electric and magnetic dipole allowed

---

[1] Mislow, K. "Introduction to Stereochemistry"; W. A. Benjamin: New York, 1965; pp 65–66, 155–160.

[2] Deutsche, C. W.; Lightner, D. A.; Woody, R. W.; Moscowitz, A. *Annu. Rev. Phys. Chem.* **1969**, *20*, 407–448.

[3] Keiderling, T. A. *Appl. Spectrosc. Rev.* **1981**, *17*, 189–226.

[4] Nafie, L. A.; Diem. M. *Acc. Chem. Res.* **1979**, *12*, 296–302.

0002-7863/82/1504-4276$01.25/0 © 1982 American Chemical Society