Journal of Organometallic Chemistry, 445 (1993) 1-5

JOM 23302

A solid state ^{7}Li NMR study of phenyllithium aggregates

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(Received September 1, 1992)

Abstract

A ^{7}Li MAS and static NMR study of mono-, di-, and tetra-meric phenyllithium aggregates was performed. The chemical shifts and quadrupolar coupling constants obtained are compared to the corresponding values in solution. There is a good agreement between the observed quadrupolar interaction in the solid state and in solution.

1. Introduction

The structure and reactivity of organolithium compounds are of fundamental interest to organic chemists, because these reagents are commonly used in organic synthesis. It has been shown that different aggregates can show considerable differences in reactivity, regiochemistry and stereochemistry [1]. Thus, it is of great importance to be able to determine the actual composition of organolithium aggregates under different reaction conditions.

There have been a number of ^{7}Li and ^{6}Li NMR studies of organolithium compounds in solution [2]. The chemical shift has been used as an indirect probe for the ion-pair state or aggregation of the studied systems. In cases where the scalar couplings between ^{6}Li or ^{7}Li and ^{13}C have been observed, the aggregation has been directly deduced from the multiplicity of the signal. In recent years, the nuclear Overhauser effect between ^{6}Li and ^{1}H nuclei has been used to establish the position of the lithium atom relative to the carbanion framework [3]. The quadrupole splitting constant (QSC) of ^{7}Li has been measured in a few cases and used as an empirical parameter to indicate the structure of the investigated system, since the QSC is dependent on the symmetry around the ^{7}Li nucleus [4]. In one paper it was noted that "the utility of QSC values could be greatly increased by obtaining additional benchmark values from measurements on crystalline solids of known crystal structure" [4d].

Quadrupole interactions in solid inorganic lithium salts have been investigated for many years [5], but the only organolithium compounds studied so far have been methyllithium and ethyllithium [6].

Previous NMR solid state studies of organolithium compounds have shown that it is possible to obtain high resolution ^{13}C NMR spectra, and that the information obtained can be used to relate known X-ray structures to structures in solution [7]. In one report, the phenyllithium system was studied [7b], since earlier the structures of three different aggregates had been determined by X-ray crystallography, namely a monomeric, a dimeric, and a tetrameric aggregation state [8].

In the present work, a solid state ^{7}Li NMR study of monomeric, dimeric and tetrameric phenyllithium aggregates was undertaken to test the validity of the assumptions used when the QSC was determined in solution. This can be accomplished by determining the quadrupolar coupling constant (QCC) and the asymmetry parameter of the electric field gradient (η) of aggregates of known crystal structure. 2-[(Dimethylamino)methyl]phenyllithium was used as a model of tetrameric stucture, since this aggregate has been shown to be tetrameric by X-ray crystallography [9]. The chemical shifts and QCC values were then compared with the shift- and QSC-values obtained in solution.

2. Results and discussion

The study of ^{7}Li NMR in the solid state is complicated owing to the quadrupole moment of ^{7}Li, which is an $I = 3/2$ nucleus. The center of gravity of the central transition ($-1/2$ to $1/2$) signal will, for example, be shifted from the "true" resonance frequency by the

0022-328X/93/$6.00

second order quadrupole interaction, according to eqn. (1) [10].

$$\nu_G - \nu_L = -(\nu_Q^2/\nu_L)[I(I+1) - 3/4](1+\eta^2/3)/30 \qquad (1)$$

where ν_G is the frequency of the center of gravity, ν_L is the Larmor frequency, ν_Q is the quadrupolar frequency, which is related to the QCC value by ($\nu_Q = 3\text{QCC}/[2I(2I-1)]$), and I is the nuclear spin.

