

$\text{CH}_3)_2$ .<sup>3,3</sup> Unfortunately, no optimization of the molecular geometry of  $(\text{LiCH}_3)_4$  was carried out and the long Li-Li distance of 2.68 Å which was used in the theoretical calculations may be largely the result of the intermolecular interactions for  $(\text{LiCH}_3)_4$  in the solid state. Suggestive, but not conclusive, evidence for the localized four-centered bond theory is the fact that in the final difference Fourier of cyclohexyllithium the largest amounts of electron density were found above each of the six smaller triangular faces and about 0.77 Å below the  $\alpha$ -carbons associated with the lithium atom faces. The residual electron density ( $0.50 \pm 05 \text{ e}/\text{Å}^3$ ) was located at the positions one would predict to be the centers of the four-centered bonds. The maximum electron density found elsewhere was  $0.38 \text{ e}/\text{Å}^3$ .

Because of the substantial evidence supporting the four-centered bond theory, the bonding proposed for cyclohexyllithium is based on the four-centered bond theory and is pictorially displayed in Figure 8. The lithium atoms are proposed to be  $\text{sp}^2$  hybridized. The  $\text{sp}^2$  orbitals lie approximately in the plane of the large lithium atom faces. Two of the  $\text{sp}^2$  orbitals are directed toward two bonding centers and the third orbital is not involved in bonding. The remaining p orbital is approximately perpendicular to the large lithium atom faces and has one of its lobes directed toward the third bonding center in which the lithium atom participates. The other lobe of the p orbital points upward from the large lithium atom face and is available to interact with bases which may associate with the "open" faces in organolithium hexamers. The vacant  $\text{sp}^2$  and p

(33) N. C. Baird, R. F. Barr, and R. K. Datta, *J. Organometal. Chem.*, **59**, 65 (1973).

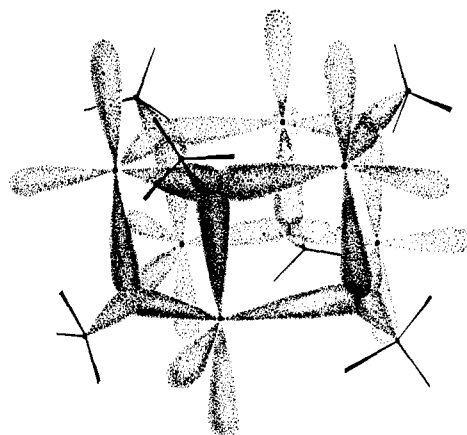


Figure 8. Proposed bonding in the  $\text{C}_6\text{H}_{11}\text{Li}$  hexamer.

orbitals may also interact with the  $\alpha$ - and  $\beta$ -hydrogen atoms resulting in coordinatively saturated lithium atoms. Therefore, the four-centered bond results from the interaction of two  $\text{sp}^2$  orbitals from two different lithium atoms, a p orbital from a third lithium atom, and an  $\text{sp}^3$  orbital from an  $\alpha$ -carbon atom.

**Supplementary Material Available.** A listing of interatomic distances, bond angles, structure factor amplitudes, and root mean square amplitude of vibration for the anisotropically refined atoms will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-74-6048.

## A Correlation of Lithium-7 Chemical Shifts of Organolithium Derivatives with Structural Effects<sup>1</sup>

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**Abstract:** The  $^7\text{Li}$  chemical shifts of a variety of organolithium derivatives have been determined using an internal proton lock as reference. Chemical shifts obtained in this manner are free of error due to magnetic susceptibility factors and provide the basis for a general standard of comparison by which all  $^7\text{Li}$  data may easily be correlated. Calculations were made in order to estimate the contributions of shielding terms that determine the  $^7\text{Li}$  chemical shifts. The results of these calculations show a reasonable correlation between the  $^7\text{Li}$  chemical shift and the substituent magnetic anisotropy term.

