Table V. Solution Structures of the Lithium Enamides **7** and **6**

anion (A)	structure	solvent (S)
6 (R = CH_3)	$ALiS_3$	$HMPT/Et_2O$; THF[a]
	$A_2Li_2S_2$	Et_2O
	$A_2Li_2S_4$	THF; $TMEDA/C_6H_6$
6 (R = *n*-Bu)	$ALiS_3$	THF
	$A_2Li_2S_4$	THF
6 (R = Pr^i)	$ALiS_3$	THF
	$A_2Li_2S_2$	Et_2O; Et_3N; THF[b]
	$A_2Li_2S_4$	THF[b]
6 (R = Bu^t)	$ALiS_2$	THF
	$ALiS_3$	THF
	$A_2Li_2S_2$	Et_2O
6 (R = $CH_3OCH_2CH_2$)	$A_2Li_2S_4$	THF
7 (R = H; *n* = 1)	$A_2Li_2S_2$	Et_2O; THF[a]
	$A_2Li_2S_4$	THF
7 (R = CH_3; *n* = 1)	$ALiS_3$	THF
	$A_2Li_2S_2$	THF[a]
	$A_2Li_2S_4$	THF
7 (R = H; *n* = 2)	$A_2Li_2S_2$	THF[a]
	$A_2Li_2S_4$	THF
7 (R = CH_3; *n* = 2)	$ALiS_3$	THF
	$A_2Li_2S_2$	THF[a]
	$A_2Li_2S_4$	THF

[a] Complete conversion to this species was not attained at the temperatures studied. [b] At certain temperatures, coexistence of $A_2Li_2S_2$, $A_2Li_2S_4$, $ALiS_3$, and, possibly, $ALiS_2$ is observed (see Figure 5).

istence. Indeed, it is conceivable that the limiting species to which we have assigned structure **4** could, in fact, be **5**. It is also not possible to say whether **10** is necessarily intermediate between **9** and **3**. It is possible that conditions exist in which lithium *N*-isopropylanilide in THF coexists as all five species, but **10** has really only been characterized in the case of the *tert*-butyl analogue. Table V summarizes the structures observed for the various systems investigated.

It is clear that, in the present series of compounds, steric factors play a dominant role in determining their degree of aggregation. This is well illustrated by the *N*-alkylanilide series in which the state of aggregation in THF at <−50 °C decreases from mainly dimer for methyl, through a mixture of monomer and dimer for *n*-butyl, to exclusively monomers for isopropyl and *tert*-butyl. A minimum degree of steric hindrance is evidently provided by pinning back the *N*-alkyl substituent by ring formation as in **7** (R = H, *n* = 1 or 2). The effect of "internal" solvation by an appropriate substituent, such as the 2-methoxyethyl group, is significant. The stabilization of a rather rigid dimer species of type **3** may well play an important role in effecting the high enantioselectivities of reagents such as **1** and **2**.

The role of the solvent is also striking in that the entire series of salts studied here exist exclusively as the dimers **4** (S = Et_2O) in diethyl ether even at temperatures as low as −120 °C. In contrast, for example, lithium indolide in THF is not completely converted from **3** to **4** even at 80 °C. The donicity of diethyl ether, as measured by its heat of complexation with boron trifluoride in methylene chloride,[49] is somewhat less than that of THF ($\Delta H°_{BF_3}$ = −78.77 and −85.36 kJ·mol^{-1}, respectively). Steric factors must, however, play an important role in the effectiveness of the solvent in solvating the dimer since lithium *N*-isopropylanilide in the much more highly donating solvent, triethylamine ($\Delta H°_{BF_3}$ = −135.9 kJ·mol^{-1}), exists only as the dimer **4**.

We have shown that the ^{13}C chemical shifts of "para" carbons are remarkably constant for the different amine structures studied here, provided the degrees of aggregation are the same. A change to lower aggregation is associated with an upfield shift of 4–5 ppm, whereas a decrease in solvation results in a 1–2 ppm shift in the opposite direction. Virtually no change is observed between *E* and *Z* isomeric dimers. The chemical shifts of carbon atoms close to the nitrogen atom are influenced by proximity effects. This is particularly noticeable in the *N*-alkylanilides in which the shifts of the two ortho carbon atoms differ by as much as 12 ppm when the rotation of the phenyl group is slow on the NMR time scale.

The observations of multiplicities due to $^6Li,^{15}N$ one-bond spin coupling are seen to provide important structural information even though the interpretation of the magnitudes of ^1Js is not obvious.

Finally, the systems studied here exhibit a rich variety of dynamic processes which are accessible on the NMR time scale, and which include amine–amide exchange, phenyl ring rotation, interaggregate exchange, and stereomutation in dimers. It is expected that kinetic studies of these processes will throw additional light on the electronic structures and reactivities of the various types of ion pairs and their aggregates.

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Lithium Quadrupole Coupling Constants and the Structures of Organic Lithium Compounds in Solution

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Abstract: The quadrupole splitting constants (QSC), defined as $(1 + \eta^2/3)^{1/2}(e^2Qq_{zz}/h)$, for ^7Li in lithium arylamides, phenolates, and enolates and for several organolithium compounds in ether and tertiary amine solvents are determined from ^7Li and ^{13}C spin–lattice relaxation data. The effect of anisotropic rotational diffusion on the apparent values of QSC is considered. Values of QSC range from 40 to 350 kHz. Empirical correlations between QSC and the degree of aggregation and solvation of lithium are presented. Large differences between QSC for tri- and tetracoordinated lithium are noted. A crude model based on a point charge approximation for calculating the principal field gradients reproduces the qualitative features of the empirical correlations. The degrees of solvation of aggregated lithium salts are discussed.

