

system was underdetermined with only four useful proton LIS and no relaxation-rate measurements.

The data presented in this work point out the difficulties in attempting to separate contact and pseudocontact components to measured lanthanide-induced shifts. The problems appear to be compounded at nuclei near the ligation site and, in light of the results presented here, several of the previously determined structures of lanthanide-carboxylates and lanthanide-amino acids should be reexamined. The trends in the LIS data we reported earlier for L-alanine are very similar to the results presented in this work for L-proline. It seems likely that inadequate separation procedures for the contact and pseudocontact shifts at C_0 and C_α in alanine led to an incorrect prediction of different lanthanide-alanine structures for cations from the first and last half of the lanthanide series. Structural differences were also noted for 3-indoylacetate² and tryptophan³ binding to lanthanide cations from the first vs. last part of the series. Plots of $\Delta_{\text{obsd}}/\langle Sz \rangle$ vs. $D/\langle Sz \rangle$ for the α -CH₂ and indole H-2 proton lanthanide induced shifts of 3-indoylacetate² clearly show the same subdivision of lanthanide cations as observed here for proline. This also suggests that the pseudocontact shifts in this ligand system contain nonaxial components (as previously pointed out by Reuben and Elgavish⁶) and these nonaxial terms are different for the light vs. heavy lanthanide cations.

Elgavish and Reuben have used relaxation data to show that sarcosine forms isostructural complexes with nine different lanthanide cations.⁵ An examination of the plots for the C_α shifts (Figure 6 in ref 14) shows the same trends as reported here for proline. Their failure to recognize the nonaxial contribution to

the C_0 and C_α shifts undoubtedly complicated their structural analysis and led them to conclude that the lanthanide cation does not bind to the carboxyl group in a unique position but rather averages between a monodentate and bidentate coordination position. This conclusion should be reevaluated in view of the results presented above.

In summary, we have shown that the separation of contact- and pseudocontact-shift contributions to observed LIS at nuclei near the lanthanide cation binding site in small molecules may often be complicated by nonaxial dipolar contributions to the pseudocontact shifts, changes in hyperfine coupling constants along the lanthanide series, or perhaps a combination of these effects. Relaxation rate data must be used to detect metal-ligand structural alterations along the cation series.⁵ A high correlation of LIS data to eq 3 does not assure conformity of the data to the axial symmetry model but merely indicates that the quantity ($A_2^0G + A_2^2G'$) is lanthanide independent.

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Registry No. L-Proline, 147-85-3; Pr(3+), 22541-14-6; Nd(3+), 14913-52-1; Eu(3+), 22541-18-0; Gd(3+), 22541-19-1; Tb(3+), 22541-20-4; Dy(3+), 22541-21-5; Ho(3+), 22541-22-6; Er(3+), 18472-30-5; Tm(3+), 22541-23-7; Yb(3+), 18923-27-8.

Aggregation of Lithium Phenolates in Weakly Polar Aprotic Solvents

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Abstract: The aggregation of lithium phenolate, 3,5-dimethylphenolate, 2,6-dimethylphenolate, and 2,6-di-*tert*-butylphenolate in dioxolane, dimethoxyethane, and pyridine has been investigated by a variety of methods including studies of vapor pressure barometry, ¹³C chemical shifts, ⁷Li nuclear quadrupole coupling constants, and ¹³C spin-lattice relaxation times. The phenolates with no ortho substituents form tetramers under most conditions. In pyridine at low concentrations and temperature the tetramers coexist with dimers. Lithium 2,6-dimethylphenolate forms dimers under all conditions studied, and lithium 2,6-di-*tert*-butylphenolate exists as a monomer or an oligomer depending on conditions. Attempts to establish solvation numbers for the aggregates from solvent ¹³C relaxation times have not been successful, and the reason for the failure, very fast solvent exchange, is discussed. The kinetics and thermodynamics of exchange between dimers and tetramers of lithium 3,5-dimethylphenolate in pyridine have been investigated, and the mechanism of interconversion has been shown to involve additional solvation of the tetramer prior to dissociation. The equilibrium 2 dimer \rightleftharpoons tetramer has $\Delta H = 7.1$ kcal mol⁻¹ and $\Delta S = 34$ cal deg⁻¹ mol⁻¹, the large entropy being due to release of solvent on formation of the tetramer.

It is established that counterions play an important role in the chemistry of enolate ions in weakly polar aprotic solvents¹ and that the structures of ion-pair aggregates must be known before the mechanisms of the reactions of enolates with electrophiles can be completely understood.^{2,3} Although X-ray crystallography can provide accurate structures for aggregates in the solid state,^{4,5} it is necessary to establish whether these structures prevail in

solution. We have used NMR spectroscopy to probe the structures in solution of aggregates of lithioisobutyrophenone.^{6,7} For some sets of conditions the existence of the tetrameric structure, which has been found for **1** (R = OCBu^t=CH₂; S = THF) in the solid state,⁴ has been established. Under other conditions, however, the presence of the dimeric species **2** could be inferred. Although there appears to be no reason to doubt these conclusions, the possible conformational flexibility within the enolate moiety in the lithioisobutyrophenone aggregates did introduce some uncertainty into the interpretation of several of the NMR phenom-

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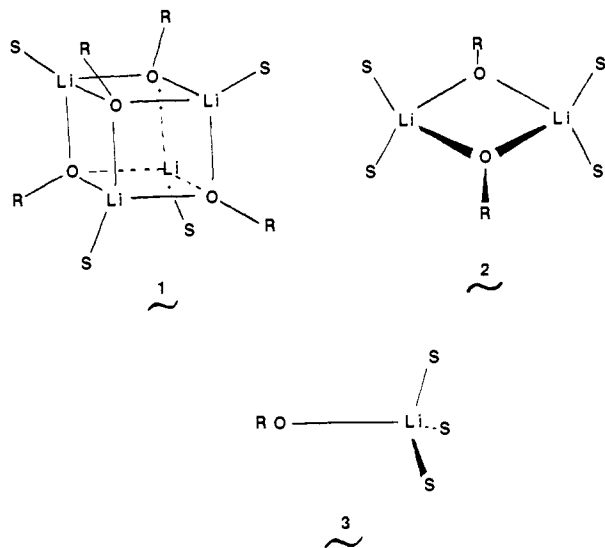
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ena. For this reason we have undertaken analogous studies of some lithium phenolates in which these uncertainties are largely avoided but which, nevertheless, are structurally closely related to the enolate system.

The principal advantage of the lithium phenolates, and their 2,6- and 3,5-dialkyl derivatives, is that the spin-lattice relaxation times of the para carbon atoms are unaffected by internal rotations of the aryl groups and therefore usually reflect the rotational diffusion of the entire aggregates. This consideration removes an important assumption made in estimating molecular volumes and ^7Li nuclear quadrupole coupling constants for lithioisobutyrophenone aggregates.⁷ For the same reason, we have included pyridine as a representative weakly polar aprotic solvent since the relaxation time for its γ carbon atom is similarly unaffected by internal rotation of the solvent molecule when bound to the aggregate.

