

¹³C Chemical shift substituent parameters for alkyllithium compounds in hydrocarbon solvents

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Abstract

¹³C chemical shift substituent parameters are presented for carbons α , β , γ , and δ to the lithium atom based on the chemical shifts of 14 ⁶Li-enriched alkyllithium compounds. The chemical shift of the carbon α to lithium depends on the branching of the alkyl group at the α -carbon and on the aggregation state of the alkyllithium compound. Increased branching results in increased upfield shifts. This is interpreted in terms of the varying electronic nature of the alkyllithium compounds. The chemical shift of the carbon β to lithium substitution is shifted downfield approximately 5 ppm from the corresponding carbon in the parent hydrocarbon, irregardless of the alkyl group or the aggregation state of the alkyllithium compound. The chemical shift of the γ -carbon depends on the steric requirements of the alkyl group. Carbons four or more bonds from lithium have the same chemical shift as those of the parent hydrocarbon. The derived chemical shift parameters are used to assign the α -carbons of two alkyllithium compounds formed from the reaction of *t*-butyllithium and trimethylvinylsilane.

Introduction

¹³C NMR spectroscopy continues to be one of the most important tools in studying alkyllithium compounds. ¹³C chemical shifts are now known for a variety of compounds [1,2] and ¹³C–⁶Li coupling is becoming increasingly useful in characterizing alkyllithium compounds in solution [2,3]. Although the assignment of the ¹³C resonances of pure alkyllithium compounds or even simple mixtures may be straight forward, it is sometimes difficult to assign the ¹³C resonances of alkyllithium compounds in reaction mixtures. This is often complicated by the relatively short lifetime of some of the lithium intermediates. Although they may have sufficient lifetimes for observation by normal 1D ¹³C NMR, short lifetimes may make 2D NMR techniques, which could provide definitive assignments, impractical.

^6Li spectra often can indicate the presence of the lithium compounds if chemical exchange is sufficiently slow, but the very small chemical shift range (ca. 2 ppm for alkyllithium compounds), a lack of resolvable lithium–proton coupling, and usually unresolvable lithium–carbon coupling make definitive assignments very difficult.

We now wish to report a simple means of assigning ^{13}C chemical shifts of alkyllithium compounds in hydrocarbon solvent by means of chemical shift substituent relationships. Although such additivity relationships are routinely used for organic compounds, they have been used less often for organometallics due to lack of data on a sufficient number of closely related compounds [4]. The relationships derived here have proven useful in our work for assigning the ^{13}C resonances of alkyllithium compounds produced in situ as well as aiding in the choice of solvent systems to avoid possible overlap of peaks. The results also suggest differences in the electronic and steric nature of the compounds as a function of branching of the alkyl group.

Results and discussion

The ^{13}C chemical shifts of 14 ^6Li -enriched alkyllithium compounds in hydrocarbon solvent are listed in Table 1. The ^{13}C chemical shifts of all of the compounds except trimethylsilylmethylithium have been reported earlier [1,3]. Figure 1 is a plot of the ^{13}C chemical shifts of the carbons α to lithium vs. the chemical shift of the corresponding carbon of the parent alkane. A linear relationship between the chemical shifts of straight-chain alkyllithium compounds and the parent hydrocarbon had previously been reported [6]. It is clear from Fig. 1 that this relationship is not restricted to only straight-chain compounds, but holds for all of the primary alkyllithium compounds. The equation for the line is:

$$C_{\alpha}(\text{primary}): \delta^{\text{RLi}} = (1.34 \pm 0.05)\delta^{\text{RH}} + (-5.9 \pm 0.9) \quad r = 0.994 \quad (1)$$

These data reemphasize the similarity of the electronic nature of all of these compounds, even though their aggregation properties differ at lower temperature [3]. It is important to note that the slope is not equal to unity. That is, the chemical shift of the α -carbon cannot be predicted merely by additive constants. Such slopes not equal to one have been observed for similar ^{13}C chemical shift relationships for Grignard reagents [7] and alcohols [8].