In the preceding paper,[1] we presented evidence that lithium arylamides exist as either, or both, monomeric and dimeric contact ion pairs in solvents such as tetrahydrofuran (THF) and diethyl ether. In addition, evidence based on the temperature and concentration dependencies of ^{13}C chemical shifts suggests that the degree of solvation of these species can change with temperature, the less highly solvated species presumably being preferred at high temperatures. We had also reported similar temperature effects for tetrameric lithium isobutyrophenone in THF and dioxolane.[2]

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Table I. Spin-Lattice Relaxation Data and Quadrupole Splitting Constants for Lithium Indolide

nucleus	$D_z f(\Omega,\mathbf{D})$					
	E^a	Z^b	av^c	T_1(calcd)^d (s)	T_1(obsd) (s)	QSC (kHz)
			0.33 M in Diethyl Ether at 30 °C			
C(4)	0.233	0.213	0.223	2.97	3.06 ± 0.02	322
C(5)	0.244	0.209	0.226	2.93	2.89 ± 0.02	315
C(6)	0.208	0.195	0.202	3.28	3.16 ± 0.03	311
C(7)	0.233	0.213	0.223	2.97	3.03 ± 0.03	320
^{7}Li	0.233	0.219	0.226		0.143 ± 0.001	317 ± 6^e
			0.73 M in THF at -80 °C			
C(4)	0.164	0.168	0.166	0.181	0.198 ± 0.010	157
C(5)	0.163	0.155	0.159	0.190	0.178 ± 0.002	147
C(6)	0.180	0.159	0.169	0.178	0.163 ± 0.003	145
C(7)	0.164	0.168	0.166	0.181	0.189 ± 0.006	155
^{7}Li	0.164	0.155	0.160		0.040 ± 0.001	151 ± 6^e

[a] D_x/D_z = 0.71 and 1.2, and D_y/D_z = 0.61 and 0.84 for the species in Et_2O and THF, respectively. [b] D_x/D_z = 0.81 and 1.20, and D_y/D_z = 0.71 and 0.95 for the species in Et_2O and THF, respectively. [c] Based on the assumption that the *E* and *Z* isomers are equally populated. [d] An average value of D_z is calculated from the four observed T_1 values, using eq 2. T_1(calcd) values are then obtained from $\langle D_z \rangle$ and the anisotropy corrections, $D_z f(\Omega,D)$. [e] The average of the four results.

For this system, the existence of the less highly solvated tetramer at high temperature followed from a consideration of the sign of a large (120–160 $J\cdot mol^{-1}\cdot K^{-1}$) entropy change for the equilibrium between the two solvates. This approach is rather indirect and does not yield absolute values for degrees of solvation. The development of alternative methods is, therefore, clearly desirable. In general, the rates of exchange of bound and bulk solvent molecules are too rapid on the NMR time scale to permit the direct observation of two or more coexisting solvates of the same aggregate. Only one example where this apparently is not the case has been reported.[3] Another approach, based on measurements of solute and solvent ^{13}C spin–lattice relaxation time (T_1), has been proposed but has been shown to be of very limited use.[4] In this paper, we will show that the ^7Li nuclear quadrupole coupling constant (Li QCC), is a parameter which is strongly dependent on the state of aggregation and also on *the degree of solvation* of the aggregate. As such, it is well suited to characterizing the structures of lithium salts in weakly polar, aprotic solvents.

^7Li QCC values have been reported for a number of inorganic[5] and carboxylic acid[6] salts, lithium alkyls,[7] and Li_nNH_{3-n}[8] from solid-state NMR measurements. Values are also known for Li_2,[9] LiH,[10] and lithium halides[9] in the gas phase. The values range from about 30 kHz for Li in some near-tetrahedral environments to 408 kHz for gaseous LiF. We have previously reported measurements of ^7Li QCC for lithioisobutyrophenone[2] and several lithium phenolates[4] in solution in weakly polar aprotic solvents, and we will assess these data, together with data for new systems, in terms of the effects of both aggregation and solvation.

^7Li QCC's for compounds in solution are obtained from ^7Li spin–lattice relaxation time which are completely dominated by the quadrupole mechanism. Effective rotational correlation times for the aggregates are required and must be determined from the T_1's of appropriately situated, proton-bearing carbon atoms. Since it will not usually be possible to define both the rotational diffusion and field gradient tensors, some assumptions will be necessary, and these must be critically analyzed for each system studied. Indeed, there are many systems for which measurements of ^7Li QCC by this method are not feasible.[11]

Experimental Section

Sample Preparation. Vacuum line techniques for the preparation of samples have been described elsewhere.[1,2,4] The amide samples were amine free.[1] The lithium enolate of α-tetralone was prepared from the corresponding *O*-trimethylsilyl ether[13] using a previously described method.[2] Phenylethynyllithium, 2-(*N*,*N*-dimethylaminomethyl)-5-methylphenyllithium,[14] and 2,6-dimethoxyphenyllithium were prepared by direct metalation of phenylacetylene, 4-(*N*,*N*-dimethylaminomethyl)toluene, and *m*-dimethoxybenzene, respectively, using less than 1 equiv of *n*-butyllithium followed by removal of the excess precursor by pumping at room temperature as in previously described experiments.[2]

NMR Spectroscopy. All experiments were carried out using a JEOL PS-100-FT spectrometer or, for very short (<0.05 s) relaxation times, a Bruker WM360 spectrometer. In the latter case, both ^7Li and ^{13}C relaxation times were carried out using a 10-mm broad band probe. Proton decoupling was accomplished using the Waltz sequence,[15] and the decoupler was kept on during ^7Li observation to avoid possible changes in temperature. The two sets of relaxation times were obtained without altering any instrumental settings, except the carrier frequency. The absolute temperatures were not determined, but the nominal values are known to be within ±2° of the true value. The relaxation times were calculated using either two- or three-parameter nonlinear least-squares programs. In most cases, at least three separate determinations of each relaxation time were made. The assignments of ^{13}C spectra were generally facilitated by semiselective proton irradiation experiments. The assignments of the proton spectra were usually straightforward.

Results

Determination of ^{7}Li QCC. In absence of symmetry, the spin–lattice relaxation time ($T_1{}^q$) of a quadrupolar nucleus, due to the quadrupole mechanism, will be a function of the quadrupole coupling constant (e^2Qq_{zz}/h) and its asymmetry parameter, $\eta = (q_{xx} - q_{yy})/q_{zz}$, where Q is the nuclear quadrupole moment and the q_{ii}'s are the diagonal elements of the field gradient tensor in its principal axis system. $T_1{}^q$ also depends on the three principal rotational diffusion constants for the molecule.[16] The same diffusion constants also enter the equation for dipole–dipole relaxation times ($T_1{}^{dd}$) for the proton-bearing carbon nuclei.[17] Thus, if assumptions can be made regarding the directions of the principal systems of axes of the field gradient and rotational diffusion tensors and for the magnitude of η, the value (e^2Qq_{zz}/h)

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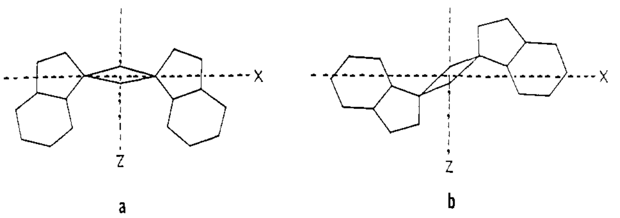
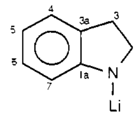


Figure 1. Definition of axes for the lithium indolide dimer, $Li_2A_2S_2$: (a) Z isomer, (b) E isomer.

