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A NUCLEAR MAGNETIC RESONANCE STUDY OF CARBON–LITHIUM BONDING IN ARYLMETHYLLITHIUMS
BENZYLLITHIUM AND 1,1-DIPHENYL-n-HEXYLLITHIUM*

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SUMMARY

The nature of carbon–lithium bonding in benzyllithium and 1,1-diphenyl-n-hexyllithium and its variation with solvent is evaluated from carbon, lithium, and proton nuclear magnetic resonance measurements. The solvent dependency of the NMR data is interpreted as evidence that the α-carbons of these arylmethyllithiums have appreciable sp^3 character which increases with decreasing solvent polarity. Anion–cation interaction accordingly increases with decreasing solvent polarity. Solvent induced changes in ligand (anion–cation) interactions are considered to be the predominant factor influencing the nature of the carbon–lithium bonding. The larger π-system of 1,1-diphenyl-n-hexyllithium is suggested to moderate the dependence of anion–cation interaction on solvent and to result in greater (than in benzyllithium) sp^2 character to the α-carbon.

INTRODUCTION

It is generally believed that in odd alternant arylmethyllithium reagents, there is extensive delocalization of the carbon–lithium bonding electrons throughout the aromatic rings. The long wavelength electronic absorption[2] and high-field displacement of aromatic protons in the ^{1}H NMR spectra of arylmethyllithium reagents[3] is evidence in support of this delocalization. Because it is part of a π-system, the criterion of maximum overlap favors the α-carbon being sp^2 hybridized which requires that the carbon–lithium bonding electrons occupy a p-orbital. Earlier ^{13}C NMR studies[4] in tetrahydrofuran solution suggested that some s-character should be ascribed to this orbital. Reported here are extensive ^{13}C, ^{7}Li, and ^{1}H NMR data for benzyllithium[5] and 1,1-diphenyl-n-hexyllithium in solvents varying in polarity from cyclohexane to hexamethylphosphoric triamide (HMPA) that permit assessing relative changes in α-carbon hybridization and carbon–lithium interaction with solvent changes. 1,1-Diphenyl-n-hexyllithium was chosen for these studies because of its substantial hydrocarbon solubility, a behavior not common to the structural analogs diphenylmethyl or triphenylmethyllithium.

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* Presented in part at the Symposium on the roles of ions and ion pairs in organic chemistry and in polymerization processes, see ref. 1.

Interpretation of the NMR data for benzyllithium shows that the α-carbon has appreciable sp^3 character which increases with decreasing solvent polarity. The changes are less than with 1,1-diphenyl-n-hexyllithium illustrating the moderating influence of the larger π-system on anion–cation interaction.

EXPERIMENTAL

^{13}C and ^7Li spectra were obtained on the previously described high resolution NMR spectrometer[6]. ^{13}C spectra were measured at 15.09 MHz and ^7Li spectra at 23.32 MHz. The INDOR technique[7] was used to obtain ^{13}C spectra of α-^{13}C-benzyllithium. Direct ^{13}C spectra were obtained for 1,1-diphenyl-1-^{13}C-n-hexyllithium.

Benzyllithium was prepared from bis(α-^{13}C-benzyl)mercury (obtained from Merck–Sharp and Dohme, Ltd. with ~58% ^{13}C enrichment) by reaction with lithium dispersion in various solvents. A particular achievement facilitating these studies is the finding that this reaction proceeds in good yield in benzene solution with heating to ~70°, and that the benzyllithium is soluble up to ~0.1 molar in aromatic hydrocarbon solvents.

1,1-Diphenyl-n-hexyllithium was prepared, as previously described[8], by reacting butyllithium (Foote Mineral Co.) with 1,1-diphenyl-1-^{13}C-ethylene (obtained from Merck–Sharp and Dohme, Ltd. with ~57% ^{13}C enrichment) in the various solvents.

