

^6Li – ^{13}C REDOR Study of the TMEDA Complex of Indenyllithium

Arne Boman,^b Ulf Edlund,^b Hans Förster^a and Dan Johnels^{b,*}

^aBruker Analytische Messtechnik, D-76287 Rheinstetten, Germany and ^bDepartment of Organic Chemistry, Umeå University, SE-901 87 Umeå, Sweden

Dedicated to Professor Göran Bergson on the occasion of his 65th birthday

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The carbon–lithium distances in the TMEDA complex of indenyllithium have been determined in the solid state by the REDOR NMR technique. The resulting position of the lithium cation relative to the carbon framework is compared with that determined by X-ray crystallography. The REDOR technique gives systematically slightly longer carbon–lithium distances compared with X-ray crystallography, as expected for a dynamic system. In this system, the observed difference in cation position was found to be 0.15 Å.

The structure and reactivity of organolithium compounds are important topics in organic chemistry, because of the frequent use of these reagents in synthesis. Consequently, the structure and aggregation of a large number of organolithium compounds have been studied experimentally, in the solid state by X-ray crystallography,¹ and in solution by different spectroscopic methods, mainly NMR spectroscopy.²

In previous papers, ^{13}C as well as $^6,^7\text{Li}$ solid state NMR investigations of organolithium complexes have been presented.³ By comparing solution and solid state NMR spectroscopy data with information from X-ray crystallography, we have tried to clarify whether the solid state structures of organolithiums are relevant models for the complexes in solution. We also explore the possibility of using solid state NMR spectroscopy as a tool for selecting suitable candidates for X-ray analysis, and to obtain direct structural information.

In the ^7Li NMR studies we have measured chemical shifts under MAS conditions and quadrupolar coupling constants under static conditions. The limited ^7Li chemical shift range restricts the usefulness of the shift parameter, as it is known that the variation due to different ligands is of the same order of magnitude as the difference due to aggregation.⁴ One exception occurs when the lithium cation is situated above an aromatic system, since the cation experiences the influence of the ring current in this case. On the other hand, the χ value is more

informative than the shift parameter, i.e. it is sensitive to both aggregation and solvation.^{3c,d,g}

The above-mentioned investigations give only indirect qualitative structural information by comparison with NMR data of complexes of known X-ray structure. In a recent paper, we used a new method in this area, the Rotational-Echo, DOuble Resonance (REDOR) method⁵ to obtain the dipolar couplings between ^6Li and ^{13}C nuclei.^{3e} This procedure gives direct structural information, as the dipole couplings obtained depend on the distance between the interacting nuclei, eqn. (1), where $r_{\text{C-Li}}$ is the carbon–lithium distance, d is the dipole coupling in Hz and the other symbols have their usual meanings.

$$r_{\text{C-Li}} = \sqrt[3]{\frac{\mu_0}{4\pi} \frac{\gamma^6\text{Li} \gamma^{13}\text{C} \hbar}{2\pi d}} \quad (1)$$

The TMEDA complex of fluorenyllithium has previously been studied with the purpose of determining the position of the lithium cation. The solid state structure of this complex was not known, but ^{13}C as well as ^7Li NMR data suggested a symmetric structure with the lithium cation positioned above the central five-membered ring.^{3a,d} This geometry was confirmed in the REDOR investigation, where the position according to REDOR of the lithium cation was determined with an error of about ± 0.2 Å. As this complex has not been investigated by X-ray crystallography, the accuracy of the REDOR method could not be confirmed.

In this paper, we present a REDOR investigation of

* To whom correspondence should be addressed.

the TMEDA complex of indenyllithium, a complex where the X-ray structure has been determined,⁶ in order to compare the relative position of the lithium cation as determined by the two methods.

Experimental

All work was carried out under an argon atmosphere. Indene was purchased from Aldrich and distilled prior to use. ⁶Li was obtained from Oak Ridge National Laboratory and used without further purification. Benzene was dried by azeotropic distillation and hexane was distilled from potassium-benzophenone before use.