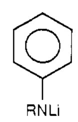
can, in principle, be determined from T_1^q and a sufficient number of spin–lattice relaxation times for proton-bearing ^{13}C nuclei having nonparallel ^{13}C–H internuclear vectors. For the ^7Li systems under investigation here, this procedure is not feasible. Several assumptions will, therefore, be necessary. The first is that rotational diffusion is effectively isotropic or that some simple model can be used to assess possible errors associated with that assumption. Secondly, it must be assumed that the $T_1^{dd}(^{13}C)$ used for determining an isotropic correlation time is unaffected by internal rotation about one or more single bonds. Finally, as we will not be able to evaluate ^7Li QCC and η separately, we must assume that $(1 + \eta^2/3)^{1/2}(e^2Qq_{zz}/h)$ is characteristic of the ^7Li environment. In the case of isotropic rotational diffusion, we have[2]

$$(1 + \eta^2/3)^{1/2}(e^2Qq_{zz}/h) = 7.0(T_1^{dd}/T_1^{q})^{1/2} \times 10^4 \text{ (Hz)} \qquad (1)$$

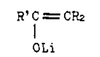
We shall refer to the left-hand side of this expression as the quadrupole splitting constant (QSC).



1

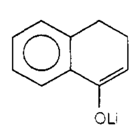


2 a,R = CH_3
b,R = Pr^i
c,R = Bu^t



$$\underset{\displaystyle OLi}{R'C}{=}CH_2$$

3 a, R = CH_3; R' = Ph
b, R = R' = H



4

Lithium Arylamides. We begin with an analysis of the data for lithium indolide, **1**, in diethyl ether which has been shown[1] to be the species $Li_2A_2S_2$ (A = anion; S = solvent). The ^{13}C relaxation times for the four unsubstituted, aromatic carbon atoms (Table I) indicate that the motions of the corresponding C,H internuclear vectors are only slightly different. It, therefore, appears that internal rotation about the N,N axis (x axis in Figure 1a) is slow compared with rotational diffusion, a conclusion which is consistent with the direct NMR observation of coexisting E and Z isomers at −110 °C. All four CH internuclear vectors, r_{CH}, lie in the same (xy) plane (Figure 1). It is expected on the basis of a simple point charge model (see below) that, for a trigonal distribution of charge about the lithium, q_{zz} will be perpendicular to the plane containing the charges (ligands) so that it too will be in the xz plane. The dipole–dipole and quadrupolar relaxation rates are controlled by the $f(\Omega,\mathbf{D})$ of the diffusion constants, $\mathbf{D}$, and the direction cosines, Ω, for the r_{CH}'s and q_{zz}, respectively. For an uncoupled, asymmetric rotor for which the principal diffusion axes are known, this function is given by[16,17]

$$f(\Omega,\mathbf{D}) = \frac{1}{3D_z}\left\{\frac{\cos^2\theta}{(D_x/D_z + D_y/D_z)} + \left[\frac{\cos^2\phi}{(1 + D_y/D_z)} + \frac{\sin^2\phi}{(1 + D_x/D_z)}\right]\sin^2\theta\right\} \qquad (2)$$

where θ and ϕ are the angles which $\mathbf{r}_{CH}$ or q_{zz} subtend with the z and x axes, respectively, and QSC is then given by

$$QSC = 7.00[T_1^{dd}f(\Omega^q,\mathbf{D})/T_1^{q}f(\Omega^{dd},\mathbf{D})]^{1/2} \times 10^4 \qquad (3)$$

Table II. Spin–Lattice Relaxation Data and Quadrupole Splitting Constants for Lithium N-Alkylanilides in Diethyl Ether at 30 °C

N-alkyl		concn, M	$T_1(C^p)$, (s)	$T_1(^7Li)$, (s)	QCC (kHz)
CH_3	**2a**	0.54	3.03 ± 0.04	0.151 ± 0.001	314
i-Pr	**2b**	0.28	2.87 ± 0.03	0.143 ± 0.001	314
t-Bu	**2c**	0.56	2.31 ± 0.08	0.116 ± 0.001	312
a	**1**	0.33	2.89 ± 0.02^b	0.143 ± 0.001	315

^{a}Lithium indolide. ^{b}C(5).

There are several models which have been developed to account for the anisotropy of rotational diffusion. The J-diffusion model[18] predicts an inverse relation ($D_i/D_j = I_j/I_i$) between the diffusion constants and the moments of inertia, and that the principal axis systems for the two sets of constants are coincident. Computation of the moments of inertia for reasonable molecular models for both the E and Z $Li_2A_2S_2$ dimers of lithium indolide etherate yields estimates of D_x/D_z and D_y/D_z. The four ^{13}C relaxation times then give values for QSC in the range 284–372 kHz. This model, however, fails to predict the *order* of the relative magnitudes of the ^{13}C relaxation times. The J-diffusion model has also been found to overestimate the effect of anisotropy.[19]

A second approach is based on the hydrodynamic model for Brownian motion of Perrin[20] which, however, has only been developed for symmetric rotors. It is, therefore, necessary to assume $D_x = D_y$, which appears to be a good approximation for the Z isomer but less good for the E isomer. The estimates of $D_\perp/D_\parallel$ are then derived from the dimensions of the axes of the assumed spheroid which in the present case is oblate. In this model, the Z isomer has the same principal axis system as the moments of inertia, whereas that for the E isomer is rotated by approximately 35° about the y axis (Figure 1b). Equation 2, or those derived by Woessner,[17] are then used to estimate the effect of anisotropy. The range for QSC is now 306–328 kHz, but this model also predicts the wrong order for the ^{13}C relaxation times.

