

Lithiated Hydrocarbons, Their Conjugate Bases, and Corresponding Radicals: A Computational Study of RLi (R = CH₃, CH₃CH₂, CH₂=CH, and HC≡C)

Lawrence M. Pratt*

Department of Chemistry, Fisk University, Nashville, Tennessee 37208

Steven R. Kass*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

kass@chem.umn.edu; lpratt@fisk.edu

Received September 30, 2003

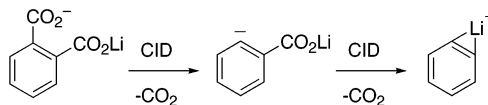
Organolithium compounds RLi (R = CH₃, CH₃CH₂, CH₂=CH, and HC≡C) and their corresponding hydrocarbons were fully optimized at the MP2/6-311+G(2df,2pd) level. Single-point energy calculations also were carried out at the CCSD(T) and B3LYP levels with the same triple split-valence basis set. Acidities, electron affinities, and bond dissociation energies are reported, and the following general results were found: (1) α -Lithio anions are ground-state triplet molecules. (2) Lithium is an acid-enhancing substituent. (3) Conjugate bases of organolithiums are stable with respect to electron loss and therefore are attractive targets for mass spectrometry investigations. (4) Lithium weakens α - and β -C–H bonds, the latter by ~ 25 kcal mol⁻¹. Consequently, radical chemistry of lithiated compounds at remote sites is a promising area for exploration.

Introduction

Anions and dianions, most commonly in the form of their lithio derivatives, play a very important role in organic synthesis. Consequently, organolithium compounds have been the subject of extensive experimental and theoretical investigations.^{1,2} It is generally accepted now that C–Li bonds are largely ionic in nature and that novel bridging structures often arise in order to minimize electrostatic interactions.^{2a,3} Aggregation, solvation, and salt effects, however, are intricately related and bedevil our understanding of these species. A detailed investigation of monomeric lithium-containing compounds in the absence of these complicating factors therefore would be of value.

Recently, a mass spectroscopic method that takes advantage of the synthetic capabilities of electrospray ionization was reported, and the conjugate bases of phenyllithium were prepared.⁴ This was accomplished, for example, by spraying the monolithium salt of terephthalate into a Fourier transform mass spectrometer

SCHEME 1



and fragmenting it in two stages (Scheme 1). The resulting σ -C₆H₄Li⁻ ion is less basic than phenyl anion, which makes lithium an acid-enhancing substituent in this case. To explore the generality of this finding and identify suitable targets for gas-phase studies, we have carried out high-level computations on a series of lithio carbanions and their corresponding hydrocarbons. More specifically, the structures, acidities, electron affinities, and bond energies of RLi (R = CH₃, CH₃CH₂, CH₂=CH, and HC≡C) are reported.

Computational Methods

Ab initio and density functional computations were carried out using Gaussian 98 or Gaussian 03 on supercomputers at the Minnesota Supercomputer Institute and on IBM, SGI, and Pentium workstations at the University of Minnesota and Fisk University.^{5,6} Geometry optimizations were carried out at the MP2 level of theory with the 6-311+G(2df,2pd) basis set using the frozen-core approximation. Each of the resulting structures were subject to a vibrational frequency analysis to ensure that all of the reported species correspond to potential energy minima and to provide zero-point energy (ZPE) and temperature corrections from 0 to 298 K. Single-point energy determinations using the same basis set were carried out at the coupled cluster level with noniterative triple excitations (CCSD(T))⁷ and with density functional theory using the B3LYP hybrid functional.⁸ All of the resulting energetic

(4) Bachrach, S. M.; Hare, M.; Kass, S. R. *J. Am. Chem. Soc.* **1998**, *120*, 12646–12649.

* Corresponding author.