The nature of organolithium derivatives is reasonably well established and has been the subject of extensive reviews.<sup>3-7</sup> An increasingly important tool in

these investigations has been the use of  $^7\text{Li}$  nuclear magnetic resonance.<sup>4,5</sup>

Brown, *et al.*,<sup>8</sup> were the first to use  $^7\text{Li}$  techniques in the study of organolithium derivatives. A surprisingly sharp resonance line for ethyllithium in benzene was observed at  $-1.00$  ppm from a 70% solution of aqueous LiBr. West and Weiner<sup>9</sup> used  $^7\text{Li}$  nmr to establish the existence of one of the first mixed organolithium species

(1) This work was supported in part by the National Science Foundation Grants G. P. 8323 and G. P. 19299.

(2) University Graduate Fellow, 1971-1973.

(3) T. L. Brown, *Advan. Organometal. Chem.*, **3**, 365 (1966).

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(6) P. West, *MTP (Med. Tech. Publ. Co.) Int. Rev. Sci.*, (1972).

(7) W. H. Glaze, *J. Organometal. Chem.*, **48**, 1 (1973).

(8) T. L. Brown, D. W. Dickerhoof, and D. A. Bafus, *J. Amer. Chem. Soc.*, **84**, 1371 (1962).

(9) M. A. Weiner and R. West, *J. Amer. Chem. Soc.*, **85**, 485 (1963).

in a solution of ethyl- and *tert*-butyllithium in benzene. Since that time,  $^7\text{Li}$  nmr has been used to determine exchange parameters in kinetics, bonding properties, degrees of aggregation, and solvation effects in a variety of organolithium compounds.<sup>10</sup>

Two important aspects of  $^7\text{Li}$  nmr studies have not as yet received attention. The first is that when  $^7\text{Li}$  chemical shifts are determined by reference to an external standard, the choice of standard (LiBr, LiCl, LiNO<sub>3</sub>, etc.) and its concentration determined the relative positions of resonance due to the differences in the magnetic susceptibilities of the sample and standard. Brown first noted that on changing the external standard from a 70 to a 7% aqueous lithium bromide solution, the chemical shift of ethyllithium changed from -1.00 to -1.28 ppm.<sup>8</sup> This is a substantial change when one considers that the range of alkylolithium chemical shifts is only about 1.2 ppm. Secondly, and perhaps more important, there is a lack of theoretical information on the parameters which determine the  $^7\text{Li}$  chemical shifts for organolithium reagents.

To this end, we have accurately measured the  $^7\text{Li}$  chemical shifts of a variety of organolithium compounds relative to an internal proton lock. In addition, we have made calculations estimating the contribution of the paramagnetic, diamagnetic, and anisotropic shielding terms to the  $^7\text{Li}$  chemical shift. The results of these calculations are in reasonable agreement with the experimental results.

### Experimental Section

Phenyllithium was obtained from Alfa Inorganics. Methylolithium was prepared according to the method of Glaze and Selman.<sup>11</sup> Synthesis of the remaining organolithiums was accomplished by means of the cleavage of the corresponding diorganomercury derivatives with lithium metal.<sup>12</sup> Lithium compounds synthesized in this manner are free from contamination due to halides, etherates, or mixed lithium compounds. The use of high vacuum techniques also minimizes impurities due to alkoxide formation. The solvents used were freshly distilled and dried over sodium-potassium alloy and stored in a high vacuum system. All samples were stored at liquid nitrogen temperatures until the spectra were obtained. Concentrations were determined either by titration or by integration of the pmr spectra on a Varian A-60-A nmr spectrometer.

The  $^7\text{Li}$  measurements were recorded on a JEOL-JNM-4H-100 spectrometer operating at 38.8 and 100 MHz. The normal  $^7\text{Li}$  probe was modified by adding a 100-MHz bridge and a second detection coil such that the two coils were concentric.