A third model, proposed by Grant et al.,[21] requires the diffusion constants to be inversely related to the dimensional ellipticities, ϵ_i, about the principal diffusion axes. The ellipticities are crudely defined as the ratios (>1) of the maximum separation of atoms along the two axes prependicular to the rotation axis. This model is consistent with the naive picture of anisotropy of rotational diffusion being related to the numbers of solvent molecules displaced by rotation about each of principal diffusion axes. It would appear to be a reasonable model for diffusion of a relatively large solute molecule in a solvent consisting of small molecules. In the present case, the diffusion axes are the same as for the Perrin model discussed above. ϵ_x, ϵ_y, and ϵ_z are then computed to be 1.64, 1.93, and 1.17, respectively, for the E isomer, and 1.41, 1.61, and 1.14, respectively, for the Z isomer. The model is too crude to provide a functional relationship between ϵ_i and D_i. Nevertheless, direct proportionality between D_i and $1/\epsilon_i$ accounts reasonably well for the relative magnitudes of the four carbon relaxation times if it is further assumed that the E and Z isomers are equally populated. The appropriate data are presented in Table I, together with the values of QSC, computed using eq 3, corresponding to the four carbon relaxation times. The averaged value of QSC is to 317 ± 6 kHz, which is not significantly different from the averaged value of 322 kHz obtained if anisotropy is ignored.

Data have also been obtained for lithium N-methyl-, N-isopropyl-, and N-*tert*-butylanilides in ether (Table II). In these systems, only the para carbon relaxation times can be used for estimating QSC, and the results are, therefore, compared with that derived for lithium indolide using the relaxation time of C(5). All of these species are believed to be $Li_2A_2S_2$, and the agreement for their QSC values is excellent. We, therefore, conclude that corrections for anisotropy are again negligible.

Lithium indolide in THF at −80 °C has been shown to exist as the tetrasolvated dimer, $Li_2A_2S_4$. For this system, q_{zz} is expected

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Table III. Spin-Lattice Relaxation Data and Quadrupole Splitting Constants for Lithium *N*-Alkylanilides in THF

N-alkyl		concn (M)	temp (°C)	T_1 (s) $^{13}C(4)$	T_1 (s) ^7Li	QSC (kHz)
CH_3	**2a**	0.19	26	1.34 ± 0.02	0.188 ± 0.005	187
i-Pr	**2b**	0.11	30	1.66 ± 0.01	0.116 ± 0.001	265
			60	2.41 ± 0.01	0.148 ± 0.001	282
		0.44	−80	0.218 ± 0.004	0.024 ± 0.001	211
			−60	0.226 ± 0.014	0.025 ± 0.001	210
			−40	0.470 ± 0.032	0.052 ± 0.001	210
			30	2.02 ± 0.04	0.133 ± 0.001	273
		0.89	30	1.34 ± 0.02	0.086 ± 0.001	276
			60	1.95 ± 0.07	0.103 ± 0.003	305
t-Bu	**2c**	0.31	−80	0.211 ± 0.020	0.023 ± 0.001	212
			−60	0.306 ± 0.030	0.030 ± 0.001	224
			30	1.76 ± 0.02	0.096 ± 0.001	300
			60	2.51 ± 0.09	0.094 ± 0.001	351[a]

[a] Corrected for anistropy.

(see below) to be coincident with the axis through the two lithium atoms. The anisotropy correction for both the *E* and *Z* isomers is small and the range of values of QSC (151 ± 5 kHz, Table I) is comparable with the propagated errors in the T_1 measurements. At higher temperatures, the tetrasolvate begins to desolvate. This results in changes in the relaxation times of C(4), C(5), and C(7) relative to C(6) from 1.21, 1.09, and 1.16 at −80 °C to 0.99, 0.87, and 0.97, respectively, at +60 °C, the high-temperature values being similar in relative magnitude to those (0.97, 0.91, 0.96) observed for the $Li_2A_2S_2$ species in diethyl ether.

Several lithium arylamides form monomeric species, $LiAS_n$. Consideration of reasonable models for both di- and trisolvates indicate that they are approximately oblate spheroids in shape with the aromatic CH internuclear vectors and the Li-N bond lying in the equatorial plane. For the $LiAS_3$ species, q_{zz} is expected to coincide with the Li-N bond, and the anisotropy correction will be negligible. In the case of the disolvate, the field gradient will be perpendicular to the equatorial plane.

Lithium *N*-isopropylanilide, **2b**, has been shown to exist as $LiAS_3$ in THF at −80 °C but is believed to convert to $Li_2A_2S_4$ and then to $Li_2A_2S_2$ as the temperature is raised. QSC data for various concentrations and temperatures are presented in Table III. Similar data are included for lithium *tert*-butylanilide, **2c**. At −80 °C, this salt is also $LiAS_3$ but it will be argued below that it is partially converted to $LiAS_2$ above room temperature. Since in the latter species q_{zz} is perpendicular to the equatorial plane of the oblate spheroid, a correction for anisotropy is needed. The ellipticity model predicts a true value of QSC which is about 10 kHz smaller than the apparent value.

Lithium Phenolates. We have previously reported QSC data for some lithium phenolates. In all cases the relaxation time of the para carbon atom, which is unaffected by internal rotation, is used to determine the correlation time. The tetrameric species will diffuse isotropically. The dimers are presumed to be $Li_2A_2S_4$ species which closely approximate oblate spheroids with $\mathbf{r}_{CH}$(para) and q_{zz} in the equatorial plane,[22] and although no X-ray structural data are available, it is reasonable to suppose that in monomers q_{zz} and $\mathbf{r}_{CH}$(para) are colinear. We have extended our earlier studies to include variable-temperature measurements (Table IV).

Table IV. Spin-Lattice Relaxation Data and Quadrupole Splitting Constants for Lithium Phenolates in Pyridine and Dioxolane

	pyridine					
	phenolate (0.5 M)			2,6-dimethylphenolate (0.2 M)		
temp (°C)	$T_1(C^p)$ (s)	$T_1(^7Li)$ (s)	QSC (kHz)	$T_1(C^p)$ (s)	$T_1(^7Li)$ (s)	QSC (kHz)
110	1.26	2.41	51	2.34	0.34	184
90	0.98	2.91	41	1.89	0.33	168
70	0.69	2.32	38	1.16	0.30	138
50	0.53	1.70	39	1.00	0.28	132
30	0.26	0.86	41	0.69	0.22	124[a]
	dioxolane					
	phenolate (0.5 M)			3,5-dimethylphenolate (0.5 M)		
	$T_1(C^p)$ (s)	$T_1(^7Li)$ (s)	QSC (kHz)	$T_1(C^p)$ (s)	$T_1(^7Li)$ (s)	QSC (kHz)
70	1.02	1.18	65	0.90	1.08	64
30	0.58	0.67	65	0.49	0.55	66
8	0.43	0.44	69	0.35	0.30	76
−8	0.30	0.22	82			
−24[b]	0.17	0.11	87			

[a] A value of 117 kHz was found for a 0.5 M solution (ref 4). [b] Some crystallization occurred below −10 °C.