All NMR samples were prepared on a vacuum line using solvents which were freshly distilled from lithium dispersion under argon, with the exception of hexamethylphosphoramide (HMPA) which was vacuum distilled from triphenylmethylsodium. Solution transfers were made under a positive argon atmosphere using Hamilton gas-tight syringes.

RESULTS

^{13}C, ^7Li and ^1H NMR data for benzyllithium in various solvents are summarized in Table 1. Analogous data for 1,1-diphenyl-n-hexyllithium are summarized

TABLE 1

NMR OF BENZYLLITHIUM

Solvent	$\delta(^{13}C)^a$ (ppm)	$J(^{13}C-^1H)$ (Hz)	$\delta(^1H)$ (ppm)^b		$\delta(^7Li)^c$ (ppm)
			Para	α-CH_2	
THF	163	132	1.8	0.79	1.06
Et_2O^d	167.6	129			
Et_2O	168.5	135	1.3	0.70	1.47
Benzene	174.5	116	~0.7	0.21	2.07
Toluene^e	172				

[a] Chemical shift of α-carbon relative to external CS_2 (neat). [b] Relative to internal toluene (all chemical shifts upfield of toluene). [c] Relative to internal butyllithium (measured independently). [d] Ether solvent containing 1.5 parts THF per mole of benzyllithium. [e] Chemical shift is for the α-carbon of toluene in THF, but because $\delta(\alpha-^{13}C)$ of carbon-1 of 1,1-diphenyl-n-hexane is invariant in this series of solvents, it is reasonable that $\delta(\alpha-^{13}C)$ toluene is also invariant with solvents (*cf.* Table 2, footnote b).

TABLE 2

NMR OF 1,1-DIPHENYL-n-HEXYLLITHIUM

Solvent	$\delta(^{13}C)^a$ (ppm)	$\Delta\delta(^{13}C)^b$ (ppm)	$\delta(^1H)$ (ppm)^c			$\delta(^7Li)^d$ (ppm)
			para	*meta*	*ortho*	
Cyclohexane	+113	−27	+1.3	(+0.5)		+8.25
Benzene	+115	−26	+1.2			+6.98
Et_3N	+110	−31	+1.5	(+0.55)		+4.99
Et_2O	+121	−20	+1.3	+0.6	+0.25	+3.5
THF	+110	−31	+1.8	+0.9	+0.5	+2.21
HMPA	+112	−29	+1.8	+0.9	+0.4	
THF^e			~+1.0	+0.5	+0.3	

^{a} Chemical shift of α-carbon relative to external CS_2 (neat). ^{b} Relative to 1,1-diphenyl-1-^{13}C-n-hexane for which $\delta(^{13}C)+141$ ppm (relative to CS_2) in cyclohexane, benzene, ether and THF. $J(^{13}C-^1H)$ 126 Hz in all of these solvents. *c* Relative to internal benzene. *d* Relative to internal butyllithium (measured independently in the respective solvents). ^{e} 0.5 Et_2Zn/RLi.