(1) (a) Hodgson, D. M. *Top. Organomet. Chem.* **2003**, *5*, 1–320. (b) Bickelhaupt, F. *Chem. Soc. Rev.* **1999**, *28*, 17–23. (c) Wakefield, B. J. *Organolithium Methods*; Pergamon Press: New York, 1988; pp 1–189. (d) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353–451. (e) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: New York, 1974; pp 1–335.

(2) (a) *Lithium Chemistry: A Theoretical and Experimental Overview*; Sapse, A.-M., Schleyer, P. v. R., Eds.; Wiley-Interscience: New York, 1995; pp 1–595. (b) Lambert, C.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1129–1140. (c) Sannigrahi, A. B.; Kar, T.; Niyogi, B. Guha; Hobza, P.; Schleyer, P. v. R. *Chem. Rev.* **1990**, *90*, 1061–1076. (d) Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *56*, 151–162.

(3) (a) Streitwieser, A. *Acc. Chem. Res.* **1984**, *17*, 353–357. (b) Ritchie, J. P.; Bachrach, S. M. *J. Am. Chem. Soc.* **1987**, *109*, 5909–5916. (c) Bachrach, S. M.; Streitwieser, A. *J. Am. Chem. Soc.* **1984**, *106*, 5818–5824.

TABLE 1. Computed MP2/6-311+G(2df,2pd) Geometries for RLi (R = CH₃, CH₃CH₂, CH₂=CH, and HC≡C) and Their Conjugate Bases^a

compd	parameter					
	C–Li	C–C	C–H _α	C–H _β	Li–C–C	Li–C–H _α
CH ₃ Li (C _{3v})	1.986 (1.959)		1.095 (1.111)			112.6 (106.2)
LiCH ₂ [−] (C _s , ¹ A)	1.907		1.100			124.0
LiCH ₂ [−] (C _{2v} , ³ A)	1.997		1.100			127.4
LiCH ₂ CH ₃ (C _s)	2.008	1.538	1.097	1.096, 1.092	117.8	108.5
LiCHCH ₃ [−] (C ₁ , ¹ A)	1.840	1.541	1.124	1.112, 1.102, 1.100	142.9	109.3
LiCHCH ₃ [−] (C _s , ³ A)	2.003	1.516	1.101	1.092, 1.099, 1.099	132.4	120.6
LiCH ₂ CH ₂ [−] (C _s)	2.029, 2.022	1.488	1.090	1.093	68.2	117.6
LiCH=CH ₃ (C _s)	1.967	1.352	1.095	1.089, 1.090	121.8	127.2
LiC=CH ₂ [−] (C _s , ¹ A)	1.859	1.354	1.106	1.100		168.4
LiC=CH ₂ [−] (C _{2v} , ³ A)	1.979	1.305		1.094	180.0	
cis-LiCH=CH [−] (D _{2h})	1.896	1.372	1.105		68.8	172.3
trans-LiCH=CH [−] (C _s)	2.004	1.317	1.085	1.090	88.6	145.6
LiC≡CH (C _{∞v})	1.909	1.237		1.065	180.0	
LiC≡C [−] (D _{2h})	1.945	1.279			70.8	

^a Bond lengths are in Å and angles are in degrees. Experimental values are in parentheses and come from ref 14f.

quantities were ZPE-corrected using a scaling factor of 0.9646.⁹ Acidities and bond dissociation energies were corrected to 298 K using standard statistical formula by scaling the harmonic frequencies by 0.9427,⁹ whereas the electron affinities and singlet–triplet gaps are given at 0 K. For CH₃Li, [−]CH₂Li, and •CH₂Li, energies were also computed using G3 theory as previously described in the literature.¹⁰ Population analyses (Mulliken and Weinhold's natural population analysis)¹¹ were carried out on MP2 wave functions.

Results and Discussion

Geometries. MP2 structures and subsequent energy calculations were carried out with the 6-311+G(2df,2pd)

(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A., Jr.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Martin, R. L.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03, Revision B.01*; Gaussian, Inc., Pittsburgh, PA, 2003.

(6) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98, Revisions A.9–11*; Gaussian, Inc., Pittsburgh, PA, 1998.