Since the real importance of this study is that it examines the efficacy of NMR methodologies for the investigation of aggregate structures, we have carried out independent determinations of degrees of association using vapor pressure barometry in order to confirm our conclusions, at least within the somewhat narrow range of conditions in which this latter method is applicable.

The study of lithium phenolates also provides an opportunity to examine the influence of anion structure on the natures of the aggregates formed. We have therefore investigated the series of salts derived from phenol, 2,6- and 3,5-dimethylphenol, and 2,6-di-*tert*-butylphenol. In the course of this study we have demonstrated the coexistence, under certain conditions, of species differing in their degree of aggregation and, in one case, have studied the kinetics of their interconversion.

Experimental Section

Nuclear Magnetic Resonance Studies. Fourier transform NMR spectra were obtained using one of the following instruments: Varian Associates CFT-20, Bruker Instruments WP-200, or Japan Electron Optics Laboratories JNM-PS100 interfaced with a Nicolet Corp. 1080 data system and associated software.

Relaxation times for both ^{13}C and ^7Li were measured using the JEOL system referred to above. The inversion-recovery method ($180^\circ-\tau-90^\circ-D$) for measuring longitudinal relaxation times (T_1) was used throughout this work. Twelve randomly ordered τ values were employed per determination, and D , the recovery time, was always at least five times as large as the calculated T_1 value. The pulse homogeneity of the JEOL two-coil ^{13}C probe is excellent. The width in microseconds of the 180° pulse was redetermined each time the carbon probe was reinstalled, by measuring the null pulse for the methyl resonance in a Gd(III)-doped *tert*-butyl alcohol sample.

The T_1 calculations were performed using the Nicolet software (NT-CFT) which accepts intensity data for a resonance as a function of τ . T_1 is then calculated by fitting the data to the two-parameter function using the method of nonlinear least squares. To be judged an acceptable T_1 determination, the value found had a standard error of 5% or less. Occasionally a point was rejected, on statistical grounds, to improve the fit of the data. Temperature of the sample was regulated to $\pm 1.0^\circ\text{C}$, as

monitored by a thermocouple in the sample cavity. Nuclear Overhauser enhancements (NOE) were determined for carbon resonances by comparing the intensities or areas of fully enhanced, broadband-decoupled resonances with their counterparts acquired under conditions of inverse gated decoupling. In the latter experiment, the broadband decoupler is only active during data acquisition, then gated off for a long (at least $10 \times T_1$) delay between scans. The same number of acquisitions and identical normalization constants were employed to obtain meaningful comparisons between the enhanced and nonenhanced spectra.

Dynamic Nuclear Magnetic Resonance Studies. For the pyridine solution of lithium 3,5-dimethylphenoxide, the variable-temperature NMR spectra revealed the presence of two species in equilibrium, one of which predominated at high ($>+30^\circ\text{C}$) temperature, the other at low temperature ($>-30^\circ\text{C}$). This phenomenon was revealed by the ^{13}C , ^7Li , and ^1H spectra. The ^1H resonance showed particularly striking changes in the methyl resonance with temperature, and this region was selected for analysis. Variable-temperature spectra were measured at 200 MHz for solutions at 0.17 and 0.35 M. Sample temperature was regulated by a thermocouple-controlled liquid nitrogen boil-off system. The actual cavity temperature was determined for each experiment by measuring the chemical shifts of a standard methanol sample, before and after each spectrum was acquired.

The 0.17 M solution showed larger changes in the temperature range examined, so these spectra were selected for simulation. The spectra were simulated using DNMR3,⁸ a program for complete line-shape analysis of spectra undergoing multisite exchange. The simulation requires as input the chemical shifts of the exchanging sites at the limit of slow exchange, the relative site populations, T_2^* (reflecting the instrumentally determined line width, estimated here from the line width of internal tetramethylsilane), and an estimate of the rate constant. The rate constants and populations for each case were first estimated, then varied slightly, until the plot of the calculated spectrum was superimposable on the experimental plot.

Viscosities. Viscosities of solutions and pure solvents were measured using a modified Canon-Fenske viscometer; the method used has been described earlier.⁷

Sample Preparation. All phenols were obtained from Aldrich Chemical Co. and recrystallized from pentane immediately prior to use, under a nitrogen atmosphere. The single exception was 2,6-di-*tert*-butylphenol, which was vacuum distilled prior to use. *n*-Butyllithium, 1.6 M in hexane, was used as obtained from Aldrich. Pyridine, obtained from Fisher, was desiccated over sodium hydroxide and, immediately prior to use, was fractionally distilled from calcium hydride, using a 20 in. Fenske column packed with glass helices.

1,3-Dioxolane and ethylene glycol dimethyl ether (DME) were obtained from Aldrich, refluxed over benzophenone sodium ketyl, and distilled immediately prior to use. They were then pipetted into storage flasks containing freshly ground calcium hydride and attached to the vacuum line.

The preparations were carried out using the previously described⁷ vacuum-line technique for filling NMR tubes, viscometer and pycnometer. Since the phenols could not be vacuum transferred, the lithium salts were prepared in the following way. A hexane solution of the appropriate amount of phenol, with a small quantity (several crystals) of 1,10-phenanthroline, was charged to the reaction vessel via syringe, which was rinsed to ensure quantitative transfer. The solution was then frozen under a strong nitrogen flow and the filling port sealed by glass-blowing. The system was evacuated while frozen and allowed to thaw under vacuum. Nitrogen was then admitted to the system, and a second port on the reaction vessel was opened and fitted with a serum cap. Stirring was commenced and *n*-butyllithium was added dropwise by syringe until the reddish endpoint just persisted. The endpoint was back-titrated with a few drops of a dilute phenol solution, and the slurry was frozen. Then the port was sealed and the preparation completed as described.

Determination of Molecular Weights from Vapor Pressure Measurements. The association numbers for phenolate solutions in pyridine and dioxolane were determined using a modification of a technique described by Fraenkel et al.⁹ for measurement of differential vapor pressures. The molal vapor pressure differentials were monitored using an MKS Instruments, Inc. baratron sensor unit, Model 145-BH, interfaced with an MKS Model 170-M electronics unit and a Kiethley millivoltmeter.

The apparatus consisted essentially of a solvent and a solution vessel connected to the two sides of the baratron. Each side was connected to a high-vacuum line via a Kontes 0-4 mm high-vacuum stopcock and to the baratron by means of a flexible Cajon/glass joint. The instrument

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was calibrated for each of the solvents employed, in the following manner. A solution (~30 mL) containing a known weight of triphenylmethane, in a known weight of solvent, was added through a side arm to the solution vessel of the baratron. The solution was frozen under a nitrogen purge and the side arm sealed by glass blowing. The solvent vessel was filled with an equivalent volume of solvent by evacuation of the solvent arm with the solution valve closed, followed by line transfer of the solvent from the reservoir to the solvent vessel. Then both arms were isolated, and the contents of the flasks were frozen. The manifold was evacuated and the contents of each flask outgassed individually by freezing and thawing cycles. The arms were then reisolated from the vacuum line, the contents thawed, and the flasks equilibrated in a recirculating constant-temperature bath (± 0.1 °C). The main valve to the vacuum line was closed and the two arms were opened briefly to each other, in order to equilibrate any residual permanent gas. The baratron was set to zero at this time. The two stopcocks were then closed and the pressure differential was recorded over the course of an hour, to the nearest 0.01 torr (1 torr = 1 V for this instrument). Typically, the readings were constant after 30 min.

