Carbanion Hybridization of Thiophosphonamide-Stabilized Anions: Remarkable Steric and Solvation Effects

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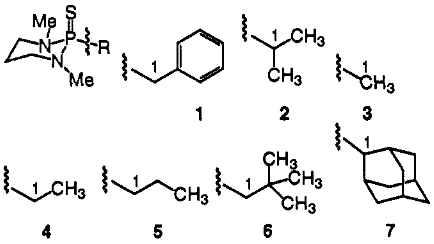
The study of structure and bonding in organolithium compounds has experienced a renaissance over the past 10–15 years. Dramatic advances in the determination of structure in the solid[1] and the solution states[2] as well as by computational analysis[3] have revealed a startling diversity of bonding arrangements, commonplace fluxional behavior, and hypercoordination. These revelations are of no small interest to the synthetic organic chemist as this panoply of structural attributes is critical for understanding the chemistry of these indispensable reagents.[4] As part of our program on the structure of phosphorus-stabilized anions,[5] we now report a study of lithiated thiophosphonamides which provides insights into the delicate balance of factors governing hybridization and bonding.

We have recently described the structures of thiophosphonamide anions derived from **1** and **2**.[5c] In solution, Li$^+$**1**$^-$ and Li$^+$**2**$^-$ displayed the following characteristics: monomeric structure; solvent-separated ion pairs; nearly planar sp^2 carbanionic carbon; and for Li$^+$**2**$^-$, a barrier of rotation of 9.1–11.4 kcal/mol. In the solid state Li$^+$**1**$^-$ showed a planar sp^2 carbanionic carbon. Subsequent examination of the adamantyl analog Li$^+$**7**$^-$ revealed a similar behavior (Table I). This anion also displayed an sp^2 carbanionic carbon, as evidenced by a large upfield shift of the ^{31}P NMR resonance, a very large increase in $^1J_{CP}$, and a small ^{7}Li NMR $W_{1/2}$ at low temperature.



Our study was initially intended to determine the rotational thermodynamic parameters of the anions. We were therefore astonished to find upon deprotonation of the methyl (**3**), ethyl (**4**), and *n*-propyl (**5**) analogs very different anionic species. Unlike the previous compounds, Li$^+$**4**$^-$ and Li$^+$**5**$^-$ showed only small changes in the $^1J_{CP}$ and $^1J_{CH}$ and the δ ^{31}P NMR resonance, indicating that the carbanionic carbon has hybridization similar to that of its neutral precursor and that little anionic charge accumulated on the carbanionic carbon and the phosphorus atoms (Table I).[5,6] Moreover, investigation of Li$^+$**3**$^-$ revealed still greater divergence. The *downfield shift* in the ^{31}P NMR and corresponding *decrease* of $^1J_{CP}$ suggest a stronger electropositive lithium interaction with the carbanionic carbon. The large $W_{1/2}$ for the ^{7}Li NMR indicated a highly asymmetric environment around the lithium cation compared to Li$^+$**1**$^-$ and Li$^+$**2**$^-$.[7] These data provide strong evidence for an sp^3 hybridized anion with some type of lithium carbon contact.

Table I. Selected NMR Data for Li$^+$**1**$^-$, Li$^+$**2**$^-$, Li$^+$**3**$^-$, Li$^+$**4**$^-$, Li$^+$**5**$^-$, and Li$^+$**7**$^-$

compd	$\Delta\delta$ ^{31}P, ppm[a,b]	Δ^1J_{CP}, Hz[a,c]	Δ^1J_{CH}, Hz[a,d]	^{7}Li $W_{1/2}$, Hz[e]
Li$^+$**1**$^-$	−15.9	90	25.8	4.0
Li$^+$**2**$^-$	−22.4	100		3.6
Li$^+$**7**$^-$	−20.4	129		2.7
Li$^+$**3**$^-$	15.4	−18	−1.8	19.6
Li$^+$**4**$^-$	3.7	4	2.1	16.0
Li$^+$**5**$^-$	−7.6	33	6.8	16.4

[a] Δ datum = (datum anion) – (datum neutral); negative numbers are upfield shifts. [b] 121 MHz ^{31}P, −105 °C, THF-d_8. [c] 125 MHz ^{13}C, −99 °C, THF-d_8. [d] HC(1), 100 MHz ^{13}C, Het2dj determined at 2.0 °C, THF-d_8. [e] 116 MHz ^{7}Li, −105 °C, THF-d_8.