Ethyl-⁶Li was prepared according to an earlier procedure,⁷ with some modifications. ⁶Li (1.08 g, 0.17 mol) was cut into small pieces and placed in a flask with 20 ml of dry benzene. The mixture was sonicated for 1 h in order to increase the reactivity of the metal by removing impurities from the surface. Bromoethane (5.97 ml, 0.08 mol) was added dropwise to the stirred mixture at 0 °C. When all of the halide had been added, stirring was continued for 6 h and the mixture was allowed to stand overnight at room temperature. The mixture was cooled to -78 °C and the solvent was removed *in vacuo*. Hexane (20 ml) was added and the solution was cannulated, leaving the solid behind. Ethyl-⁶Li was recrystallised from hexane twice and then dissolved in 50 ml of hexane. The homogenous solution was titrated using 1-pyreneacetic acid⁸ yielding a concentration of 0.15 M of ethyl-⁶Li.

Indene (150 mg, 1.3 mmol) was mixed with 2 ml of hexane and 150 mg (1.3 mmol) of TMEDA. To this mixture were added 9.51 ml (1.35 mmol) of the ethyl-⁶Li solution, at ambient temperature, whereupon a white precipitate immediately formed. The mixture was cooled to -20 °C, and the solvent was removed by cannulation and the solid residue was dried *in vacuo*, yielding a yellow-white powder. The resulting TMEDA complex of indenyl-⁶Li was placed in a rotor for REDOR measurements in an argon filled dry-box.

The REDOR spectra were acquired with a Bruker DMX 400 NMR instrument, equipped with a 4 mm probe triple tuned to ¹H, ⁶Li and ¹³C. With the sample spinning at 10 kHz, 512 scans were acquired per increment. 64 rows were obtained with an increment of four rotor periods. The proton decoupling RF power level was 90 kHz. The ¹³C π -pulse was 9.25 μ s and the ⁶Li π -pulse was 15 μ s.

The experiment was conducted and analysed as previously described,^{3e} except for a slight modification of the pulse sequence, which is shown in Fig. 1. The experiment is run twice, with and without the ⁶Li π -pulses. The experiment without the ⁶Li pulses was performed in order to estimate the T₂ value. The large number of rotor synchronized ⁶Li π -pulses makes this experiment sensitive to the spectrometer set-up.

The experiment was run in a 2D fashion, where the number of dephasing rotor cycles increased in the first

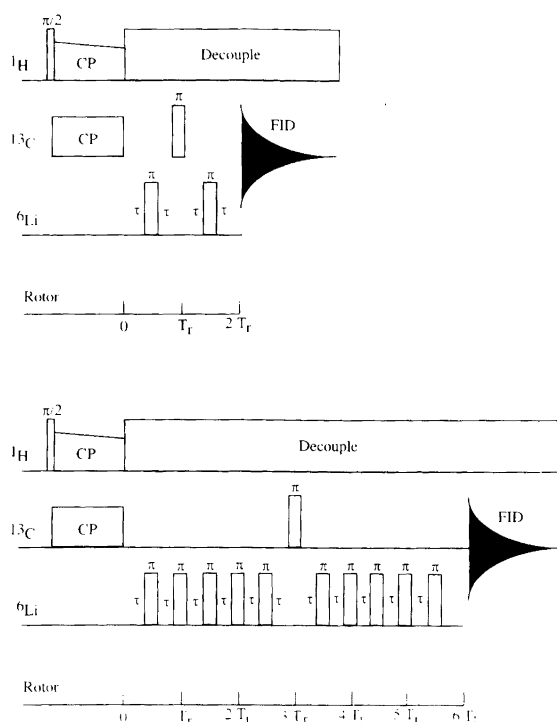


Fig. 1. The first two increments in the REDOR pulse sequence, where the dephasing delay is increased by adding more rotor periods and ⁶Li π -pulses.

dimension. By the use of ⁶Li enriched material and natural abundance ¹³C, the sample preparation was simplified, since no ¹³C enrichment was necessary. Furthermore, a single experiment determined the dipole couplings between all ¹³C nuclei and the ⁶Li cation. This is helpful in the structural determination as several distance constraints are obtained in one experiment.

