(III)[10] and 1.890 (10) Å in dichlorobis(2-amino-2-methyl-3-butanonoximato)cobalt(III).[11] Therefore, we might expect that the Co–N distance (1.99 Å) in the $D_{3h}$ conformation of CoL$^+$ would be considerably longer than optimum. The Co–N distance may be decreased by twisting the ligand about the threefold axis. Calculations made assuming retention of $D_3$ symmetry and planarity of the dimethylglyoximate groups show that a twist of 50° of one BO$_3$ group with respect to the other would decrease the Co–N distance to 1.89 Å. This corresponds to a twist of the CoN$_6$ coordination polyhedron of 22° from trigonal prismatic toward trigonal antiprismatic (pseudooctahedral). In fact, the CoL$^+$ cation is found to deviate only slightly from a $D_3$ conformation, with a twist of 51.5° between the two BO$_3$ groups. However, as in CoL, there is a significant deviation of the dimethylglyoximate groups from planarity. The mean angles of twist about the pseudo-threefold axis (the F–B–Co–B–F axis) are C1, 4.1°; C2, 4.4°; N, 15.6°; and O, 25.8°, while twist angles calculated from the model with retention of planarity are C1, 3.8°; C2, 5.6°; N, 11.8°; and O, 25.8°. The observation that the mean angle of twist of the nitrogen atom, 15.6°, is so much greater than the angle, 11.8°, calculated from the model may be due to the well-known preference of Co$^{3+}$ for octahedral coordination. As in the case of the CoL molecule, we may describe the conformation of the CoL$^+$ cation in terms of the twisting about the several bonds which are required to go from the $D_{3h}$ conformation to the observed conformation. The bond twists (with signs appropriate for the cation with the cobalt atom at $^1/_4$, $^1/_4$, $^1/_4$) are: B1–O1, −12.2°; O1–N1, +37.2°; N1–C11, −6.4°; C11–C11′, −10.7° (defined in terms of the nitrogen atoms) or 9.1° (defined in terms of the methyl carbon atoms, C12) and B1–O3, −11.1°; O3–N3, +30.0°; N3–C31, −7.4°; C31–C21′, −9.5° (defined in terms of the nitrogen atoms) or −10.0 (defined in terms of the methyl carbon atoms, C32 and C22′); C21–N2′, −8.3°; N2′–O2′, +43.3°; O2′–B1′, −12.7°. The loss of the threefold symmetry in CoL$^+$ is most conveniently illustrated by the X$_2$–Co–X$_3$ angles (in projection as viewed down the threefold axis) between pairs of atoms, one from each of the two dimethylglyoximate groups related by the twofold symmetry axis of the cation. These angles are: O2–Co–O3, 118.3°; N2–Co–N3, 117.4°; C21–Co–C31, 112.5°; C22–Co–C32, 108.9°. Thus, the two "arms" of the cage which are related by the twofold axis have been drawn toward another and away from the third arm. We suggest that this has been caused by an attractive interaction between these two arms and the two fluorine atoms, F21 and F21′, from the adjacent BF$_4^-$ ion, as shown in Figure 1. This is indicated by the fact that the distances of each of these fluorine atoms from the closest atoms of one of the arms are O3, 3.12; N3, 2.95; C31, 3.27 Å and from those of the other arm are N3′, 3.41; C31′, 3.13; C21, 3.01; C22, 3.36; N2, 3.41 Å.

The B–F bond distances in the BF$_4^-$ anion are normal, mean value 1.369 (7) Å, and the ion shows a small but significant distortion from regular tetrahedral symmetry.

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# Structural Effects on Lithium-7 Relaxation Times of Organometallic Compounds in Solution[1]

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*Received September 8, 1970*

**Abstract:** The lithium-7 spin–lattice relaxation times in a series of organolithium compounds of known aggregation have been measured in various solvents. These measurements provide lower limits for the $^7$Li line widths, which range from 0.05 Hz for symmetrical tetrahedral species to 30 Hz for some larger or smaller aggregates at low temperatures. The measurements suggest that the tetramer of (CH$_3$)$_3$SiCH$_2$Li is distorted away from a tetrahedral structure, and that tetrameric CH$_3$Li also loses its high symmetry above 0°. Quadrupolar broadening becomes a dominant factor in low-temperature lithium-7 high-resolution nmr studies of nontetrahedral organolithium species. This broadening is partly responsible for the difficulties encountered in studies of spin–spin coupling and exchange processes in such species.

