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^{7}Li Solid-State NMR of Organolithium Compounds: Dependence of ^{7}Li Quadrupolar Coupling, $\chi(^7\text{Li})$, on the Structural Angle C−Li−C

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Because of their importance for organic synthesis, organolithium compounds belong to the systems most extensively studied with respect to reactivity and structure. While in solution NMR spectroscopy is the method of choice for structural investigations,[1] numerous X-ray measurements have been performed to uncover the structure of organolithium compounds in the solid.[2] More recently, the quadrupolar coupling constant of lithium-7, $\chi(^7\text{Li}) = e^2Qq/h$ (where Q is the quadrupole moment, q the field gradient at the nucleus, e the elementary charge, and h Planck's constant), as determined from ^{7}Li solid-state NMR spectra, emerged as an additional and promising parameter for structural work in this field.[3,4] The sensitivity of the nuclear quadrupole interaction for the bonding situation around the ^{7}Li nucleus allows, for example, discrimination between contact and solvent separated ion pairs,[3] and the measured $\chi(^7\text{Li})$ values also correlate with the aggregation state of the organolithium compound.[5]

We have shown that $\chi(^7\text{Li})$ in lithiated amines correlates linearly with the N−Li−N structural angle, ∠(N−Li−N), which was determined by X-ray investigations:[4]

$$\chi(^7\text{Li}) = (4.1 \pm 0.5)[\angle(\text{N−Li−N})] - (110.8 \pm 69.0) \quad (1)$$

This empirical relation can give important information about the structure of solid lithium amides in cases where X-ray determinations fail because suitable crystals are not available. For example, dimeric structures with N−Li−N angles of 90° can be distinguished from ring compounds with larger internal angles on this basis.

It was therefore of interest to evaluate the possibility that a similar correlation exists in organolithium compounds between $\chi(^7\text{Li})$ and the C−Li−C bond angle, ∠(C−Li−C). For this purpose we investigated a selected number of systems where X-ray determinations allowed us to extract the particular bond angle: phenyllithium*tmeda (**1**),[6] mesityllithium*dee (**2**),[7] tris(trimethylsilyl)methyllithium (ligandfree) (**3**),[8] tetrakis(η^6-2,4,6-triisopropylphenyl)tetralithium (**4**),[9] tris(trimethylsilyl)methyllithium*tmeda (**5**),[10] and tris(trimethylsilyl)methyllithium*thf (**6**)[11] (Chart 1). With the exception of **4**, the selection is limited, as in the case of the lithium amides studied earlier,[4] to systems with a unique X−Li−X angle (X = N, C) as found in monocyclic and many dimeric structures. **1**−**6** were synthesized according to literature procedures and solid-state ^{7}Li MAS NMR spectra were run at 116 MHz under ^{1}H decoupling with rotational frequencies of 4 kHz. The quadrupolar coupling constants $\chi(^7\text{Li})$ (kHz) were extracted from magic angle spinning (MAS) sideband patterns using the program QUASAR.[12] The spectral simulation also yielded the anisotropy parameter for the quadrupolar interaction, the chemical shift anisotropy, and the respective anisotropy parameter. The results are collected in Table 1, together with the structural C−Li−C angles from the X-ray work.

Chart 1. Compounds Studied

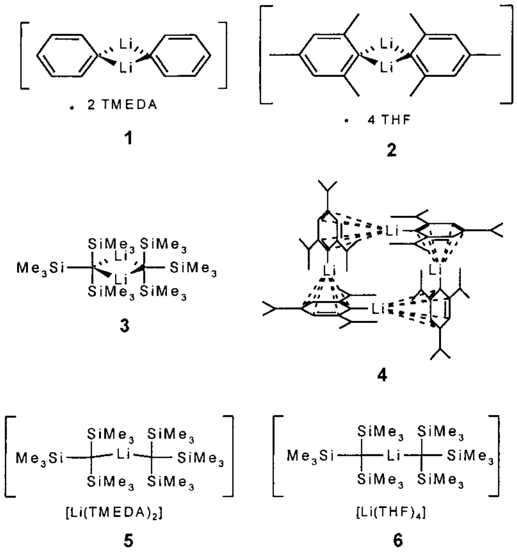

Table 1. ^{6}Li Chemical Shifts, Structural Angles, Quadrupolar Coupling Constants $\chi(^7\text{Li})$, ^{7}Li Chemical Shift Anisotropy, and Respective Anisotropy Parameters

compd	δ(^{6}Li)[a] (ppm)	∠(C−Li−C) (deg)	$\chi(^7\text{Li})$[b] (kHz)	η[c,f]	CSA[d,f] (ppm)	η_{CSA}[e,f]
1	1.9	106	156[g]	0.81	−20	0.6
2	−3.2	114	264	0.74	−16	0.6
3	0.6	118	252	1.00	−17	0.7
4	−6.3	143[h]	334[i]	0.09	−63	0.2
5	−0.1	174	460	0.06	−22	0.2
6	−0.8	180	478	0.12	1	0.0