The most interesting feature of Fig. 1 is that the chemical shifts of the α -carbons for primary, secondary, and tertiary compounds vs. those for the parent alkanes do not fall on the same line. Increased branching at the α -carbon results in an upfield shift. This is in contrast to Grignard reagents [7] or alcohols [8], where compounds derived from all types of alkyl groups fall on the same line. Not only is there a chemical shift as a function of branching of the alkyl group, but there is also a chemical shift as a function of aggregation state. Unlike some of the ^{13}C spectra reported earlier for secondary alkyllithium compounds containing natural-abundance lithium (93% ^7Li) [9], the ^{13}C resonance of the α -carbon of ^6Li -enriched secondary alkyllithium compounds is resolved into resonances for the tetrameric and hexameric aggregation states. For each of the secondary compounds in this study, the α -carbon of the tetramer is shifted upfield relative to the hexamer by

Table 1

Room temperature ^{13}C chemical shifts of alkyllithium compounds in cyclopentane

Compound	R-group	Aggregation ^a	$\delta(^{13}\text{C})$ (ppm) ^b						
			C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	CH ₃
1	-C-C	6, 8, 9	0.3	10.7					
2	-C-C-C	6, 8, 9	16.1	22.4	22.3				
3	-C-C-C-C	6, 8, 9	11.7	30.9	31.5	13.0			
4	-C-C-C-C-C-C	6, 8, 9	12.3	29.1	37.9	31.6	22.8	13.8	
5	$\begin{array}{c} \text{C} \\ \\ -\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	6	8.2	38.8	34.7	21.5			
6	$\begin{array}{c} \text{C} \\ \\ -\text{C}-\text{C}-\text{C} \end{array}$	6	27.4	29.3	29.3				
7	$\begin{array}{c} \text{C} \\ \\ -\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	6	23.5	35.9	36.6	11.8			25.4 (γ)
8	$\begin{array}{c} \text{C} \\ \\ \text{C} \\ \\ -\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	6	19.2	42.1	31.5	10.8			
9	$\begin{array}{c} \text{C} \\ \\ -\text{C}-\text{Si}-\text{C} \\ \\ \text{C} \end{array}$	4, 6	-4.1	-	2.7				
10	$\begin{array}{c} \text{C} \\ \\ -\text{C}-\text{C} \end{array}$	4	6.2	22.9					
		6	10.3						
11	$\begin{array}{c} \text{C} \\ \\ -\text{C}-\text{C}-\text{C}^{\text{c}} \end{array}$	4	16.2	31.0	15.3				18.6 (β)
		6	20.2	30.6	15.1				18.1 (β)
		2	9.8						
12	$\begin{array}{c} \text{C} \\ \\ -\text{C}-\text{C}-\text{C}-\text{C} \end{array}$	4	12.5	41.0	23.4	13.7			18.7 (β)
		6	16						
13	$\begin{array}{c} \text{C} \\ \\ -\text{C}-\text{C} \end{array}$	4	10.7	32.6					
14	$\begin{array}{c} \text{C} \\ \\ \text{C} \\ \\ \text{C} \\ \\ -\text{C}-\text{C}-\text{C} \\ \\ \text{C} \end{array}$	4	13.8	36.9	5.7				27.7 (β)

^a Aggregation states, from ref. 3. Multiple aggregates are usually resolved only at low temperature.^b Carbons are numbered from lithium substitution. ^c From ref. 1.

approximately 4 ppm. Each of these types of compounds gives a straight line, distinct from that for the primary compounds:

$$\text{C}_\alpha(\text{secondary hexamer}): \delta^{\text{RLi}} = (1.1 \pm 0.2)\delta^{\text{RH}} + (-7 \pm 4) \quad r = 0.985 \quad (2)$$

$$\text{C}_\alpha(\text{secondary tetramers}): \delta^{\text{RLi}} = (1.1 \pm 0.1)\delta^{\text{RH}} + (-11 \pm 3) \quad r = 0.994 \quad (3)$$

