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^{13}C Spin-Echo NMR Spectroscopy with Gated ^{6}Li Decoupling: Spectral Editing for Simple Alkyl- and Aryllithium Compounds – Scope and Limitations

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Abstract: J-modulation of ^{13}C NMR signals by $^{1}J(^{13}C,^{6}Li)$ has been used to characterize the multiplicity of NMR signals of lithiated carbons in phenyl- and *n*-butyllithium.

The diagnostic value of line splittings due to $^{13}C,^{6}Li$ scalar spin-spin coupling over one bond in ^{13}C NMR spectra of dissolved organolithium compounds for the characterization of aggregation states is amply documented$^{1)}$. In particular, the resonances of lithiated carbons in simple alkyl- and aryllithium systems show multiplicities and intensity distributions that correspond to the well-known multiplets caused by coupling to neighbouring spin-1 nuclei: 1:1:1-triplets for $^{13}C,^{6}Li$ spin systems of monomers, 1:2:3:2:1 quintets for $^{13}C,^{6}Li_2$ spin systems of dimers, and 1:3:6:7:6:3:1 septets for $^{13}C,^{6}Li_3$ spin systems of static tetramers.

From the viewpoint of NMR spectroscopy, the situation for these spin systems is completely similar to that found for CD-, CD_2- and CD_3-groups in deuteriated or partially deuteriated compounds where the deuteron (^{2}H) is the spin-1 nucleus. However, while scalar $^{13}C,^{2}H$ splittings in small and medium-sized organic molecules are usually well resolved, the dynamic behaviour of organolithium compounds in solution very often masks the multiplet pattern due to residual line broadening as a consequence of chemical exchange. Furthermore, since the measurements have to be performed in the majority of cases at low temperatures, additional broadening effects are introduced due to solvent viscosity. These aspects are of special importance in cases where a distinction has to be made between a possible quintet or septet structure. While the 1:1:1 ^{13}C triplet of monomers can usually be recognized fairly easily even under unfavourable conditions, the outer lines of the ^{13}C septet of a tetramer are already so low in intensity that they may not be resolved and a quintet structure is erroneously indicated. Finally, the analysis will become difficult if ^{13}C multiplets of several aggregates severely overlap.

In the case of deuteriated compounds, various one-dimensional NMR techniques, among them simple spin-echo sequences, have been employed for spectral editing, that is $^{13}C,^{2}H$ multiplet analysis$^{2)}$. From the two possible versions of spectral editing for $^{13}C,^{6}Li_n$ spin systems by J-modulated spin-echo FT spectroscopy (SEFT$^{3)}$), the experiment that uses gated ^{13}C decoupling with ^{6}Li observation has already been successfully described$^{1,4)}$. It has the advantage of high intensity for the detected signal in the phase selection step, where the expression $I(^{13}C) = I_o(-1)^n$ holds$^{3)}$. However, the experiment is confined to ^{13}C-labelled compounds, because under conditions of ^{13}C decoupling the ^{13}C satellite signal coincides with the large ^{6}Li resonance of the $^{6}Li,^{12}C$ isotopomers.

It was, therefore, of interest to investigate the alternative approach: gated ^{6}Li decoupling with ^{13}C observation. While the possibility to work on the natural abundance level is an attractive feature of this version of the SEFT experiment, the intensities obtained in the phase selection step follow now the expression $I(^{13}C) = I_o(-1/3)^n$ $^{1,2)}$ and the expected relative intensities are rather low: -0.33 for the triplet, $+0.11$ for the quintet, and only -0.04 for the septet (Fig. 1). These numbers are even further attenuated by relaxation processes, especially for the higher multiplets because the magnitude of $^{1}J(^{13}C,^{6}Li)$ decreases$^{1)}$ and the evolution time 1/2J increases. Clearly, as we already stated$^{1)}$, there are practically no chances to detect signals for $^{13}C,^{6}Li_n$ spin systems with $n > 3$.