With the main valve closed, the solution arm was opened and approximately 1.5 mL was distilled into a reservoir. The solution arm was closed, and the reservoir was removed, weighed, pumped dry, and reweighed in order to ascertain the weight of solvent removed. The newly concentrated solution and the solvent were equilibrated, as before, and a new value of Δp was determined. Several concentrations were measured in this way. A plot of Δp vs. solution molality was thus generated and was used for that solvent and temperature to estimate the apparent molalities of unknown solutions. The temperatures used were slightly less than ambient in order to prevent condensation of solvent vapor in the upper parts of the apparatus.

Phenolate solutions of known titer were prepared in the solution arm in a manner similar to that described for the NMR solutions. A known quantity of phenol, in hexane, was charged to the solution flasks, under nitrogen purge. *n*-Butyllithium was added dropwise, with stirring, to give the phenanthroline endpoint. The contents were frozen and sealed, and the hexane was removed by prolonged pumping and heating. Then equal known weights of the ether solvent were line-transferred separately into the solvent and solution flasks, yielding approximately a 0.3 M solution of the phenolate in the latter. The two flasks were outgassed and equilibrated at the calibrated temperature as before, and Δp was determined. This value was used in conjunction with the calibration plot, to yield an apparent molality, which was then compared with the actual molality, yielding an association number, n , for the salt in question.

2,6-Dimethylanisole. The phenol (5.0 g, 0.04 mol) was dissolved in an aqueous solution of NaOH (1.7 g, 0.04 mol). The solution was chilled to ice-bath temperature and dimethyl sulfate (4.8 mL, 0.05 mol) was added dropwise. The solution clouded immediately. The mixture was heated at reflux for 1 h, then cooled, and 10% NaOH (10 mL) was added. A light yellow oil separated which was extracted with ether (2 \times 30 mL). The combined extracts were washed with brine and dried (Na_2CO_3). The ether was removed to furnish a yellow oil. The crude product was distilled under reduced pressure to yield the pure 2,6-dimethylanisole (2.5 g, 45%), bp 40 °C (1 mm), η^{20}_D 1.5036 (lit.¹⁰ 1.5053).

3,5-Dimethylanisole. An analogous preparation gave 3,5-dimethylanisole (4.0 g, 72%), bp 30 °C (0.2 mm), η^{20}_D 1.5126 (lit.¹⁰ 1.5129).

2,6-Di-*tert*-butylanisole. To a chilled, stirred slurry of NaH (Alfa, 2 g, 50% oil dispersion) in ether (150 mL) was added a solution of the phenol (8.5 g, 0.04 mol) in dry ether (50 mL), dropwise over 15 min. The mixture was allowed to warm and stirred for 2 h during which time the gray color discharged. The slurry was recharged to ice-bath temperature and dimethyl sulfate (5.0 mL, 0.052 mol) was added dropwise over 15 min. The solution was cooled and aqueous NaOH (50 mL, 10%) was added, giving a clear, two-phase mixture. This was extracted with ether (3 \times 25 mL). The extracts were combined, washed with brine, and dried (Na_2CO_3). Evaporation furnished a viscous yellow oil (9 g), which was distilled to yield 2,6-di-*tert*-butylanisole (8 g, 88%), bp 96 °C (0.15 mm), η^{20}_D 1.5046 (lit.¹¹ 1.5044).

Results

Differential Vapor Pressure Barometry. Measurements of differential vapor pressure were carried out at 290 K, which was somewhat below ambient temperature, and at concentrations in the range 0.08–0.5 M. The results are summarized in Table I. The principal source of error in the degree of association n is in the determination of the concentration of the phenolate (see Experimental Section), but we estimate that the reported values

Table I. Degree of Association (n) of Lithium Phenoxide in Two Solvents at 17.5 °C

substituents	dioxolane		pyridine	
	concn (M)	n	concn (M)	n
H	0.49	3.7	0.39	3.9
3,5-Me ₂	0.44	3.8		
2,6-Me ₂	0.46	2.2	0.51	1.7
2,6-Bu ^t ₂	0.08	0.9	0.39	0.9
2,6-Bu ^t ₂	0.09	1.0		
2,6-Bu ^t ₂	0.11	1.2		
2,6-Bu ^t ₂	0.13	1.2		
2,6-Bu ^t ₂	0.16	1.3		
2,6-Bu ^t ₂	0.21	1.5		
2,6-Bu ^t ₂	0.41	2.0		

are within the $\pm 10\%$ of the true values.

At room temperature and at concentrations of 0.4–0.5 M in dioxolane, both lithium phenolate and 3,5-dimethylphenolate are tetramers, as is the former salt in pyridine. Of course, low concentrations of smaller aggregates cannot be excluded, and, as will be shown later, lithium 3,5-dimethylphenolate in pyridine under these conditions does indeed exist as a mixture of tetramer and dimer although at 0.44 M and 290 K the former is the major species.

Lithium 2,6-dimethylphenolate is clearly essentially dimeric in both solvents. It has also been found¹² by cryoscopy to be dimeric ($n = 1.9 \pm 0.2$) in dioxane at 11 °C over the concentration range 0.015–0.081 M.

Lithium 2,6-di-*tert*-butylphenolate is monomeric in pyridine at 0.4 M concentration. In dioxolane this salt is monomeric at 0.08 M but becomes aggregated as the concentration is increased. The concentration dependence of the degree of aggregation is far too steep to be accommodated by a monomer–dimer equilibrium. Indeed, the data do not even fit the formation of a tetramer. It appears likely, therefore, that this salt tends to form linear polymeric aggregates at higher concentrations. It is, however, known to crystallize from diethyl ether as a cyclic dimer with one ether molecule per lithium,⁴ and a tetrahydrofuran solvate (one THF per Li) of its 4-methyl homologue exists as a dimer in benzene.¹³ It is possible that linear or macrocyclic oligomers, unlike the cyclic dimer, can accommodate two solvent molecules per lithium, thus favoring the oligomerization at high concentrations.

Molecular Volumes from Spin–Lattice Relaxation Times. In our studies of lithioisobutyrophenone⁷ we sought to establish the degree of aggregation in various solvents from estimates of molecular volume based on ¹³C T_1 and viscosity data. The procedure involved several assumptions which are not readily justified. In particular, the effective correlation times for reorientation of the C, H bond vectors could have been affected by internal rotation and might not have reflected the motion of the aggregate as a whole. Since, for phenolates, rotation of the aromatic ring does not reorient the C, H bond vector for the para carbon atom, its relaxation time should allow the determination of a correlation time for the entire aggregate, and these systems therefore provide an opportunity for critically evaluating the efficacy of the T_1 vs. viscosity method for determining molecular volumes.