High-resolution lithium-7 nmr has been of great value in the study of organolithium compounds in solution. Although the quadrupole moment of the $^7$Li nucleus is large, the "natural" line widths are often sufficiently narrow for the study of inter- and intra-

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**Table I.** Systems Used in This Study

| Designation in Figure 1 | Compound | Solvent | Concentration[a] | Degree of association[b] | Ref |
|---|---|---|---|---|---|
| A | $CH_3Li$ | $(C_2H_5)_2O$ | 0.90 | 4[c,d] | *k* |
| B | $C_2H_5Li$ | $(C_2H_5)_2O$ | 1.90 | 4[e] | 6 |
| C | $(CH_3)_3CLi$ | Toluene | 3.06 | 4[f] | 2 |
| D | $(CH_3)_3SiCH_2Li$ | Toluene | 0.35 | 4[f] | *l* |
| E | $C_2H_5Li$ | Toluene | 0.81 | 6[f] | *l* |
| F | $(CH_3)_3COLi$ | Toluene | 0.50 | 6[f] | *g* |
| G | $(CH_3)_3SiCH_2Li$ | Hexane | 0.89 | 6[h] | *l* |
| H | $C_6H_5Li$ | $(C_2H_5)_2O$ | 0.64 | 2[c,d] | *i, k* |
| I | $C_6H_5CH_2Li$ | Toluene | 0.072 | 2[f] | 2 |
| J | $C_6H_5CH_2Li$ | $(C_2H_5)_2O$ | 1.32 | 1,[d] 2[c] | *j, k* |

[a] Molar concentration as monomer. [b] Nearest whole number. [c] Measured in diethyl ether. [d] Measured in tetrahydrofuran. [e] Inferred from exchange with methyllithium in diethyl ether. [f] Measured in benzene. [g] G. E. Hartwell and T. L. Brown, *Inorg. Chem.*, **5**, 1257 (1966). [h] Measured in cyclohexane. [i] T. V. Talahaeva, A. N. Rodionov, and K. A. Kocheshkov, *Proc. Acad. Sci. USSR*, **154**, 47 (1964). [j] G. Wittig, F. J. Meyer, and G. Lange, *Justus Liebigs Ann. Chem.*, **571**, 167 (1951). [k] P. West and R. Waack, *J. Amer. Chem. Soc.*, **89**, 4395 (1967). [l] H. L. Lewis and T. L. Brown, *ibid.*, **92**, 4664 (1970).

molecular exchange processes involving the various associated species in solution.[2-4] To date, all the exchanging systems studied have included at least one tetrameric aggregate, a species whose intermolecular exchange processes are slower and whose line widths are generally narrower than for larger or smaller aggregates. When using $^7Li$ nmr to study exchange processes, it would be desirable to know the relaxation broadening so that contributions to the line width from chemical exchange and unresolved scalar coupling to $^1H$ or $^{13}C$ nuclei could be unambiguously measured. Lithium-7 line widths have been reported for ethyllithium,[5,6] *tert*-butyllithium,[5] methyllithium,[6] trimethylsilylmethyllithium,[7] and *n*-butyllithium[8] in various solvents. The increased line width of the $^7Li$ resonance at low temperatures has been shown to be due, at least in part, to unresolved lithium–proton coupling, which becomes increasingly important with the slowing of inter- and intramolecular exchange. However, quadrupolar broadening is also greatest at low temperatures. The quadrupolar contribution to the line width, $1/\pi T_2$, is given, in hertz, by[9]