The field was usually locked on the proton resonance of the solvent. If the solvent spectra contained multiplets, the field was locked on a given line of the multiplet. The proton spectra was scanned immediately after the measurement of the  $^7\text{Li}$  resonance to confirm that the lock had not shifted to another line of the multiplet during the measurement. The  $^1\text{H}$  and  $^7\text{Li}$  frequencies were determined using a Hewlett Packard 5245L counter with a 5251A plug-in unit. The observed resonances were reproducible to better than  $\pm 0.04$  ppm for samples with a concentration above 0.03 *M*. The model used for the molecular orbital calculations for the calculation of nmr parameters was the same as that previously described.<sup>13</sup>

### Results and Discussion

The observed chemical shifts of lithium nuclei in organolithium derivatives can be attributed to the following shielding terms

$$\sigma_{\text{obsd}} = \sigma_{\text{solvent}} + \sigma_{\text{dia}} + \sigma_{\text{para}} + \sigma_{\text{sa}} + \sigma_{\text{aa}} \quad (1)$$

(10) See ref 4, 5, and 6 and references therein.

(11) W. H. Glaze and C. M. Selman, *J. Org. Chem.*, **33**, 1987 (1968).

(12) J. B. Smart, R. Hogan, P. A. Scherr, M. T. Emerson, and J. P. Oliver, *J. Organometal. Chem.*, **64**, 1 (1974).

(13) J. B. Smart, R. Hogan, P. A. Scherr, L. Ferrier, and J. P. Oliver, *J. Amer. Chem. Soc.*, **94**, 8371 (1972).

In the above equation, the terms correspond to the contributions to the observed shielding by solvent effects, local diamagnetic, local paramagnetic, substituent anisotropy, and aggregation anisotropy, respectively. To simplify the calculations, the effect of the solvent was assumed to be constant within a series and was neglected.

The local diamagnetic term was calculated using the formula<sup>14</sup>

$$\sigma_{\text{dia}} = \sum_{\mu} P_{\mu\mu} \frac{4\pi e^2}{3mc^2} \int_0^{\infty} r \rho(r) dr \quad (2)$$

where the sum is over the atomic orbitals ( $\mu$ ) on the lithium and  $P_{\mu\mu}$  are the diagonal terms of the population density matrix as determined by INDO molecular orbital calculations.<sup>15</sup> The radial distribution functions,  $\rho(r)$ , were calculated by the method of Herman and Skillman<sup>16</sup> from atomic wave functions for lithium in the  $2s^1 2p^1$  configuration.

The local paramagnetic term was calculated using eq 3. The value of  $\langle r^{-3} \rangle$  was evaluated from the

$$\sigma_{\text{para}} = \frac{2e^2 h^2}{2m^2 c^2 \Delta E} \left\langle \frac{1}{r^3} \right\rangle [(P_{xx} + P_{yy}) - \frac{1}{2}(P_{zz}P_{yy} + P_{xx}P_{yy} + P_{xx}P_{zz}) + \frac{1}{2}(P_{yz}P_{zy} + P_{xy}P_{yx} + P_{xz}P_{zx})] \quad (3)$$

calculated lithium atomic orbitals, and the average excitation energy ( $\Delta E$ ) was taken to be 6.2 eV.<sup>13</sup> The diamagnetic and paramagnetic terms were calculated for tetrameric ethyllithium and for monomeric, dimeric, tetrameric, and hexameric methylolithium. The results of these calculations are listed in Table I. Since the

Table I. Calculated Values for the Local Diamagnetic and Paramagnetic  $\sigma$  Terms<sup>a</sup>

	$\sigma_{\text{dia}}$	$\sigma_{\text{para}}$	$\sigma_{\text{d}} + \sigma_{\text{p}}$	$\sigma_{\text{d}} + \sigma_{\text{p}}$ relative to tetramer
MeLi				
Monomer	3.924	-2.398	1.526	0.01
Dimer	5.303	-3.706	1.597	0.08
Tetramer	6.050	-4.534	1.516	0.00
Hexamer	6.43	-4.80	1.63	0.11
EtLi				
Tetramer (crystal structure)	6.085	-4.539	1.496	-0.02

lithium chemical shifts were computed on a relative scale, only relative changes in the calculated values with regard to aggregation and substitution were considered. As indicated in column 4, Table I, this relative change is small for changes in aggregation for the alkyl derivatives.