The method involves the application of the Stokes–Einstein equation

$$V_m = 4\pi r_s^3/3 = kT\tau_c/\eta \quad (1)$$

in which τ_c is the correlation time for isotropic rotational diffusion and η is the bulk viscosity. The former is obtained from the equation

$$1/T_1^{\text{DD}} = \gamma_{\text{H}}^2 \gamma_{\text{C}}^2 \hbar^2 r_{\text{C,H}}^{-6} \tau_c \quad (2)$$

where T_1^{DD} is the dipole–dipole relaxation time for a carbon atom with an attached proton and $r_{\text{C,H}}$ is the vibrationally averaged internuclear distance which is assumed to be 110.7 pm for an

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Table II. Spin-Lattice Relaxation Times (T_1 , s) of Para Carbon Atoms, Viscosities (η , cP), Microviscosity Constants (f), and Molecular Volumes ($10^{-9}V_m$, pm³) for Lithium Phenolates (0.5 M) in Three Solvents at 30 °C

substituent	dioxolane				dimethoxyethane ^a				pyridine			
	T_1	η	f	V_m	T_1	η	f	V_m	T_1	η	f	V_m
H	0.61	0.7156	0.39	1.3	0.77	0.5347	0.36	1.4	0.26	1.0641	0.40	1.8
3,5-Me ₂	0.44	0.7293	0.41	1.6					0.27	1.0370	0.40	1.8
2,6-Me ₂	0.82	0.7784	0.36	0.9	1.27	0.5350	0.33	0.95 ^b	0.50	1.1157	0.35	1.1
2,6-Bu ^t ₂	0.57	0.7648	0.37	1.3 ^d					0.44	1.1134	0.37	1.2 ^c

^a 25 °C. ^b 0.6 M. ^c 0.25 M. ^d 0.2 M.Table III. ¹³C Chemical Shifts (δ , ppm, from Me₄Si) and $\Delta\delta$ ($\delta - \delta_{\text{anisole}}$) for Lithium Phenolates (0.5 M)

substituents	dioxolane			dimethoxyethane			pyridine		
	T (°C)	δ	$\Delta\delta$	T (°C)	δ	$\Delta\delta$	T (°C)	δ	$\Delta\delta$
H <i>o</i>	-40	119.8	+5.1	-60	120.2	+5.3			
<i>m</i>		130.2	0.0		129.6	-0.6			
<i>p</i>		115.3	-6.0		114.4	-6.0			
<i>o</i>	35	119.7	+5.0	35	120.2	+5.3	35	120.6	+5.9
<i>m</i>		130.1	-0.1		129.6	-0.6		130.2	-0.1
<i>p</i>		115.1	-6.2		114.4	-6.0		114.3	-6.7
3,5-Me ₂ <i>o</i>							-32	117.9	+5.3
<i>m</i>								138.7	-0.9
<i>p</i>								113.9	-9.2
<i>o</i>	35	117.7	+5.3				58	118.8	+6.2
<i>m</i>		139.1	-0.6					138.7	-0.9
<i>p</i>		117.0	-6.0					116.5	-6.6
2,6 Me ₂ <i>o</i>	-42	125.5	-6.0	-10 ^a	125.0	-6.2	2	126.1	-5.2
<i>m</i>		128.5	-1.0		128.2	-1.2		128.9	-0.7
<i>p</i>		112.4	-12.0		111.7	-12.6		111.9	-12.5
<i>o</i>	35	125.5	-6.0	25 ^a	124.9	-6.3	35	126.3	-5.0
<i>m</i>		128.6	-0.9		128.2	-1.2		128.9	-0.7
<i>p</i>		112.8	-11.6		111.7	-12.6		112.1	-12.3
2,6-Bu ^t ₂ <i>o</i>	-78 ^c	137.0	-7.3						
<i>m</i>		124.4	-2.9						
<i>p</i>		108.4	-15.3						
<i>o</i>	35	138.4	5.9				35 ^b	137.8	-6.3
<i>m</i>		125.2	-2.1					124.9	-2.5
<i>p</i>		113.4	-10.3					108.6	-15.4

^a 0.6 M. ^b 0.25 M. ^c 0.20 M.

aromatic C-H bond.¹⁴ Equation 1 is valid only for spherical molecules which are large compared with solvent molecules. For systems involving smaller solute molecules, but for which $\tau_c/\tau_{FR} > 5$ (τ_{FR} is the free rotor correlation time), it is suggested¹⁵ that the Geier-Wirtz equation

$$f^{-1} = 6r_0/r_s + (1 + r_0/r_s)^{-3} \quad (3)$$

(r_0 , r_s are the effective radii of the solvent and solute molecules, respectively) can be used to derive a microviscosity correction f which can be incorporated into the denominator of the right-hand side of eq 1, which can then be solved iteratively for r_s and hence V_m . The appropriate data and results are presented in Table II.

For the cubic tetramers **1** rotational diffusion is necessarily isotropic. Models show that the dimers **2** should also diffuse isotropically. The value of r_s for lithium phenolate in pyridine is 50 pm smaller than estimated for a sphere which would just contain the postulated structure. This probably is about as good as could be expected in view of the highly approximate nature of the Geier-Wirtz correction. The increase in the size of the attached solvent molecules in going from dioxolane to pyridine is reflected in the values of r_s . With the smaller solvent, dioxolane, there is also an increase in the volume in going from phenolate to 3,5-dimethylphenolate, but with the larger solvent pyridine this is not observed. The smaller volumes of the dimers are clearly demonstrated by their r_s . Indeed, it would appear that one can distinguish between tetramers and dimers on the basis of their relative molecular volumes determined in this way.

Interpretation of the data for lithium 2,6-di-*tert*-butylphenolate is more difficult. First, the size of the phenolate is substantially

different. The result for the species in dioxolane is further complicated by the fact that the solution contains a mixture of monomer and higher aggregates. The monomeric species, which prevails in pyridine solution, is not necessarily an isotropic rotor. The probable structure **4** is approximately an oblate spheroid. It is possible to correct r_s for the anisotropy of rotational diffusion of the oblate spheroid using the treatment outlined by Woessner.¹³ This reduces the value used in Table II to 620 pm for the sphere of equivalent volume which, however, is still substantially larger than 550 pm estimated for the enclosed volume of the oblate spheroid. It should be pointed out that the above treatment assumes the stick boundary condition and ignores inertial effects.¹⁵ Violation of either of these assumptions could lead to a larger measured molecular volume.