[a] Relative to LiBr 1 Mr in H_2O; experimental. error <0.2 ppm. [b] Estimated maximum error ±0.3 kHz. [c] Asymmetry parameter of the electric field gradient. [d] Chemical shift anisotropy. [e] Asymmetry parameter of the chemical shift anisotropy. [f] Estimated error 10%. [g] A value of 147 kHz was measured earlier from a static ^{7}Li spectrum.[13] [h] ∠(C−Li−C) = ∠[C(1)−Li-C(1′)]. [i] Values of 320 and 303 kHz were reported for ^{7}Li powder spectra of **4** by other groups.[14,5]

The correlation between the experimental $\chi(^7\text{Li})$ and ∠(C−Li−C) data is given in Figure 1 and shows again a linear behavior as in the case of lithium amides.[4] The dependence is characterized by eq 2, which has nearly the same slope as eq 1, while the

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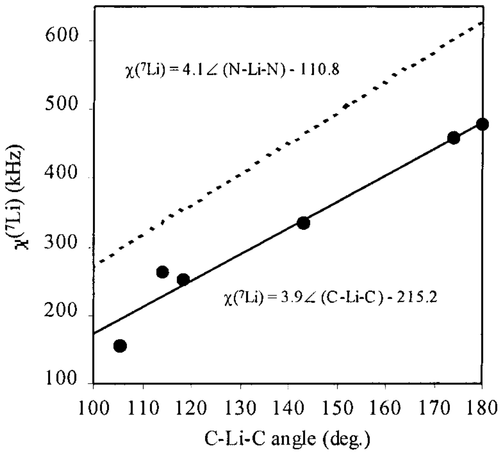

Figure 1. Correlation between $\chi(^7\mathrm{Li})$ and the structural angle ∠(C−Li−C) for **1**−**6**; the dotted line results for lithium amides[4]

different intercept results from the larger magnitude of the quadrupolar coupling constants in the case of the amides:

$$\chi(^7\mathrm{Li}) = (3.9 \pm 0.4)[\angle(\mathrm{C{-}Li{-}C})] - (215.2 \pm 55.6) \quad (2)$$

or

$$\angle(\mathrm{C{-}Li{-}C}) = (0.25 \pm 0.03)\chi(^7\mathrm{Li}) + (58.8 \pm 8.6)$$

That eq 2 also holds for **4** indicates that systems with higher Li coordination may indeed be covered by this relation; however, this aspect needs further confirmation by additional measurements. The fact that the carbon and nitrogen systems display practically the same slope means that the angular dependence is governed by purely geometrical factors and supports the finding[15] that both bonds are largely ionic. The different magnitude of the $\chi(^7\mathrm{Li})$ value in both series, on the other hand, can be attributed to the different charge separation in the C−Li and N−Li bonds. According to results of calculations[15] and a straightforward consideration of the electronegativities for nitrogen and carbon, the N−Li bond is more polar than the C−Li bond. Atomic charge densities obtained from ab initio calculations[16] for simple model systems (Table 2) support this conclusion. The calculated charge separation in the N−Li bond is in all cases larger than that in the C−Li bond of the corresponding system. Since $\chi(^7\mathrm{Li})$ is proportional to the z-component of the electric field gradient at the Li nucleus the more polar bond is expected to yield the larger χ value.

Table 2. Calculated Atomic Charge Densities ρ for Monomeric Model Systems at the HF Level[a]

	C−Li				N−Li		
	ρ_C[b]	ρ_Li[c]	$\Delta\rho$		ρ_N[d]	ρ_Li[c]	$\Delta\rho$
CH_3Li	−1.41	0.82	2.23	NH_2Li	−1.62	0.90	2.52
CH_3CH_2Li	−1.13	0.82	1.95	CH_3NHLi	−1.37	0.91	2.27
CyHexCH_2Li[e]	−1.11	0.83	1.94	*CyHex*NHLi[e]	−1.36	0.91	2.27
$(CH_3)_2CHLi$	−0.86	0.82	1.68	$(CH_3)_2NLi$	−1.28	0.92	2.20
i-Pr$_2$CHLi	−0.86	0.83	1.69	*i-Pr*$_2$NLi	−1.15	0.92	2.06
*CyHex*Li[e]	−0.87	0.83	1.70	*Pip*Li[f]	−1.14	0.92	2.06

[a] Basis set 6-31G**; standard bond lengths and angles as input.[16] [b] Natural charge on lithiated carbon. [c] Natural charge on lithium. [d] Natural charge on lithiated nitrogen. [e] *CyHex* = Cyclohexyl. [f] *Pip* = Piperidide.

Apart from the angular dependence of $\chi(^7\mathrm{Li})$, systems **5** and **6** nicely demonstrate the usefulness of this parameter for the discrimination between lithium cations in contact and solvent-separated ion pairs with large differences for the respective quadrupolar interactions. For **5** and **6** we find $\chi(^7\mathrm{Li})$ 126 and 19 kHz, respectively, for the solvent-separated lithium cations which reside in a more symmetric environment as compared to the lithium cations in close contact with organic ligands which yield the $\chi(^7\mathrm{Li})$ values given in Table 1.

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