accuracy with which this method can determine the basicity of a free radical, even given an infinitely dense basicity scale. We estimate this error to be ±2 kcal mol^{-1}, which is comparable in magnitude to the error introduced into the kinetic method by the approximation of radical-radical recombination activation energies.[3]

Conclusion

It has been demonstrated that the ion cyclotron double resonance bracketing experiment yields reliable values for the heats of formation of free radicals. In addition, our experience provides evidence for the validity of the general method for the determination of the thermochemical stabilities of transient neutral molecules.

Acknowledgments. We are pleased to thank Mr. Steven Pollack and Professor Joseph Thomas (California State University, Fullerton) for synthesizing the cyclopropene. We are also indebted to Professor Robert Taft (University of California, Irvine) for providing us with the unpublished proton affinity data. D.J.D. would like to thank the University of California for a Reagents Intern Fellowship. This work was supported in part by grants from the National Science Foundation.

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Study of Complexation of Polydentate Amido Ethers with Lithium Ions by Nuclear Magnetic Resonance Spectroscopy. 1. Solvent Effects

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Abstract: The complexation of lithium ions with polydentate amido ethers was investigated by ^1H and ^7Li magnetic resonance spectroscopy, including studies of spin-lattice relaxation times. Methylene chloride, nitromethane, acetonitrile, and pyridine were used as solvents. The tetradentate amido ether *N,N′*-diheptyl-*N,N′*,5,5′-tetramethyl-3,7-dioxanonanediamide (NDA) and the bidentate *N*-methylheptyl-3-oxapentanamide (PMA) were used as ligands. It was found that NDA acts as a much more effective complexing agent of lithium ions than its bidentate analogue PMA. For NDA the 1:1 complex represents the dominant species. However, it was shown that "sandwich"-type as well as bislithiated complexes may also be formed. The exchange rate between various forms is fast on the NMR scale. The stability constants, chemical shifts, and relaxation times of various complexes were calculated. The stability constants increase in the order of decreasing "donicities" of the solvent media. Inspection of ^1H NMR spectra revealed that conformation of amidic groups of the ligands is not affected by the complexation. The rotation around the C-N bond of NDA is, however, considerably restricted in the complexed species. It was found that the deviation from cubic symmetry is much less pronounced in a "sandwich"-type complex than in the 1:1 complex of NDA. Conductivity measurements were conducted for the latter complex in order to determine the degree of association of the complexed lithium with the perchlorate counterions. It was found that, even in such a high dielectric constant solvent as nitromethane, a large fraction of the complexed lithium ions was associated with their counterions, at the concentration range investigated by NMR.

Introduction

Tetradentate amido ethers were designed by Simon and his co-workers[1-3] as ionophores for alkali and alkaline-earth cations. The high complexing ability of these ligands is apparently due to cooperative interactions involving the ethereal and the amidic groups Their selectivity is strongly affected by minor differences in the molecular structure.[4]

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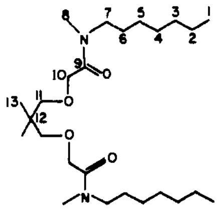

Figure 1.

N,N' - Diheptyl - *N,N'*,5,5'-tetramethyl-3,7-dioxanonanediamide (NDA) (see Figure 1) has been shown to bind preferentially lithium ions.[5] Steric restrictions imposed upon the segmental motions of the methylene groups, adjacent to the centrally located tertiary carbon atom, are apparently responsible for the selectivity of this ligand toward small lithium ions.

NMR technique is a powerful tool for the study of complexing interactions. An insight into the structural features of the complexes formed and information about their stoichiometry and thermodynamic parameters can be gained from such measurements.

Results of ^{1}H NMR and ^{7}Li NMR investigation of the complexes of NDA with lithium salts in various solvents are discussed in the present paper.

Experimental Section

N,N'-Diheptyl-*N,N'*,5,5'-tetramethyl-3,7-dioxanonanediamide (NDA) and *N*-methylheptyl-3-oxapentanamide (PMA) were prepared according to the general procedure described by Simon et al.[1] 2,2'-Dimethyl-1,3-hydroxypropane (DMHP) (Fluka puriss) and methoxyacetyl chloride (BDH, Analar) were used as starting materials for the preparation of NDA and PMA, respectively. DMHP was reacted with freshly prepared[6] ethyl diazoacetate (EDA). *N*-Heptylmethylamine (Fluka, purum) was used in the final amidation step.

Experimental conditions adopted in Simon's laboratory[7] for the preparation of NDA were slightly modified. Namely, 20% molar excess of EDA was used for the preparation of the intermediate ester, which was hydrolyzed in a 3.5 M soluton of KOH in a 4:1 (v/v) water-methanol mixture (reflux, 2 h). Free acid was extracted with ether and converted by an excess of $SOCl_2$ into the corresponding acyl chloride. NDA, formed as a result of the amidation of the intermediate acyl chloride, was extracted with chloroform. The chloroform solution was washed with 5% aqueous HCl followed by 5% $NaHCO_3$ and solvent was evaporated. The overall yield for the four-step synthesis of NDA was 50%. NDA was purified on a silica gel column (100 g of Kieselgel 60, Merck, per 1 g of NDA) with ethyl ether as eluent (ca. 200 mL of ether/1 g of NDA).

Deuterated solvents (Merck, 99.9% deuteration) were dried for 48 h on molecular sieves (type 4).

Solvents for ^{7}Li NMR experiments were freshly distilled in a dry nitrogen atmosphere before use. Nitromethane (Aldrich, spectrograde) and methylene chloride (Fluka, spectrograde) were dried for 48 h over molecular sieves (type 4). Acetonitrile and pyridine (Fluka, puriss) were refluxed over calcium hydride and granulated barium oxide, respectively.

Lithium perchlorate (Fisher, Analar) was dried for 48 h under high vacuum (10^{-4} Torr) at 90 °C. Thermogravimetric analysis of samples of $LiClO_4$, dried by this procedure, proved that absolutely dry anhydrous salt was thus obtained.

Solutions were prepared under a "blanket" of dry nitrogen. Absence of traces of water was checked by gas chromatography with a "para pack" Type Q column. Viscosities were determined with an Ubbelohde viscosimeter. The solubility of lithium salts in methylene chloride at 25 °C was determined by stirring for 48 h (under dry nitrogen) an excess of the dry salt with 1 L of dry solvent. The thus obtained solutions were filtered under a "blanket" of dry nitrogen. The solvent was distilled off and the residue was dissolved in 10 mL of water. An atomic absorption spectrophotometer (Varian 1200) was used for the lithium determinations.

The ^{1}H NMR spectra were recorded at 270 MHz on a Bruker WH-270 spectrometer operating in the Fourier transform mode, using 2-mm o.d. sample tubes. The deuterium signals of the solvents served as internal locks and Me_4Si as the internal reference. Constant temperatures (within ±0.5 °C) were maintained by means of a Bruker temperature control unit calibrated with ethylene glycol.