¹³C Chemical Shifts. Data for the ortho, meta, and para carbon atoms are presented in Table III. Since the introduction of alkyl substituents will influence the shielding of the aromatic carbons, even if they do not effect the degree of aggregation and/or solvation, it is convenient to compare the chemical shifts of the salts with those of the corresponding *O*-methyl ethers. $\Delta\delta = (\delta_{\text{salt}} - \delta_{\text{anisole}})$ should then more accurately reflect the effects of aggregation and solvation on the shielding of, and hence the charge densities at, the ring carbon atoms. Examination of $\Delta\delta$ for systems for which the degree of aggregation is clearly established by the barometric measurements reveals that for the para carbon atoms, in particular, this parameter is highly characteristic of the degree of aggregation, being approximately -6, -12, and -15 ppm for the tetramers, dimers, and monomers, respectively.

The results indicate that lithium phenolate and 3,5-dimethylphenolate are tetrameric in ether-type solvents even at low temperatures. The salts are also tetrameric in the more basic solvent pyridine at room temperature, but the 3,5-dimethyl derivative shows evidence of dimer formation at low temperature.

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Table IV. ${}^7\text{Li}$ and ${}^{13}\text{C}$ (Para) Spin-Lattice Relaxation Times (s) and Quadrupole Splitting Constants (kHz) for Lithium Phenolates (0.5 M) at 30 °C

substituents	dioxolane			dimethoxyethane			pyridine		
	$T_1({}^7\text{Li})$	$T_1({}^{13}\text{C})$	QSC	$T_1({}^7\text{Li})$	$T_1({}^{13}\text{C})$	QSC	$T_1({}^7\text{Li})$	$T_1({}^{13}\text{C})$	QSC
H	0.59	0.59	69	0.86	0.77	66	0.86	0.26	39
3,5-Me ₂	0.47	0.48	70				1.01	0.27	36
2,6-Me ₂	0.18	0.815	147	0.26	1.27	154 ^a	0.18	0.50	116
2,6-Bu ^t ₂	0.062	0.57	212 ^a				0.075	0.43	167 ^b

^a 0.6 M. ^b 0.25 M; a mixture of monomer and oligomer. ^c 0.2 M; a correction for anisotropic rotational diffusion (see text) gives 162 kHz.

The thermodynamic and kinetic parameters for this equilibrium are reported below.

Lithium 2,6-dimethylphenolate appears to be dimeric in all three solvents even at low temperatures, although poor solubility precluded measurements for pyridine solutions below 0 °C.

As expected from the barometric studies, lithium 2,6-di-*tert*-butylphenolate is monomeric in dioxolane at low temperatures and concentrations, but is evidently more highly aggregated at higher temperatures and concentrations. The chemical shifts do not, however, distinguish between the dimer and acyclic or macrocyclic oligomers. The spectrum of this salt in pyridine at room temperature provided chemical shift values for the monomeric species.

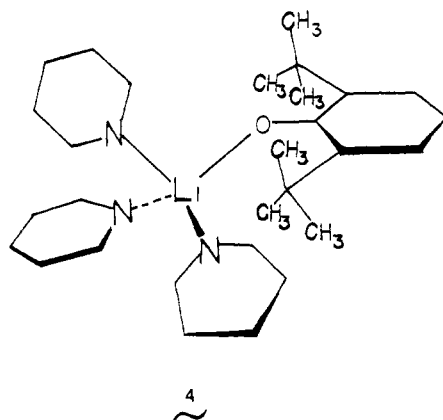
${}^7\text{Li}$ Quadrupole Splitting Constants (QSC). This parameter

$$\text{QSC} = (1 + \eta^2/3)^{1/2}(e^2Qq_{zz}/h) \quad (4)$$

(where $\eta = (q_{zz} - q_{xx})/q_{yy}$, and q_{ii} are elements of the electric field gradient tensor) is expected to vary considerably with the symmetry of the distribution of negative charges in the immediate vicinity of the lithium cation and should therefore be characteristic of the structure of the aggregate. QSC can be determined from ${}^7\text{Li}$ spin-lattice relaxation times using the equation

$$1/T_1({}^7\text{Li}) = (2\pi^2/5)(\text{QSC})^2\tau_c \quad (5)$$

The term τ_c in eq 5 is the isotropic correlation time in eq 3, so the evaluation of QSC also requires a knowledge of the spin-lattice relaxation time of the para carbon atom. Equation 5 is valid for the tetramers and dimers which are isotropic rotors. It is also valid for the monomers provided that the C(ipso)-O-Li angle is 180° since in this case the C-H bond vector and q_{zz} are colinear. The situation is more complex if this angle is, say, 109.5°, since now $r_{\text{C,H}}$ and q_{zz} subtend different angles (ca. 80 and 30°, respectively) to the short axis of the oblate spheroid which approximately describes the shape of the structure 4. The method



of Woessner¹³ can be used to correct the two relaxation times. These calculations indicate that the correction for anisotropy reduces QSC by only 3%. A more serious problem is that in the "bent" structure 4, q_{zz} and $r_{\text{C,H}}$ are reoriented by internal rotations about C-O and Li-O bonds, respectively. If the rates of these rotations are comparable to or faster than rotational diffusion, they could influence the calculated value of QSC. Since internal reorientation of the bulky trisolated lithium cation about the C-O bond is expected to be slower than the analogous reorientation of the di-*tert*-butylphenolate ion about the Li-O bond, the cal-

culated value of QSC will be too low.

The values of QSC and the relaxation times from which they were calculated are presented in Table IV. It can be assumed that the local gradients associated with the lone pairs of the negatively charged oxygen atoms of the phenolate ions will be significantly greater than those provided by the solvent donor atoms and will hence dominate q_{zz} . QSC would approach zero for a tetrahedral array of phenolate ions around lithium. As each ligand is successively replaced by the solvent, there will be an increase in q_{zz} , reaching a maximum when only one anion remains and falling to zero for the tetrahedrally solvated free cation. These trends are observed for each of the solvents studied (of course, solvent-separated ions are not found in these weakly polar solvents). In fact, the results in Table IV provide good evidence for the structures postulated for 1-3.

It is also predicted that as the donor properties of the solvent approach that of the anion, QSC will decrease for all three structures. This too is borne out by the results, since for pyridine, which has a Gutmann donor number (DN) of 33.1,¹⁶ the QSC's are considerably smaller than found for the ether solvents (DN ~ 20) for each type of aggregate.

Attempted Determination of Solvation Numbers. Solvation no doubt plays a crucial role in controlling the degree of aggregation, and an effective method of measuring the solvation number for cations in aggregates in pure solvents would be most useful. Since the degree of aggregation may vary with concentration and temperature (see below), it is not possible to determine limiting values of solvent properties in the bound state by extrapolative procedures. It is therefore necessary to select a property for which the value will change greatly in going from the free to the bound state and for which limiting values can be estimated. For the solvent pyridine, the dipole-dipole spin-lattice relaxation time (T_1^{DD}) of the γ carbon atom appeared to satisfy these requirements since estimates of the limiting values can be made which, because of the great disparity in the size of the solute and solvent molecules, differ by approximately two orders of magnitude.

