The Nature of Carbon–Lithium Bonding in Benzyl-lithium and its Variation with Solvent

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WE report ^{13}C, ^{7}Li, and ^{1}H n.m.r. results which permit evaluation of carbon–lithium bonding in benzyl-lithium. ^{13}C-Resonance uniquely allows direct examination of the carbon atom involved in bonding. The solvent is shown to have a profound influence on the anion–cation interaction and hybridization of the α-carbon.

In odd alternant molecules, such as benzyl-lithium, the criterion of maximum overlap is typically cited as evidence that the α-carbon is sp^2-hybridized. This requires that the carbon–metal bonding electrons occupy a *p*-orbital. Earlier studies suggested some *s*-character should be ascribed to this orbital.[1]

The ^{13}C chemical-shift data and its solvent dependence, the ^{13}C–^{1}H spin–spin coupling constants, and ^{1}H measurements of charge densities show that the α-carbon in benzyl-lithium has substantial sp^3 character, which shows a marked increase in benzene solution compared with that in tetrahydrofuran (THF). Hybridization in diethyl ether is intermediate. The changes in ^{7}Li chemical-shift in these solvents indicate appreciable increase in anion–cation interaction with decreasing solvent polarity. The degree of anion-cation interaction is believed to be the driving force for sp^3 hybridization, which counteracts the possible gain in stability arising from maximum delocalization.

α-^{13}C Enriched benzyl-lithium was prepared from enriched dibenzylmercury and lithium: this reaction proceeds in good yield in benzene solution with heating to *ca.* 70°, and benzyl-lithium is soluble up to *ca.* 0·1 M. The n.m.r. spectra were obtained with the spectrometer of Baker and Burd.[2] INDOR techniques[3] were used to obtain ^{13}C spectra.

If $CH_2{=}^{13}CHPh$, (δ_{CS_2} 59)[4] is taken as a reference for sp^2 benzyl and $Ph^{13}CH_3$ (δ_{CS_2} 172 p.p.m.)[1] as a reference for sp^3 species, the change from sp^2 to sp^3-C causes a change in $\delta(^{13}C)$ of 112 p.p.m. The dependence of $\delta(^{13}C)$ on charge density (ρ) is given[5] by $\delta = 160\rho$ for sp^2-C: theory suggests this should also be a reasonable approximation for sp^3-C.[6]

^{1}H Chemical-shift studies in THF[7] permit assessment of negative charge density on the phenyl ring. The change in aromatic ^{1}H chemical-shift values of benzyl-lithium relative to those of benzene indicates that *ca.* 0·6 electron density is delocalized on the ring.[8] If we assume a unit negative charge on the benzyl moiety this leaves a net maximum of 0·4 excess electron-density on the α-C.† Similar evaluation in benzene shows the excess electron-density on the ring to be *ca.* 0·2 *e*, substantially reduced from that in THF solution. Assuming $\rho_{\alpha\text{-C}}$ to be reduced in proportion leads to a net maximum of *ca.* 0·1–0·2 e on

N.m.r. data for [α-^{13}C]*benzyl-lithium*

Solvent	α-CH$_2$ (p.p.m.) $\delta(^{13}C)$[a]	$\delta(^1H)$[b]	$J(^{13}C\text{-}H)$	$\delta(^7Li)$ (p.p.m.)[c]
THF	163·0	0·79	132	1·06
Et_2O	168·5	0·70	135	1·47
Benzene	174·5	0·21	116	2·07
[Me-^{13}C]Toluene[d]	172·0		126	

[a] Relative to external neat CS_2; [b] relative to internal toluene CH_3; [c] relative to internal n-butyl-lithium; [d] In THF, but $\delta(^{13}C)$ (1,1-diphenyl[1-^{13}C]hexane) is invariant in the above solvents relative to external CS_2; thus, $\delta(^{13}C)$ ([Me-^{13}C] toluene) is almost certainly invariant in these solvents.

α-C of benzyl-lithium in benzene. The observed down-field shift of the methylene protons with solvent change from THF to benzene supports this reasoning. To account for the $\delta(\alpha\text{-}^{13}C)$ of benzyl-lithium in benzene as being a result of an sp^2 hybridized reagent would require an unreasonable value of *ca.* 0·8 *e* excess charge density on the α-C atom.

Although the upfield displacement of benzyl-lithium relative to toluene is less than that found for methyl-lithium[9] relative to methane (*i.e.*, 9—13 p.p.m.), the upfield displacement is in accord with the behaviour expected for substantially sp^3-hybridized benzyl-lithium. Similarly, appreciable sp^3 character is required to account for $\delta\alpha(^{13}C)$ in THF without an unreasonable high α-C charge density.

The ^{7}Li-chemical shift moves appreciably upfield with change in solvent from THF to benzene. This is interpreted as due to a substantial increase in anion–cation interaction with transfer of electron density from the benzyl moiety to lithium. The C–Li bonding in benzyl-lithium is probably largely σ in nature, this being most pronounced in benzene.

The ^{13}C–^{1}H spin–spin coupling constants vary with the hybridization of the carbon,[10] increasing with increasing *s*-character in the C–H orbital. The greater the *s*-character of the C–H orbitals, the more *p*-character in the C–Li orbital. Values of $J(^{13}C\text{–}H)$ are several Hz smaller for species bearing partial negative charge density than in neutral species.[1] The finding that $J(^{13}C\text{–}H)$ for α-C–H of benzyl-lithium in benzene is smaller than that of toluene is in agreement with these species having similar α-C-hybridization [*cf.* $J(^{13}C\text{–}H)$ 98 Hz for methyl-lithium, 125 Hz for methane].[9] The increase in $J(^{13}C\text{–}H)$ for α-C–H in THF solution is in accord with increased sp^2 character for α-C in this solvent, *i.e.*, more *p*-character in the C–Li orbital. This arises from a reduction in interaction energy between incipient anion–cation pair as a result of the reduced Lewis-acid strength[11] of the more (than in benzene) solvated positively polarized lithium ligand.

Solvent-induced changes in electronic transition energy in odd alternant lithium reagents are considered to arise primarily from changes in cation-anion interaction,[11] which reflect relative stabilization of the ground state.‡ We now report that the absorption maximum of benzyl-lithium at 330 nm. in THF[12] shifts to 292 nm. in benzene. This corresponds to a change of *ca.* 11 kcal. mole^{-1} in transition energy. Ligand interaction-induced hybridization changes within a π-system should have the same effect on transition energy as steric distortion of a π-system,[13] and result in blue shifts.[14]

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† Note that $\rho_{\alpha\text{-C}}$ is expected to be less than this maximum value to the extent that C–Li ion-pair interaction occurs.
‡ The excited-state energies are less sensitive to cation–anion interactions because of their being a single electron C–Li bond.

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