$$1/\pi T_2 = (4\pi/3)S(S + 1)(eQq)^2\tau_Q \qquad (1)$$

where $T_2$ is the transverse relaxation time, $S$ is the spin of the nucleus ($^3/_2$ for $^7Li$), $eQq$ is the quadrupole coupling constant in hertz, and $\tau_Q$ is the rotational correlation time of the molecule in seconds. For simplicity, we have assumed that the rotational reorientation is isotropic. Equation 1 must be suitably modified if the motion is anisotropic.[10] Quadrupolar broadening of $^7Li$ line widths has been estimated[5] but not measured directly. To determine this contribution, we have measured the temperature dependence of the longitudinal relaxation time $T_1$ of the $^7Li$ nucleus in a series of organolithium compounds with known degrees of aggregation. Since $T_1 \geq T_2$, $1/\pi T_1$ provides a lower limit to the $^7Li$ line width. The results indicate that $1/\pi T_1$ can vary from less than 0.05 Hz to more than 30 Hz depending on structure and temperature. In addition, measurements of $T_1$ provide valuable information about the aggregation of organolithium compounds in solution.

## Experimental Section

*tert*-Butyllithium and lithium *tert*-butoxide were obtained from Alfa Inorganics, Inc., and ethyllithium was obtained from the Foote Mineral Co. These compounds and trimethylsilylmethyllithium[11] were sublimed before use. Benzyllithium was prepared from dibenzylmercury in benzene.[12] Phenyllithium and methyllithium were prepared from the corresponding mercury compounds in diethyl ether at 0°.

Solutions were prepared in an argon atmosphere glove box, frozen with liquid nitrogen, and sealed under vacuum. The samples were stored in Dry Ice until needed. Concentrations were determined after the measurements were done, by hydrolysis of the solutions and titration with standard HCl.

The $^7Li$ spin–lattice relaxation times were measured at 10.748 MHz on a modified Magnion pulsed nmr apparatus, by means of the 180°–$\tau$–90° pulse sequence,[13] using several $\tau$ values in each case. The sample tubes had an inside diameter of 6 mm. In all cases, the single-scan signal-to-noise ratio was not sufficient for accurate determinations. A Fabri-Tek 1074 digital signal averager was used for signal accumulation. The number of scans varied from 8 to 1024 depending on concentration and temperature. The estimated maximum error in the $T_1$ values varied from ±5 to ±25%. A dewar insert of our own design was used with a temperature controller obtained from NMR Specialties, Inc. Temperature stability of better than ±0.5° was achieved.

## Results and Discussion

Table I lists the compounds studied and the solvents used. For several of the compounds, the degree of association has been determined in benzene and cyclohexane. Because of the relatively high melting points of these solvents, toluene and hexane were used instead. It is safe to assume that the degree of association will

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not change appreciably when going from benzene to toluene, and from cyclohexane to hexane. The $^7$Li $T_1$ of 0.36 $M$ $(CH_3)_3SiCH_2Li$ in benzene at room temperature was found to be identical with that in toluene (sample D, Table I).

Figure 1 is an "Arrhenius" plot of $1/\pi T_1$, against the reciprocal absolute temperature. The relaxation rates vary by more than two orders of magnitude, yielding "natural" line widths ranging from 0.05 to 30 Hz. The values in Figure 1 can be used to establish the smallest measurable line broadening arising from lithium–proton or lithium–carbon-13 coupling, or from chemical exchange. With the exception of $(CH_3)_3SiCH_2Li$ in toluene (sample D), the tetrameric species have much smaller natural line widths than the other aggregates.

In order to relate the results in Figure 1 with structural factors, we must consider the various mechanisms that may contribute to $^7$Li spin-lattice relaxation. These are the quadrupolar, dipole–dipole, and spin-rotation relaxation mechanisms.[14] Each dipole–dipole contribution is proportional to the square of the gyromagnetic ratio of each of the nuclei involved, to the inverse sixth power of their distance, and to a correlation time for rotational or translational reorientation. Using typical correlation times for small molecules,[14] we have estimated the dipolar contribution to be much smaller than the experimental values of $1/T_1$. Contributions from the spin–rotation mechanism have a temperature dependence opposite to that observed in all the solutions except methyllithium in ether (sample A) at high temperatures. Thus we can safely assume the quadrupolar relaxation mechanism given by eq 1 for all solutions, with the possible exception of sample A.