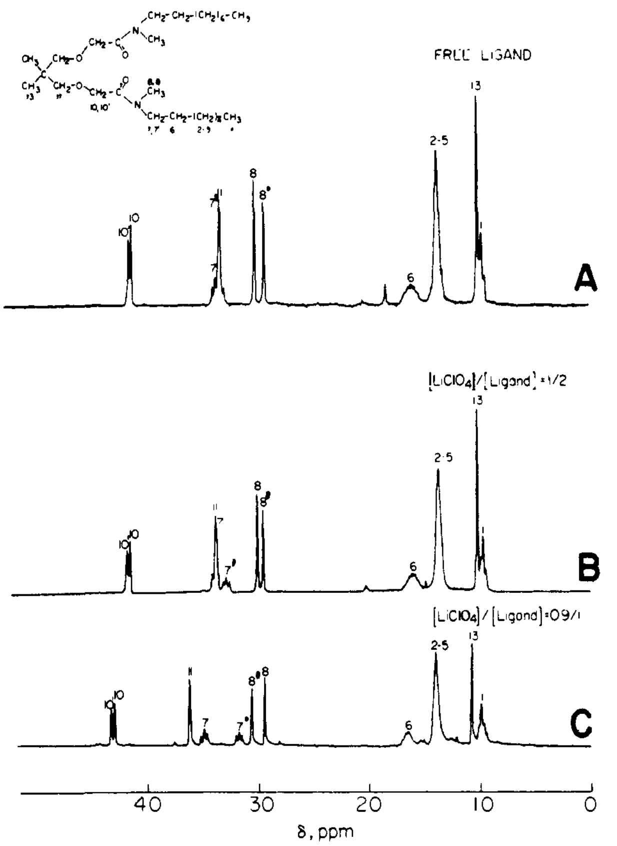

Figure 2. ^{1}H NMR spectra of 0.02 M solutions of NDA in methylene chloride in presence of $LiClO_2$: (A) free ligand; (B) [$LiClO_4$]/[NDA] = 1/2, [$LiClO_4$]/[NDA] = 0.9/1.

^{7}Li NMR spectra at 34.98 MHz were measured on a Bruker WH-90 spectrometer equipped with a variable probe using 10-mm o.d. sample tubes. A 4.0 M solution of $LiClO_4$ was used as an external reference. Both the WH-270 and WH-90 spectrometers were equipped with Nicolet 1180 computers (with 32K and 16K memory, respectively).

T_1 spin-lattice relaxation times were measured by the inversion recovery method using a π-π-$\pi/2$ pulse sequence with varying τ within an automatic program. The T_1 values were obtained with ±10% accuracy from the slope of a plot of ln $[(I_\infty - I)/I_\infty]$ vs. τ, where I denotes the signal intensity.

NMR measurements of the ^{1}H chemical shifts of the NDA complexes were performed on solutions prepared by mixing 0.02 M solutions of NDA in nitromethane or in acetonitrile with 0.02 M NDA + 0.1 M $LiClO_4$ in the same solvent. In case of methylene chloride a saturated solution with respect to lithium was used as the second solution and it contained 0.02 M NDA + 0.0181 M of $LiClO_4$.

$LiClO_4$ (0.1 M) + 1.0 M NDA in nitromethane, acetonitrile, or pyridine were added to the 0.1 M $LiClO_4$, in the same solvent, for measurements of the ^{7}Li spin-lattice relaxation times as a function of the [NDA]/[$LiClO_4$] molar ratio.

Results and Discussion

Methylene chloride, nitromethane, acetonitrile, and pyridine have been chosen as solvents for the present investigation of complexation of NDA with lithium ions. Donicities[8] of the first three solvents are lower and that of pyridine is higher than the donicities of the ethereal and of the amido groups responsible for the complexing power of NDA.

Methylene chloride may be regarded as an inert medium in which solvation of the cations is negligible. Indeed the solubility of lithium salts in this solvent is extremely low (1.1×10^{-6}, 1.2×10^{-6}, and 1.6×10^{-6} M for LiCl, $LiClO_4$, and LiSCN, re-

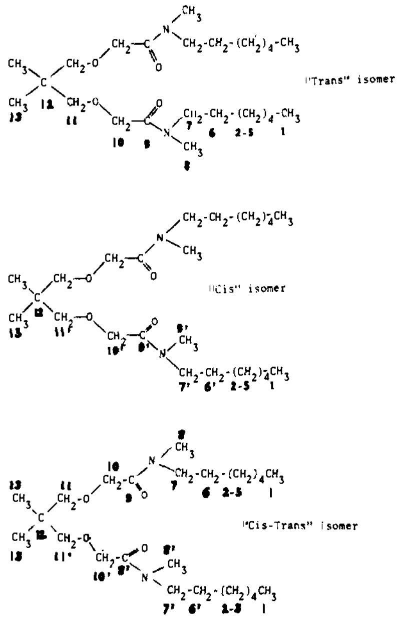

Figure 3. The isomeric forms of NDA.

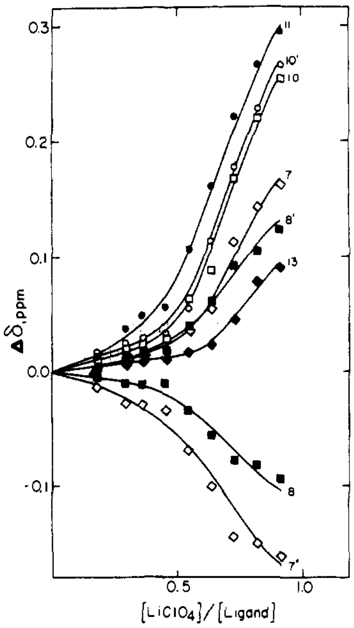

Figure 4. Increments of chemical shifts of ^1H signals of NDA vs. $[LiClO_4]/[NDA]$ ratio, 0.02 M solutions of NDA in methylene chloride. Full lines correspond to the computed values. Numbers at the right indicate signal assignment (cf. Figure 3).

spectively). A drastic increase in the solubility is, however, observed upon addition of NDA. This effect is due to the complexation of NDA with lithium ions.[5]

^1H NMR spectra of NDA in methylene chloride solutions containing various amounts of $LiClO_4$ are shown in Figure 2. The numbers above the peaks indicate their assignment (cf. Figure 3). Since the rotation about the C-N bond of the amide group is restricted,[9] peaks corresponding to the "trans" and to the "cis" forms appear in the spectra.