Despite these limitations, an experimental test of the $^{13}C\{^{6}Li\}$-SEFT experiment was of interest. It could be useful in certain cases for the characterization of monomers of organolithium compounds where a triplet splitting is found. With respect to dimers and tetramers, where a decision between a quintet and a septet structure becomes necessary, the detection of a positive ^{13}C spin-echo signal would also be helpful since it proves the presence of a quintet. We thus investigated the experiment with the monomer of phenyllithium and the dimer and tetramer of *n*-butyllithium.

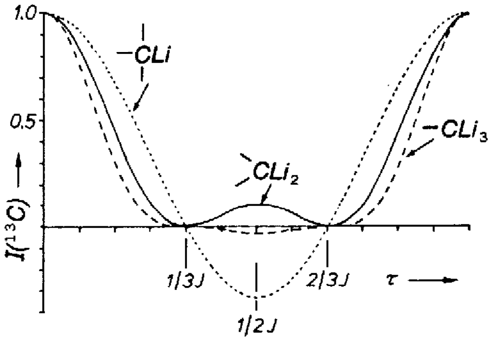
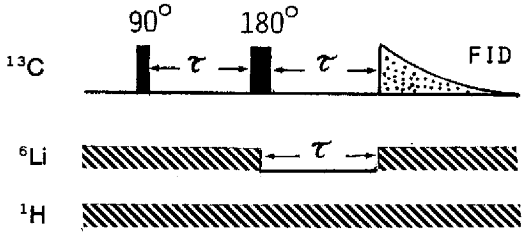


Fig. 1. Time dependence of ^{13}C magnetization for various $^{13}C,^6Li_n$ spin systems in a spin-echo experiment with gated ^6Li decoupling; relaxation during the echo sequence has been neglected; $I(^{13}C) = I_0[^1/_3 + ^2/_3\cos(2\pi J\tau)]^n$ after Ref. 2d.

Results

Spectral editing for the $C_6H_5{}^6Li$ PMDTA monomer. The compound was prepared in hexane (2.1 M) as described[5] and measured at −100 °C in THF-d_8 with a Bruker WH 400 FT-NMR spectrometer operating at a ^{13}C frequency of 100.61 MHz. After optimizing the field homogeneity under ^2H field/frequency lock, the spectrometer was unlocked and the ^2H transmitter coil was tuned to the ^6Li frequency of 58.883 MHz. This HF signal was derived from a Schomandl MS 100 frequency synthesizer and amplified by the heterodecoupler which allowed gating. ^1H broadband decoupling was used throughout.

Fig. 2 shows the triplet of C-1 and the same signal under ^6Li decoupling conditions. The spin-echo sequence (1) was then used with a delay τ = 1/2J of 35 ms, derived from the measured $^{13}C,^6Li$ coupling of 14.8 ± 0.3 Hz:



(1)

The inverted signal detected (Fig. 2c) had a relative intensity of 0.081 I_0, that is only 25% of the theoretical value. It is thus considerably reduced by relaxation. Since field inhomogeneity contributions to the effective transverse relaxation rate $1/T_2^*$ are minimized by the spin-echo sequence, the observed signal loss must mainly be due to T_2 processes caused by chemical exchange.

In order to elucidate the experiment further, a number of standardisized spectra with 200 transients were recorded using various spin-echo delays. The results (Fig. 3) clearly demonstrate that the time dependence of ^{13}C magnetization follows the predictions (Fig. 1), but emphasize at the same time the importance of transverse ^{13}C relaxation. Therefore, the accessibility of the slow exchange region for inter-aggregate processes will set the limit for a successful application of the SEFT technique.