(7) (a) Hampel, C.; Peterson, K.; Werner, H.-J. *Chem. Phys. Lett.* **1992**, *190*, 1–12. (b) Deegan, M. J. O.; Knowles, P. J. *Chem. Phys. Lett.* **1994**, *227*, 321–326. (c) Knowles, P. J.; Hampel, C.; Werner, H.-J. *J. Chem. Phys.* **1993**, *99*, 5219–5227; erratum: *J. Chem. Phys.* **2000**, *112*, 3106.

(8) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(9) Pople, J. A.; Scott, A. P.; Wong, M. W.; Radom, L. *Isr. J. Chem.* **1993**, *33*, 345–350.

(10) Curtiss, L. A.; Raghavachari, K.; Redfern, P. C.; Rassolov, V.; Pople, J. A. *J. Chem. Phys.* **1998**, *109*, 7764–7776.

basis set. This large triple split-valence basis set contains diffuse functions, which are needed to adequately describe negative ions, and higher angular momentum terms for representing small-ring bridged structures. The latter orbitals also are important in minimizing basis set superposition errors that can arise in lithium-containing compounds¹² and for obtaining accurate reaction energies using coupled cluster theory.¹³ Full details for the geometries of methyl, ethyl, vinyl, and ethynyllithium (RLi, R = CH₃, CH₃CH₂, CH₂=CH, and HC≡C), their conjugate bases, and the corresponding radicals are provided in the Supporting Information, and a summary of the key structural parameters for RLi and their conjugate bases is given in Table 1; these species also are illustrated in Figure 1.

None of the lithiated acids nor their α-deprotonated ions form bridged compounds, and their geometries are in accord with previously available results carried out using a variety of theoretical models and basis sets.^{2,13b,14} Each of the β-lithio carbanions is predicted to form a cyclic species, as is often the case with lithium compounds.² Moreover, vinylithium leads to two different β-anions, a cis species and a trans one.

Thermochemistry. Singlet–Triplet Gaps. Schleyer et al. have suggested on the basis of low-level computations (MP2/6-31+G(d)//HF/4-31G) that [−]CH₂Li is a ground-state triplet and can be viewed as having CH₂[−]Li• character (i.e. the HOMO is a singly occupied σ* orbital

(11) (a) Carpenter, J. E.; Weinhold, F. *THEOCHEM* **1988**, *46*, 41–62. (b) Reed, A. E.; Curtiss, L. A.; Weinhold, F. *Chem. Rev.* **1988**, *88*, 899–926.

(12) (a) Del Bene, J. E. *J. Phys. Chem.* **1996**, *100*, 6284–6287. (b) Feller, D.; Glendening, E. D.; Kendall, R. A.; Peterson, K. A. *J. Chem. Phys.* **1994**, *100*, 4981–4997. (c) Bachrach, S. M.; Ritchie, J. P. *J. Am. Chem. Soc.* **1989**, *111*, 3134–3140. (d) Bachrach, S. M.; Streitwieser, A., Jr. *J. Am. Chem. Soc.* **1984**, *106*, 2283–2287.

(13) (a) Bartlett, R. J.; Stanton, J. F. In *Reviews in Computational Chemistry*; Lipkowitz, K. B., Boyd, D. B., Eds.; WCH: New York, 1994; Vol. 5, pp 65–169. (b) Scalmani, G.; Bredas, J. L.; Barone, V. *J. Chem. Phys.* **2000**, *112*, 1178–1191.

(14) (a) Spitznagel, G. W.; Clark, T.; Chandrasekhar, J.; Schleyer, P. v. R. *J. Comput. Chem.* **1982**, *3*, 363–371. (b) Chandrasekhar, J.; Pople, J. A.; Seeger, R.; Seeger, U.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 3651–3655. (c) Kaufmann, E.; Raghavachari, K.; Reed, A. E.; Schleyer, P. v. R. *Organometallics* **1988**, *7*, 1597–1607. (d) Wiberg, K. B.; Sklenak, S. *Organometallics* **2001**, *20*, 771–774. (e) Breiding, J.; Thiel, W. *J. Mol. Struct.* **2001**, *599*, 239–254. (f) Grotjahn, D. B.; Pesch, T. C.; Xin, J.; Ziurys, L. M. *J. Am. Chem. Soc.* **1997**, *119*, 12368–12369.