Inspection of Figure 2 reveals that the isomer with NCH_3 in trans position to the carbonyl oxygen is favored over the "cis" isomer ($I_8 > I_{8'}$, $I_7 > I_{7'}$, and $I_{10} > I_{10'}$). The relative intensity of the peaks corresponding to the two isomers is not affected by the complexation of NDA with $LiClO_4$, though considerable shifts in their positions are noted. Obviously, the complexed lithium ion is located within the "cavity" formed by the four oxygen atoms and its presence does not affect the conformation of the amidic group.

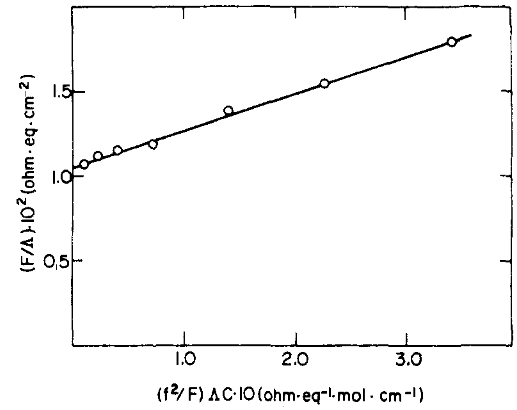

Figure 5. Fuoss plot of the conductivities at 25 °C of the complexed $LiClO_4$ in nitromethane at a constant $NDA/LiClO_4$ ratio of 1.1/1.

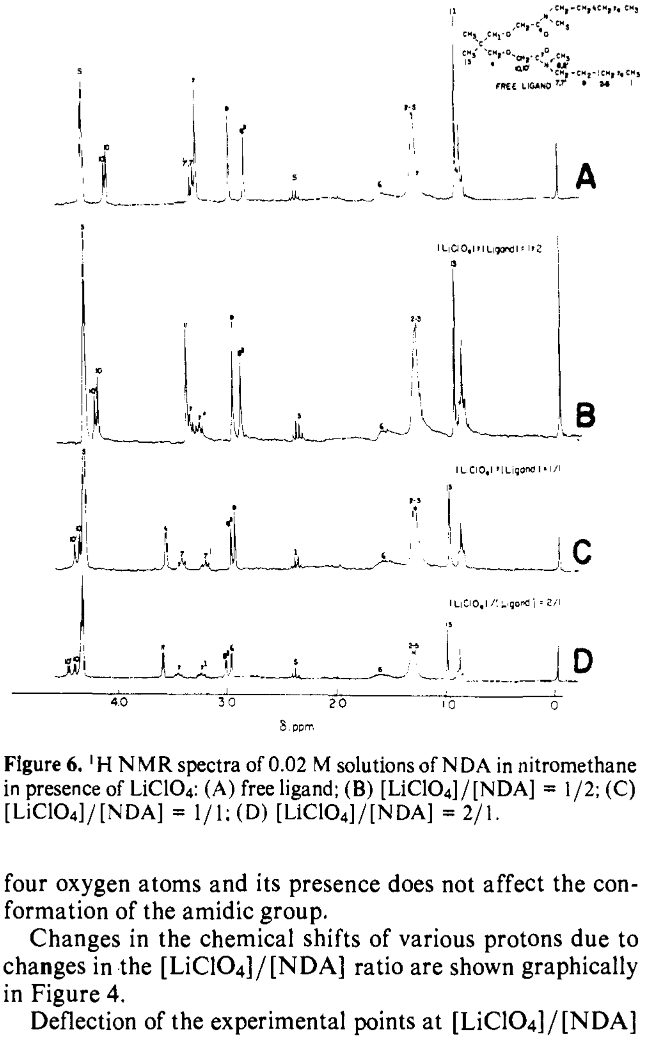

Figure 6. ^1H NMR spectra of 0.02 M solutions of NDA in nitromethane in presence of $LiClO_4$: (A) free ligand; (B) $[LiClO_4]/[NDA] = 1/2$; (C) $[LiClO_4]/[NDA] = 1/1$; (D) $[LiClO_4]/[NDA] = 2/1$.

Changes in the chemical shifts of various protons due to changes in the $[LiClO_4]/[NDA]$ ratio are shown graphically in Figure 4.

Deflection of the experimental points at $[LiClO_4]/[NDA] \sim 0.5$ seems to indicate that more than one complex may be formed in this solvent. We suggest that the following equilibria must be considered:

$$\mathrm{Li^+,ClO_4^- + NDA \overset{K_1''}{\rightleftharpoons} (NDA)Li^+,ClO_4^-} \qquad (1)$$

$$\mathrm{(NDA)Li^+,ClO_4^- + NDA \overset{K_2''}{\rightleftharpoons} (NDA)_2Li^+,ClO_4^-} \qquad (2)$$

The observed changes in the chemical shifts call for a comment. The donicity of amides has been reported to be much greater than that of ethers.[8] One could expect, therefore, that the complexed lithium ion interacts more strongly with the carbonyl than with the ethereal oxygens. Nevertheless, the largest

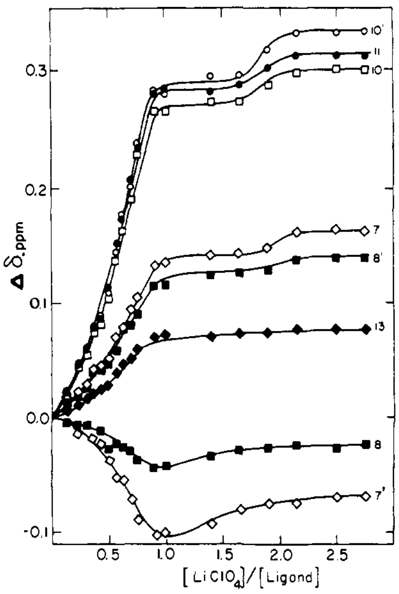

Figure 7. Increments of chemical shifts of ^{1}H signals of NDA vs. $[LiClO_4]/[NDA]$ ratio, 0.02 M solutions of NDA in nitromethane. Full lines correspond to the computed values. Numbers at the right indicate signal assignment (cf. Figure 3).

downfield shift due to complexation is observed for the no. 11 peak, which is assigned to the CCH_2O protons.

Apparently, deshielding of the methylene protons of OCH_2CO (peaks no. 10 and 10′), due to the proximity of the cation, is partially compensated by changes in the anisotropy effect of the adjacent carbonyl. The observed changes in the chemical shifts of the NCH_3 and NCH_2– protons are somewhat unusual. While protons in the cis positions to the carbonyl group (7 and 8′) are shifted downfield, upfield shifts are observed for the NCH_3 and NCH_2 protons in trans position to the carbonyl group (7′ and 8). Similar behavior was observed even in the very diluted solutions of NDA–$LiClO_4$ and NDA–LiSCN in the high dielectric constant solvents, such as nitromethane and acetonitrile. The observed upfield shifts cannot be ascribed, therefore, to the proximity of the counterions to those protons and must be attributed to changes in the inductive and anisotropy effects due to complexation.