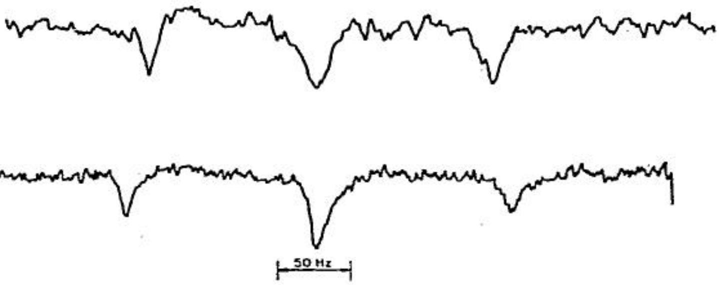
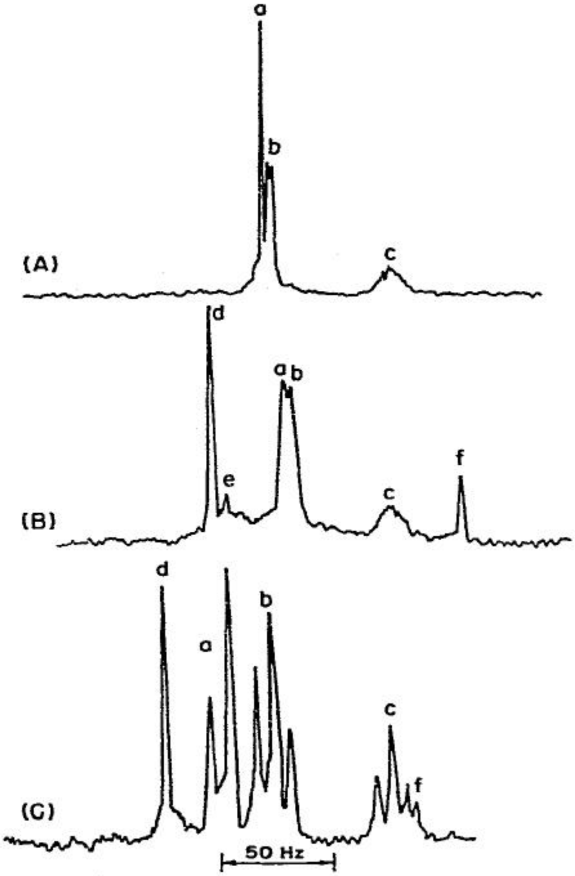


Fig. 1. ^{13}C INDOR spectra of benzyllithium in (A) benzene and (B) THF.

in Table 2. Example ^{13}C NMR spectra for benzyllithium are shown in Fig. 1, which illustrates the difference in $^{13}C-^1H$ spin–spin coupling constants in the solvents benzene and THF. Example ^{1}H NMR spectra for 1,1-diphenyl-n-hexyllithium in three solvents are illustrated in Fig. 2. Of particular interest and a source of uncertainty in evaluating charge density distribution is the finding that the spectrum changes from an essentially first order pattern in THF to a non-first order pattern in the nonpolar solvents triethylamine and cyclohexane. An unidentified impurity resonance, (e), was found to increase with time in solutions containing excess 1,1-diphenylethylene, but was absent from solutions containing equimolar butyllithium and 1,1-diphenylethylene. The first order spectrum observed in THF, which is like that of triphenylmethyllithium[3], changes in less coordinating solvents to a spectrum (Fig. 2) much like that reported for diphenylmethyllithium[3]. Examination of the spectrum of 3,3′,5,5′-tetradeuterio-1,1-diphenyl-n-hexyllithium in cyclohexane (Fig. 3) established that the order of the protons is *ortho, meta, para* (moving upfield from benzene), as was established for the first order spectrum in THF. $\delta(^{13}C)$ was unaffected by excess 1,1-diphenyl-1-^{13}C-ethylene.

In contrast to the $^{13}C-^7Li$ spin–spin coupling observed for methyllithium in donor solvents[9], no $^{13}C-^7Li$ coupling was observed for benzyllithium or 1,1-diphenyl-n-hexyllithium at temperatures as low as −100° in THF solution or at ambient tem-