Spectral editing for the n-$C_4H_9{}^6Li$ dimer and tetramer. The solution of both aggregates in THF-d_8 was prepared following published procedures[6] and was measured as described above. At −100 °C a quintet and a septet were clearly resolved (Fig. 4a)[7] and yielded coupling constants of 7.9 ± 0.1 and 5.5 ± 0.2 Hz, respectively. A delay of 63 ms was used for the spin-echo sequence (1) and a positive signal was detected for the quintet (Fig. 4c). Spectral editing for the septet was not attempted, since an experiment on a more concentrated solution which showed only the septet of the tetramer was unsuccessful even after collecting more than 4000 transients.

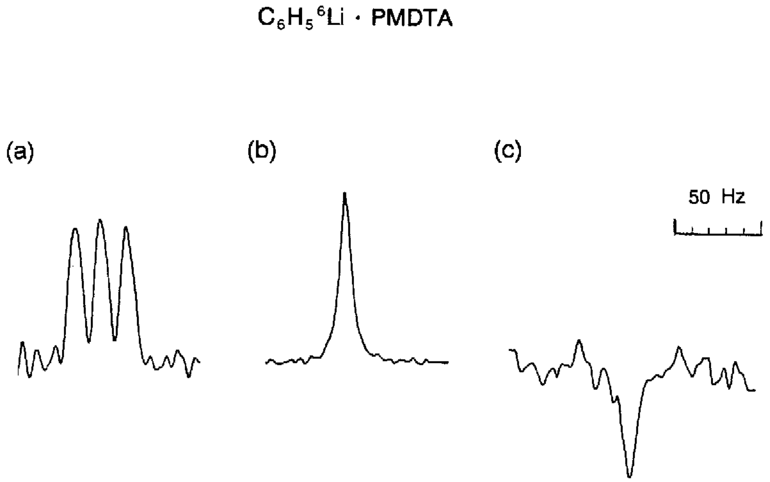


Fig. 2. (a) 100.6 MHz ^{13}C-NMR signal of C-1 in ^6Li-phenyllithium•PMTDA at -100 °C; $^1J(^{13}C,^6Li)$ = 14.8 Hz; (b) the same signal with ^6Li decoupling;
(c) the same signal after application of the $^{13}C\{^6Li\}$-SEFT experiment (1) with τ = 35 ms; total exp. time 14 min.

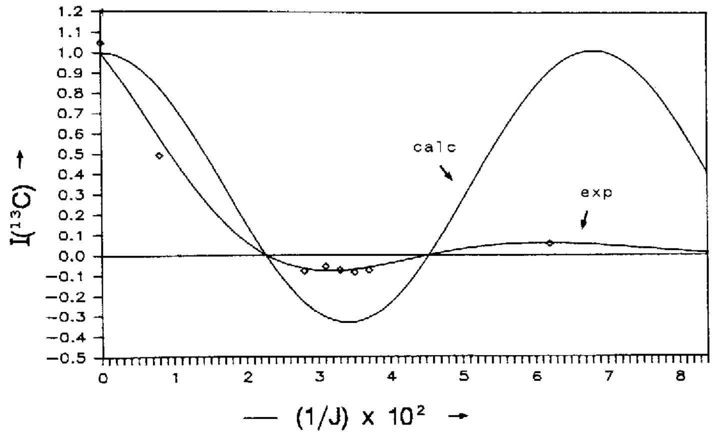


Fig. 3. Time dependence of transverse ^{13}C magnetization $I(^{13}C)_{exp}$ (◇) of ^6Li-phenyllithium•PMTDA in a $^{13}C\{^6Li\}$-SEFT experiment of type (1) at -100 °C; $I(^{13}C)_{calc}$ see Fig. 1.