Complexes in Nitromethane (DN = 2.7). The association of complexed lithium ions with the perchlorate counterions was implicitly assumed for the low dielectric constant methylene chloride ($\epsilon = 9.1$). Such an assumption may not be justified for a high dielectric constant solvent such as nitromethane ($\epsilon = 35.9$). Conductance measurements were, therefore, performed in order to obtain information about the state of ionic association of the NDA complex in this solvent. The dissociation constant, $K_d = (1.25 \pm 0.03) \times 10^{-2}$ M, for the reaction $(NDA)Li^+,ClO_4^- \rightleftarrows (NDA^+)Li^+ + ClO_4^-$ was obtained from the Fuoss plot shown in Figure 5. The Fuoss plot was derived from the experimentally determined conductivities by a computer iteration procedure described elsewhere.[10] Accordingly, in 0.1 N solutions used for ^{7}Li NMR measurements, 70% of the complexed species is in the form of $(NDA)Li^+,ClO_4^-$ and 30% is unassociated with the counterion. In 0.02 M solutions investigated by ^{1}H NMR the fraction of the associated complex decreases to 46%.

^{1}H NMR spectra of NDA in nitromethane are shown in Figure 6. In this solvent the solubility of $LiClO_4$ is appreciable and solutions with $[LiClO_4]/[NDA] \geqslant 2$ could also be prepared. In such solutions an additional small splitting of the 7–11 peaks is observed.

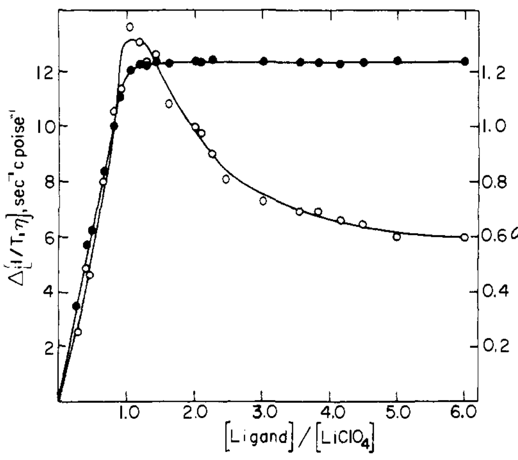

Figure 8. Increments of normalized relaxation rates and of chemical shifts of ^{7}Li vs. $[NDA]/[LiClO_4]$ ratio, 0.1 M solutions of $LiClO_4$ in nitromethane. Full lines correspond to the computed values. ○, $\Delta(1/T_1\eta)$; ●, $\Delta\delta$.

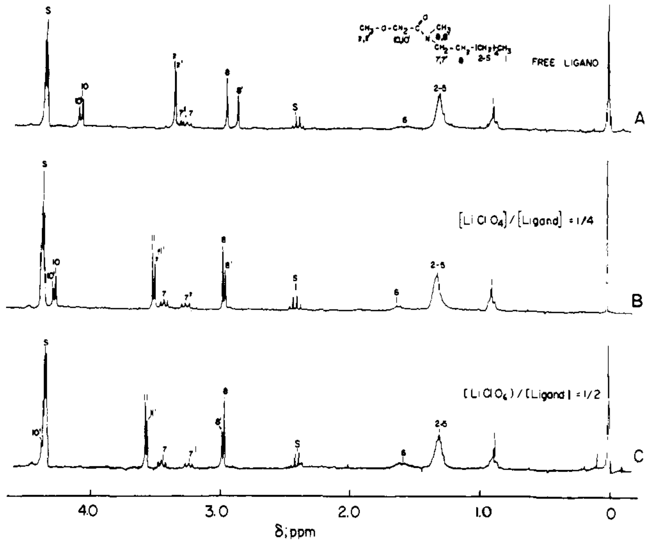

Figure 9. ^{1}H NMR spectra of 0.02 M solutions of PMA in nitromethane in presence of $LiClO_4$: (A) free PMA: (B) $[LiClO_4]/[PMA] = 1/4$; (C) $[LiClO_4]/[PMA] = 1/2$.

Measurements of $\Delta\delta$ vs. r (where $r = [LiClO_4]/[NDA]$), shown in Figure 7, reveal deflections at $r \sim 0.5$, $r = 1$, and $r \sim 2$. The observed changes in the chemical shifts at $r \sim 2$ indicate that the 1:1 complex can further react with an excess of the lithium salt to form a bislithiated complex:

$$(NDA)Li^+,ClO_4^- + Li^+,ClO_4^- \overset{K''_{0.5}}{\rightleftarrows} (NDA)(Li^+,ClO_4^-)_2 \tag{3}$$

or

$$(NDA)Li^+ + Li^+,ClO_4 \rightleftarrows (NDA)(Li_2{}^+,ClO_4^-) \tag{3a}$$

Such bislithiated complexes were not obtained in methylene chloride. Apparently, the value of $K''_{0.5}$ is not sufficiently large to compensate for the extremely low solubility of the "free" $LiClO_4$ in methylene chloride.

Deflections at $r = 0.5$ observed for both methylene chloride and nitromethane systems seem to indicate that "sandwich"-type complexes may be formed in both solvents (cf. eq 2). A supporting evidence for this conclusion was provided by measurements of the spin-lattice relaxation times of the complexed ^{7}Li. A plot of $1/T_1\eta$ vs. r' (where $r' = 1/r$) is shown in Figure 8. The observed maximum at $r' \simeq 1$ indicates that a "sandwich"-type complex less deviating from cubic symmetry than the 1:1 complex is formed upon addition of an excess of NDA. The relatively low ($1/T_1\eta = 3.4$ s^{-1} cP^{-1}) re-

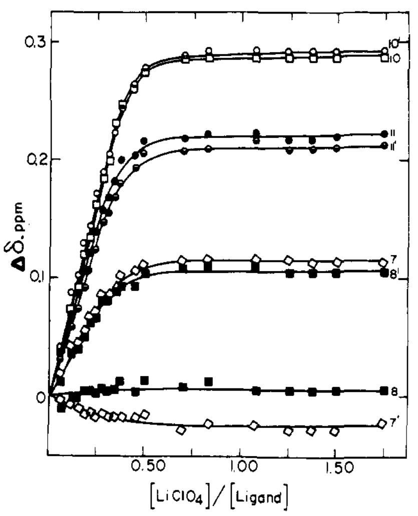

Figure 10. Increments of chemical shifts of ^{1}H signals of PMA vs. [$LiClO_4$]/[PMA] ratio, 0.02 solutions of PMA in nitromethane. Full lines correspond to the computed values. Numbers at the right indicate signal assignment.