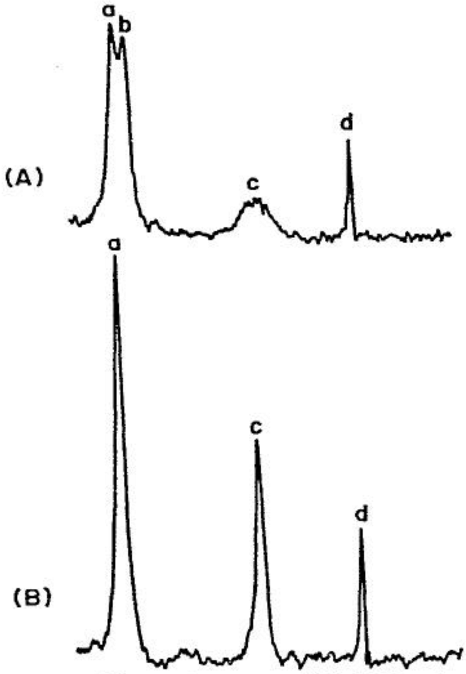


Fig. 2. ^1H NMR of 1,1-diphenyl-n-hexyllithium in (A) triethylamine, (B) cyclohexane, and (C) THF. a, b, and c designate the *ortho*, *meta*, and *para* aromatic proton resonances; d and f, the aromatic and vinyl resonances of excess 1,1-diphenylethylene in the solutions; and e, an unknown impurity.

Fig. 3. ^1H NMR of (A) 1,1-diphenyl-n-hexyllithium in cyclohexane. a, b, and c designate the *ortho*, *meta*, and *para* aromatic proton resonances and d, the vinyl resonance arising from excess 1,1-diphenylethylene in solution; (B) 3,3′,5,5′-tetradeuterio-1,1-diphenyl-n-hexyllithium in cyclohexane.

peratures in hydrocarbon solutions. The low solubility of these reagents in hydrocarbon solvents precluded observation of ^7Li spectra at low temperatures. The lack of observable coupling in THF is suggested to result from rapid ^7Li exchange even at $-100°$, or alternatively, the ionic character of the carbon–lithium bond may preclude the occurrence of coupling. Favoring the former is that lithium exchange between benzyllithium and lithium bromide is rapid at temperatures at which the analogous exchange between methyllithium and lithium bromide is slow. In hydrocarbon solution, the broad ^7Li resonance (line width $\geqslant 10$ Hz) may obscure coupling.

DISCUSSION

Substantial experimental and theoretical evidence indicates that ^1H and ^{13}C chemical shifts and $J(^{13}C–^1H)$ values are effective measures of the hybridization and charge density on the examined carbon[10]. Use of both ^{13}C and ^{1}H NMR data permits evaluation of carbon hybridization in molecules where both charge and hybridization change simultaneously. The ^{13}C chemical shifts for sp^2- and sp^3-hybridized carbon is respectively $\sim +50$ and $+160$ ppm from carbon disulfide. Representative data are summarized in Table 3. Increasing charge density on a carbon of given hybridization results in an upfield shift of ^{13}C resonance. The conversion constant of $\sim$160–200 ppm/electron established for sp^2-carbon*, apparently is also applicable for sp^3-carbon[14].

TABLE 3

CARBON CHEMICAL SHIFTS AND COUPLING CONSTANTS FOR sp^2 AND sp^3 HYBRIDS

Compound	$\delta(^{13}C)^a$ (ppm)	$J(^{13}C-^{1}H)$
C_6H_6	+ 65.0	159
$Ph^{13}CH{=}CH_2$	+ 57.0^b	
$H_2C{=}^{13}CPh_2$	+ 42.7	
$Ph^{13}CH_3$	172	126
$Ph_2{}^{13}CH_2$	157	126
$Ph_2{}^{13}CH$-n-C_5H_{11}	141	126

[a] Chemical shift of α-carbon (excepting benzene) relative to external CS_2 (neat). [b] Ref. 17.

The data summarized in Tables 1 and 2 permit evaluating the nature of carbon–lithium bonding in benzyllithium and 1,1-diphenyl-n-hexyllithium over a wide range of solvent environments. In these odd alternant molecules, delocalization of negative charge occurs throughout the π-electronic system. The extent of delocalization, reflected in the proton NMR shifts, is moderated by anion–cation interaction. Polar solvents interact with the lithium cation, moderate its Lewis acid strength and facilitate charge separation[8].

Studies of the solvent dependency of the electronic absorption spectra of 1,1-diphenyl-n-hexyllithium established that the λ_{max} shifts from 410 mμ in hexane to 496 mμ in THF. This reflects increased charge delocalization in the anion caused by increased solvation of the lithium cation in more polar solvents. The proton NMR spectrum of diethylzinc/1,1-diphenyl-n-hexyllithium mixtures showed that interaction of the organolithium with the Lewis acid, diethylzinc, decreases the charge delocalization[12]. The change in fractional charge density occurring at each of the ring protons varies with the organolithium/diethylzinc ratio, and it is probable that a corresponding change in charge density occurs at the α-carbon.