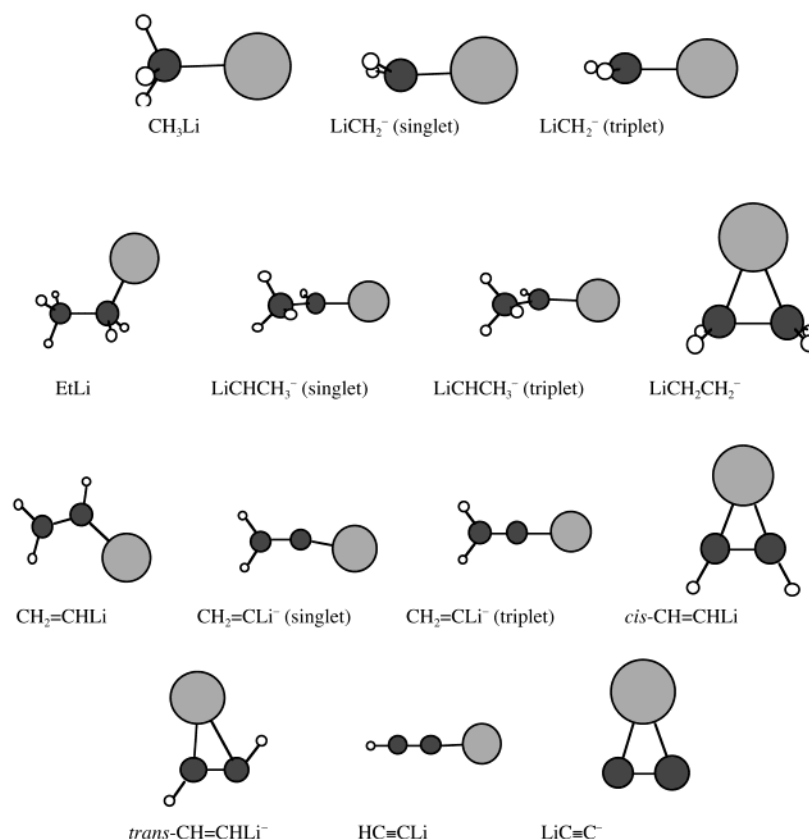


FIGURE 1. Computed MP2/6-311+G(2df,2pd) structures of RLi ($R = \text{CH}_3$, CH_3CH_2 , $\text{CH}_2=\text{CH}$, and $\text{HC}\equiv\text{C}$) and their conjugate bases.

residing almost entirely on lithium).^{14a} Not surprisingly, we find the same result at the MP2 level for CH_2Li and the other two α -anions (CH_3CHLi^- and $\text{CH}_2=\text{CHLi}^-$) that were explored. This method is not very reliable, however, for obtaining singlet–triplet gaps or even predicting ground-state multiplicities; therefore, B3LYP and CCSD(T) calculations with the same large 6-311+G(2df,2pd) basis set were carried out. In addition, all three methods (MP2, B3LYP, and CCSD(T)) were calibrated with methylene ($\text{CH}_2\cdot$), vinylidene ($\text{CH}_2=\text{C}\cdot$), and *o*-benzyne (*o*- C_6H_4), since these compounds have well-established singlet–triplet gaps and encompass both singlet and triplet ground states.¹⁵ As seen in Table 2, the coupled cluster calculations do an excellent job for the three test cases, whereas the other two methods do not. Nevertheless, all three methods predict that the α -lithio carbanions are ground-state triplets, and the singlet–triplet gaps span from 3.2 to 6.3 kcal mol⁻¹ at the CCSD(T) level.¹⁶ Like the parent ion, each of these species can be thought of as $\text{R}\cdot\text{Li}\cdot$ given their HOMOs (a σ^* orbital largely on lithium), the absence of charge on lithium (Table 3), and the location of the odd electron as given by the Mulliken population spin densities. It is interesting that there is not more evidence for a $\text{R}:\text{Li}^-$ configuration, given that the electron affinity of lithium (0.618069