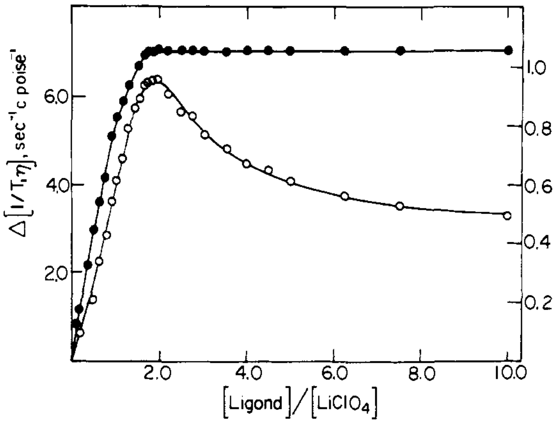

Figure 11. Increments of normalized relaxation rates and of chemical shifts of ^{7}Li vs. [PMA]/[$LiClO_4$] ratio, 0.1 M solutions of $LiClO_4$ in nitromethane. ○, $\Delta(1/T_1\eta)$; ●, $\Delta\delta$. Full lines correspond to the computed values.

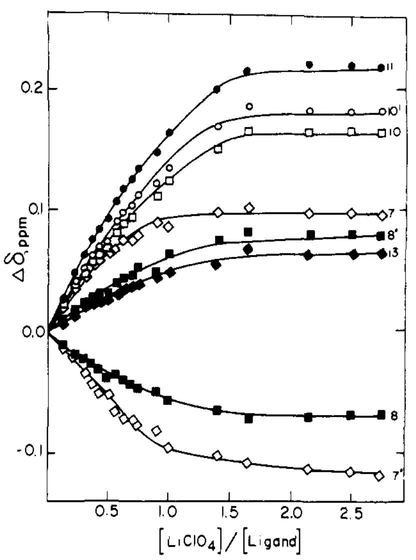

Figure 12. Increments of chemical shifts of ^{1}H signals of NDA vs. [$LiClO_4$]/[NDA] ratio, 0.02 solutions of NDA in acetonitrile. Full lines correspond to the computed values. Numbers at the right indicate signal assignment (cf. Figure 3).

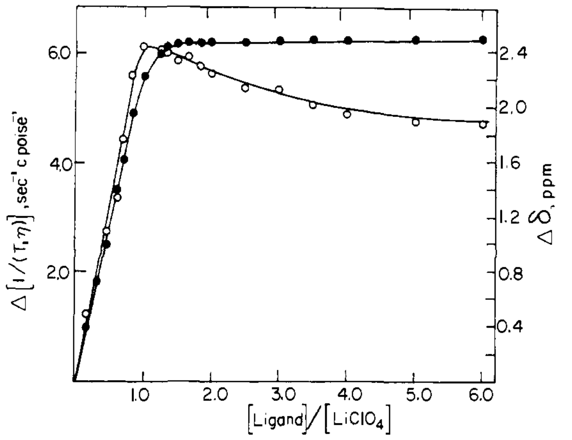

Figure 13. Increments of normalized relaxation rates and of chemical shifts of ^{7}Li vs. [NDA]/[$LiClO_4$] ratio, 0.1 M solutions of $LiClO_4$ in acetonitrile. ○, $\Delta(1/T_1\eta)$; ●, $\Delta\delta$. Full lines correspond to the computed values.

laxation rate in such a complex may be due to a considerable separation of the ^{7}Li ion from its counterion. Jackman and Szeverenyi pointed out[11] that for a nucleus such as ^{7}Li spin-lattice relaxation is completely dominated by the quadrupole mechanism. The difference between the quadrupole splitting constant of the monolithiated and "sandwich"-type complex is probably even greater than indicated by the respective relaxation rates; hence a longer correlation time may be expected for the large "sandwich"-type complex than for the smaller 1:1 complex.

NMR measurements in nitromethane were also taken for the amido ether PMA, which can be regarded as a bidentate analogue of the tetradentate NDA. As may be seen from Figure 9, changes in the ^{1}H NMR spectrum of PMA caused by addition of $LiClO_4$ are analogous to those observed for the NDA system. Results of measurements of $\Delta\delta$ vs. r and of $1/T_1\eta$ vs. r' (where $r' = 1/r$ = [PMA[/[$LiClO_4$]) are shown in Figures 10 and 11, respectively. It is evident that complexes with stoichiometries corresponding to two PMA molecules per $LiClO_4$ and to four PMA molecules per $LiClO_4$ may be formed in this system. These complexes are to some extent analogous to the 1:1 and to "sandwich"-type complexes of NDA.

Complexes in Acetonitrile (DN ≈ 14.1). Measurements of $\Delta\delta$ vs. r and of $1/T_1\eta$ vs. r' for the NDA-$LiClO_4$ system are shown in Figures 12 and 13, respectively. They reveal that both the 1:1 and the sandwich-type 1:2 complexes of $LiClO_4$ with NDA may be formed in acetonitrile. The formation of the bislithiated 2:1 complex is, however, not observed. Apparently, in acetonitrile, a solvent characterized by donicity approaching that of the ethereal solvents, the free energy of solvation of lithium ions is higher than that of interaction of the monolithiated NDA with a second lithium ion.

Complexation in Pyridine (DN = 33.1). Measurements of $1/T_1\eta$ vs. r' shown in Figure 14 indicate that in this solvent the donicity of which is larger than that of the amidic and of the ethereal groups, the complexing ability of NDA is rather limited and apparently only the 1:1 complex may be formed. The extrapolated value of $1/T_1\eta$ for this complex is 12 s^{-1} cP^{-1}, and the equilibrium constant of complexation $K_1'' = 1.1$ M^{-1} (cf. Table IV).

Calculation of the Equilibrium Constants. The intrinsic chemical shifts of the complexes, their longitudinal relaxation times, and the corresponding equilibrium constants were calculated by computer iteration procedure. The experimentally determined chemical shifts and $1/T_1\eta$ values depicted graphically in Figures 4, 7, 8, and 10–14 were used in the computations. The extrapolated intrinsic chemical shifts are summarized in Tables I and II, intrinsic values of $1/T_1\eta$ in