It is interesting to speculate upon the cause of the relatively slow quadrupolar relaxation rates in the tetrameric species of methyl-, ethyl-, and *tert*-butyllithium (samples A–C). From eq 1 it follows that these tetramers must have smaller $^7$Li quadrupole coupling constants and/or appreciably shorter correlation times than the other alkyllithium species in Table I. It is unlikely that a short correlation time is chiefly responsible for the slow relaxation rate of samples A–C. For example, *tert*-butyllithium in toluene (sample C) relaxes more slowly than ethyllithium in toluene (sample E). If this difference results mainly from variations in the correlation time, it would indicate that the ethyllithium hexamer (mol wt 216) is reorienting more slowly than the *tert*-butyllithium tetramer (mol wt 256). In all likelihood the variations in Figure 1 reflect to a great extent variations in $^7$Li quadrupole coupling constants of the various aggregates. The long relaxation times in all but one of the tetrameric species indicate a small electric field gradient at the $^7$Li nucleus, and thus a small $eQq$ in these species. The crystal structure of methyllithium[15] indicates a tetrahedral geometry for the tetramer, in which the $^7$Li atom is located along a threefold axis of symmetry. The tetrahedral structure of the methyllithium tetramer in solution has been verified below −50° by means of exchange studies[6] in diethyl ether and $^7$Li–$^{13}$C scalar coupling in diethyl ether and tetrahydrofuran.[16] Such a tetrahedral structure does not necessarily require a small $^7$Li quadrupole coupling constant, but our results show that the $^7$Li $eQq$ value is indeed small in a tetrahedral tetramer. We have not attempted to evaluate $eQq$ because of the lack of independent *experimental* evaluations of the rotational correlation times. The use of the Debye equation to compute $\tau_Q$ from macroscopic viscosity data often leads to large errors.[14]

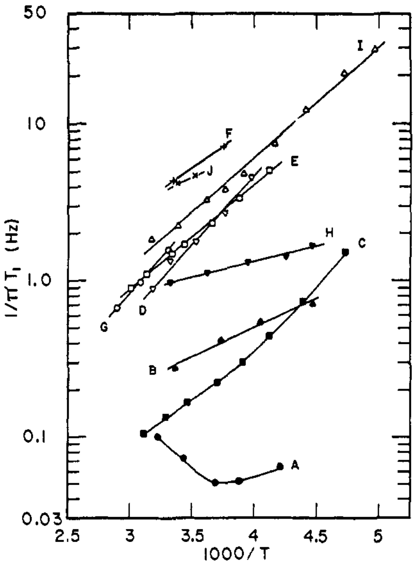

Figure 1. Arrhenius plot of the $^7$Li spin–lattice relaxation times of organolithium compounds in solutions. The compounds and solvents are shown in Table I.

An explanation for the relatively fast $^7$Li relaxation of tetrameric $(CH_3)_3SiCH_2Li$ is that, unlike the other tetramers, this species does not have tetrahedral symmetry but is distorted toward a more open configuration. This explanation is in agreement with the more facile dissociation of $(CH_3)_3SiCH_2Li$, noted in exchange studies with *tert*-butyllithium.[4–7] In addition, the $(CH_3)_3SiCH_2Li$ tetramer, with its relatively open structure, can easily accept a dimer to form a hexameric species at high concentrations in aromatic solvents.[17]

The peculiar temperature dependence of the $^7$Li spin-lattice relaxation in methyllithium (sample A) may be either due to an increasing contribution from spin rotation at high temperatures[14] or to changes in the average quadrupolar contribution arising from changing aggregation or structure. Although more work is necessary to settle this question, we favor the latter explanation. Colligative measurements at 25° show a concentration-dependent degree of aggregation ranging from nearly four at 0.2 $M$ to nearly three at 1.2 $M$.[18] This behavior was explained by assuming solvation of the tetramer by the ether. The increase in $eQq$ at high temperatures may have several origins. It may arise from a dissociation of the tetrahedral tetramer into species of lower symmetry such as dimers, monomers, or ions such as $Li_4(CH_3)_3^+ + CH_3^-$. It may even be due to a simple distortion toward a nontetrahedral tetramer as proposed for $(CH_3)_3SiCH_2Li$.