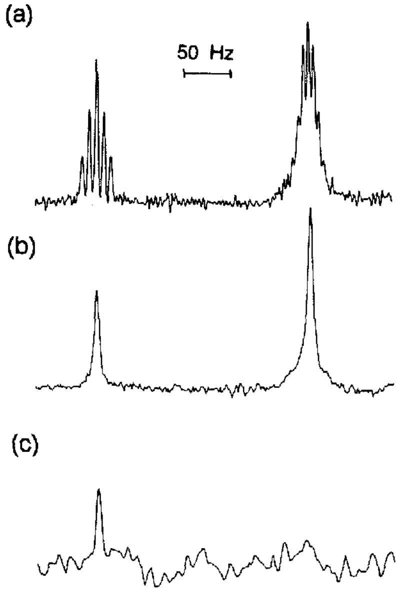


Fig. 4. (a) Quintet and septet in the 100.6 MHz ^{13}C NMR spectrum of the dimer and tetramer of n-butyllithium-^{6}Li at −100 °C in THF-d_8 (0.5 M); 3980 transients;
(b) as (a) but with ^{6}Li decoupling; 400 transients;
(c) spin-echo experiment (1) with τ = 63 ms; 5364 transients; total exp. time 6.2 hrs.

Conclusions. The successful demonstration of spectral editing for $^{13}C^{6}Li$ and $^{13}C^{6}Li_2$ spin systems described here adds a further option to the series of NMR experiments that are available today for studies of the solution structure of organolithium compounds$^{1)}$. The experiment is limited by fast transverse ^{13}C relaxation, but may be of value in certain cases where it proves difficult to determine the multiplicity of simple $^{13}C,^{6}Li$ multiplets. Since quite often spin coupling between ^{13}C and ^{7}Li can also be resolved, the corresponding SEFT experiment with J-modulation of ^{13}C magnetization by $^{1}J(^{13}C,^{7}Li)$ is an interesting alternative. It has – neglecting relaxation – the advantage of unit intensities for the phase selection step with an evolution time of 1/J. Because the ratio $\gamma(^{7}Li)/\gamma(^{6}Li)$ is 2.64, there is even an additional plus due to shorter evolution delays. Work along these lines is in progress.

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Literature

1) For a review see H. Günther, D. Moskau, P. Bast, and D. Schmalz, *Angew. Chem.* **99**, 1242 (1987); *Angew. Chem. Int. Ed. Engl.* **26**, 1212 (1987).
2) (a) P. Schmitt, J. R. Wesener, and H. Günther, *J. Magn. Reson.* **52**, 511 (1983); (b) J. R. Wesener and H. Günther, *Org. Magn. Reson.* 21, 433 (1983); (c) J. R. Wesener, P. Schmitt, and H. Günther, *Bull. Magn. Reson.* **5**, 232 (1983); (d) J. R. Wesener, P. Schmitt, and H. Günther, *J. Am. Chem. Soc.* **106**, 10 (1984); (e) M. R. Bendall, D. T. Pegg, J. R. Wesener, and H. Günther, *J. Magn. Reson.* 59, 223 (1984).
3) D. L. Rabenstein and T. T. Nakashima, *Anal. Chem.* 51, 1465A (1979); for a review see R. Benn and H. Günther *Angew. Chem.* **95**, 381 (1983); *Angew. Chem. Int. Ed. Engl.* 22, 350 (1983).
4) H.-J. Gais, J. Vollhardt, H. Günther, D. Moskau, H.-J. Lindner, and S. Braun, *J. Am. Chem. Soc.* 110, 978 (1988).
5) W. Bauer, W. R. Winchester, and P. v. R. Schleyer, *Organometallics* 6, 2371 (1987); U. Schürmann, J. Kopf, and E. Weiss, *Angew. Chem.* **97**, 222 (1985); *Angew. Chem. Int. Ed. Engl.* **24**, 215 (1985); PMDTA = pentamethyldiethylenetriamine.
6) D. Seebach, R. Hässig, and J. Gabriel, *Helv. Chim. Acta* **66**, 308 (1983).
7) The $^{13}C,^{7}Li$ splitting for the tetramer has recently been resolved by W. Bauer, T. Clark, and P. v. R. Schleyer, *J. Am. Chem. Soc.* **109**, 970 (1987).

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