The shift of the center of gravity is, according to eqn. (1), related to the quadrupole interaction and inversely proportional to the Larmor frequency. The second order effect is thus smaller at higher magnetic field strengths. The quadrupole shifts of the resonance frequency in organolithium compounds are expected to be small (up to approximately 1.5 ppm at the resonance frequency of 38.92 MHz used) owing to the small electric quadrupole moment of ^{7}Li. However, since the chemical shift range of ^{7}Li is small, the resulting quadrupole shift must be taken into account. The few reports of studies in which ^{6}Li and ^{7}Li chemical shifts were investigated by the MAS technique concerned lithium-containing glasses and polymer electrolytes [11].

However, other parameters of chemical significance can also be obtained in the solid state, such as the QCC, and η. These parameters are related to the QSC values, which can be determined in solution, by use of the relationship (2) [4d]:

$$\text{QSC} = (1+\eta^2/3)^{1/2}\text{QCC} \qquad (2)$$

The QSC values can be derived in solution by measuring the relaxation time of ^{7}Li, a relaxation which is dominated by the quadrupole mechanism. However, the effective rotational correlation time of the system must be determined by measuring the relaxation time

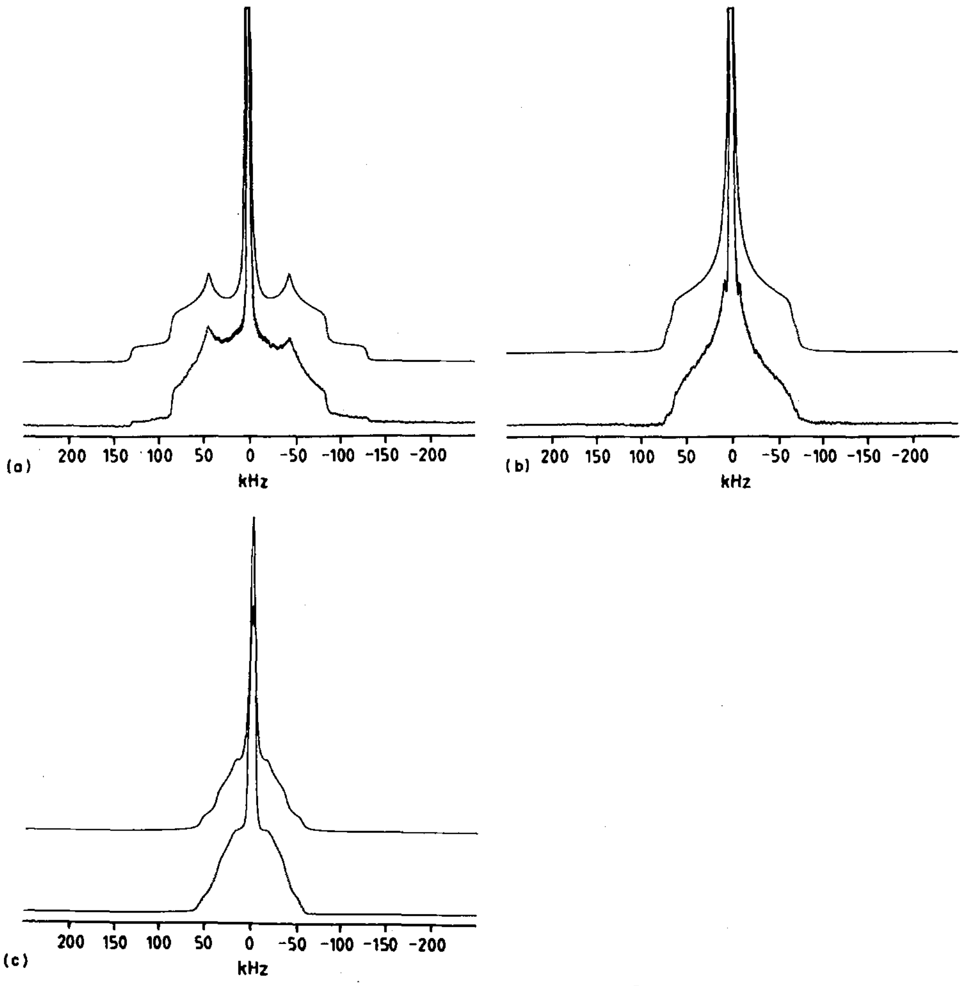

Fig. 1. Experimental and simulated (above) static solid state powder ^{7}Li NMR spectra of (a) PMDTA-coordinated and (b), TMEDA-coordinated phenyllithium; (c) 2-[(dimethylamino)methyl]phenyllithium.