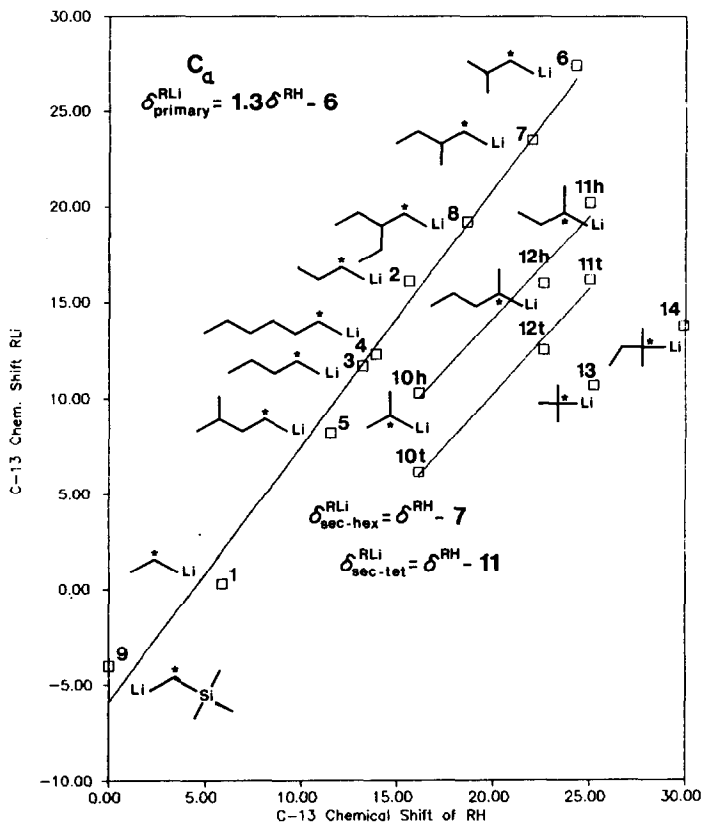


Fig. 1. ^{13}C chemical shifts of the α -carbons of alkyllithium compounds vs. the parent alkane; h, hexameric aggregate; t, tetrameric aggregate.

This suggests that the chemical shift of the α -carbon may help in the assignment of aggregation states of some unknown compounds.

Dixon had suggested earlier [10] based on PRDDO (partial retention of diatomic differential overlap) molecular orbital calculations, that alkyllithium tetramers have a greater carbon–lithium charge separation than hexamers. More recent theoretical studies suggest carbon, lithium bonding is primarily ionic in nature [11]. In either case, the data in Fig. 1 suggest that not only do the alkyl groups of the tetramers have greater anionic character relative to those of the hexamers, but that the alkyl groups of branched-chain hexamers are more anionic than straight-chain hexamers.

Although chemical exchange with other aggregation states could contribute to a downfield shift of the primary compounds or to an upfield shift of the secondary compounds, exchange is not the primary factor in the difference in chemical shift of the two types of compounds. The chemical shift of the hexameric secondary compounds does move slightly downfield as the interaggregate exchange is stopped at low temperature, but never reaches as far downfield as those for the primary hexamers. On the other hand, the more downfield shift of the primary alkyllithiums is not simply due to contributions from rapid exchange with higher aggregation states, as shown by their non-exchange chemical shift values in Table 2. In addition,

Table 2
Low temperature ^{13}C chemical shifts of C_α carbons

Compound	Temperature	Aggregation state ^a		
		9	8	6
1	-60 °C	2.8	1.8	-0.2 ppm
2	-82	18.5	17.2	15.5 ppm
3	-70	(13-14.5) ^b		11.5 ppm
4	-80	(13-15) ^b		11.9 ppm

^a From ref. 3. ^b Nonamer and octamer peaks are obscured by overlapping methyl resonance.

it should be noted that several of the branched primary alkyllithium compounds exist only as hexamers and are not undergoing interaggregate exchange (6, 8) [3], yet they also fall on the same line as the remainder of the primary lithium compounds.

^{13}C chemical shifts have been observed thus far for only two tertiary alkyllithium compounds. Additional branching at the α -carbon clearly produces increased shielding of the α -carbon relative to the parent alkane. Attempts to extend this series to additional tertiary compounds have thus far been unsuccessful.

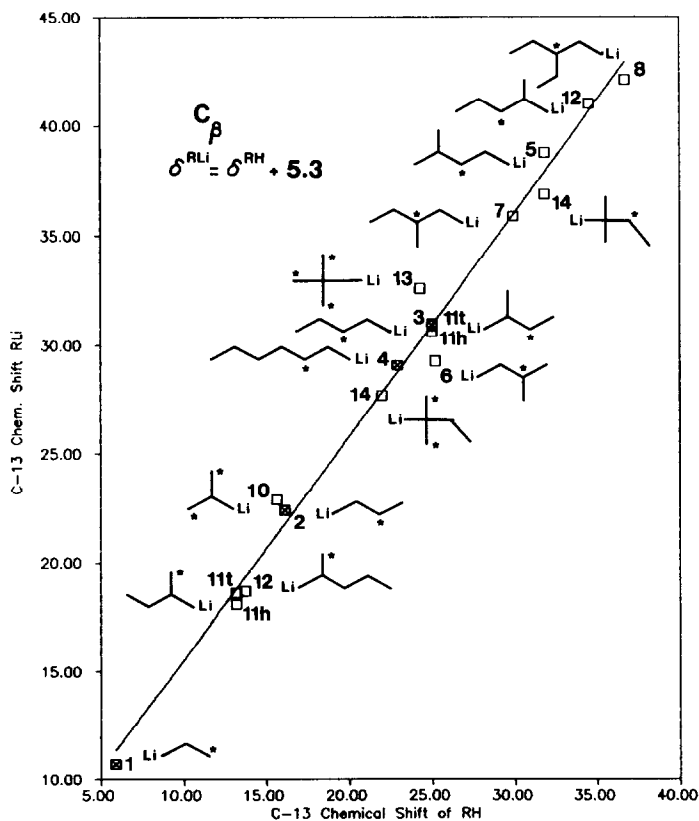


Fig. 2. ^{13}C chemical shifts of RLi vs. RH for β -carbons. X denotes a straight-chain alkyllithium compound.