TABLE 2. Computed Singlet–Triplet Gaps^a

compd	MP2	B3LYP	CCSD(T)	expt
$\text{CH}_2\cdot$	15.0	11.0	9.9	9.05 ± 0.06^b
$\text{CH}_2=\text{C}\cdot$	-52.0	-49.5	-48.2	-47.60 ± 0.14^c
<i>o</i> - C_6H_4	-44.8	-31.5	-36.9	-37.5 ± 0.3^d
LiCH_2^-	14.8	16.9	3.6 (3.8) [2.5] ^e	
LiCHCH_3^-	17.5	17.0	6.3	
$\text{LiC}\equiv\text{C}^-$	14.8	16.9	3.2	

^a All values are in kcal mol⁻¹ and are ZPE-corrected. Positive numbers indicate a triplet ground state, while negative values indicate a singlet ground state. ^b Reference 15a. ^c Reference 15b. ^d Reference 15c. ^e The parenthetical value was obtained using the 6-311+G(3df,3pd) basis set and the number in square brackets was obtained via G3 theory.

± 0.000044 eV) is larger than for vinylidene ($\text{CH}_2=\text{C}\cdot$; 0.4466 ± 0.0016 eV) and virtually the same as for methylene ($\text{CH}_2\cdot$; 0.652 ± 0.006 eV).¹⁷

Acidities. The acidities of methane, ethane, ethylene, and acetylene are well-reproduced at the MP2, B3LYP, and CCSD(T) levels, so it is not surprising that these three methods also are in reasonable accord for methyl, ethyl, vinyl, and ethynyllithium.^{17,18} More specifically, when the acidities are computed for going from the ground-state of RLi to the ground-state of its conjugate base (a spin forbidden process for the α -anions), there is

(15) (a) McKellar, A. R. W.; Bunker, P. R.; Sears, T. J.; Evenson, K. M.; Saykally, R. J.; Langhoff, S. R. *J. Chem. Phys.* **1983**, *79*, 5251–5264. (b) Ervin, K. M.; Ho, J.; Lineberger, W. C. *J. Chem. Phys.* **1989**, *91*, 5974–5992. (c) Wenthold, P. G.; Squires, R. R.; Lineberger, W. C. *J. Am. Chem. Soc.* **1998**, *120*, 5279–5290.

(16) This appears to be a general result for α -lithio anions.

(17) All of the cited thermochemistry, unless otherwise noted, comes from the following reference: Bartmess, J. E. In *Secondary NIST Chemistry WebBook, NIST Standard Reference Database Number 69*, Mallard, W. G., Linstrom, P. J., Eds.; National Institute of Standards and Technology: Gaithersburg, MD (<http://webbook.nist.gov>).

TABLE 3. Computed Natural Population Analysis Charges and Mulliken Atomic Spin Densities^a

compd	Li	C(α)	C(β)
CH ₃ Li	0.86	-0.86	
CH ₂ Li ⁻ (singlet)	0.44	-1.46	
CH ₂ Li ⁻ (triplet)	-0.01 (0.87)	-0.99 (1.13)	
CH ₃ CH ₂ Li	0.83	-0.75	-0.08
CH ₃ CHLi ⁻ (singlet) ^b	0.20	-1.03	-0.17
CH ₃ CHLi ⁻ (triplet)	-0.01 (0.86)	-0.82 (1.14)	-0.16 (0.00)
CH ₂ =CHLi	0.89	-0.73	-0.16
CH ₂ =CLi ⁻ (singlet)	0.46	-1.14	-0.42
CH ₂ =CLi ⁻ (triplet)	0.02 (0.93)	-0.63 (0.66)	-0.39 (0.40)

^a Hydrogen atom contributions have been summed into the carbon atoms to which they are attached. Parenthetical values are for the Mulliken spin densities. ^b These results were obtained with the 6-311G(2df,2pd) basis set since the NPA procedure in Gaussian 03 gave spurious charges in this case (i.e., -1.66 electrons).