The determination of T_1^{DD} requires measurements of relaxation times and nuclear Overhauser enhancements. The solvation number, N , is given by eq 6 which requires estimates of T_1^{DD} .

$$N = [1/T_1^{\text{DD}}(\text{obsd}) - 1/T_1^{\text{DD}}(\text{free})]/X_b[1/T_1^{\text{DD}}(\text{bound}) - 1/T_1^{\text{DD}}(\text{free})] \quad (6)$$

(bound) and $T_1^{\text{DD}}(\text{free})$. X_b is the mole fraction of bound solvent.

Consider, first, the pyridine solvated tetramer 1 (R = OPh). It is clear that the phenolate ion and the pyridine occupy essentially identical sites in the aggregates, and the T_1 s of the para and γ carbon atoms should therefore be equal since neither is affected by internal rotation and the aggregate should undergo isotropic rotation diffusion. Thus $1/T_1^{\text{DD}}(\text{bound})$ is set equal to $1/T_1(\text{para})$. $T_1^{\text{DD}}(\text{free})$ is assumed equal to the value for the solvent at the same temperature. The resulting value of N is 0.69 (Table V) instead of the expected 1.0. The propagated error in the calculation is 0.03 so the difference is significant. A similar result ($N = 0.85$) is found for lithium 3,5-dimethylphenolate. In the case of the dimeric 2,6-dimethyl system, 1.3 is found rather than 2.0, and for the monomeric lithium 2,6-di-*tert*-butylphenolate the value is 1.4 compared to 3.0, although it is conceivable that this latter salt is only disolvated. Thus, while the observed values of N exhibit

Table V. T_1 (s) and NOE Data for $\delta^{13}\text{C}$, and T_1 (s) for Para ^{13}C Used in Computation of the Solvation Numbers N by eq 6 for Lithium Phenolates (0.5 M) in Pyridine

substituents	T ($^{\circ}\text{C}$)	T_1^{obsd} (s)	NOE	T_1^{DD} (s)	T_1^{DD} (Para) (s)	N
H	30	7.2 ± 0.1	1.95 ± 0.02	7.3 ± 0.1	0.263 ± 0.009	0.69 ± 0.03
	50	8.6 ± 0.1	1.78 ± 0.03	9.6 ± 0.2	0.485 ± 0.016	0.85 ± 0.06
3,5-Me ₂	30	7.0 ± 0.3	1.90 ± 0.06	7.3 ± 0.2	0.27 ± 0.01	0.72 ± 0.04
	50	9.1 ± 0.3	1.84 ± 0.04	9.8 ± 0.4	0.40 ± 0.01	0.68 ± 0.05
2,6-Me ₂	30	7.3 ± 0.1	1.94 ± 0.05	7.5 ± 0.2	0.50 ± 0.01	1.30 ± 0.06
2,6-Bu ₂ ^a	30	9.1 ± 0.5	1.73 ± 0.06	10.4 ± 0.7	0.45 ± 0.01	1.43 ± 0.15
	50	10.1 ± 0.3	1.69 ± 0.10	11.8 ± 0.4	0.59 ± 0.03	1.47 ± 0.20
pyridine	30	23.6 ± 0.3	1.60 ± 0.4	29.2 ± 0.9		
	50	17.5 ± 0.2	1.27 ± 0.11	27.2 ± 2.3		

^a 0.25 M.

the expected trend for the systems studied, the absolute magnitudes are consistently low by 30–40%.

There are a number of assumptions embodied in eq 6 which must be examined. First is the value of T_1^{DD} (bound). The assumption that the γ carbon of pyridine in the aggregate has the same T_1 as the para carbon atom of the phenolate is subject to direct experimental verification. It proved possible to prepare a 1:1 solvate by exhaustively pumping down a pyridine solution of lithium phenolate and dissolving the residue in benzene- d_6 . Integration of its carbon spectrum established the phenolate–pyridine ratio as 1:1. The ^{13}C chemical shifts for the phenolate residue showed that the species was a tetramer. The concentration of the salt was sufficiently high to permit a crude T_1 experiment which indicated that the para and γ carbon atoms have the same relaxation times (0.32 s at 30 $^{\circ}\text{C}$).

The assumption regarding the value of T_1^{DD} (free) is not strictly valid since there is an approximately 20% increase in the viscosities of 0.5 M solutions of these salts over that of the pure solvent. However, rotational diffusion of the small solvent molecules is expected to conform to "slip" boundary conditions,¹⁴ and, as found for benzene,¹⁷ their correlation times should vary only slightly with viscosity. In any case, a viscosity correction would only lower the value of N .

Inherent in eq 6 is the assumption that exchange between free and bound solvent does not contribute to the relaxation time of the bound solvent molecule. In the regime in which the exchange and relaxation rates are comparable, both contribute to the observed relaxation time which is then given by the Swift–Connick equation¹⁸

$$1/T_1^{\text{DD}}(\text{obsd}) = (1-p)/T_1^{\text{DD}}(\text{free}) + p/[T_1^{\text{DD}}(\text{bound}) + \tau_{\text{ex}}] \quad (7)$$

in which p is the fraction of bound solvent molecules and τ_{ex} their lifetime. For the systems being considered, τ_{ex} would have to be of the order of 0.1 s to raise the solvation numbers to their expected values. In fact, we expect τ_{ex} to be orders of magnitude smaller. The rate constants for the complexation of Na^+ with dibenzo-18-crown-6 in several nonaqueous solvents including weakly polar ones such as dimethoxyethane are of the order of $10^8 \text{ s}^{-1} \text{ M}^{-1}$,¹⁹ and it is known that in aqueous solution the rates of complexation of Li^+ and Na^+ with a variety of polydentate ligands are very similar.²⁰ We conclude that the rate of exchange of simple solvent molecules is at least as fast as $10^8 \text{ s}^{-1} \text{ M}^{-1}$.

There remains another possibility, namely, that the solvent exchange rate is of the order of rotational diffusion rate of the aggregate. The value of τ_{c} for the tetramers is approximately 200 ps, and the above estimate of the rate of exchange suggests that the lifetime of a bound solvent is less than 10^4 ps and could well be in the range of 100–1000 ps. If this is the case, the effective correlation time for the bound solvent will be modified by the

Table VI. Ratios of T_1 (Ortho and/or Meta) to T_1 (Para) for the Protonated Carbon Atoms in Lithium Phenolates (0.5 M) at 27 $^{\circ}\text{C}$

substituent	dimethoxyethane		
	dioxolane	pyridine	
H	4.45	2.62	5.95
2,5-Me ₂	2.33		4.60
2,6-Me ₂	1.41	1.27 ^a	
2,6-Bu ₂	1.53		<i>b</i>

^a 0.6 M. ^b Signal of the meta carbon atom overlapped a solvent peak.

exchange process, and the assumption that the T_1 's for the γ and para carbons are equal is no longer valid. The former will be longer, resulting in a low value of N calculated by eq 6. A simple picture is one in which pyridine is attached to the aggregate for periods which are less than the mean time for reorientation through 2π radians of the aggregate (more correctly, times which are shorter than the time constant for decay of the rotational correlation function of the aggregate) and therefore does not fully experience its correlation time. Of course, this does not apply to the pyridine solvate in benzene where exchange is presumably nonexistent. The situation in which exchange and rotational diffusion occur with similar rates has been formally treated by several workers,^{21–23} and it has been shown that the actual correlation time (τ_{c}) must be replaced by an effective correlation time (τ_{eff}) given by the equation

$$\tau_{\text{eff}}^{-1} = \tau_{\text{c}}^{-1} + \tau_{\text{ex}}^{-1} \quad (8)$$

If lithium phenolate has one pyridine/ Li^+ and if only the primary solvation shell need be considered, τ_{ex} would need to be approximately $2.3\tau_{\text{c}} = 460$ ps in order to obtain the values we have calculated for N .

