Structure and Bonding in Alkyl-lithium Compounds in Hydrocarbon Solution

By L. DENNIS MCKEEVER* and RICHARD WAACK

(*Physical Research Laboratory,* 1712 *Building, The Dow Chemical Company, Midland, Michigan* 48640)

WE report ^{13}C and ^{7}Li n.m.r. data[†] which define the structure of the t-butyl-lithium tetramer and elucidate the nature of carbon–lithium bonding in t-butyl- and n-butyl-lithium in hydrocarbon solution.[‡] ^{13}C–^{7}Li spin–spin coupling is observed in the ^{7}Li n.m.r. spectrum of α-^{13}C-enriched t-butyl-lithium in cyclohexane solution over the temperature range -20 to $+80°$ (Figure). Observation of coupling at these relatively high temperatures supports the suggested slow intermolecular exchange between certain alkyl-lithium species in hydrocarbon solution.[1] ^{13}C-^{7}Li coupling was established by collapsing the multiplet by irradiating the ^{13}C at 15·089597 MHz.

Interpretation of the spectrum, analogous to that in previous studies of ^{13}C–^{7}Li scalar coupling in methyl-lithium in donor solvents,[2] provides definitive support for the tetrameric structure suggested for t-butyl-lithium in hydrocarbon medium.[3] The calculated n.m.r. spectrum is in accord with the previously suggested[2,3] "cubic" structure for the tetramer, *i.e.*, one in which the lithium atoms are situated at opposite corners of a cube with the α-carbons occupying the other corners such that each lithium interacts with three neighbouring alkyl groups and *vice*-versa. The ratio of line intensities (relative to the centre line of the multiplet) for the observed spectrum is 1·00, 0·81, 0·47, 0·08. For slow intra-aggregate exchange (7-line spectrum with Lorentzian line shapes), calculated ratios are 1·00, 0·81, 0·41, 0·13, and for rapid intra-aggregate exchange (but with no interaggregate exchange) a 9-line spectrum with intensity ratios, 1·00, 0·83, 0·49, 0·20 is calculated. Although the coupling pattern defines the structure of the tetramer, the observed line intensity ratios are not sufficiently precise to distinguish between slow and rapid intra-aggregate exchange. The latter, however, is reported to obtain.[4]

^{13}C–^{7}Li scalar coupling is *not* observed for [α-^{13}C]-n-butyl-lithium in n-hexane, cyclohexane, or benzene solution. The ^{7}Li resonance of *ca.* 0·5M-n-butyl-lithium in n-hexane solution broadens from 3 to 20 Hz. over the temperature range $+20$ to $-70°$ and line narrowing does not occur upon

---

[†] ^{7}Li spectra were measured at 23·322 MHz. and ^{13}C at 15·089 MHz. on the high-resolution n.m.r. spectrometer described by E. B. Baker and L. W. Burd, *Rev. Sci. Instr.*, 1957, **28**, 313; 1963, **34**, 238. An FTI Model 1052 computer was used for time-averaging.

[‡] n-Butyl- and t-butyl-lithium were prepared in sealed evacuated tubes by reaction of the alkyl chloride or bromide with an excess of lithium dispersion in the various hydrocarbon solvents. Residual lithium was removed by filtration through a fritted disc.

Nuclear magnetic resonance of C_4H_9Li

Compound	Solvent	$\delta(^7Li)$[a] (p.p.m.)	$\delta(^{13}C)$[b] (p.p.m.)	$J(^{13}C-^7Li)$ (Hz.)	$J(^{13}C-^1H)$ (Hz.)
Bu^tLi	Cyclohexane	−0·96	+182	11	—
Bu^tLi	Toluene	−0·26	—	*ca.* 10	—
Isobutane	Neat	—	+169[c]	—	—
Bu^nLi	Hexane	−1·76	+182	—	100
Bu^nLi	Ether	−0·71	+182	14	98
n-Butane	Neat	—	+181[d]	—	125

[a] Relative to external 0·5M-LiBr in tetrahydrofuran.

[b] Relative to external carbon disulphide.

[c] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1961, **35**, 722.

[d] E. G. Paul and D. M. Grant, *J. Amer. Chem. Soc.*, 1963, **85**, 1701.

irradiation of the ^{13}C. $^{13}C-^7Li$ coupling is, however, observed in [α-^{13}C]-n-butyl-lithium in diethyl ether solution at −70° (Table). Although the spectrum is not especially well defined in this medium, the relative spectral line intensities are in accord with a cubic[2,3] geometry for the n-butyl-lithium tetramer.

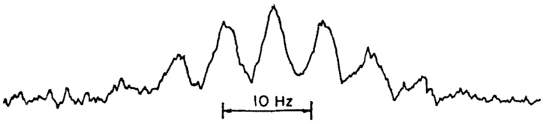

FIGURE. ^7Li *n.m.r. spectrum (room temperature) of* ca. 0·1M-[α-^{13}C] (57%) *t-butyl-lithium in cyclohexane solution (averaged* 300 *times).*

The absence of scalar $^{13}C-^7Li$ coupling in n-butyl-lithium in hydrocarbon solvents is noteworthy. n-Butyl-lithium is reported to be predominantly hexameric[6] in hydrocarbon solution over a wide concentration range.[7] Assuming the previously suggested octahedral structure[8] for the hexamer obtains $J^{13}C-^7Li$ is expected to be in the 10—15 Hz. range.[2] Quadrupolar relaxation of the ^7Li nuclear spin states[9] would obscure coupling only if the coupling constant were much smaller. The absence of scalar $^{13}C-^7Li$ coupling is suggested to arise from rapid interaggregate exchange. Although Lewis and Brown[7] report that the hexamer is the predominant species in solution, interaggregate exchange also may occur between lower or even higher (but low-concentration) polymeric species.