Table V. Spin-Lattice Relaxation Data and QSC for Lithio-α-tetralone (0.4 M), 4, in THF

temp (°C)	T_1 (s) C(5)	C(6)[a]	C(7)[a]	C(8)	^7Li	QSC (kHz)
−50	b	b	0.10	0.10	0.07	84
−30	b	b	0.18	0.17	0.12	83
−10	0.28	0.29	0.27	0.25	0.24	71
10	0.38	0.43	0.41	0.40	0.50	63
30	0.58	0.64	0.62	0.57	0.68	64
50	0.73	0.86	0.79	0.68	0.80	65

[a] The assignments of C(6) and C(7) may be reversed. [b] The C(5) and C(6) resonances are incompletely resolved at this temperature.

Table VI. Spin-Lattice Relaxation Data for Lithioisobutyrophenone (0.5 M), 3a, in Dioxolane and THF

temp (°C)	T_1 (s) C^p	T_1 (s) ^7Li	QSC (kHz)
	Dioxolane		
−45.0	0.089 ± 0.001	0.046 ± 0.001	97
−30.5	0.128 ± 0.002	0.066 ± 0.001	97
−24.5	0.146 ± 0.001	0.070 ± 0.002	101
−17.0	0.183 ± 0.005	0.074 ± 0.001	110
4.0	0.317 ± 0.001	0.114 ± 0.001	117
20.0	0.450 ± 0.007	0.132 ± 0.002	129
30.0	0.526 ± 0.005	0.150 ± 0.001	131
40.0	0.606 ± 0.008	0.167 ± 0.001	133
46.0	0.664 ± 0.012	0.177 ± 0.001	136
	THF		
−80.0	0.062 ± 0.003	0.050 ± 0.001	78
−60.0	0.087 ± 0.003	0.044 ± 0.003	98
−40.0	0.172 ± 0.003	0.063 ± 0.003	116
40.0[a]	0.68	0.20	136

[a] Reference 2.

Lithium Enolates. Measurements of QSC for lithioisobutyrophenone, **3a**, as a tetramer and as a dimer–tetramer mixture have been reported previously.[2] Although the tetramer is expected to diffuse isotropically, the reorientation of $\mathbf{r}_{CH}$(para), which must be used to define the correlation time, may be affected by internal rotation about the C–O bond. Indeed, Wen Jeng Quan and Grutzner[23] have shown that the vinyl groups in tetrameric lithioacetaldehyde, **3b**, rotate about eight times faster than overall rotational diffusion at 1 °C. Furthermore, they find a value of QSC of 65 kHz which is substantially less than the value (135 kHz) we have reported for lithioisobutyrophenone in the same solvent (THF). In order to probe this problem further, we have now examined lithio-α-tetralone, **4**, in which the aromatic ring is locked, although the group as a whole can still rotate about the C–O bond. Relaxtion data for this system are presented in Table V. There is some evidence for fast rotation about the C–O bond at 50 °C, but the effect becomes negligible at the lower temperatures. We have also determined QSC for lithioisobutyrophenone in both dioxolane and THF as a function of temperature; these results are presented in Table VI. These values closely correlate with the proton chemical shift data which were originally used as evidence for desolvation.[2] Since there is very little change

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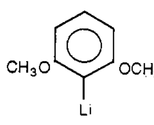
Table VII. Spin-Lattice Relaxation Data and QSC's for Some Organolithium Compounds

compound	solvent	concn (M)	temp (°C)	T_1 (s) C(4)	T_1 (s) ^{7}Li	QSC (kHz)
phenyllithium	THF-d_8	1.1	26	1.13	0.21	162
	Et_2O	6.0	26	0.46	0.08	168
	Et_2O	0.2	26	2.42	0.19	250
5	benzene-d_6	1.0	26	0.77	0.56	82
6	benzene-d_6	1.0	26	0.63	0.23	116
PhC≡CLi	THF	1.0	26	0.86	0.56	87
			−40	0.21	0.09	107

in the apparent values of QSC in the range 20–46 °C and since rotation of the enolate residue is likely to be more hindered than for the α-tetralone enolate residue, we regard these values as characteristic of the limiting species present at high temperatures.

Organolithium Compounds. We have determined the QSC values for phenyllithium under several sets of conditions in which it is either a tetramer or dimer ($Li_2A_2S_4$). The former species is isotropic and the latter an oblate spheroid with q_{zz} and $\mathbf{r}_{CH}$(para) in the equatorial plane, so that in neither case is an anisotropy correction needed. Also included in this series are the aryllithium derivatives **5** and **6**, both of which have been examined in benzene solution. The former has been shown by T_1 mapping and ^{13}C chemical shift studies to be tetrameric.[24] The second derivative **6** has been established by van Koten and his collaborators[14] to be a distorted cubic tetramer in the solid state and also to be tetrameric in both benzene and diethyl ether solution. The assumption of isotropic rotational diffusion appears valid, particularly in view of the fact that all three protonated carbon atoms have essentially the same T_1.



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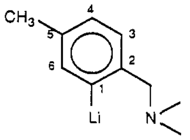

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Finally, we have examined lithium phenylacetylide in THF. This appears to be mainly a tetramer at room temperature, but at −40 °C small concentrations of what appears to be a dimer are formed. Exchange of this species with the tetramer occurs slowly on the ^{13}C chemical shift time scale at and below this temperature. The dimer is not expected to approximate well to an oblate spheroid, and the assumption of isotropy would probably result in an underestimate of QSC. Data for these compounds are contained in Table VII.

Discussion

Although some uncertainties exist regarding the influence of anisotropic rotational diffusion on the estimates of Li QSC's, the maximum errors introduced from this source are quite small. This is partly a consequence of the square root dependence of QSC on $T_1(^{13}C)/T_1(^7Li)$ and partly because the molecules under investigation are reasonably globular in shape. We point out, however, that failure to recognize the possible influence of *internal* rotation could lead to serious errors. Thus, using the ortho or meta ^{13}C relaxation times of lithium phenolate in pyridine[4] would have resulted in a 250% error in QSC! This means that the present technique is not universally applicable and, for example, could not be used for determining QSC's for para-substituted lithium phenolates or for many alkyllithium compounds.