Although charge densities in the ring can be evaluated from proton NMR data[3], evaluation of charge density on the α-carbon is less certain. Assuming unit negative charge on the organic moiety, the maximum α-carbon charge is evaluated by difference using the *para*-proton shift as a probe. Evaluation of the chemical shift and coupling constant data of benzyllithium in THF (*cf.* Table 1) indicates that a substantial degree of sp^3 character be attributed to the α-carbon[5]. The upfield shift of $\delta(^{13}C)$ in changing from the polar solvents, which interact strongly with the

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* Derivation of this relationship assumed negligible ion-pair interaction. The proportionality constant of 160 is, thus, a minimal value.

positively polarized lithium, to nonpolar hydrocarbon solvents is in accord with increasing sp^3 character for the α-carbon with this change in solvent environment. In contrast to benzyllithium, ^{13}C shifts of 1,1-diphenyl-n-hexyllithium (Table 2) are nearly constant. The changes in the ^1H and ^7Li chemical shifts with solvent are instructive in interpreting this behavior. Summarized in Table 4 are approximated ring charge densities* for 1,1-diphenyl-n-hexyllithium. The change from polar (THF) to nonpolar (benzene) solvent results in a charge reduction of $\sim 30\%$ in the aromatic rings, based on both *para* and total ring charge densities. A similar reduction of charge on the α-carbon is considered to occur with this solvent change. Assuming the α-carbon charge changes in proportion to that on the rings, the maximum excess charge on the α-carbon is indicated to be ~ 0.1 electron in hydrocarbon solvents.

TABLE 4

NEGATIVE RING CHARGE DENSITIES ON 1,1-DIPHENYL-n-HEXYLLITHIUM DETERMINED FROM ^1H CHEMICAL SHIFTS

Solvent	Σ_q			Σ_q total
	para	*meta*	*ortho*	
Cyclohexane	0.24	0.37		0.61
Benzene	0.22			
Et_2O	0.24	0.22	0.09	0.55
Et_3N	0.28	0.41		0.69
THF	0.34	0.33	0.20	0.87
HMPA	0.34	0.33	0.15	0.82

Hückel and SCF–MO calculations predict an α-carbon excess charge of ~ 0.4 and 0.32 respectively for an sp^2 hybridized 1,1-diphenyl-n-hexyllithium[16]. Proton data which yield smaller values are presumably a more realistic estimate of this charge. However, because of the anion–cation interaction, there presumably is *not* unit charge on the organic moiety. Interpretation of the NMR data (particularly the high-field ^{13}C resonance) suggests that a substantial fraction of sp^3 character be ascribed to the α-carbon. The degree of sp^3 character increases with decreasing solvent polarity. Assuming relative changes in excitation energy are small, the constancy of $\delta(^{13}C)$ in solvents of different polarity may reflect the balance between charge polarization and sp^3 character of the α-carbon.

Supporting the suggestion, that the donor–acceptor type interaction between incipient anion and cation is solvent dependent, is a substantial upfield displacement of the ^7Li resonance (Table 2) in changing from polar to nonpolar solvents. The lithium resonance is interpreted to be sensitive to the anion–cation interaction and the electron density at lithium as a result of electronic charge delocalization in the carbon–lithium bond.

The bonding concepts proposed for benzyllithium and 1,1-diphenyl-n-hexyllithium are thought to be general and to apply to other odd-alternant arylmethyl-

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* Using the relationship $\Delta = 10.7\,p$. Unit charge density on the anionic species is assumed, see ref. 11 and 15.

lithiums. The size of the π-system influences the nature of the solvent dependency of carbon–lithium bonding in these molecules.

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