

69. The ${}^6\text{Li}$, ${}^6\text{Li}$ -INADEQUATE Experiment: A New Tool for 1D- and 2D-NMR Studies of Organolithium Compounds¹⁾

by Oswald Eppers, Thomas Fox, and Harald Günther*

Fachbereich 8, OC II, Universität Siegen, Postfach 10 12 40, D–5900 Siegen

Dedicated to Prof. *Adalbert Maercker* on the occasion of his 60th birthday

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The 1D- and 2D- ${}^6\text{Li}$, ${}^6\text{Li}$ -INADEQUATE experiments are described as new tools for the detection of scalar coupled nonequivalent ${}^6\text{Li}$ nuclei in organolithium clusters. Practical applications of these sequences are demonstrated for the ${}^6\text{Li}$ -NMR spectra of (*E*)-1-lithio-2-(2-lithiophenyl)-1-phenylhex-1-ene (**1**) and (*E*)-2-lithio-1-(2-lithiophenyl)-1-phenylpent-1-ene (**2**), where signals due to dimers and monomers can be distinguished. The performance of the 2D- ${}^6\text{Li}$, ${}^6\text{Li}$ -INADEQUATE and the ${}^6\text{Li}$, ${}^6\text{Li}$ -COSY-45-LR experiment are compared. The ${}^6\text{Li}$ chemical shifts of **1** and **2** are discussed.

Introduction. – Aside from chemical shifts, nuclear *Overhauser* effects, and relaxation times, scalar spin-spin coupling constants are the most important parameters available from high-resolution NMR spectra of liquids. While, in many cases, detailed information with respect to configuration and bonding can be extracted from the magnitude of homo- and/or heteronuclear *J* values, sometimes simply the proof of the existence of spin-spin interactions allows conclusions which are relevant for the solution of a structural problem. Such situations are met quite frequently in the field of organolithium compounds, where aggregation effects yield a variety of oligomers which exist, however, mostly in fast, reversible equilibrium. It is then only at low temperature (usually below -70°) in the limit of slow *intra*- as well as *inter* aggregate exchange that individual species can be recognized [2]. In the absence of splittings due to heteronuclear ${}^6\text{Li}$, X spin-spin coupling, clusters of different size (dimers, tetramers, *etc.*) and structure give rise to distinct *singulets* in the ${}^{6,7}\text{Li}$ -NMR spectra. On the other hand, recent research on polyolithium compounds [3] has shown that quite a number of dilithiated systems may contain nonequivalent Li sites that also lead to different ${}^{6,7}\text{Li}$ signals with *singulet* character [4] [5]. The observation of spin-spin coupling between ${}^{6,7}\text{Li}$ nuclei then becomes an important criterium for distinguishing the two situations, since scalar Li, Li interactions can only be expected for nuclei in the same cluster. An assignment of the ${}^{6,7}\text{Li}$ -NMR signals to individual aggregates is then possible.

While the experimental strategy for the analysis of the structural problem outlined above is, thus, straightforward, its practical realization mostly proves difficult because of the small magnitude of Li, Li coupling constants. Firstly, the spin- $3/2$ nucleus ${}^7\text{Li}$ is hardly suitable for the measurement of homonuclear spin-spin coupling because of its

¹⁾ NMR Spectroscopy of Organolithium Compounds, Part XIII. Part XII: [1].

quadrupole moment that leads to fast spin-lattice relaxation associated with line-broadening effects and the possibility of relaxation decoupling. More favourable in this respect is ${}^6\text{Li}$, which has the smallest quadrupole moment of all nuclides. Various spin-spin interactions between ${}^6\text{Li}$ and other nuclei in organolithium compounds have thus been observed. From these parameters, ${}^6\text{Li}, {}^{13}\text{C}$ [6] [7] and ${}^6\text{Li}, {}^{15}\text{N}$ [8] [9] interactions are of sizeable magnitude and easy to detect. In lithiated organophosphorous compounds, ${}^7\text{Li}, {}^{31}\text{P}$ interactions have frequently been measured [10], while a ${}^6\text{Li}, {}^{29}\text{Si}$ coupling was only reported once [11]. ${}^6\text{Li}, {}^1\text{H}$ [12] interactions observed so far are smaller than 1 Hz and their existence has been deduced in many cases only on the basis of line widths considerations (*cf. e.g.* [13]). As for ${}^6\text{Li}, {}^6\text{Li}$ coupling constants, which are of interest in the present context, a resolved ${}^6\text{Li}$ multiplet due to homonuclear ${}^6\text{Li}, {}^6\text{Li}$ J coupling has recently been reported for the first time [1]. Before, these parameters were detected indirectly through the 2D-COSY experiment [4], where the appearance of cross peaks proves the existence of scalar interactions. Their direct observation now led to the introduction of the ${}^6\text{Li}, {}^6\text{Li}$ -INADEQUATE experiment [1] as an interesting alternative to ${}^6\text{Li}, {}^6\text{Li}$ -COSY spectroscopy, and the potential of this new method for structural research in the field of organolithium compounds as well as its practical applications are discussed in the present contribution.