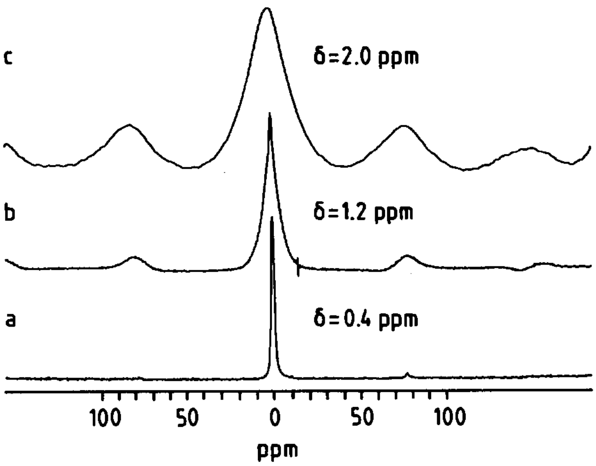

Fig. 2. MAS solid state ^{7}Li NMR spectra of (a) PMDTA coordinated and (b) TMEDA coordinated phenyllithium; (c) 2-[(dimethylamino) methyl]phenyllithium.

for some other nucleus for which the contribution of the dipole mechanism dominates, usually ^{13}C, and on the assumption that both nuclei have the same correlation time. In some instances, the relaxation time of ^{6}Li has been determined to determine the contribution of other relaxation mechanisms to the ^{7}Li [4e]. The QSC values obtained were used as empirical parameters to distinguish between different aggregates or solvates and ion-pair structures.

The measurement of QCC values in the solid state, on the other hand, does not require any of the above mentioned assumptions, and gives additional information in the form of η [12]. Furthermore, the measurement of the QCC and the asymmetry parameter can be of great value from a theoretical point of view, since they are related to the distribution of electric charge in the surroundings of the nucleus, arising from nuclear charge and the distribution of electrons in chemical bonds. To determine experimentally the orientation of the principal axes of the field gradient, however, a relatively large single crystal has to be used, and studied at different angles in the magnetic field. Growing such a crystal is a fundamental problem when dealing with highly reactive organolithium species. In some cases the principal axes can be deduced from a known crystal structure (often a cylindrically symmetric case with $\eta = 0$; if the field gradient is spherically symmetric, for instance if it has a cubic symmetry, the quadrupole interaction vanishes). Moreover, the dynamic processes that occur in solution, namely fast exchange between different aggregates, may affect the measured QSC values, such processes are avoided in the solid state.

In the present study the monomeric species was isolated as the *N,N,N',N',N''*-pentamethyldiethylenetriamine complex (PMDTA), and the dimer as the *N,N,N',N'*-tetramethylethylenediamine (TMEDA) complex. Because of the loose coordination of the diethyl ether (DEE) ligand in the previously isolated tetrameric aggregate [8c], this complex was avoided in the present investigation, and instead the 2-[(dimethylamino)-methyl]phenyllithium was included as a tetramer model [9].

The QCC values were determined by a spin-echo sequence ($90°_x$–τ–$90°_y$) on the microcrystalline samples [13]. These static spectra together with simulated powder spectra are depicted in Figure 1(a)–(c). The singularities are clearly recognized in these spectra. However, there are differences in the intensities between the experimental and simulated spectra at the outer regions of the satellite transitions. These discrepancies are caused by non-uniform exitations and/or finite pulse lengths; *i.e.* quadrupole interactions can not be entirely ignored during the pulse [14]. The ^{7}Li chemical shifts were determined from the MAS experiment. As seen in Fig. 2, the signals are relatively broad (82–945 Hz), preventing an exact determination of the chemical shifts. This could be due to motonal processes, as also observed in the ^{13}C solid state NMR spectra [7b]. The