We will first show that QSC can be used as an empirical parameter to distinguish between monomers, dimers, and tetramers and their various solvates. We will then show that the values of QSC are in qualitative agreement with predictions based on simple point charge models. Finally, we will comment on the effects of solvent donicity on QSC.

Tetramers. Lithium phenolate and its 3,5-dimethyl homologue are characterized by small (<100 kHz) values of QSC (Table IV). It has been estalbished[4] that in pyridine, at least, the species is the solvated tetramer $Li_4A_4S_4$, the first coordination sphere of each lithium cation consisting of three anions and one solvent molecule. A similar arrangement is found[25] in crystalline lithium formate monohydrate for which QSC is approximately 70 kHz.[6a] In THF, both lithio-α-tetralone (Table V) and lithioacetaldehyde[23] have values (64 and 65 kHz at 30 °C) which fall in this range. The value for lithioisobutyrophenone, however, is substantially higher (136 kHz at 40 °C). This salt is known to be substantially desolvated in dioxolane at room temperature,[2] but the value decreases as the temperature is lowered (Table VI) reaching a value of 97 kHz at −45 °C at which temperature it is more highly solvated. In contrast, QSC for lithium phenolate and lithio-α-tetralone exhibit a small increase as the temperature of their ether solutions is lowered (Tables IV and V). The origin of this latter effect is not known. These species, however, are generally distorted cubic structures, and it is possible that at lower temperatures vibrational interconversion of the distorted topomers may become comparable in rate to rotational diffusion which could lead to a decrease in the ^{7}Li relaxation time[26] and an increase in the apparent value of QSC.

The quadrupole coupling constants for ^{7}Li in crystalline methyllithium fall in the same range (48 kHz; $\eta = 0$).[7b] Although not solvated, the fourth coordination site is occupied by sharing of a carbon atom from a neighboring $[LiCH_3]_4$ cluster.[27] Ethyllithium, which consists of distorted $[LiEt]_4$ units,[28] has a larger value (83 kHz; $\eta = 0.79$).[7b] The value of QSC for lithium phenylacetylide in THF (Table VII) indicates that it too is a solvated tetramer. The true value of QSC may, in fact, be even smaller since some dimer, which is directly observable at −45 °C, may still be present at room temperature.

Lithioisobutyrophenone in both THF[2] and dioxolane (Table VI) has a QSC of approximately 135 kHz which is evidently characteristic of a less solvated species, perhaps Li_4A_4. In view of this, 6.0 M phenyllithium in diethyl ether, which is known to be tetrameric,[29] is probably also Li_4A_4 since its QSC is 168 kHz. The aryllithium compounds **5** and **6** are formally unsolvated tetramers. Their ortho substituents, however, provide the fourth ligand, and their values of QSC (Table VII) are more characteristic of solvated tetramers. In the case of **6**, the aggregate is considerably distorted from the ideal cubic symmetry[14a] which probably accounts for its higher QSC value.

Dimers. Lithium indolide provides benchmark values for the species $Li_2A_2S_4$ (155 kHz; S = THF; −80 °C) and $Li_2A_2S_2$ (314 kHz; S = Et_2O). The environment of lithium in the former species is similar to that found in crystalline $CH_3CO_2Li{\cdot}2H_2O$,[30] in which each lithium cation is associated with two acetate ions and two water molecules, and for which a value of 154.6 kHz ($\eta = 0.9$) has been found for the quadrupole coupling constant.[31] We have observed similar values for lithium 2,6-dimethylphenolate in pyridine at room temperature (Table IV) and in dioxolane (147 kHz)[4] and dimethoxyethane (154 kHz).[4] The QSC for this salt in pyridine increases at elevated temperatures, indicating desolvation to the $Li_2A_2S_2$ species is beginning to occur. A similar result is observed for lithium indolide in THF. The observed QSC values correlate well (Figure 2) with the concentration-independent ^{13}C chemical shift difference $\Delta\delta = \delta_{C(5)} - \delta_{C(7)}$, which senses the change in solvation of the lithium cation.[1] Again, only partial conversion to $Li_2A_2S_2$ is attained at the highest available temperature.

Phenyllithium in THF-d_8 also appears to be the species $Li_2A_2S_4$ at room temperature since it is a dimer[29] and its QSC value is 162 kHz. The solution was, however, too unstable to permit

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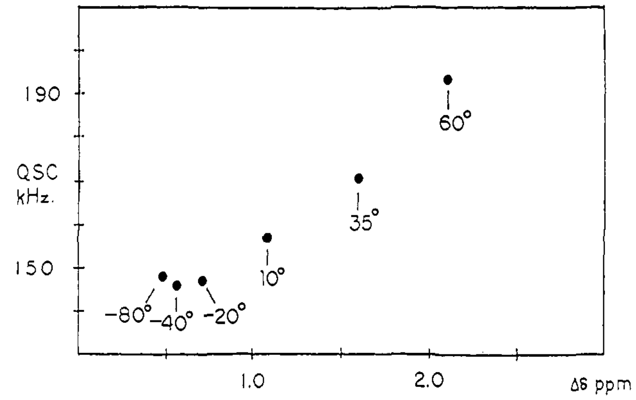

Figure 2. Correlation of QSC with $\Delta\delta = \delta_{C(5)} - \delta_{C(7)}$ as a function of temperature for lithium indolide in THF.

measurements at higher temperatures.

Although no value for an $Li_2A_2S_2$ species in the solid state is available, several lithium arylamides in diethyl ether have QSC values in the narrow range 310–320 kHz (Table II), and evidence for dimeric structures is unequivocal.[1] Phenyllithium which is 0.2 M in diethyl ether evidently exists substantially as $Li_2A_2S_2$ since its apparent QSC is 250 kHz, and it probably is still contaminated with the Li_4A_4 species which predominates at 6.0 M concentration.[29]

Monomers. No study of lithium quadrupole coupling constants for monomers in the solid state has been reported. Monomeric lithium isopropyl- and *tert*-butylanilides have been observed in THF at low temperatures,[1] and values for QSC at -80 °C of 211 and 212 kHz, respectively, have been determined (Table III). The structures of these species are assigned as $LiAS_3$. In the case of the isopropyl salt, raising the temperture causes conversion to $Li_2A_2S_4$ which appears to be almost completely converted to $Li_2A_2S_2$ at 60 °C. In contrast, the monomeric *tert*-butyl salt appears, on the basis of ^{13}C chemical shifts changes, to be partially converted at 60 °C to $LiAS_2$. This interpretation is dramatically supported by the value of 351 kHz at that temperature. This is the highest value we have observed, and the limiting value has not been reached at 60 °C.