Results and Discussion. – A. *General Considerations.* The INADEQUATE experiment (for a review, see [14]), originally developed to facilitate the measurement of homonuclear ${}^{13}\text{C}, {}^{13}\text{C}$ coupling constants [15], is a double quantum-based pulse sequence which also yields, in its 1D as well as in its 2D version [16] (*Eqns. 1* and *2*, respectively, with $A = 1/4J$), correlation information. It is, thus, an important assignment aid in ${}^{13}\text{C}$ -NMR [17], but also in ${}^1\text{H}$ - [17] [18], ${}^{29}\text{Si}$ - [19] or ${}^{183}\text{W}$ - [20] NMR. Even in the solid state, ${}^{29}\text{Si}, {}^{29}\text{Si}$ - and ${}^{119}\text{Sn}, {}^{119}\text{Sn}$ -INADEQUATE experiments have been possible [21] [22].

1D-INADEQUATE [15]

$$90^\circ - - A - - 180^\circ - - A - - 90^\circ, 90^\circ, \text{FID}(t_2) \quad (1)$$

2D-INADEQUATE [16]

$$90^\circ - - A - - 180^\circ - - A - - 90^\circ - - t_1 - - 135^\circ, \text{FID}(t_2) \quad (2)$$

For quadrupolar nuclei the INADEQUATE experiment has, to the best of our knowledge, not been used so far. Our preliminary results [23] already indicated, that its application in ${}^6\text{Li}$ -NMR is promising for several reasons: 1) enrichment of organolithium compounds with ${}^6\text{Li}$ is easily achieved, and there are no limitations due to low sensitivity like in the case of less abundant nuclei; 2) the *anti*-phase character of the INADEQUATE signals facilitates the detection of small coupling constants hidden in the line widths of 1D signals and even allows the determination of their magnitude. This is a clear advantage over the COSY experiment, where cross-peak structures are difficult to resolve, if spin-spin coupling becomes small; 3) again compared to the COSY experiment, the absence of diagonal peaks in the 2D-INADEQUATE spectra greatly facilitates the detection of correlation signals; 4) with their built-in double quantum filter, the INADEQUATE experiments eliminate signals of impurities or *singulets* of clusters with isochronous ${}^6\text{Li}$ nuclei. An equivalent result can only be obtained with the COSY-DQF version [23] (see, however, the discussion on p. 889).

The use of a fixed delay Δ in *Sequences 1* and *2* that depends on the scalar coupling constant may be seen as disadvantage of the INADEQUATE experiment. This limitation is, however, less severe in practice, because estimates for the approximate magnitude of the respective coupling constants are usually available, and a complete signal loss due to a mismatch for the spin-evolution time $1/4J$ is seldom observed.

In the 1D-INADEQUATE experiment for spin-1 nuclei, *anti*-phase magnetization for an AX system ($A = I, X = S$) is obtained after an evolution period of $1/4J$, thus $\Delta = 1/8J$ in *Eqn. 1*. On the basis of a product operator treatment [24]²⁾, and the appropriate operators for spin-1 nuclei [25], the magnetization obtained after the spin-evolution time 2Δ (neglecting the center line, which is stationary in the on-resonance rotating frame and the 180° refocussing pulse) is given by

$$\sigma_1 = (\hat{I}_x \hat{S}_z + \hat{I}_z \hat{S}_x) \sin(2\pi J 2 \Delta) + (\hat{I}_y \hat{S}_z^2 + \hat{I}_z^2 \hat{S}_y) \cos(2\pi J 2 \Delta) \quad (3)$$

With $2\Delta = 1/4J$, we obtain

$$\sigma_2 = \hat{I}_x \hat{S}_z + \hat{I}_z \hat{S}_x \quad (4)$$

The next 90° pulse creates double-quantum coherence

$$\sigma_3 = \hat{I}_x \hat{S}_y + \hat{I}_y \hat{S}_x \quad (5)$$

which is transformed into observable single-quantum magnetization by the last 90° pulse

$$\sigma_4 = -(\hat{I}_x \hat{S}_z + \hat{I}_z \hat{S}_x) \quad (6)$$

Both nuclei, thus, yield *anti*-phase magnetization, and the magnetization of the center line, not shown in *Eqn. 3–6*, is eliminated by the phase cycle. An *anti*-phase doublet with a splitting of $2J(A,X)$ is observed for the A and X resonance, respectively.