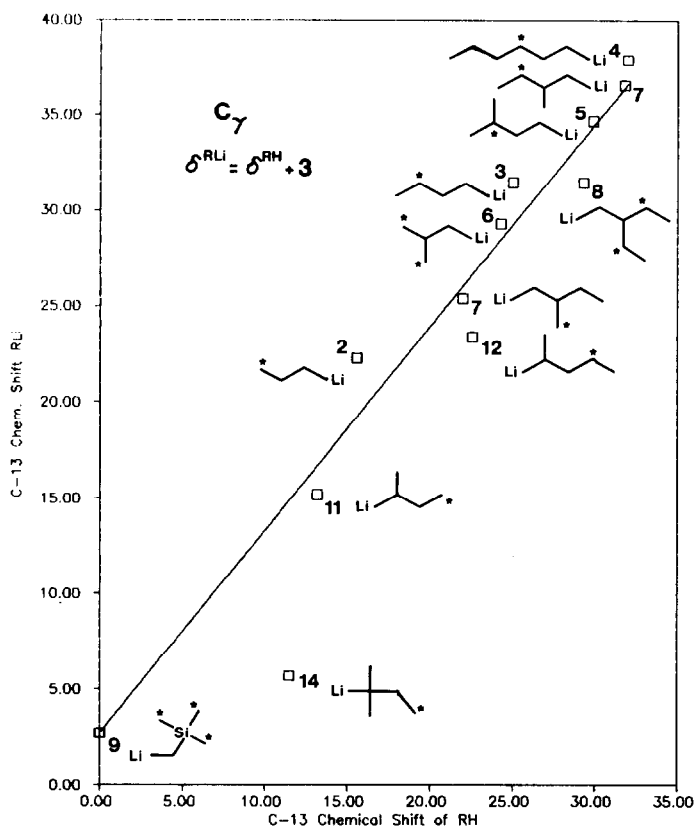


Fig. 3. ^{13}C chemical shifts of RLi vs. RH for γ -carbons. 14 was not included in the least-squares fit.

Plots for carbons β , γ , and δ to lithium substitution are shown in Fig. 2–4. The β carbons for the straight-chain alkyl lithium compounds show a good linear relationship, as reported earlier [6]. Inclusion of the remainder of the β -carbons introduces additional scatter, but all of the β carbons fall on the same line.

$$C_{\beta}(\text{st. chain only}): \delta^{\text{RLi}} = (1.06 \pm 0.04)\delta^{\text{RH}} + (4.7 \pm 0.7) \quad r = 0.999 \quad (4)$$

$$C_{\beta}: \delta^{\text{RLi}} = (1.03 \pm 0.03)\delta^{\text{RH}} + (5.3 \pm 0.7) \quad r = 0.994 \quad (5)$$

Unlike the relationship for the α -carbons, there is no apparent difference in this relationship as a function of type or length of branching or the nature of the β carbon.

Stucky originally suggested [12], based on X-ray crystal data, that interactions between the hydrogens on the β -carbons and the lithium atoms might play a role in determining the structure of the lithium aggregate, although later data [13] contradicted that hypothesis. The ^{13}C chemical shift data reported here suggests there is relatively little or no interaction between the hydrogens on the β carbons and the lithium atoms, or at least that the interaction is constant over the compounds studied.