TABLE 4. Calculated MP2, B3LYP, and CCSD(T) Acidities

compd (HX)	$\Delta H_{\text{acid}}^{\text{HX}}^a$			
	MP2	B3LYP	CCSD(T)	expt
CH ₄	418.1	417.3	420.2	416.8 ± 0.7 ^b
CH ₃ CH ₃	420.4	420.1	422.5	420.1 ± 2.0 ^c
CH ₂ CH ₂	409.4	409.0	410.7	408.8 ± 0.3 ^b
C ₂ H ₂	378.9	378.3	379.6	378.3 ± 0.1 ^b
CH ₃ Li	402.3	400.3	401.6 (400.7) ^d	
CH ₃ CH ₂ Li				
α	397.7	394.9	397.2	
β	395.4	393.8	394.4	
CH ₂ =CHLi				
α	391.1	388.0	391.2	
β (cis)	398.2	397.9	400.5	
β (trans)	399.3	405.5	399.8	
HC≡CLi	390.4	391.5	391.1	

^a All values are in kcal mol⁻¹ and are at 298 K. Each acidity corresponds to a ground-state to ground-state transformation, even when the process is formally spin forbidden. ^b Reference 18. ^c Reference 17. ^d The parenthetical value is the acidity calculated using G3 theory.

good accord among the three levels of theory (Table 4). If the spin-allowed process is considered for ⁻CH₂Li, CH₃CHLi⁻, and CH₂=CLi⁻, then the acidities are smaller (larger numbers), and the MP2 and B3LYP results differ significantly from the CCSD(T) data. This difficulty in the MP2 and B3LYP acidities is due to their failure to reproduce the singlet anion energies, presumably because they do not account for the multiconfiguration description of these ions. Regardless, we find that methyl, ethyl, and vinyl lithium are more acidic than their corresponding hydrocarbons. Consequently, a previous report on phenyllithium that indicates that it is more acidic than benzene is not an isolated phenomenon,⁴ and in general, lithium is an acid-*enhancing* substituent!¹⁹

For the α-position in organolithium, the increased acidity is due to favorable electrostatic interactions and the π-electron-accepting ability of lithium due to its empty p-orbitals.^{2,3,14a} The former effect is reflected in the natural population analysis (NPA) charges (Table 3),²⁰ while the latter is consistent with the 0.08–0.17 Å contraction in the C–Li bond distance upon deprotonation. Likewise, the β-anions derived from ethyl and vinyl lithium are stabilized by ion-triplet formation and

(18) Ervin, K. M.; DeTuri, V. F. *J. Phys. Chem. A* **2002**, *106*, 9947–9956.

TABLE 5. Calculated MP2, B3LYP, and CCSD(T) Electron Affinities

compd (HX)	EA(X) ^a			
	MP2	B3LYP	CCSD(T)	expt ^b
CH ₄	-1.2	1.8	-2.6	1.8 ± 0.7
CH ₃ CH ₃	-6.6	-5.7	-8.3	-6.0 ± 2.1
CH ₂ CH ₂	19.7	16.5	14.9	15.4 ± 0.6
C ₂ H ₂	80.4	74.2	70.6	68.5 ± 0.1
CH ₃ Li	7.3	10.2	7.9 (10.0) ^c	
CH ₃ CH ₂ Li				
α	7.7	10.0	7.9	
β	-9.8	-8.2	-6.4	
CH ₂ =CHLi				
α	12.7	12.1	10.2	
β (cis)	-0.4	1.7	0.3	
β (trans)	6.8	-0.5	6.5	
HC≡CLi	60.5	40.4	36.4	