TABLE 1. ^{7}Li chemical shifts, quadrupolar coupling constants, asymmetry parameters, corrected ^{7}Li chemical shifts and calculated quadrupolar splitting constants for various phenyllithium aggregates, together with ^{7}Li chemical shifts, and quadrupolar splitting constants in solution

Ligand	δ^7Li	$\delta_{corr}{}^7$Li [a]	$\delta_{solution}{}^7$Li [b]	QCC/kHz	η	QSC/kHz [c]	QSC$_{solution}$/kHz [d]	State of aggregation [e]
PMDTA	0.4	1.6	1.07	260	0.32	264	–	$LiAS_3$
TMEDA	1.2	1.6	1.87	147	0.78	161	162 [f]	$Li_2A_2S_4$
CH_2NMe_2 [g]	2.0	2.2	3.58 [h]	112	0.38	115	116	$Li_4A_4S_4$

[a] The chemical shifts were corrected according to eqn. (1). [b] Solution ^{7}Li NMR chemical shifts were determined in toluene-d_8. [c] The QSC-values were calculated according to eqn. (2). [d] QSC-values from reference 4d. [e] As defined in the text. [f] In THF-d_8 without added ligand. [g] Internal coordination of the substituent in the 2-[(dimethylamino)methyl]phenyllithium system. The ^{13}C NMR spectrum, recorded as previously reported [7b], consisted of 7 resonances at 45 broad (b); 68 (b); 126.1; 128.5; 138.3 (b); 151.5 and 175 ppm (very broad), in accordance to solution data of the corresponding 4-methylsubstituted compound [15]. [h] Measured for the corresponding 4-methyl-substituted compound in toluene-d_8 owing to the low solubility of the parent compound [15].

distortions of the line are small compared to the natural linewidths, owing to the relatively small QCC of ^{7}Li.

The measured and corrected chemical shifts according to eqn. (1) are listed in Table 1 together with the QCC-, η- and QSC-values calculated from eqn. (2). The corresponding values measured in solution are also included.

No QCC or QSC data have been determined previously for a monomeric lithium carbanion. However, isopropylanilide is believed to exist as a monomeric species, solvated by three solvent molecules ($LiAS_3$; A = anion, S = solvent), in tetrahydrofuran (THF) at low temperature [4d]. A QSC value of 211 kHz has been reported for this species. The QSC value for the PMDTA complex obtained in the present study is 264 kHz. This complex is formally a $LiAS_3$ complex, since the PMDTA is a terdentate ligand [8a]. However, in the few cases in which the same type of aggregate has been studied, the QSC value seems to be larger for carbanions than for amides [4d]. This may be the reason for the discrepancy between the QSC values for these $LiAS_3$ aggregates. Attempts were made earlier to predict the QSC value of monomeric aggregates by a simple point charge model, but the predictions were sensitive to the Li–A–S angles, and no definite conclusions were reported [4d].

Two greatly different QSC-values were reported for dimeric phenyllithium, *viz.* 250 kHz in DEE solution and 162 kHz in THF solution [4d]. It was proposed that this difference is due to different solvation of the dimers in DEE and THF. In the former case a dimer solvated by two solvent molecules, $Li_2A_2S_2$ was suggested and in the latter a dimer solvated by four solvent molecules, $Li_2A_2S_4$. The TMEDA-coordinated dimer in the solid state has formally a $Li_2A_2S_4$ structure [8b], since the TMEDA is bidentate. The QSC-value obtained in this study of the TMEDA dimer (161 kHz) is in good agreement to the QSC-value determined in THF solution (162 Hz) (Table 1).