Table I. Intrinsic Chemical Shifts (δ, ppm) of the Ligand Protons

solvent	system	$H_{10'}$	H_{10}	H_7	$H_{7'}$	$H_{11\text{-}11'}$	H_8	$H_{8'}$	H_{13}
nitrometh-	NDA[a]	4.138	4.115	3.330	3.330	3.297	3.002	2.860	0.934
ane	$(NDA)_2 \cdot LiClO_4$	4.23 ± 0.05	4.19 ± 0.04	3.37 ± 0.04	3.30 ± 0.04	3.39 ± 0.04	2.98 ± 0.03	2.89 ± 0.03	0.94 ± 0.01
$\epsilon = 35.9$	$NDA \cdot LiClO_4$	4.43 ± 0.05	4.39 ± 0.05	3.45 ± 0.04	3.22 ± 0.04	3.60 ± 0.04	2.95 ± 0.03	3.00 ± 0.03	1.01 ± 0.01
DN = 2.7	$NDA(LiClO_4)_2$	4.45 ± 0.05	4.41 ± 0.05	3.46 ± 0.04	3.26 ± 0.04	3.62 ± 0.04	2.98 ± 0.03	3.02 ± 0.03	1.01 ± 0.01
	PMA[a]	4.097	4.069	3.233	3.259	3.347/3.352	2.949	2.866	
	$(PMA)_4 \cdot LiClO_4$	4.26 ± 0.05	4.24 ± 0.05	3.31 ± 0.04	3.24 ± 0.03	3.47 ± 0.04/ 3.49 ± 0.04	2.95 ± 0.03	2.93 ± 0.03	
	$(PMA)_2 \cdot LiClO_4$	4.39 ± 0.05	4.36 ± 0.05	3.33 ± 0.04	3.23 ± 0.03	3.55 ± 0.04/ 3.57 ± 0.04	2.95 ± 0.03	2.98 ± 0.03	
acetonitrile	NDA[a]	4.072	4.051	3.249	3.258	3.239	2.918	2.819	0.896
$\epsilon = 38.0$	$(NDA)_2 \cdot LiClO_4$	4.13 ± 0.04	4.11 ± 0.04	3.31 ± 0.04	3.20 ± 0.03	3.31 ± 0.03	2.89 ± 0.03	2.85 ± 0.03	0.92 ± 0.01
DN = 14.1	$NDA \cdot LiClO_4$	4.26 ± 0.04	4.22 ± 0.05	3.36 ± 0.04	3.14 ± 0.03	3.46 ± 0.04	2.84 ± 0.03	2.90 ± 0.03	0.96 ± 0.01
methylene	NDA[a]	4.061	4.039	3.228	3.278	3.233	2.928	2.844	0.911
chloride	$(NDA)_2 \cdot LiClO_4$	4.10 ± 0.04	4.06 ± 0.04	3.29 ± 0.04	3.20 ± 0.03	3.28 ± 0.03	2.92 ± 0.03	2.86 ± 0.03	0.92 ± 0.01
$\epsilon = 9.08$	$NDA \cdot LiClO_4$	4.34 ± 0.05	4.30 ± 0.05	3.45 ± 0.04	3.06 ± 0.03	3.54 ± 0.04	2.83 ± 0.03	2.98 ± 0.03	1.01 ± 0.01

[a] Directly measured values.

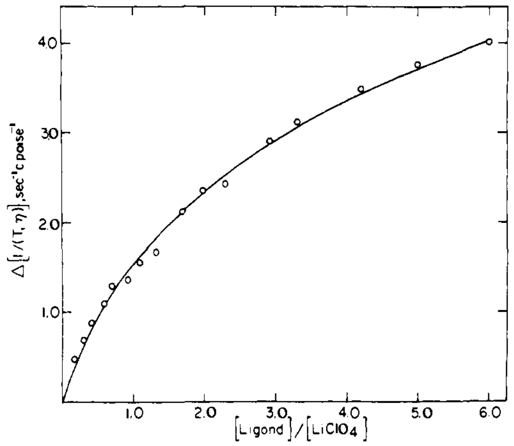

Figure 14. Increments of normalized relaxation rates of ^7Li vs. $[NDA]/[LiClO_4]$ ratio, 0.1 M $LiClO_4$ in pyridine. Full line corresponds to the computed values.

Table II. The Intrinsic Chemical Shifts (δ, ppm) of ^7Li

	solvent	
	nitromethane	acetonitrile
$LiClO_4$[a]	0.16	2.65
$(NDA)_2LiClO_4$	1.35 ± 0.05	0.25 ± 0.05
$NDA \cdot LiClO_4$	1.35 ± 0.05	0.25 ± 0.05
$NDA(LiClO_4)_2$	0.72 ± 0.05	
$(PMA)_4LiClO_4$	1.24 ± 0.05	
$(PMA)_2 \cdot LiClO_4$	1.24 ± 0.05	

[a] Directly measured value.

Table III. The Intrinsic $1/T_1\eta$ (s^{-1} cP^{-1}) of ^7Li

	solvent		
	nitromethane	acetonitrile	pyridine
$LiClO_4$[a]	0.33	0.23	0.90
$(NDA)_2 \cdot LiClO_4$	3.4 ± 0.2	2.9 ± 0.2	
$NDA \cdot LiClO_4$	13.9 ± 0.1	6.5 ± 0.2	12.0 ± 0.2
$NDA(LiClO_4)_2$	2.6 ± 0.2		
$(PMA)_4 \cdot LiClO_4$	2.8 ± 0.3		
$(PMA)_2 \cdot LiClO_4$	5.9 ± 0.2		

[a] Directly measured value.

Table III, and the values of equilibrium constants in Table IV. Solid lines in the graphs correspond to points computed from the equilibrium constants and from the extrapolated intrinsic chemical shifts or intrinsic relaxation times.

The procedure described by Reuben et al.[12,13] for the conditions of fast exchange between the free ligand and its bounded states was used for the mathematical analysis of the experimental data.

The complexation of NDA in pyridine was treated as 1:1 case, characterized by the single equilibrium

$$NDA + LiClO_4 \xrightleftharpoons{K_1''} (NDA)Li^+,ClO_4^- \quad \text{(cf. eq 1)}$$

The complexation of NDA in acetonitrile and in methylene chloride was treated as case 2 defined[12] by two equilibria (cf. eq 1 and 2). Similarly treated was the complexation of PMA in nitromethane, which was assumed[14] to be described by the equilibria

$$2PMA + LiClO_4 \xrightleftharpoons{K_1'} (PMA)_2Li^+,ClO_4 \qquad (4)$$

$$2PMA + (PMA)_2Li^+,ClO_4 \xrightleftharpoons{K_2'} (PMA)_4Li^+,ClO_4 \qquad (5)$$

It has been shown in the preceding section that three equilibria must be considered (cf. eq 1–3) for the complexation of NDA in nitromethane. Experimental data in this system were analyzed by dividing them into two parts. It was assumed that in the concentration range $[NDA] > LiClO_4$ the system is defined by the equilibria K''_1 and K''_2, while in the concentration range $[NDA] < LiClO_4$ the system is defined by the equilibria K''_1 and $K''_{0.5}$. Each part was treated as case 2. Such an approximation is justified when $K_{0.5} \ll K_1 \gg K_2$. This indeed seems to be the case in the presently investigated system (cf. Table IV). The standard deviation of the experimental points from values computed by the above-described procedures did not exceed 3% (cf. Figures 4, 6, 7, and 10–14). Moreover, the difference between any individual experimental point and its computed value did not exceed 1.5σ. The reliability of the thus determined equilibrium constants estimated by the saturation factor analysis[13,15] is indicated in Table IV.