Results and discussion

In the solid state ¹³C NMR spectrum six peaks were observed, as shown in Fig. 2. The signals can be assigned by comparison with solution NMR data.⁹ The C-4 and C-7 carbons give rise to separate signals due to the unsymmetrical arrangement of the TMEDA ligand relative to the carbanion framework.⁶ The shift differences for the pairs C-1,3; C-6,5 and C-3a,7a are too small to be resolved at the magnetic field used. The absence of

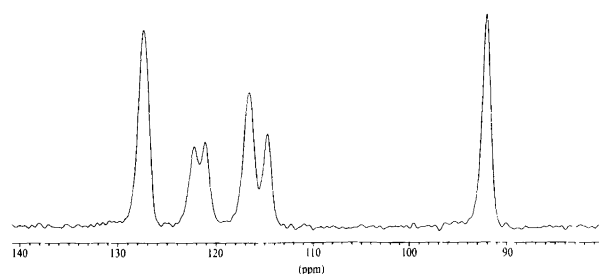


Fig. 2. The ¹³C CP/MAS spectrum of the aromatic region of the TMEDA complex of indenyllithium.

signal overlap arising from carbons with different C–Li distances, eliminates the need for the use of the REDOR transform.¹⁰ This transform can be used to deconvolute different dipolar couplings under favourable circumstances.

The non-linear least-squares fitting procedure to the experimental signal decays give the results presented in Table 1. The distances reported in the X-ray study are also given in Table 1.

It should be pointed out that the Li cation in the X-ray study is slightly unsymmetrically positioned relative to the carbon framework, of the order of ca. 0.004 Å. This is smaller than the expected resolution of the REDOR experiment. Mean values of the distances are therefore reported in Table 1.

Best fits to the REDOR decay for C-1,3 and C-5,6 are shown in Fig. 3. The signal for C-1,3 shows the typical undulation of a relatively strongly dipolar coupled nucleus, whereas the dipolar coupling to C-5,6 is much smaller. The dependence of the dipolar coupling constant of the C–Li distance is shown in Fig. 4. The practical limit is about 50 Hz or 4.5 Å, provided that there are strongly dipolar coupled nuclei in the system. The limited distance range is caused by the small gyromagnetic constant of ${}^6\text{Li}$.

As evident from Table 1, the REDOR method systematically overestimates the Li–C distances by ca. 0.2 Å on average. However, the error becomes larger for longer distances, i.e. smaller dipolar couplings, due to the inherent difficulty of accurately determining small dipolar coupling constants.

If all distance constraints are used in the optimisation of the lithium position, the difference between the two lithium positions is ca. 0.3 Å. A distance optimisation using the C–Li dipolar couplings above 100 Hz gives a better fit. The result is shown in Fig. 5, where the darker lithium cation correspond to the position according to X-ray crystallography and the lighter grey cation corresponds to the position according to REDOR. In this

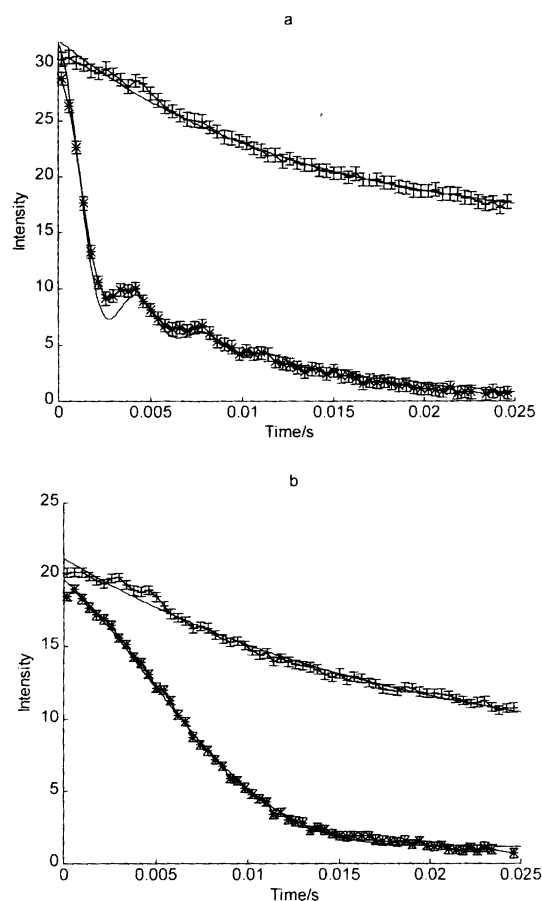
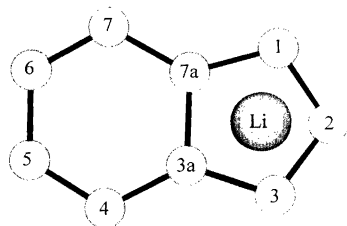