^a All values are in kcal mol⁻¹ and are at 0 K. ^b Experimental values come from ref 17. ^c The parenthetical value is the EA calculated using G3 theory.

covalent bridging interactions. In the former case, the β-anion is more stable than the α ion by 1–3 kcal mol⁻¹. This order is reversed for vinyl lithium and the preference for the α-anion is ~9 kcal mol⁻¹, presumably because bridging is less effective due to increased strain in the three-membered ring (e.g. the strain energies of cyclopropane and cyclopropene are 27.7 and 53.7 kcal mol⁻¹, respectively).²¹ The same reasoning (i.e. increased strain) also can account for the 12 kcal mol⁻¹ smaller acidity of ethynyllithium compared to acetylene. These results are for monomeric gas-phase species, but they suggest that the deprotonation of lithiated compounds maybe easier than one might expect and that such transformations could be synthetically more useful than currently is the case.

Electron Affinities. To generate lithiated carbanions in the gas phase, so that one can study their intrinsic reactivities and thermodynamic properties, the corresponding radicals must have positive electron affinities (i.e. the loss of an electron from the anion must be endothermic).²² This is a problem for many alkyl anions, since their radicals typically have small or even negative electron affinities. Consequently, the electron affinities for methyl, ethyl, vinyl, and ethynyl radicals and their lithiated derivatives were computed (Table 5). As expected, both the B3LYP and CCSD(T) results are in good accord with the experimental values for the hydrocarbon radicals, although the predicted electron affinity is too large for HC≡C• by 5.7 kcal mol⁻¹ (B3LYP) and too small for CH₃• by 4.4 kcal mol⁻¹ (CCSD(T)); the other errors are ≤1.1 (B3LYP) and 2.3 (CCSD(T)) kcal mol⁻¹. MP2 does surprisingly well for methyl, ethyl, and vinyl radical (error ≤ 4.3 kcal mol⁻¹) but is in error by 11.9 kcal mol⁻¹ for ethynyl radical. All three approaches, however, clearly

(19) Similar results have been noted for the conversion of a monolithio compound to a dilithio species. (a) Streitwieser, A., Jr.; Swanson, J. T. *J. Am. Chem. Soc.* **1983**, *105*, 2502–2503. (b) Schleyer, P. v. R.; Kos, A. J.; Kaufmann, E. *J. Am. Chem. Soc.* **1983**, *105*, 7617–7623. (c) Bachrach, S. M. *J. Am. Chem. Soc.* **1986**, *108*, 6406–6407. (d) Bachrach, S. M.; Miller, J. V., Jr. *J. Org. Chem.* **2002**, *67*, 7389–7398.

(20) In general, the Mulliken charges are ~0.3 smaller than those from the natural population analysis.

(21) Cohen, N.; Benson, S. W. *Chem. Rev.* **1993**, *93*, 2419–2438.

(22) Actually, it is possible to observe ions with negative electron binding energies, but they are so short-lived that nobody has been able to study the reactivity of such species.

TABLE 6. Calculated MP2, B3LYP, and CCSD(T) Bond Dissociation Energies

compd (HX)	BDE (HX) ^a			
	MP2	B3LYP	CCSD(T)	expt ^b
CH ₄	103.2	105.4	104.0	104.99 ± 0.03
CH ₃ CH ₃	100.2	100.7	100.6	101.1 ± 0.4
CH ₂ CH ₂	115.3	111.7	112.0	110.7 ± 0.6
C ₂ H ₂	145.3	138.6	136.3	133.3 ± 0.1
CH ₃ Li	96.0 [46.3]	96.9 [45.4]	95.9 (96.8) [45.8]	[48.0] ^c
CH ₃ CH ₂ Li				
α	91.6 [39.4]	91.0 [36.3]	91.3 [38.4]	[40.4] ^c
β	71.8	71.7	74.1	
CH ₂ =CHLi				
α	90.0 [63.1]	86.3 [55.6]	87.6 [58.3]	
β (cis)	84.0	85.9	87.2	
β (trans)	92.3	91.2	92.4	
HC≡CLi	138.0 [118.1]	118.2 [107.8]	113.8 [107.9]	