Lithium 2,6-di-*tert*-butylphenolate in pyridine has been shown[4] to be a monomer with a QSC of 167 kHz. It is evidently the species $LiAS_3$, and the low value of QSC is related to the nature of the solvent (see below).

Summary of Empirical Correlations. It is clear that Li QSC is sensitive to the degree of aggregation and particularly to the degree of solvation of the aggregate. In fact, QSC values appear to offer one of the more promising methods for establishing the degree of solvation of lithium salts in weakly polar solvents. For a given aggregate structure, QSC is not highly dependent on the nature of anion but is sensitive to the nature of the solvent. The conclusions are summarized in Table VIII.

The Point Charge Model. To the extent that the systems under investigation can be regarded as ionic complexes one might expect to be able to make qualitative predictions on the basis of a point charge model. This approach has been used by Akitt and McDonald[32] and by Knop and his co-workers[33] to discuss the possible arrangements of ligands in coordination compounds which will lead to a zero electric field gradient (efg) at a given point.

Provided the principal axis system for the efg tensor is known from symmetry,[34] as is the case for all the systems we will discuss, the principal efg's, q_{ii}, are given by

$$q_{ii} = \textstyle\sum_j C_j(3\cos^2\theta_{ij} - 1)/\mathbf{r}_j^3 \qquad (4)$$

where θ_{ij} is the angle between the *i*th axis and the line joining the *j*th charge, of sign and magnitude C_j, and the origin (the lithium nucleus under consideration), and $\mathbf{r}_j$ is the distance of that charge from the origin. To simplify the present discussion, we initially assume all charges in the first coordination sphere are equidistant from the lithium nucleus. We further assume that $C_j = \pm 1$ for ions and -1 or $-^3/_4$ for solvent molecules, S.[35] Finally, in order to compare the various systems, we set the calculated q_{zz} and measured QSC equal to unity for the $Li_2A_2S_2$ species.

Table VIII. Approximate QSC Values (kHz) for Lithium Salts of Organic Carbon, Nitrogen, and Oxygen Acids in Ethers and Tertiary Amines

species	C	N		O	
	(ethers)	(ethers)	(3° amines)	(ethers)	(3° amines)
$Li_4A_4S_4$	85			65	40
$Li_4A_4S_n$	116, 168			105	>51
$Li_2A_2S_4$	162	155		150	120
$Li_2A_2S_2$	>250	315	306		>184
$LiAS_3$		210		210	167
$LiAS_2$		>351			

The geometry adopted for $Li_4A_4S_4$ is that found for the THF solvate of α-lithiocyclopentanone,[36] and the same skeletal geometry is assumed for Li_4A_4. The geometric *z* axis is defined as the local threefold axis through the lithium nucleus under consideration. For the dimers, the Li_2A_2 system is taken as a rhombus with the commonly observed[37,38] A–Li–A angle of 105°. For $Li_2A_2S_4$ the two pairs of S are placed in the plane containing the lithium atoms and perpendicular to the Li_2A_2 rhombus. The S–Li–S angles are set at 114°, and the *z* axis is defined as perpendicular to Li_2A_2 with the origin at the lithium under consideration. For $Li_2A_2S_2$, each S lies on the Li–Li axis, and the *z* axis is again taken as perpendicular to the Li_2A_2 plane.

The field gradients for the monomeric species $LiAS_3$ are extremely sensitive to the A–Li–S angle, and no geometry is available from the literature. We have, therefore, performed calculations for 110, 120, and 130°. Since monomers only form with anions which are sterically crowded, it is likely that the true angle is substantially greater than the tetrahedral angle. The *z* axis is the threefold symmetry axis. The $LiAS_2$ species is assumed planar, and the *z* axis is taken perpendicular to the plane. As the principal efg is in the *z* direction, its value is independent of the valence angles.

The results of these crude calculations are presented in Table IX. It is seen that the qualitative order is in rather good agreement with that of the observed QSC values. In particular, the model accounts well for the large QSC values observed by the tricoordinate lithium systems. The model is too crude to merit further refinement except to note that the assumption of equal Li–A bond lengths throughout the series is incorrect. It is known that the bond lengths decrease significantly with decreasing aggregation, and correction for this would, for instance, raise the computed values for $LiAS_2$ by as much as 30%.[39]

The fact that efg's for these systems are largely controlled by the number and disposition of the ligands of the lithium cations provides strong support for the conclusions we have reached re-

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[34] In the absence of symmetry it is still possible to construct the field gradient tensor from the Cartesian coordinates of the charges. Diagonalization of the tensor then gives the principal field gradients and the orientation of the principal axis system.

[35] It is expected that the major contribution to the field gradient will arise from the lone pair of electrons in the orbital directed toward the lithium ion. The formal net charge of the ligand, being effective at a greater distance, will make a smaller contribution. Actually, varying the effective charge of *S* from $-^1/_2$ to -1 does not alter the qualitative conclusions for the systems under discussion.

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[39] The Li–N bond length in $Li_2A_2S_2$ with A = 2,4,6-tri-*tert*-butylanilide and S = Et_2O is 2.041 Å, compared to 1.895 Å in the analogous monomer, $LiAS_2$, where S_2 is the bidentate ligand, tetramethylethylenediamine.[38] Similar trends between monomers and dimers, and dimers and tetramers are presented in Table I of ref 38.

Table IX. Estimated Relative Magnitudes of the Principal Field Gradients (q_{zz}), Their Asymmetry Parameters (η) and Directions, and Relative Observed QSC's for Lithium Salt Aggregates

	C = −1.0			C = $-^3/_4$			
species	q_{zz}	η	dir[a]	q_{zz}	η	dir[a]	QSC
$Li_4A_4S_4$	0.2	0.9	‖	0.1	1	⊥	0.21
Li_4A_4	0.6	0.4	⊥	0.6	0.4	⊥	0.43
$Li_2A_2S_4$	0.6	0.5	⊥	0.7	1	‖	0.60
$Li_2A_2S_2$	(1.0)	0	‖	(1.0)	0.3	‖	(1.00)
$LiAS_3$[b]							
110°	0.0	0	‖	0.2	0	‖	0.67
120°	0.5	0	‖	0.6	0	‖	
130°	1.1	0	‖	1.1	0	‖	
$LiAS_2$	1.2	0	‖	1.1	0.3	‖	>1.12

[a] Direction of q_{zz} with respect to the geometric z axis as defined in text. [b] Calculated for the ALiS angles shown.