Fig. 3. (a) Signal decay, with and without ${}^6\text{Li}$ pulses, of the C-1,3 and (b) C-5,6 signals of the TMEDA complex of indenyllithium, as a function of the decay time.

case the difference between the Li positions according to X-ray and REDOR reduces to 0.15 Å. The optimised distances, r_{opt} reported in Table 1, are from this optimisation of the lithium position. A minimum requirement

Table 1. Parameters determined from the REDOR experiment of the TMEDA complex of indenyllithium.^a



Carbon No.	δ	d/Hz	T_2/ms	$r_{\text{REDOR}}/\text{\AA}$	$r_{\text{opt}}/\text{\AA}$	$r_{\text{X-ray}}/\text{\AA}$
1, 3	92	310(13)	13(2.6)	2.43(0.03)	2.43	2.31
2	115	324(15)	14(3.1)	2.39(0.06)	2.39	2.28
3a, 7a	127	281(18)	17(9.6)	2.51(0.06)	2.51	2.38
4	121	93(6)	15(3.4)	3.63(0.07)	3.46	3.35
7	122	87(6)	15(3.7)	3.71(0.09)	3.46	3.36
5, 6	117	50(2)	18(2.8)	4.46(0.06)	4.18	4.08

^aValues in parenthesis correspond to 3σ .

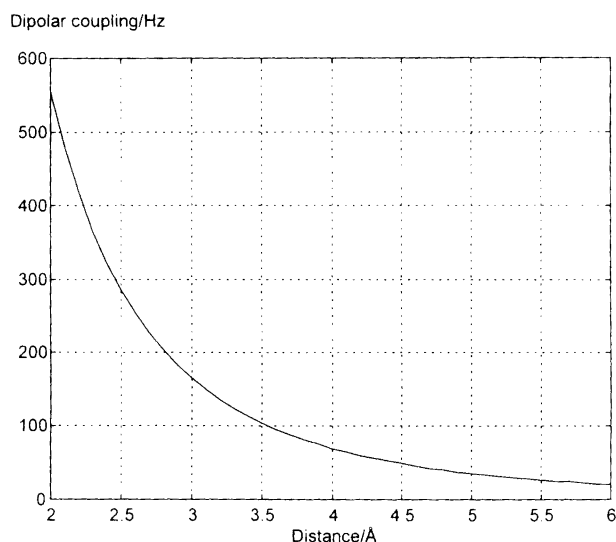


Fig. 4. The ${}^6\text{Li}$ - ${}^{13}\text{C}$ dipolar coupling as a function of carbon-lithium distance.

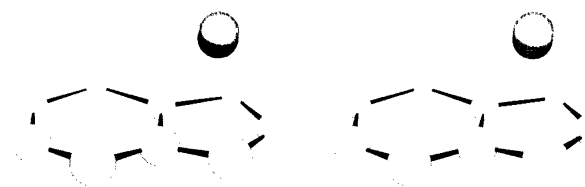


Fig. 5. A stereo view of the lithium position relative to the indenyl framework, as determined by X-ray crystallography (dark grey) and REDOR NMR spectroscopy.

to obtain a reliable geometry is C-Li couplings of three assigned carbons, preferably with large dipole couplings.

The observed difference between the REDOR lithium position and the position according to X-ray crystallography, can be explained by dynamic effects, and from instrumental imperfections. A recent theoretical investigation showed that NMR and X-ray distances are expected to differ to some degree. Dynamic processes have different influences on X-ray and REDOR, especially at higher temperatures.¹¹ In this system the TMEDA ligand is likely to be involved in dynamic processes, similar to those investigated in detail in some related organolithium complexes.¹² This dynamic process could change the position of the lithium cation to an extent that affects the observed dipolar coupling.

In conclusion, the above comparison between distances obtained by X-ray crystallography and the REDOR experiment shows that the ${}^{13}\text{C}$ - ${}^6\text{Li}$ REDOR technique is a valuable tool for the structural characterisation of organolithium complexes. Contrary to X-ray crystallography, there is no need for single crystals. However, although the C-Li distances are slightly overestimated by the REDOR technique, the precision is sufficient to discriminate between various possible lithium positions in the complexes. The extension of the REDOR method

to multiple spin situations¹³ will increase the use and generality of REDOR experiments to structural studies of organolithium compounds, including aggregates and multiply charged carbanionic species.

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