As mentioned, the 2-[(dimethylamino)methyl]phenyllithium was used as a model for a tetrameric structure, internally solvated by four ligands, $Li_4A_4S_4$. The QSC-value of the corresponding 4-methyl-substituted compound measured in benzene-d_6 solution was reported previously [4d]. This derivative was used because of the low solubility of the parent compound in solvents that favour tetramers [15]. It was assumed that methyl substitution would not affect the tetrameric stucture to any major extent, nor the quadrupolar interaction, and, as is evident from Table 1, the agreement is good between the solution and solid state QSC values. The QSC values of these aggregates are, however, slightly higher than those reported for other $Li_4A_4S_4$ structures. A reasonable assumption to account for this slight increase in QSC is that the structure in the 2-[(dimethylamino)methyl]phenyllithium is somewhat distorted from cubic symmetry [4d].

QCC-values have recently been determined by multiexponential quadrupolar relaxation methods for 20% phenyllithium in cyclohexane/DEE (70/30) [16]. Values in the range of 92–138 kHz were obtained, depending on the method used. This species should be a tetrameric aggregate, since it is known from previous studies that phenyllithium has a tetrameric structure in toluene containing one equivalent DEE and in neat DEE [17], as well as in cyclohexane/DEE 2/1 [18]. However, the QSC-value for tetrameric phenyllithium in neat diethyl ether is 168 kHz [4d]. The reason for the discrepancy between these two results is not clear, but it could be due to differences in solvation, as discussed above.

The use of ^{7}Li NMR chemical shifts as an empirical parameter to distinguish between different types of aggregates in the solid state is hampered by the relatively large linewidths. The use of higher field NMR instruments should reduce the second order quadrupolar interaction, as mentioned earlier. This, together with the increased resolution, will give more accurate chemical shift determinations. A better approach might be to use the ^{6}Li isotope, since the quadrupole moment of ^{6}Li is only 0.5% of that of ^{7}Li. The relaxation time for ^{6}Li is expected to be longer than that for ^{7}Li and, in unfavourable cases, where the quadrupolar relaxation mechanism dominates, a relaxation time up to 667 times longer can be expected for ^{6}Li [4e], which will make the determination of QCC more difficult. The diagnostic use of Li NMR chemical shifts is however, limited by the above mentioned problems in conjunction with the small chemical shift range. Furthermore, it has been shown that solvent (ligand) and substituent effects can be larger than shift differences between different types of aggregates [17,19].

3. Conclusions

It has been shown that there is excellent agreement between the QSC-values determined for solution and the for the solid state. This means that in the systems investigated the solid state stucture is more or less retained in solution. Moreover, the present results place the earlier assumptions used in the calculation of QSC-values in solution on a firmer base. Limiting QSC-values for monomeric aggregates of the $LiAS_3$ type are also reported.

However, more work is needed to extend the empirical application of QSC-values for solutions by determining more limiting QSC-values of aggregates of known solid state structures. The effects of various ligands, *e.g.* ethers compared with tertiary amines, on the QSC-values needs further investigation, together with the effects of different types of anions, namely lithio-carbanions, -enolates and -amides.

4. Experimental details

The monomeric and dimeric aggregates were prepared as described previously [7b]. The 2[(dimethylamino)methyl]phenyllithium was prepared by the published method [9]. All the compounds were handled under an argon atmosphere, and the NMR rotors were filled under argon in a glovebox.

The solid NMR data were obtained with a Bruker MSL 100 NMR spectrometer, operating at a frequency of 38.92 MHz. Both static and MAS spectra were obtained with proton decoupling, using a 7 mm broad band Bruker MAS probe. The pulse power was selected to maximize the free induction decay under MAS conditions at a pulselength of 3.5 μs. The repetition time was 45–60 s in both types of experiments. The samples were rotated at a speed of 3 kHz in the MAS experiments.

Solution NMR spectra were recorded in 0.4 M toluene-d_6 solution and with a Bruker ACP 250 NMR spectrometer. The ^{7}Li NMR chemical shifts are referenced to external 1.0 M LiCl in H_2O.

The simulations were made with the FTNMR software, Hare Research Inc. A line-broadening of 4–6000 Hz was used and 10000 orientation/transition were calculated.

Acknowledgements

The Swedish Natural Science Research Council is acknowledged for financial support, and Prof. U. Edlund and Dr. P.-O. Eriksson for helpful discussions.

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