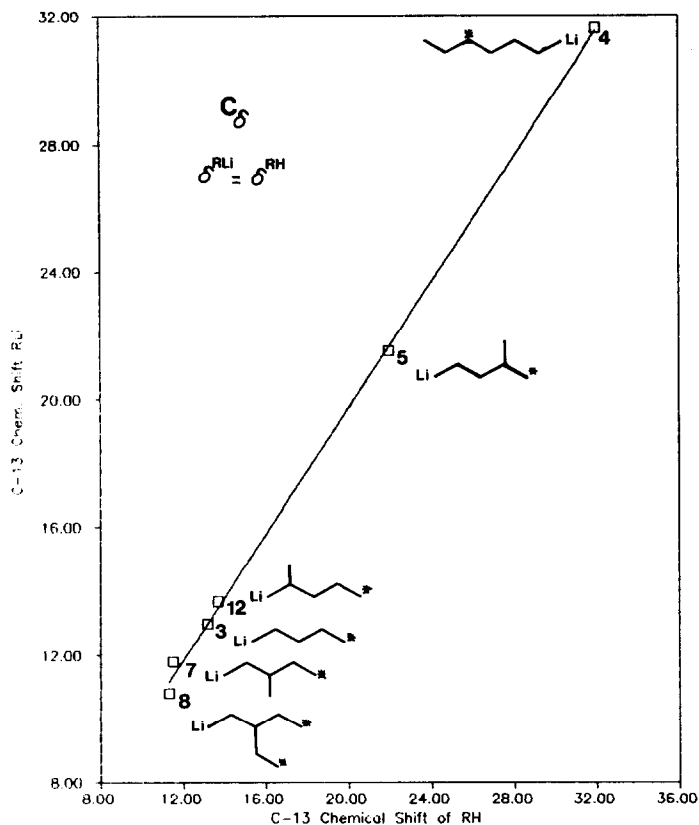


Fig. 4. ^{13}C chemical shifts of RLi vs. RH for δ -carbons.

The carbons γ to lithium in straight-chain alkyl lithium compounds have an excellent correlation with the parent alkanes:

$$C_{\gamma}(\text{st. chain only}): \delta^{\text{RLi}} = (0.95 \pm 0.02)\delta^{\text{RH}} + (7.5 \pm 0.5) \quad r = 0.9998 \quad (6)$$

Substitution of lithium for hydrogen produces a downfield (positive) chemical shift. This is opposite to "normal" γ -effects, in which substitution of an atom for H at the γ position leads to an upfield shift [14].

Inclusion of the branched-chain compounds, excluding *t*-pentyllithium, results in a reasonable correlation:

$$C_{\gamma}: \delta^{\text{RLi}} = (1.06 \pm 0.07)\delta^{\text{RH}} + (2.7 \pm 1.6) \quad r = 0.983 \quad (7)$$

However, fitting this data to a single line is misleading. This analysis ignores an apparent alkyl group dependence of the chemical shifts. The straight-chain compounds (2–4) and isopentyllithium (5) are shifted downfield by 5.2–6.7 ppm. These compounds have the least amount of steric strain, as indicated by their ability to form higher aggregation states (see Table 1). The remainder of the primary compounds (7 and 8), which are more sterically crowded due to branching, are shifted downfield by 1.8–4.8 ppm. The secondary compounds (11 and 12) are shifted downfield by only 0.8–2.0 ppm. The only tertiary compound with a γ -carbon, 14, is shifted upfield 5.8 ppm.

Analysis of the ^{13}C NMR spectrum, however, supports the mass spectral results. There are two new broad resonances at 1.5 ppm and at approximately 14 ppm in the ^{13}C NMR spectrum of the reaction mixture of *t*-butyllithium and vinylsilane. Since the broadness of the lines is likely due to unresolved ^{13}C - ^6Li coupling, these are assumed to be α -carbons. Based on a chemical shift in the parent hydrocarbon of approximately 11 ppm, equations 2 and 3 predict an α -chemical shift for **15** of 0–4 ppm. The resonance at 1.5 ppm was thus assigned to the α -carbon of **15**. Based on a parent hydrocarbon chemical shift of 28 ppm, the α -carbon would be approximately at 12.5 ppm. We have thus assigned the resonance at 14 ppm to the α -carbon of **16**. The magnitudes of these resonances as a function of time further support these assignments. A full discussion of the ^{13}C and ^6Li NMR spectra and the reaction of trimethylvinylsilane with *t*-butyllithium will be presented elsewhere [20].

Experimental

All alkyllithium compounds were prepared as described elsewhere [3] from the corresponding bis(alkyl)mercury compound and ^6Li metal (greater than 95% isotopic enrichment). All samples are 2 *M* in cyclopentane except ethyllithium, which was 0.3 *M* based on monomer. The ^{13}C NMR spectra were measured at 22.6 MHz on a JEOL FX-90Q or at 75.4 MHz on a Varian VXR-300. Chemical shifts are expressed relative to TMS by assigning internal cyclopentane to 25.8 ppm [5]. The chemical shifts for *sec*-butyllithium- ^6Li (**11**) were taken from the literature [1] and corrected to internal cyclopentane at 25.8 ppm by subtracting 0.7 ppm [1b]. The chemical shifts of the parent hydrocarbons were taken from the literature [5]. The correlations were derived from a linear least-squares fit of the data. Errors in the slope and y-intercept are for one standard deviation.

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