The anisotropy term was calculated by the McConnell equation with a correction term for nonpoint dipoles as given in eq 4.<sup>17</sup> These calculations assumed free rotation of the alkyl group about the carbon-to-lithium axis

(14) J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill, New York, N. Y., 1959.

(15) J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, N. Y., 1970.

(16) F. Herman and S. Skillman, "Atomic Structure Calculations," Prentice-Hall, Englewood Cliffs, N. J., 1973.

(17) J. W. ApSimon, W. G. Craig, P. V. Demarco, D. W. Mathieson, L. Saunders, and W. B. Whalley, *Tetrahedron*, **23**, 2339 (1967).

$$\sigma_{\text{anisotropic}} = \frac{1}{3R^3}[\Delta\chi_1(1 - 3 \cos^2 \theta) + \Delta\chi_2(1 - 3 \sin^2 \theta \sin^2 \gamma)] \quad (4)$$

and averaged the effect of substituent groups equally over all angles of rotation. The change in  $\sigma_{\text{anisotropic}}$  for each of the previously mentioned aggregation states results from sequentially changing each proton on the  $\alpha$ -carbon to another methyl group. This generates the ethyl, isopropyl, and *tert*-butyl groups, respectively. The results of these calculations are shown in Table II.

**Table II.** Change in  $\sigma_{\text{anisotropic}}$  due to Change in Alkyl Groups (ppm)

	Monomer	Dimer	Tetramer	Hexamer
Me $\rightarrow$ Et	0.64	0.196	0.304 <sup>a</sup> 0.366 <sup>b</sup>	0.330 <sup>a</sup> 0.370 <sup>b</sup>
Et $\rightarrow$ <i>i</i> -Pr	0.64	0.196	0.304 <sup>a</sup> 0.366 <sup>b</sup>	0.330 <sup>a</sup> 0.370 <sup>b</sup>
<i>i</i> -Pr $\rightarrow$ <i>t</i> -Bu	0.64	0.196	0.304 <sup>a,c</sup> 0.366 <sup>b,c</sup> 0.016 <sup>a,d</sup>	0.330 <sup>a,c</sup> 0.370 <sup>b,c</sup>

<sup>a</sup> Eclipsed (sighting from the carbon to the center of the lithium aggregate, the three lithiums forming a face and the three atoms bonded to the  $\alpha$ -carbon above that face are eclipsed). <sup>b</sup> Staggered. <sup>c</sup> Li-C bond length = 2.3 Å. <sup>d</sup> Li-C bond length = 2.5 Å in the *t*-Bu compound and 2.3 Å in the *i*-Pr derivative. The choice of 2.5 Å was taken as a reference point to show how the anisotropy changes with bond length and does not indicate a belief that the actual bond length is 2.5 Å.

**Table III.**  $\sigma$  Terms for Aromatic and Charge Delocalized Organolithiums

	Me Li	Vinyl Li	Phenyl Li	Allyl Li	Benzyl Li
$\sigma_{\text{dia}}$	5.303	5.685	5.770	6.188	
$\sigma_{\text{para}}$	-3.706	-4.048	-4.181	-4.398	
$\sigma_{\text{d}} + \sigma_{\text{p}}$	1.597	1.637	1.589	1.790	1.790 <sup>a</sup>
$\sigma_{\text{anisotropic}}$	(0.0)	-0.1801	-1.6732	0.5156	-0.1266

<sup>a</sup> Assumed to be equal to allyl due to structural similarity.

Thus, it can be seen from Tables I and II that in non-interacting solvents, with fixed states of aggregation, the predominant effect that accounts for differences in chemical shifts between alkylolithiums is the substituent anisotropy term.

The change in shielding due to changes in the anisotropy of the lithium framework was not calculated. Experimental results, which will be discussed in detail later, indicate that this change is small for the change from hexamer to tetramer. The changes in anisotropy due to aggregation for the tetramer, dimer, and monomer would be impossible to distinguish from the solvent effect.