^a All values are in kcal mol⁻¹ and are at 298 K. The parenthetical value is the BDE calculated using G3 theory and the results in brackets correspond to the R–Li BDEs. ^b Experimental values come from Blanksby, S. J.; Ellison, G. B. *Acc. Chem. Res.* **2003**, *36*, 255–263. ^c MP4/6-311++G(3df,2p)//MP2(full)/6-31G(d,p) result from ref 23.

indicate that the α-anions and the conjugate base of ethynyllithium are bound species. This makes these ions attractive candidates for mass spectrometry studies. The β-anions derived from ethyl and vinyl lithium are a different story and give mixed results. All three methods predict that LiCH₂CH₂⁻ is unbound but are more ambiguous when it comes to LiCH=CH⁻. The cis ion may have a small positive electron binding energy [0.3 kcal mol⁻¹ (B3LYP) and 1.7 kcal mol⁻¹ (CCSD(T))] but could be unbound [−0.4 kcal mol⁻¹ (MP2)], and the same holds for the trans derivative [−0.5 kcal mol⁻¹ (B3LYP), 6.5 kcal mol⁻¹ (CCSD(T)), and 6.8 kcal mol⁻¹ (MP2)].

Bond Dissociation Energies. No additional calculations were needed to compute the carbon–hydrogen bond energies (ΔH_{298}°) of RH and RLi, so these quantities are tabulated in Table 6.

Lithium is also found to stabilize radicals, and the β-position is affected to a greater extent than the α-position. This can be explained, at least in part, by the bond-weakening effect of a β-carbanion center resulting from the formation of a two-center–three-electron bond upon homolytic cleavage (e.g., CH₃CH₂⁻ → •CH₂CH₂⁻ + H•).

As a result of this large effect (~25 kcal mol⁻¹), the β-C–H bond dissociation energy of ethyllithium is predicted to be only 74 kcal mol⁻¹ at the CCSD(T) level! This corresponds to an extremely weak C–H bond and suggests that appropriate substituents may reduce the bond strength further. Consequently, it may be possible to carry out radical chemistry at remote (β) sites on lithiated compounds. Further computations and experiments are underway to explore this possibility.

Carbon–lithium bond energies also were computed (Table 6) for completeness sake and because these quantities have been previously calculated at a high level of theory (MP4/6-311++G(3df,2p)//MP2(full)/6-31G(d,p)) for methyl and ethyllithium.²³ In both cases, there is good accord among the MP2, B3LYP, CCSD(T), and literature MP4 results.

Conclusion

High-level ab initio and density functional calculations were carried out on organolithium compounds (RLi) and their corresponding hydrocarbons. The acidities and C–H bond dissociation energies of these species are reported, as are the electron affinities of the corresponding radicals. We have found that (1) α-lithio anions have triplet ground states, (2) lithium is an acid-enhancing group, (3) the conjugate bases of RLi are stable with respect to electron detachment and therefore are good candidates for mass spectrometry studies, (4) lithium weakens α- and β-C–H bond energies, the latter by ~25 kcal mol⁻¹. This has far-reaching implications with regard to carrying out radical chemistry on lithium-containing molecules.

Acknowledgment. Support from the National Science Foundation, the donors of the Petroleum Research Foundation, as administered by the American Chemical Society, and the Minnesota Supercomputer Institute are gratefully acknowledged. We also appreciate a summer supplement from the Petroleum Research Foundation to S.K. for the support of L.P., which helped make this work possible.

Supporting Information Available: Computed energies and structures (xyz coordinates). This material is available free of charge via the Internet at <http://pubs.acs.org>.

JO035432H

(23) Sana, M.; Leroy, G.; Wilante, C. *Organomet.* **1991**, *10*, 264–270.