Internal Rotation of Phenolate Residues. The ratios of ortho (meta):para relaxation times for the protonated carbon atoms of the phenolate residues are recorded in Table VI. It is clear that for the tetramers the barriers to internal rotation, which these ratios reflect, are small. Even the large value observed for lithium phenolate in pyridine does not distinguish between diffusion-controlled internal rotation and a jump process²⁴ involving six equally populated conformations.

Two trends are of interest. First, it is clear that ortho substituents, in addition to producing dimers or monomers, significantly reduce the rate of internal rotation. Secondly, dimethoxyethane causes restricted internal rotation in the tetramer. Presumably, this solvent is attached through only one of its oxygen atoms, leaving the remainder of the chain free and in a situation in which it encumbers the phenolate residue.

Dynamic NMR of Lithium 3,5-Dimethylphenolate in Pyridine. As indicated in Table III, the chemical shift of the para carbon atom changes as the temperature of the solution is lowered from

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Table VII. Rate and Equilibrium Data for the Process 2 Dimer \rightleftharpoons Tetramer for Lithium 3,5-Dimethylphenolate (0.17 M) in Pyridine

T ($^{\circ}\text{C}$)	K (M^{-1})	$[\text{D}]$ (M)	$10^3 k_1$ ($\text{s}^{-1} \text{M}^{-1}$)	k_{-1}^a (s^{-1})
227	4.3	0.053	0.32	74
<i>b</i>	4.7	0.094		
248	17	0.042	1.13	67
263	39	0.029	3.8	98
299	201	0.014	31	150
313	344	0.0094	67	190

^a Calculated from K and k_1 . ^b 0.35 M.

60 to -32 $^{\circ}\text{C}$. This change accompanied by changes in line shape is indicative of the presence of two species undergoing exchange at a rate comparable with the NMR chemical shift time scale. Similar phenomena are observed in the ^7Li and ^1H spectra for this system. The latter spectrum, for example, shows two C-Me signals at low temperatures, and for a 0.17 M solution the temperature-dependent changes in signals are convenient for studying the exchange process by dynamic NMR line-shape analysis. It has been possible to simulate the observed spectra by treating the system as an unequally populated two-site exchange problem, in which both populations and rate of exchange are a function of temperature. The observed and computed spectra are shown in Figure 1.

The rate constants yield $\Delta H^{\ddagger} = 8.2 \pm 0.04$ kcal mol $^{-1}$ and $S^{\ddagger}_{298} = -10.4 \pm 0.3$ cal deg $^{-1}$ mol $^{-1}$ for the activation parameters for the conversion of the low- to the high-temperature species. On the basis of their ^{13}C chemical shifts and the barometric results, these two species are assigned the structures of the dimer and tetramer, respectively.

Assuming the equilibrium to be 2 dimer \rightleftharpoons tetramer and using the experimentally determined populations of the two species, equilibrium constants, K , were calculated for each temperature (see Table VII). The proposed equilibrium allows prediction of the relative populations of the two species according to the following expression

$$X_T = (2KM + 1 - \sqrt{4KM + 1}) / 2KM \quad (9)$$

where X_T is the mole fraction of tetramer and M is the total concentration of phenolate. It proved possible to determine populations at two concentrations at 227 K, and the results are consistent with the proposed equilibrium but, of course, do not exclude other equilibria of the type $2A_n \rightleftharpoons A_{2n}$. The k vs. T data give $\Delta H = 7.1 \pm 0.1$ kcal mol $^{-1}$ and $\Delta S = 33.9 \pm 0.5$ cal deg $^{-1}$ mol $^{-1}$. Formation of the tetramer is thus spontaneous above 210 K, and the activation parameters for the dissociation of the tetramer to the dimer are $\Delta H^{\ddagger} = 1.2 \pm 0.05$ kcal mol $^{-1}$ and $\Delta S^{\ddagger} = -44.5 \pm 0.5$ cal deg $^{-1}$ mol $^{-1}$.

Discussion

Methodology for Investigating Ion-Pair Aggregates. There is no doubt that colligative methods remain the best means of establishing the degree of aggregation of organic salts in solution in weakly polar solvents. A disadvantage of all such methods is the limited range of concentrations and temperatures over which they can be applied. In this respect vapor pressure barometry has an advantage over ebullioscopic and cryoscopic methods and is particularly well adapted for examining air- and moisture-sensitive compounds over quite a wide range of concentrations. Since it is most readily applicable at or below room temperature, it is somewhat complementary to ebullioscopy.

The use of ^{13}C spin-lattice relaxation times for determining molecular volumes and hence degrees of aggregation has some potential, particularly in cases in which colligative methods are inapplicable, for instance, in mixed solvent systems. There are, however, too many assumptions involved to allow absolute molecular volumes to be determined. The method is nevertheless useful for determining relative molecular volumes once T_1 vs. η data are available for one set of conditions (solvent, T , concentration, etc.) for which one degree of aggregation has been established. It may be applied over a wide temperature range