Similar calculations were also performed on some aromatic and charge delocalized systems. The results of these calculations are given in Table III.

In order to verify the general conclusions of the calculations, the chemical shifts of a large number of organolithiums were observed and are shown in Figure 1. All of the chemical shift measurements are relative to an internal proton standard. Details of this technique are discussed in the experimental section. Although all of the chemical shifts are relative to an internal tetramethylsilane, the <sup>7</sup>Li resonance position of lithium bromide (0.7 g/ml) was chosen as our arbitrary zero point in order to bring our values into reasonable

correspondence with the literature. In this regard, negative values of chemical shifts in Figure 1 indicate resonances which are downfield of lithium bromide. Another important consideration is the fact that all of the lithium compounds, except the menthyl, phenyl, and methylcuprate derivatives were synthesized from the corresponding mercury compounds. This ensures lithium derivatives that are halide free. While no quantitative study has been made on the changes in chemical shifts due to the presence of halide, initial observations on such derivatives as lithium methylcuprate and *tert*-butyllithium indicate substantial changes in chemical shift due to the presence of halide.

One of the major conclusions of the calculations is that substituent anisotropy is the major factor in determining the differences in chemical shifts between organolithiums. Examination of Table II indicates that a change in chemical shift of 0.30–0.37 ppm is expected for each sequential change of a proton on the  $\alpha$ -carbon to a methyl group providing that no other factors such as solvent or aggregation state are being changed. A comparison of the observed and calculated differences in the chemical shifts of methyl-, ethyl-, isopropyl-, and *tert*-butyllithium is shown in Table IV. Examination of this table indicates that agreement is quite good for changing the methyl to ethyl groups or changing the ethyl to isopropyl substituents in ether. Changing the isopropyl to a *tert*-butyl group, however, produces a serious discrepancy between the calculated

**Table IV.** Calculated and Observed Chemical Shift Changes for Methyl-, Ethyl-, Isopropyl-, and *tert*-Butyllithium

	Ether solvent		Cyclopentane solvent	
	$\Delta\delta_{\text{calcd}}$	$\Delta\delta_{\text{obsd}}$	$\Delta\delta_{\text{calcd}}$	$\Delta\delta_{\text{obsd}}$
Me $\rightarrow$ EtLi	0.33 <sup>a</sup>	0.42		
Et $\rightarrow$ <i>i</i> -PrLi	0.33 <sup>a</sup>	0.48	0.23 <sup>c</sup>	0.65
<i>i</i> -Pr $\rightarrow$ <i>t</i> -BuLi	0.33 <sup>a</sup>	-0.03	0.33 <sup>a</sup>	0.23
	0.02 <sup>b</sup>		0.02 <sup>b</sup>	

<sup>a</sup> Average of eclipsed and staggered forms. <sup>b</sup> Value obtained by elongating the Li-C bond from 2.3 to 2.5 Å. <sup>c</sup> Undergoes change in aggregation.

and observed results. To explain this anomalous result, an argument similar to that used to explain the ultra-violet transition in *tert*-butyllithium will be invoked.<sup>13</sup>

Because of steric repulsions between *tert*-butyl groups, the Li- $\alpha$ -carbon bond length must be increased by at least 0.10 Å to relieve strain as previously shown.<sup>13</sup> Equation 4 indicates that the anisotropy term is an inverse function of the distance cubed and any increase in the Li-C bond length would have the effect of reducing the anisotropy term, as is observed in Table IV. There is also evidence<sup>4</sup> to support the idea that the steric crowding in *tert*-butyllithium prevents the solvent from interacting effectively with the lithium core. This would result in a different solvent effect on the chemical