^{13}C chemical shifts for t-butyl- and n-butyl-lithium and $J(^{13}C-^1H)$ values for n-butyl-lithium are summarized in the Table. In view of the considerations of Spiesecke and Schneider,[10] $\delta(^{13}C)$ is not expected to be appreciably affected by the magnetic anisotropy of the neighbouring polymeric group. The butyl-lithium data, analogous to those reported for methyl-lithium,[2] are interpreted to imply substantial (but polar) covalent carbon–lithium bonding. Previous ^{13}C n.m.r. studies of arylmethyl-lithiums, where substantial electron delocalization occurs, illustrated that appreciable differences between $\delta(^{13}C)$ for the organolithium and the corresponding hydrocarbon occur.[11] The downfield shifts of the organolithiums relative to the hydrocarbons were interpreted in terms of the partial sp^2 character of the carbon bound to lithium.

Based on the very similar ^{13}C chemical shifts of n-butyl- and t-butyl-lithium (relative to the corresponding hydrocarbons) substantial sp^3-hybridization of the α-carbon is inferred. Furthermore, since the relationship between charge density and $\delta(^{13}C)$ for sp^3-hybridized carbon,[12] like that for sp^2-carbon,[13] is indicated to be *ca.* 160 p.p.m. per electron, the excess of charge density on the α-carbon is indicated to be small, implying predominantly covalent carbon–lithium bonding.

$J(^{13}C-^1H)$ values for n-butyl-lithium, like those for methyl-lithium,[14] are appreciably smaller than those reported for the corresponding sp^3-hybridized hydrocarbon. As noted previously,[2,11,15] negative charge is indicated to reduce $J(^{13}C-^1H)$ values.

It appears that carbon–lithium bonding in alkyl-lithiums,[2] unlike arylmethyl-lithiums,[11] is not appreciably altered by relatively severe changes in the solvent environment. Self-solvation of these reagents to form polymeric species is preferred.

We thank Drs. M. Exner, L. M. Huber, and E. B. Baker for assistance, and Professor T. L. Brown and his students for preprints of their recent studies.

(*Received, May 9th,* 1969; *Com.* 642.)

---

[1] M. Weiner and R. West, *J. Amer. Chem. Soc.*, 1963, **85**, 485; T. L. Brown and J. A. Ladd, *J. Organometallic Chem.*, 1964, **2**, 373.

[2] L. D. McKeever, R. Waack, M. A. Doran, and E. B. Baker, *J. Amer. Chem. Soc.*, 1968, **90**, 3244; 1969, **91**, 1057.

[3] M. Weiner, G. Vogel and R. West, *Inorg. Chem.*, 1962, **1**, 654.

[4] G. E. Hartwell and T. L. Brown, *J. Amer. Chem. Soc.*, 1966, **88**, 4625.

[5] P. West and R. Waack, *J. Amer. Chem. Soc.*, 1967, **89**, 4395.

[6] D. Margerison and J. P. Newport, *Trans. Faraday Soc.*, 1963, **59**, 2058.

[7] H. L. Lewis and T. L. Brown, *J. Amer. Chem. Soc.*, 1969, **91**, in the press.

[8] T. L. Brown, R. L. Gerteis, D. A. Bafus, and J. A. Ladd, *J. Amer. Chem. Soc.*, 1964, **86**, 2135.

[9] T. L. Brown and J. A. Ladd, *J. Organometallic Chem.*, 1964, **2**, 373; E. A. C. Lucken, *ibid.*, 1965, **4**, 252.

[10] H. Spiesecke and W. G. Schneider, *J. Chem. Phys.*, 1962, **35**, 722.

[11] R. Waack, M. A. Doran, E. B. Baker, and G. A. Olah, *J. Amer. Chem. Soc.*, 1966, **88**, 1272; R. Waack, L. D. McKeever, and M. A. Doran, *Chem. Comm.*, 1969, 117.

[12] T. Yonezawa, I. Morishima, and H. Kato, *Bull. Chem. Soc. Japan*, 1966, **39**, 1398; B. V. Cheney and D. M. Grant, *J. Amer. Chem. Soc.*, 1967, **89**, 5319; T. D. Alger, D. M. Grant, and E. G. Paul, *ibid.*, 1966, **88**, 5397; W. J. Horsley and H. Sternlicht, *ibid.*, 1968, **90**, 3738.

[13] P. C Lauterbur, *Tetrahedron Letters*, 1961, **274**; H. Spiesecke and W. G. Schneider, *ibid.*, p. 468.

[14] A. W. Douglas, *J. Chem. Phys.*, 1966, **45**, 3465.

[15] R. M. Hammaker, *J. Mol. Spectroscopy*, 1965, **15**, 506.