To support this hypothesis, Li$^+$**3**$^-$ and Li$^+$**4**$^-$ were investigated using ^{6}Li–^{1}H heteronuclear NOE spectroscopy (HOESY).[8] In both cases, a strong heteronuclear NOE between HC(1) and the lithium atom was found. However, the strongest evidence for the lithium–carbon interaction came from observation of direct ^{6}Li–^{13}C coupling.[9] Upon the cooling of solutions of ^{6}Li- and ^{13}C-labeled anions, C(1) appeared as a triplet in the ^{13}C NMR spectra at very low temperature (in Me$_2$O)[10] (^{6}Li$^+$**3**$^{*-}$, $^1J_{^{13}C^6Li}$ = 7.0 Hz at −123 °C; ^{6}Li$^+$**4**$^{*-}$, $^1J_{^{13}C^6Li}$ = 6.2 Hz at −139 °C). Further, upon irradiation of the ^{6}Li signal, the ^{13}C triplet collapsed to a singlet, assuring the origin of the ^{6}Li–^{13}C coupling. Collectively, *these data unequivocally demonstrate the existence of a lithium carbon contact in Li$^+$**3**$^-$, Li$^+$**4**$^-$, and Li$^+$**5**$^-$ in solution.*

The spectroscopic studies clearly demonstrate that a range of carbanion hybridization is possible within the same family of compounds.[11] Thus the degree of pyramidalization of the carbanion is not uniquely determined by the nature of the stabilizing group and other factors must also be considered: (1) the electronic asymmetry of the local environment, (2) the degree of charge delocalization, (3) the accessibility of localized charge to metal cation contact, and (4) the degree of solvation of the attendant cation. The symmetry of the thiophosphonamide unit precludes significant pyramidalization due to electronic distortion and the planarity of the benzyl anion Li$^+$**1**$^-$ is easily understood due to charge delocalization. However, the dichotomy of aliphatic carbanion hybridization between the isopropyl (Li$^+$**2**$^-$) and adamantyl (Li$^+$**7**$^-$) compounds (sp^2 limit) and the methyl (Li$^+$**7**$^-$), ethyl (Li$^+$**4**$^-$), and *n*-propyl (Li$^+$**5**$^-$) compounds (sp^3 limit) illustrates the importance of the factors 3 and 4 above. Thus, the steric encumbrance around the carbanionic centers in Li$^+$**2**$^-$ and Li$^+$**7**$^-$ prevents the lithium and its attendant solvent molecules from forming a contact ion pair.

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(1) (a) Setzer, W. N.; Schleyer, P. v. R. *Adv. Organomet. Chem.* **1985**, *24*, 353. (b) Seebach, D. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1624. (c) Williard, P. G. In *Comprehensive Organic Synthesis: Additions to C-X π-Bonds, Part 1*; Schreiber, S. L., Ed.; Pergamon Press: Oxford, 1991; Vol. 1, Chapter 1.1.

(2) (a) Wardell, J. L. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. A., Eds.; Pergamon Press: Oxford, 1982; Vol. 1, p 43. (b) Wakefield, B. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. A., Eds.; Pergamon Press: Oxford, 1982; Vol. 7, p 1. (c) Fraenkel, G.; Hsu, H.; Su, B. M. In *Lithium: Current Applications in Science, Medicine and Technology*; Bach, R. O., Ed.; Wiley: New York, 1985; p 273. (d) Collum, D. B. *Acc. Chem. Res.* **1993**, *26*, 227.

(3) (a) Schleyer, P. v. R. *Pure Appl. Chem.* **1984**, *56*, 151. (b) Kranz, M.; Dietrich, H.; Mahdi, W.; Müller, G.; Hampel, F.; Clark, T.; Hacker, R.; Neugebauer, W.; Kos, A. J.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1993**, *115*, 4698 and references cited therein.

(4) (a) Wakefield, B. J. *Organolithium Methods*; Academic Press: San Diego, CA, 1988. (b) Boche, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 277. (c) Brandsma, L.; Verkruijsse, H. D. *Preparative Polar Organometallic Chemistry*; Springer-Verlag: Berlin, 1987; Vol. 1.

(5) (a) Denmark, S. E.; Dorow, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 864. (b) Denmark, S. E.; Miller, P. C.; Wilson, S. R. *J. Am. Chem. Soc.* **1991**, *113*, 1468. (c) Denmark, S. E.; Swiss, K. A. *J. Am. Chem. Soc.* **1993**, *115*, 3826.

(6) Bernardi, F.; Schlegel, H. B.; Whangbo, M.-H.; Wolfe, S. *J. Am. Chem. Soc.* **1977**, *99*, 5633.

(7) Since ^{7}Li has a medium quadrapole moment (Q = −0.037, I = $^3/_2$), narrow ^{7}Li lines usually indicate symmetric (tetrahedral) enviroments.

(8) (a) Bauer, W.; Schleyer, P. v. R. *Magn. Reson. Chem.* **1988**, *26*, 827. (b) Bauer, W.; Clark, T.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1987**, *109*, 970. (c) Bauer, W.; Feigel, M.; Müller, G.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 6033. (d) Bauer, W.; Müller, G.; Pi, R.; Schleyer, P. v. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 1103.