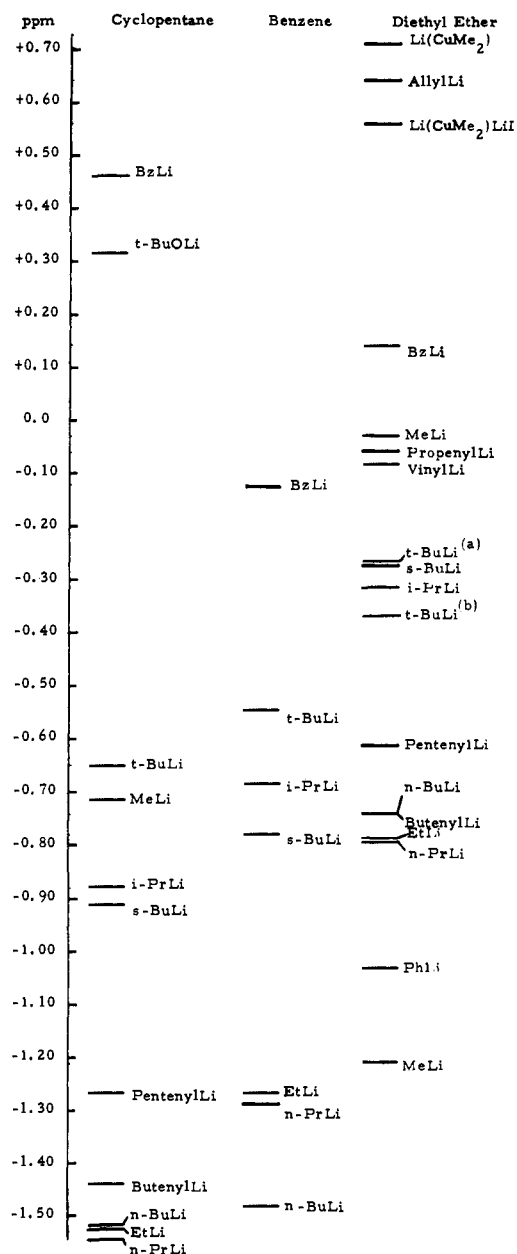


Figure 1.  ${}^7\text{Li}$  chemical shifts relative to TMS lock: (a) value obtained for  $t\text{-BuLi}$  prepared from  $(t\text{-Bu})_2\text{Hg}$ , (b) value obtained for commercial sample of  $t\text{-BuLi}$ .

shift of the *tert*-butyl as compared to other alkyl-lithium derivatives. One can assume that the difference in solvent effect between isopropyl- and *tert*-butyllithium will be greatest in polar interacting solvent such as diethyl ether while the differences will be minimal in a noninteracting solvent such as cyclopentane. Thus, in changing the alkyl group from isopropyl to *tert*-butyl in cyclopentane, the observed difference in chemical shift is 0.1 ppm less than the calculated prediction while in diethyl ether the observed change is 0.36 ppm less than calculated. This suggests that the difference between calculated and observed results in cyclopentane is due primarily to a reduction of the anisotropy term because of Li-C bond elongation while the reduction of the observed *vs.* the calculated results in ether reflect both a reduction in the anisotropy term due to bond elongation and a significant change in the solvent effect between the isopropyl- and *tert*-butyllithium.

*tert*-Butyllithium also proved to be anomalous in another manner. A sample of *tert*-butyllithium obtained commercially or prepared in the manner of Weiner and West<sup>9</sup> was observed to have a  ${}^7\text{Li}$  chemical shift at  $-0.65$  ppm. Only one line was obtained with a width at half height of 3 Hz. When this same compound was prepared by exchange with di-*tert*-butylmercury, two resonances were observed at  $-0.65$  ppm ( $\nu_{1/2} = 16$  Hz) and  $-0.13$  ppm ( $\nu_{1/2} = 6$  Hz). The occurrence of this upfield peak was at first thought to be due to alkoxide impurities. All future syntheses contained the same two peaks, and, in addition, the resonance due to *tert*-butyllithium exposed to air was shown to occur at  $+0.31$  ppm. When the solvent was changed to diethyl ether, only a single broad resonance was observed at  $-0.21$  ppm. This implies the presence of an extraneous component that underwent exchange in diethyl ether solvent.