Inspection of the values of equilibrium constants listed in Table IV reveals that they increase with the decrease in solvent basicity, but are unrelated to the dielectric constants of the solvent medium. In solvents of low basicity, bislithiated and "sandwich"-type complexes of NDA may also be formed. The preferred species in all solvents is, however, the 1:1 complex, in which the complexed lithium ion is located within the

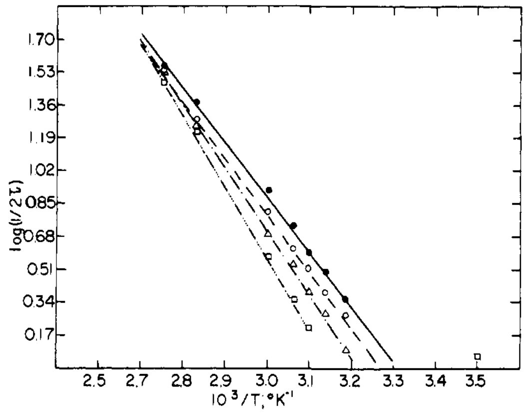

Figure 15. Semilogarithmic plots of rate constants of rotation around the C-N bond of NDA in nitromethane vs. reciprocals of absolute temperatures: ●, uncomplexed NDA: ○, 2[NDA]/[$LiClO_4$]; △, NDA·$LiClO_4$; □, NDA·$(LiClO_4)_2$.

Table IV. Stability Constants of the $LiClO_4$-NDA Complexes

solvent	$K''_{0.5}$, M^{-1}	K''_1, M^{-1}	K''_2, M^{-1}
methylene chloride		~10^6 (?)	200 ± 25
nitromethane	50 ± 10	$10^5 < K < 10^6$	17 ± 3
acetonitrile	none	(1 ± 0.3) × 10^3	10 ± 2
pyridine	none	1.1 ± 0.1	none

"cavity" formed by the four oxygen atoms of NDA. Observations made in this laboratory seem also to indicate that the formation of the "sandwich"-type complex in methylene chloride may be inhibited by the presence of minute amounts of water. Apparently, partial hydration of the lithium ion complexed with NDA may prevent its interaction with the second NDA molecule.

Equilibrium constants K'_1 and K'_2 (see eq 4 and 5) for the PMA-$LiClO_4$ system in nitromethane have been found to be 50 and 10 M^{-2}, respectively. A direct comparison of these equilibrium constants with the values of K''_1 and K''_2 in the NDA system is impossible because the PMA constants are of the second and the analogous NDA constants are of the first order, respectively. Nevertheless, it is obvious that NDA acts as a much more effective complexing agent of lithium ions than its bidentate analogue PMA.

Restricted Rotations around the C-N Bond in NDA and in Its Complexes. ^1H NMR spectra of NDA and of its complexes in nitromethane around δ ~3 ppm have been recorded in the temperature range 40-95 °C. Signals due to NCH_3 coalesce at 65 °C and at 55 °C in free NDA and in the "sandwich"-type complex, respectively. A considerable broadening of the lines was noted at higher temperatures for the 1:1 and for the bislithiated complexes. However, their coalescence temperature could not be reached in nitromethane (bp 100.8 °C). Rates of exchange, $1/\tau$, between the cis and trans positions of NCH_3 and the corresponding rate constants of rotation around the C-N bond, $k = 1/2\tau$, were calculated from the line-shape analysis[16,17] of the NCH_3 signals. Semilogarithmic plots of $1/2\tau$ vs. reciprocals of absolute temperatures are shown in Figure 15. Energies of activation derived from the slopes of these lines are listed in Table V together with the respective frequency factors. A significant increase in the energy of activation of rotation around the C-N bonds of NDA is noted for the 1:1 and for the bislithiated complexes. It seems that the partial double bond character of the C-N bond increases considerably as the result of interaction of the amidic carbonyls of NDA with a lithium ion. This effect is, however, very small in the PMA system. Apparently the weakness of the $LiClO_4$-PMA complexes should be considered in terms of enthalpy as well as of entropy.

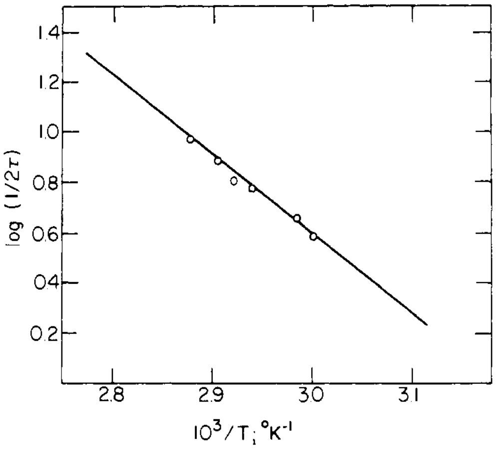

Figure 16. Bislithiated NDA complex in nitromethane. Semilogarithmic plot of $1/2\tau$ for the fine splitting of the OCH_2CO signals vs. reciprocals of absolute temperatures.

Table V. Restricted Rotation around the C-N Bond of NDA, PMA, and Their Complexes in Nitromethane. Energies of Activation and Frequency Factors

system	E_a, kcal/mol	log A
NDA	12.9 ± 0.5	9.4 ± 0.3
2[NDA]/[$LiClO_4$]	13.3 ± 0.5	9.6 ± 0.3
NDA·$LiClO_4$	15.0 ± 0.6	10.6 ± 0.3
NDA$(LiClO_4)_2$	16.8 ± 0.7	11.7 ± 0.4
PMA	8.9 ± 0.4	7.7 ± 0.2
2[PMA]/[$LiClO_4$]	9.3 ± 0.4	6.8 ± 0.2

It has been pointed out in the first part of this discussion that additional fine splitting of the *O*-methylene, *N*-methylene, and *N*-methyl signals is observed in the bislithiated NDA complex formed in nitromethane (cf. Figure 6). Such splittings indicate that a process slow on the NMR time scale must be responsible for the nonequivalency of the two "arms" of NDA. Pretsch observed similar splittings in a calcium complex of a tetradentate amido ethereal ligand analogous to NDA and attributed them to the presence of two amidic groups on the same ligand molecule. He suggested[18] that the fine splittings of the 7, 7′, 8, 8′, 10, 10′, and 11 signals of the bislithiated complex, observed by us, may be explained in the same way.