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It is interesting to compare the observed $^7$Li high-resolution nmr line width of methyllithium in diethyl ether with the natural line width predicted in Figure 1. The former varies from about 3.5 Hz below −50° to about 0.7 Hz at 0° and higher.[6] The latter is 0.1 Hz or less at all temperatures measured (−35° to 38°). Clearly the line broadening is not dominated by spin relaxation. The major factor is probably unresolved lithium–proton scalar coupling as proposed. The decrease in broadening on warming to 0° is consistent with a dissociative process enabling intermolecular exchange.

# Correlations between Carbon-13 and Boron-11 Chemical Shifts. III. Pairwise Interaction Parameters[1]

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**Abstract:** $^{11}$B chemical shifts for a variety of tetracoordinate boron resonance nuclei are shown to be pairwise additive with respect to attached substituent groups as has been observed for $^{13}$C shifts of tetracoordinate carbon resonance nuclei. Assuming $^{11}$B and $^{13}$C shifts to be generally pairwise additive for tetracoordinate resonance nuclei, a total of 13 common $^{11}$B and $^{13}$C pairwise additivity parameters is obtained which are shown to be linearly related. The slope of the linear equation relating the $^{13}$C and $^{11}$B pairwise parameters is quantitatively accounted for by a consideration of the ratio of the paramagnetic contribution to the chemical shift for $BH_4^-$ and $CH_4$. The chemical shifts of the hydroxy-substituted hydroborate intermediates, $BH_n(OH)_{4-n}^-$, with $n$ = 1–3, are predicted as an example of the potential utility of the correlation. Finally, in view of the correlation between the pairwise parameters, a prediction is made concerning possible similarities in the chemistry of $BH_3CO$ and its isoelectronic carbon analog, $CH_3CO^+$.

Nmr studies involving $^{13}$C and $^{11}$B nuclei have long been hampered by features unfavorable toward magnetic resonance measurements.[3] Recently, however, advances in instrumentation, such as field-frequency stabilization techniques[4–7] and pulsed and Fourier-transform nmr spectroscopy,[8] have been increasing the number and application of nmr studies of these nuclei, especially for $^{13}$C. In view of this, linear correlations in chemical shift or chemical shift parameters between these two nuclei would be expected to have considerable utility as an empirical tool. In addition, such correlations would imply closely related theoretical interpretations of the chemical shift for these nuclei, thus providing checkpoints for the testing of chemical shift theories.

One linear correlation in chemical shift between these two nuclei has been reported.[9] For $^{13}$C shifts in alkanes and the corresponding $^{11}$B shifts in the isoelectronic amine–boranes, the equation relating the $^{13}$C and $^{11}$B shifts was found to be

$$\delta_{^{13}\mathrm{C}} = 1.44\delta_{^{11}\mathrm{B}} + 86.0 \qquad (1)$$

where $^{13}$C shifts are in ppm from benzene and $^{11}$B shifts are ppm from boron trifluoride diethyl etherate. The average deviation for some ten observed $^{13}$C shifts calculated from the observed $^{11}$B shifts by this equation was 1.96 ppm (in chemical shift) out of a range in $^{13}$C shifts of 50 ppm. Other studies[1a,10,11] have further emphasized the close relationships existing between $^{13}$C and $^{11}$B chemical shifts, although these have been limited mainly to saturated hydrocarbons and analogous boron–nitrogen compounds.

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(1) (a) Previous paper in this series: J. M. Purser and B. F. Spielvogel, *Inorg. Chem.*, 7, 2157 (1968); (b) presented in part at the 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968.

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(3) $^{13}$C has low natural abundance (1.1%), long values of relaxation time, and a poor natural sensitivity ($\mu$ = 0.70220 nuclear magneton). Although $^{11}$B has the higher natural abundance of the two boron isotopes and has a somewhat higher natural sensitivity ($\mu$ = 2.688 nuclear magnetons) than $^{13}$C, line broadening is observed for $^{11}$B ($I$ = $^3/_2$) because of its quadrupole moment. See J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. II, Pergamon Press, Elmsford, N. Y., 1966, pp 970 and 980.

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