(9) (a) Seebach, D.; Hässig, R.; Gabriel, J. *Helv. Chim. Acta* **1983**, *66*, 308. (b) Seebach, D.; Gabriel, J.; Hässig, R. *Helv. Chim. Acta* **1984**, *67*, 1083.

(10) No coupling could be observed in THF to the freezing point of the solutions.

(11) This behavior has also been noted in α-lithiosulfones;[4b] however, the trend is quite different.

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Table II. Effect of Temperature and HMPA on Hybridization

compd	T, °C	$\Delta\delta$ ^{31}P, ppm[a,b]	Δ^1J_{CP}, Hz[a,c]	Δ^1J_{CH}, Hz[a]
sp^2 range		$-15.9 \rightarrow -22.4$	$90 \rightarrow 129$	25.8
Li^+**6**$^-$	−114	−19.9	80	31.7[d]
Li^+**6**$^-$	−94	−18.2	64	20.4[e]
Li^+**6**$^-$	−5	−7.4	19	7.6[e]
$Li(h)_4^+$**6**$^-$	−100	−14.3	90	31.1[d]
$Li(h)_4^+$**4**$^-$	−100	−9.3	88	29.0[f]
$Li(h)_4^+$**3**$^-$	−100	1.3	72	21.6[f]
$Li(h)_4^+$**3**$^-$	−5	8.1	36	12.4[f]
sp^3 range		$15.4 \rightarrow -7.6$	$-18 \rightarrow 33$	$-1.8 \rightarrow 6.8$

[a] Δ datum = (datum anion) − (datum neutral); negative numbers are upfield shifts. [b] 121 MHz ^{31}P, THF-d_8. [c] 125 MHz ^{13}C, −105 °C, THF-d_8. [d] 125 MHz ^{1}H-coupled DEPT. [e] 125 MHz ^{13}C, Het2dj. [f] 500 MHz ^{1}H (^{13}C enriched).

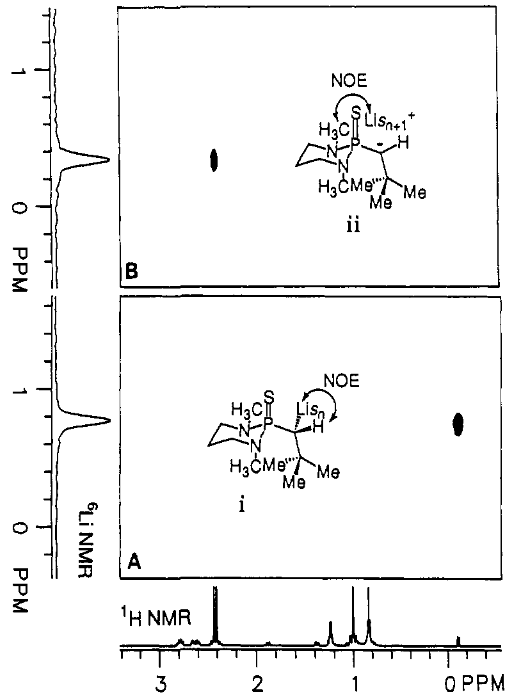

Figure 1. ^{6}Li–^{1}H HOESY spectra of Li^+**6**$^-$ (THF-d_8, ^{6}Li NMR was externally referenced to 1 M LiCl in D_2O). Spectrum A, −5 °C; spectrum B, −94 °C. The ^{1}H spectrum depicted is at −5 °C, and some resonances have been truncated.

To test this hypothesis, we prepared the neopentyl phosphonamide **6**. The NMR spectra of Li^+**6**$^-$ at −5 °C (THF-d_8) showed little change in $^1J_{CP}$ and $^1J_{CH}$, strongly suggesting an sp^3 hybridized carbanionic carbon with a lithium contact (Table II).[12] This conclusion was verified by a ^{6}Li–^{1}H HOESY experiment which revealed a large heteronuclear NOE between the HC(1) and lithium, Figure 1. When the solution of the anion was cooled, the diagnostic indicators of hybridization changed continuously. At lower temperature (−94 °C), the spectra of Li^+**6**$^-$ were characteristic of an sp^2 hybridized carbanion, i.e., a larger upfield ^{31}P NMR shift and increased $^1J_{CP}$ and $^1J_{CH}$. Furthermore, a ^{6}Li–^{1}H HOESY experiment revealed *no* heteronuclear NOE between the HC(1) and the lithium but, rather, between the *N*-methyl protons and the lithium! At still lower temperature, the hybridization changed further in the direction of the sp^2 limit as seen in the significant increase in $^1J_{CP}$ and $^1J_{CH}$.[13] Thus, at −5 °C in THF, Li^+**6**$^-$ displays the characteristics of an sp^3 carbanion (with lithium contact), while at −94 °C it has the properties of an sp^2 carbanion. This remarkable temperature dependence of hybridization can be understood in terms of the differential solvation of two contact ion pairs, Figure 1. The carbon contact ion pair i must have fewer solvent molecules than the heteroatom contact ion pair ii, which in turn has fewer solvent molecules than the solvent-separated ion pair. As the solution is cooled, the sequestering of solvent is coupled with a sliding of the lithium moiety from carbon to the N–P–S region and ultimately to separation. That the rehybridization process is a consequence of a change in solvation is supported by the calculated $\Delta H = -3.2$ kcal/mol and $\Delta S = -16.4$ eu for the equilibrium [sp^3] $\rightleftarrows$ [sp^2] (from the temperature dependence of $^1J_{CP}$).