Table X. Thermodynamic Parameters for Solvation and QSC Values for Lithioisobutyrophenone, **3a**

	QSC (kHz)				
solvent	low temp	high temp	ΔH^a ($kJ \cdot mol^{-1}$)	ΔS^a ($J \cdot mol^{-1} \cdot deg^{-1}$)	$\Delta H^\circ{}_{BF_3}$ ($kJ \cdot mol^{-1}$)
dioxolane[b]	97	135	−43	−162	−68.6[c]
THF[d]	78	136	−31	−131	−90.4[e]

[a] For addition of solvent. [b] Reference 42. [c] Reference 41. [d] Reference 2. [e] Reference 40.

garding the structures and degrees of solvation of aggregates.

Solvent Effects. In our discussion to this point, we have, for simplicity, implicitly assumed that intermediate degrees of solvation of tetramers $Li_4A_4S_{4-n}$ ($n \neq 4, 0$), and the dimer $Li_2A_2S_3$, do not represent the limiting species we have observed. We need now to consider this question as well as the interrelated problem of the effects of Lewis basicity and steric properties of the solvent on QSC.

The data for both lithium phenolate (Table IV) and 3,5-dimethylphenolate[4] tetramers in pyridine are for limiting species characterized by a QSC of approximately 40 kHz. Since lower limits of 0.7 and 0.86 solvent/lithium, respectively, have been established for these species,[4] we believe they have $Li_4A_4S_4$ structures, analogous to those of lithium enolate THF solvates in the solid state.[36] The corresponding value for lithium phenolate in dioxolane is 65 kHz at 30 °C. Maria and Gal[40] have established a reliable scale of Lewis basicities based on $-\Delta H^\circ{}_{BF_3}$, the enthalpy of complex formation with BF_3 at 25 °C. The values for dioxolane[41] and pyridine[40] are 68.6 and 128.1 $kJ \cdot mol^{-1}$, respectively. Presumably, pyridine is bound more closely to the lithium cation, resulting in a more nearly tetrahedral distribution of negative charge. An alternative explanation is that the limiting species in dioxolane is $Li_4A_4S_3$, and, at present, it is not possible to distinguish between these two possibilities.

Tetrameric lithioisobutyrophenone exists as two limiting species in both dioxolane (<−50°; >40 °C)[42] and THF (<−80°; >30 °C),[2] and the QSC values and ΔH and ΔS for the interconversion of the limiting species are presented in Table X. Since the Lewis basicity of THF is substantially higher than that of dioxolane, consideration of the values of ΔH and ΔS leads to the conclusion that, in dioxolane, the change in solvation involves more solvent molecules than in THF. In principle, the number of solvent molecules involved in these transitions can be determined from chemical shift vs. temperature data, but, in practice, this is difficult since it requires a knowledge of chemical shifts for the intermediate as well as for the limiting species. Since QSC for the low-temperature solvates are similar to that found for lithium phenolate in dioxolane at −24 °C (Tables IV and VI), it is likely that they are $Li_4A_4S_4$. The values of ΔS for their formation from the less solvated species are substantially more negative than for the conversion of monomeric contact ion pairs to solvent-separated ion pairs in similar solvents,[43] a process which presumably involves the addition of only one solvent molecule. We conclude, therefore, that the high-temperature species are $Li_4A_4S_{4-n}$ with n being 4 or 3 and 3 or 2 for dioxolane and THF, respectively. This does, however, raise the question of why QSC is the same for the desolvated species in the two solvents. It is possible that partial solvation distorts the tetramer skeleton from its normal geometry sufficiently to affect QSC.

The situation with dimers is clearer. The fact that lithium indolide and *N*-methyl-, *N*-isopropyl-, and *N*-*tert*-butylanilides all have essentially the same value (312–317 kHz) for QSC in diethyl ether, in spite of their widely differing steric demands, indicates that complete conversion to $Li_2A_2S_2$ has occurred. Further loss of solvent is highly unlikely. It is of interest to note that the same species is observed for lithium *N*-isopropylanilide in triethylamine (QSC = 306 kHz). Triethylamine ($-\Delta H^\circ{}_{BF_3}$ = 135.9 $kJ \cdot mol^{-1}$) is a much more powerful Lewis base than diethyl ether ($-\Delta H^\circ{}_{BF_3}$ = 78.8 $kJ \cdot mol^{-1}$). In this situation, however, the effective basicity of triethylamine is, presumably, considerably reduced by steric hindrance.

Conclusions

Provided systems are chosen carefully to avoid problems associated with internal rotations of groups, ^7Li quadrupole splitting constants for organic lithium salts can be reliably determined from a knowledge of ^7Li and ^{13}C carbon relaxation times. The values of QSC are found to be characteristic of the degree of aggregation and of the degree of primary solvation of the aggregate and provide one of the few available probes for the latter. The values of QSC in various situations agree qualitatively with those predicted on the basis of simple point charge models. The utility of QSC values could be greatly increased by obtaining additional benchmark values from measurements on crystalline solids with known crystal structures. In view of the success of theoretical methods in predicting the structures of organic lithium compounds,[37,44] it would also appear highly desirable to extend such calculations to include estimates of ^7Li quadrupole coupling constants and their asymmetry parameters.

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Registry No. 1, 59092-48-7; **1** (*E*-dimer), 109362-19-8; **1** (*Z*-dimer), 109361-21-9; **2a**, 35954-01-9; **2b**, 86952-90-1; **2c**, 99806-37-8; **3a**, 62416-34-6; **3b**, 67285-39-6; **4**, 74074-96-7; **5**, 2785-97-9; **6**, 109242-40-2; PhOLi, 555-24-8; 2,6-$(CH_3)_2C_6H_3OLi$, 24560-29-0; PhLi, 591-51-5; $PhC{\equiv}CLi$, 4440-01-1; $PhC{\equiv}CH$, 536-74-3; 3-$CH_3OC_6H_4OCH_3$, 151-10-0; 4-$(CH_3)_2NCH_2C_6H_4CH_3$, 4052-88-4; ^7Li, 13982-05-3; 2-(*N*,*N*-dimethylaminomethyl)-5-methylphenyllithium, 109242-41-3.

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