An intriguing possibility is that this resonance arises from the formation of a stable mercurate as observed in  $\text{LiSi}(\text{CH}_3)_3\text{-Hg}[\text{Si}(\text{CH}_3)_3]_2$  by Schaaf and Oliver<sup>18</sup> and as proposed by Seitz and Hall<sup>19</sup> for the  $\text{LiCH}_3\text{-Hg}(\text{CH}_3)_2$  system. Another reasonable possibility is that isobutene has been eliminated and  $\text{LiH}$  formed giving rise to the new resonance. These possibilities have not been investigated, but the extraneous resonance clearly does not arise from halide impurity since lithium halides undergo rapid exchange under the conditions employed to give a single resonance line.

Table V shows an excellent correspondence between

Table V. Calculated and Observed Chemical Shift for SiMe Unsaturated Organolithium Derivatives

	$\Delta\delta_{\text{calcd}}^a$	$\Delta\delta_{\text{obsd}}^b$
Vinyl	0.0	0.0
Phenyl	-1.54	-0.95
Allyl	+0.85	+0.80
Benzyl	+0.21	+0.22

<sup>a</sup> Differences in chemical shift are all relative to the vinyl compound. <sup>b</sup> Ether solvent.

the observed and calculated shifts for the aromatic and charge delocalized species. These results are a bit fortuitous due to the paucity of information concerning the nature of the derivatives in solution. We have assumed all of the compounds to be dimers and selected among the various geometries on the basis of INDO molecular orbital calculations. The geometries for the vinyl and phenyl compounds have the  $\pi$  system in the Li-C-Li-C plane, rather than perpendicular to the plane. For the allyl compound, the energy was minimized with respect to the angles  $\alpha$  and  $\beta$  shown in Figure 2. The geometry of the benzyllithium as determined by Stucky, *et al.*,<sup>20</sup> was used as the basis for the dimer. The similarity in the various Li-C distances in the calculated geometry of the allyl compound with experimental geometry of the benzyl compound as determined by X-ray diffraction should be noted.

The agreement between the calculated and observed  ${}^7\text{Li}$  chemical shifts (Table V) seems to indicate that the

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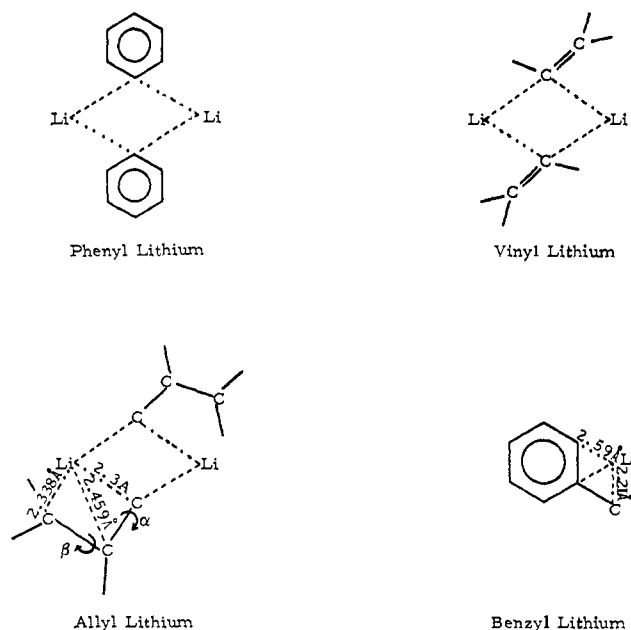


Figure 2.

calculated geometries are reasonable approximations and support postulations<sup>20, 21</sup> that the bonding in these charge delocalized lithium systems while mainly ionic also includes delocalization over the  $\pi$  cloud of the anion.