The enlarged signals of OCH_2CO protons (having the most pronounced fine splitting) were recorded in the temperature range 40-95 °C. Values of $1/2\tau$ have been computed from the line-shape analysis of these signals. Their semilogarithmic plot vs. $1/T$ is shown in Figure 16. The slope of the straight line, thus obtained, yields ~14 kcal/mol as the energy of activation of the corresponding exchange process. In view of uncertainties involved in line-shape analysis of ^1H NMR signals separated by 3.5 Hz only, the difference between this value and the value of 16.8 ± 0.7 kcal/mol, calculated previously as the energy of activation of rotation around the C-N bond in the bislithiated complex, cannot be regarded as significant. The observed additional splittings in the bislithiated complex must be attributed, therefore, to the differences between the cis and the trans environment in the symmetric isomers "cis" and "trans" and in the asymmetric isomer "cis-trans" (cf. Figure 3).

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Dynamic Behavior and Aggregation of Propyllithium from ^{13}C and ^{6}Li NMR at High Field

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Abstract: High-field ^{13}C NMR of propyllithium-*1*-^{13}*C*-*1*-^{6}*Li* (**4**) at equilibrium in cyclopentane shows splitting due to ^{13}C-^{6}Li spin coupling, and reveals the existence of several organolithium species with aggregation numbers of 6, 8, and 9 whose distribution varies with temperature and which all undergo fast *intraaggregate* carbon-lithium bond exchange. Equilibrium constants and thermodynamic data connecting the aggregates are given. Above 250 K mainly hexamer is present. Increasing temperature causes averaging of the ^{13}C-^{6}Li coupling and chemical shifts due to progressively faster interaggregate carbon-lithium bond exchange. NMR line-shape analysis for the ^{13}C NMR data from **4** and for the ^{6}Li line shapes of propyllithium-*1*-^{6}*Li* show exchange to result from the collision of two aggregates.

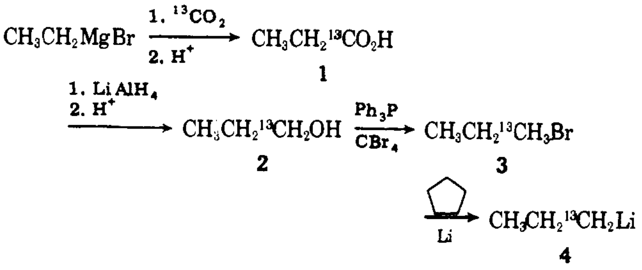
Alkyllithium compounds exist in solution as hexamers[2] or tetramers[3] and undergo fast inversion at carbon bonded to lithium[4] as well as interaggregate carbon-lithium bond exchange.[5,6]

Certain alkyllithium compounds, methyllithium[7] or *n*-butyllithium,[8] in ether exhibit directly bonded ^{13}C-^{7}Li scalar coupling at low temperatures. This has been used to confirm the tetrahedral character of methyllithium and *n*-butyllithium etherates. Thus, in principle, where it can be observed, from the multiplicity of the splitting due to $J(^{13}C_1-^{7}Li)$, one can identify the character of the carbon-lithium bridged bond and from its averaging the dynamics of carbon-lithium bond exchange. It turns out that in many cases, for *n*-alkyllithiums in hydrocarbon solvent, although ^{13}C NMR of carbon bonded to lithium undergoes broadening with decreasing temperature, splitting is not observed.[9] The proposal that the couplings are averaged out by ^{7}Li quadrupole-induced relaxation[9] was recently confirmed by comparing the ^{13}C NMR spectrum of propyllithium-^{7}*Li* with that of propyllithium-^{6}*Li*. The ^{6}Li sample showed splitting of the C$_1$ carbon resonance at 240 K, while the ^{7}Li sample had only broad peaks.[10] Evidently, the quadrupole moment of ^{6}Li in this system is too insignificant to affect the NMR in a noticeable way.[11]

In this article, we show how high-field ^{13}C and ^{6}Li NMR can be used to identify fluxional aggregates of alkyllithium compounds (in hydrocarbon solvent), some present only at low temperatures, and to identify their association numbers. It will be shown that ^{13}C and ^{6}Li NMR of organolithiums enriched with ^{13}C and ^{6}Li is the method of choice to investigate structure and dynamic behavior of organolithium compounds.

Results and Discussion

Isotopically enriched 1-bromopropane-*1*-^{13}*C*, 90%, was prepared according to the scheme below. NMR data for the intermediates **1–3** are listed in Table I. Reaction of the bromide **3** in cyclopentane with lithium-6 shavings, 95.6% ^{6}Li, ca. 4.4% ^{7}Li, cleanly gave the lithium compound **4** in 95% yield.



$$\mathrm{CH_3CH_2MgBr} \xrightarrow[2.\ \mathrm{H^+}]{1.\ ^{13}\mathrm{CO_2}} \underset{\mathbf{1}}{\mathrm{CH_3CH_2{}^{13}CO_2H}} \xrightarrow[2.\ \mathrm{H^+}]{1.\ \mathrm{LiAlH_4}} \underset{\mathbf{2}}{\mathrm{CH_3CH_2{}^{13}CH_2OH}} \xrightarrow[\mathrm{CBr_4}]{\mathrm{Ph_3P}} \underset{\mathbf{3}}{\mathrm{CH_3CH_2{}^{13}CH_2Br}} \xrightarrow[\mathrm{Li}]{} \underset{\mathbf{4}}{\mathrm{CH_3CH_2{}^{13}CH_2Li}}$$

Figure 1 shows ^{13}C NMR line shapes for C$_1$ of propyllithium-*1*-^{13}*C*-*1*-^{6}*Li* (**4**), 0.5 M in cyclopentane, previously obtained at 22.526 MHz at several temperatures.[10] With decreasing temperature, the C$_1$ resonance broadens and splits, and by 245 K two new resonances develop to lower field at the expense of the original absorptions. The same sample at 67.89 MHz gave the ^{13}C resonance for C$_1$ of **4** shown in Figure 2. Notice how the lower field peaks seen at 22.625 MHz now consist of four distinguishable resonances. Use of a resolution enhancement technique (plotting of the first derivative) on two of these spectra, Figure 3, shows each of the resonances to be split. These results demonstrate the existence of at least five different propyllithium species.

We previously reported that the ^{7}Li NMR (23.32 MHz) of "normal" propyllithium, 1 M in cyclopentane, consists of a single line whose width increases from 2 Hz at 320 K to >60 Hz at 180 K, the result of ^{7}Li quadrupole relaxation whose rate increases with decreasing temperature.[10] In contrast, ^{6}Li NMR at 39.73 MHz for the species $(\mathrm{CH_3CH_2{}^{12}CH_2{}^{6}Li})_n$ (**5**) prepared 0.5 M in cyclopentane from normal 1-bromopropane and lithium-6 shavings, 96%, gives five sharp lines of width 0.5-2 Hz at 180 K over a span of 33 Hz; see Figure 4. With increasing temperature the highest field resonance increases in

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