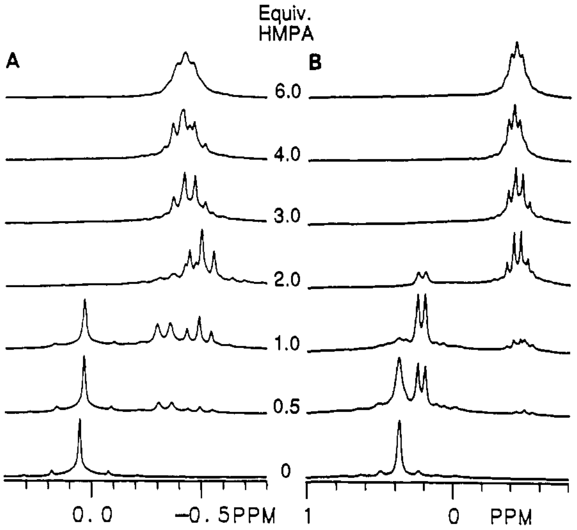

Figure 2. ^{7}Li NMR spectra (THF/Et_2O, −123 °C, externally referenced to 1 M LiCl in D_2O) of HMPA titrations. Spectral stack A, Li^+**2**$^-$; spectral stack B, Li^+**4**$^-$.

Since lithium solvation was shown to be crucial to the hybridization of the anions, we probed the nature of the association employing hexamethylphosphoric triamide (HMPA(*h*)) titrations,[14] Figure 2. With Li^+**2**$^-$ (and Li^+**1**$^-$) we found behavior characteristic of solvent-separated and/or weak contact ion pairs in THF. On the other hand, Li^+**4**$^-$ (and Li^+**3**$^-$ and Li^+**5**$^-$) displayed characteristics of a contact ion pair. After two or more equivalents of HMPA were added, the carbon–lithium contacts in Li^+**4**$^-$ (and Li^+**3**$^-$ and Li^+**5**$^-$) were heterolyzed to solvent-separated ion pairs. These new anions are for the most part sp^2 hybridized, e.g., $Li(h)_4^+$**4**$^-$ showed a large increase in $^1J_{CP}$ and $^1J_{CH}$. However, $Li(h)_4^+$**3**$^-$ still showed a significant temperature dependence of hybridization reminiscent of Li^+**6**$^-$.

In summary, we have demonstrated the importance of steric encumbrance and solvation in the hybridization of lithiated thiophosphonamide anions. The continuum of hybridization states dramatically illustrates the balance of steric, electronic, and medium effects on the nature of the carbon-lithium bond. The manifestation of these differences in hybridization and bonding in chemical reactivity are under examination.

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Supplementary Material Available: Preparation and full spectroscopic characterization of **1–7**, **3**-^{13}*C*, and **4**-^{13}*C* and tables of ^{1}H, ^{7}Li, ^{13}C, and ^{31}P NMR spectra for Li^+**1**$^-$ to Li^+**7**$^-$ (112 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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[12] The data presented in Table II are compared to the ranges for sp^2- and sp^3-type anions from Table I and are well documented elsewhere: (a) Albright, T. A. *Org. Magn. Reson.* **1976**, *8*, 489. (b) Duangthai, S.; Webb, G. A. *Org. Magn. Reson.* **1983**, *21*, 125. (c) Webb, G. A.; Simonnin, M.-P.; Seyden-Penne, J.; Bottin-Strzalko, T. *Magn. Reson. Chem.* **1985**, *23*, 48.

[13] The values for $Li(h)_4^+$**6**$^-$ in THF at −114 °C closely approximated those for the HMPA separated ion pair $Li(h)_4^+$**6**$^-$ at −100 °C.

[14] Reich, H. J.; Borst, J. P. *J. Am. Chem. Soc.* **1991**, *113*, 1835 and references cited therein.