We did not calculate the change in anisotropy due to differences in aggregation. Since the change in aggregation is usually associated with a change in solvent, experimental estimates for this shift due to changing aggregation are masked by the solvent shifts. One exception to this, however, is the isopropyl lithium system. Brown<sup>22</sup> has shown that isopropyl lithium is essentially tetrameric below 0.03  $M$  in cyclopentane but approaches hexamer at higher concentrations. The calculated  $\sigma_{\text{dia}}$  and  $\sigma_{\text{para}}$  terms (Table I) indicated *ca.* 0.1 ppm difference between hexamer and tetramer, and the substituent anisotropy term should be the same since the alkyl group does not change. Therefore, if the anisotropy term due to difference in aggregation states is large, then two resonances should be observed for isopropyl lithium above 0.03  $M$ . Observation of lithium resonance for isopropyl lithium over the same concentration range used in Brown's cyroscopic studies is shown in Figure 3. The results show that only one resonance is observed, and the line position is invariant within experimental error. The failure to observe two peaks does not necessarily conflict with the concept of hexamer-tetramer equilibrium. It may simply be that our calculation of 0.1 ppm difference between hexamer and tetramer based on the paramagnetic and diamagnetic terms is an overestimation and the two peaks simply

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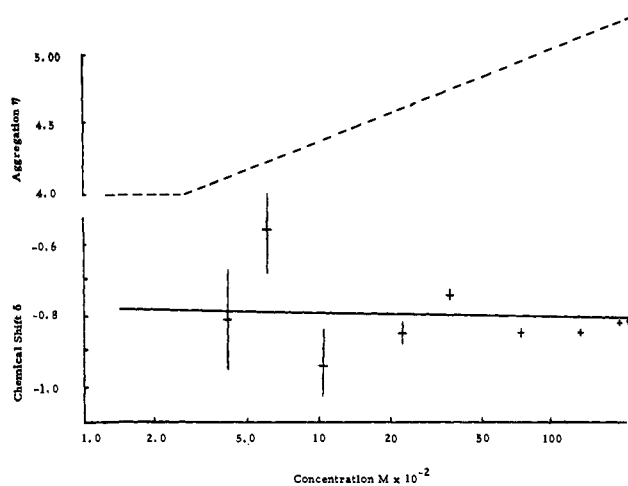
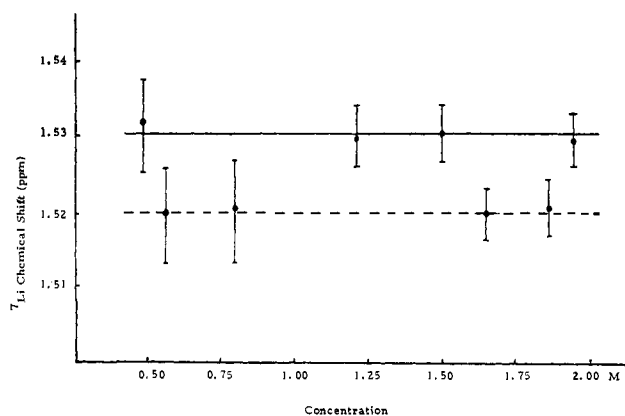


Figure 3. Lithium resonance for isopropyl lithium.

Figure 4.  $^7\text{Li}$  Chemical shifts for alkylolithiums.

cannot be resolved or, more likely, the hexamer is in rapid equilibrium with the tetramer and the small difference in chemical shift between the two is not sufficient to cause a measurable change in chemical shift.

In more qualitative terms, the  $^7\text{Li}$  chemical shifts of alkylolithiums, as shown in Figure 4, are concentration independent in cyclopentane. Covalent derivatives such as the alkylolithiums have chemical shifts downfield of lithium bromide while the chemical shifts of ionic derivatives are upfield. A general trend that is noted, however, is that almost all of the organolithiums show an upfield shift on going from cyclopentane to ether. Finally, the major factor which determines the  $^7\text{Li}$  chemical shift in similar lithium aggregates is the anisotropy associated with the substituent groups.

With a more detailed understanding of what brings about differences in chemical shifts between organolithiums,  $^7\text{Li}$  nmr can be used as a powerful tool to distinguish subtle perturbations such as metal-olefin interactions<sup>12</sup> and solvation around the lithium atom.<sup>23</sup>

(23) R. Hogan, P. Scherr, A. Weibel, and J. P. Oliver, unpublished results.