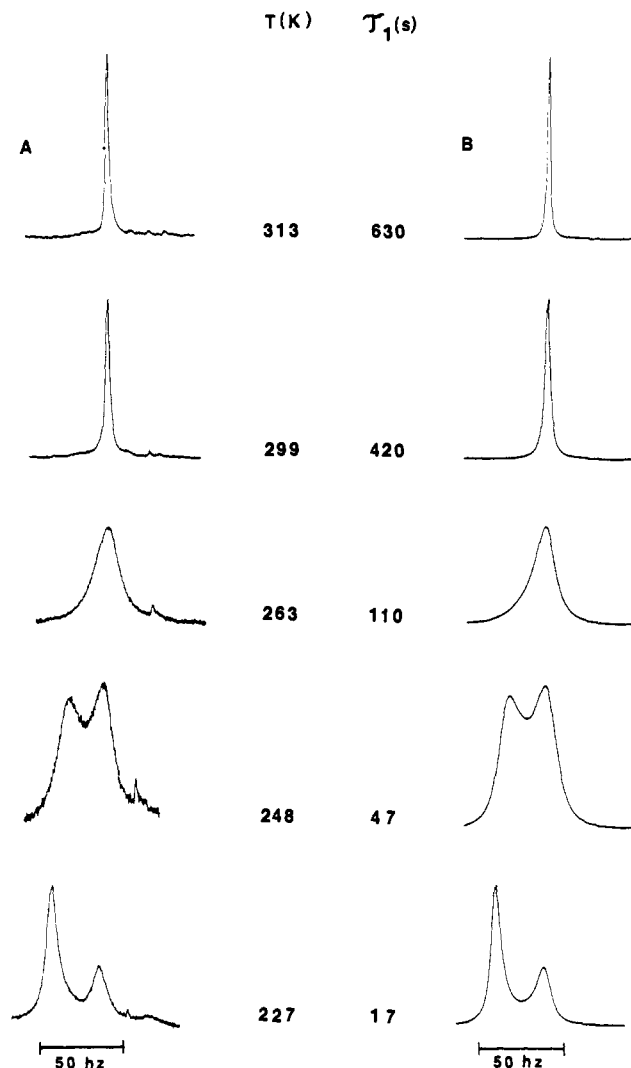


Figure 1. Experimental (A) and calculated (B) 200-MHz ^1H NMR spectra of the Ar-CH $_3$ region of 0.17 M lithium 3,5-dimethylphenolate in pyridine, as a function of temperature. The separation of the two peaks at low temperature is 27.8 Hz.

although the measurement of viscosities at low temperatures would require modification of the simple technique employed here. It must be emphasized how important it is that the relaxation time used be unaffected by internal rotation within the aggregate. From the data in Table VI, it is readily seen that large errors in relative molecular volumes of lithium phenolate in the three solvents would have been introduced if the relaxation times of the ortho (or meta) carbon atoms had been employed. Of course, this is an extreme case but the problem is nevertheless a real one. In addition, it is necessary to consider whether the aggregate may undergo anisotropic rotational diffusion and, if so, to apply an approximate correction using the method of Woessner.¹³

In the present context of the phenolate ions and the enolate ions studied earlier,^{2,7,25} ^{13}C chemical shift data have proved to be characteristic of the structures of aggregates, irrespective of the nature of the solvent, although the method is probably inherently incapable of distinguishing between various monocyclic aggregates (or sizable oligomers). In general, it may be anticipated that ^{13}C chemical shifts will be useful for studying the structures of aggregates involving anions which allow π delocalization of the negative charge. If the charge can be delocalized to a remote center, the qualitative effect on $\Delta\delta$ in the progression of structures 1-3 can be readily predicted. This is not necessarily true for less remote carbon atoms since proximity effects also come into play. Thus, in lithium phenolate, the ortho positions are deshielded (Table III) relative to anisole whereas the para position, as expected, is shielded.

The nuclear quadrupole splitting is also highly characteristic of the structures of the aggregates and also in a way which can be qualitatively predicted. Again, it is important that the relaxation time used for the determination of the rotational correlation time should not be influenced by internal rotations although QSC varies only as $\tau_c^{1/2}$. It is probable that the reason for the apparent QSC's for dimeric and especially tetrameric lithioisobutyrophenone being significantly larger (178 and 133 kHz, respectively, for ether-type solvents⁷) than their phenolate counterparts is due in part to the effect of internal rotation of the enolate ion about the C–O bond on the relaxation time of its para carbon atom.

Attempts to establish absolute solvation numbers from solvent ¹³C relaxation times have been unsuccessful. It appears that this is a consequence of solvent exchange occurring at a rate comparable with rotation diffusion. This situation is believed to exist for aqueous solutions of alkali metal cations^{21,22} but definitive data are not available for nonaqueous solutions. This method of determining solvation numbers is therefore at present not a useful one.

Factors Influencing the Degree of Aggregation. The series of phenolates investigated makes it clear that steric hindrance is one important factor in controlling the size of aggregates. As pointed out by Seebach, Amstutz, and Dunitz,⁵ there is a strong electrostatic driving force for the formation of a tetramer over less highly aggregated species. In the absence of ortho substituents such a structure readily accommodates the phenolate residues as is evident from the observation of comparatively free rotation of the aryl group about the C–O bond axis. The introduction of two ortho methyl groups dramatically changes this situation, and we find that the dimeric structure **2** is preferred. Models indicate that this is a consequence of reduced steric interactions between the methyl groups and solvent molecules on adjacent lithium cations in **2** as compared with **1**. The steric crowding is further exacerbated in the 2,6-di-*tert*-butyl derivative, and, although a dimer can still form, it appears to involve only monosolvation of lithium⁴ resulting in three-coordinate Li⁺. As a result, monomeric ion pairs are encountered in pyridine at room temperature and in dioxolane at low temperatures. Inspection of models for the monomeric structures **3** and **4** reveals that the Li⁺ can attain a coordination number of 4.

Electronic factors must also be important, particularly the ability of the conjugating system to reduce the negative charge density on oxygen. In this context, a comparison of the data for lithioisobutyrophenone⁷ with those of the phenolates is interesting.

The enolate moiety should have approximately the same steric requirements as the 2,6-dimethylphenolate and yet it is tetrameric in dioxolane. Even in dimethoxyethane, where the chelation effect favors the dimer, it forms a mixture of dimer and tetramer. Evidently, the negative charge is more strongly localized on oxygen in the enolate than in the phenolate ion so that the former requires greater stabilization through ion pairing and therefore shows a greater tendency toward tetramer formation. Further work is necessary to establish more precisely the role of electronic effects.

Dimer–Tetramer Equilibrium. Role of the Solvent. It is interesting that conversion of the tetramer to the dimer results in a decrease in entropy for the system lithium 3,5-dimethylphenolate in pyridine. This must be the result of loss of solvent translational freedom and is consistent with the solvation by one and two molecules of pyridine per lithium for the tetramer and dimer, respectively.

The tendency toward dimer formation is greater for pyridine than for dioxolane, reflecting the higher Gutmann DN value for the former. This effect presumably influences the dimer–tetramer equilibrium constant through the enthalpy term. We can extend this reasoning to the dimer–monomer equilibrium for 2,6-di-*tert*-butylphenolate, in which solvent-mediated breakdown of the aggregate is more favored enthalpically (occurs at higher temperature) in pyridine than in dioxolane.

The very large negative entropy of activation for the dissociation of the tetramer to the dimer indicates that the mechanism for the process involves a prior additional solvation of the tetramer rather than dissociation followed by further solvation of the product.

The requirement for prior solvation of Li⁺ in the breakdown of tetramer to dimer is reminiscent of the observation⁷ that the lithioisobutyrophenone tetramer in dioxolane is in equilibrium with a more highly solvated structure at low temperatures. Presumably at still lower temperatures, the increased solvation would result in a similar breakdown of that tetramer to two dimers. The fact that the dissociation in phenolates occurs in a higher temperature range is, again, suggestive of greater charge delocalization in these salts, compared with simple enolates.

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Registry No. Lithium phenolate, 555-24-8; lithium 3,5-dimethylphenolate, 83859-28-3; lithium 2,6-dimethylphenolate, 24560-29-0; lithium 2,6-di-*tert*-butylphenolate, 55894-67-2; pyridine, 110-86-1; dioxolane, 646-06-0; dimethoxyethane, 110-71-4.