In the 2D-INADEQUATE experiment, the term σ_3 evolves in the rotating frame during the evolution time t_1 with the sum of the *Larmor* frequencies ω_I and ω_S :

$$\begin{aligned} \sigma_5 = & (\hat{I}_x \cos\omega_I t_1 - \hat{I}_y \sin\omega_I t_1)(\hat{S}_y \cos\omega_S t_1 + \hat{S}_x \sin\omega_S t_1) \\ & + (\hat{I}_y \cos\omega_I t_1 + \hat{I}_x \sin\omega_I t_1)(\hat{S}_x \cos\omega_S t_1 - \hat{S}_y \sin\omega_S t_1) \end{aligned} \quad (7)$$

Eqn. 7 can be transformed into

$$\sigma_6 = (\hat{I}_x \hat{S}_y + \hat{I}_y \hat{S}_x) \cos(\omega_I + \omega_S) t_1 + (\hat{I}_x \hat{S}_x + \hat{I}_y \hat{S}_y) \sin(\omega_I + \omega_S) t_1 \quad (8)$$

by well-known trigonometric relations³⁾. Using a 135° read pulse [26] yields

$$\begin{aligned} \sigma_7 = & -1/\sqrt{2} (\hat{I}_x \hat{S}_y + \hat{I}_x \hat{S}_z + \hat{I}_y \hat{S}_x + \hat{I}_z \hat{S}_x) \cos(\omega_I + \omega_S) t_1 \\ & + \hat{I}_x \hat{S}_x - 1/2 (\hat{I}_y \hat{S}_y + \hat{I}_y \hat{S}_z + \hat{I}_z \hat{S}_y + \hat{I}_z \hat{S}_z) \sin(\omega_I + \omega_S) t_1 \end{aligned} \quad (9)$$

and, after retaining only observable components,

$$\sigma_8 = -1/\sqrt{2} (\hat{I}_z \hat{S}_x + \hat{I}_x \hat{S}_z) \cos(\omega_I + \omega_S) t_1 - 1/2 (\hat{I}_y \hat{S}_z + \hat{I}_z \hat{S}_y) \sin(\omega_I + \omega_S) t_1 \quad (10)$$

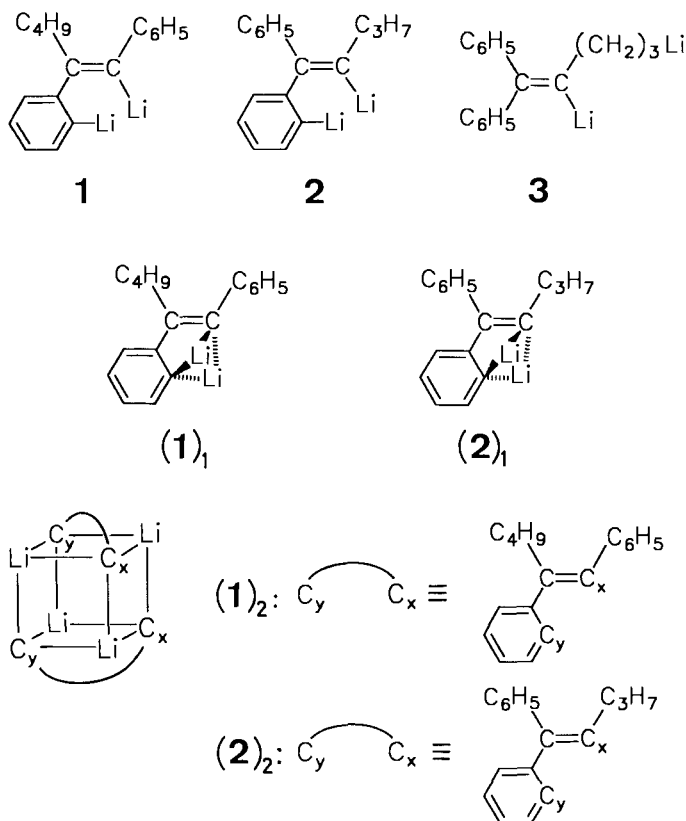
The first term constitutes *anti*-phase x magnetization of the I and the S spin, respectively, which has been modulated by $\cos(\omega_I + \omega_S)$ during t_1 . The second term represent *anti*-

²⁾ Contrary to [24], we use for convenience the right-handed coordinate system with clockwise rotation of transverse components.

³⁾ $\sin(\alpha + \beta) = \sin\alpha \cos\beta + \cos\alpha \sin\beta$ and $\cos(\alpha + \beta) = \cos\alpha \cos\beta - \sin\alpha \sin\beta$.

phase y magnetization of both spins modulated during t_1 by $\sin(\omega_l + \omega_s)$. This allows quadrature detection in F_1 , and this domain contains the double-quantum frequencies $\omega_{DQ} = \omega_l + \omega_s$ for individual AX systems, while, in F_2 , *anti-phase doublets* with a splitting of $2J(A,X)$ are measured at $\omega_2 = \omega_l$ and ω_s . Consequently, the AX spin systems are separated along F_1 .

B. Experimental Results. For an experimental test of the ${}^6\text{Li}, {}^6\text{Li}$ -INADEQUATE experiment two related compounds, (*E*)-1-lithio-2-(2-lithiophenyl)-1-phenylhex-1-ene (**1**) and (*E*)-2-lithio-1-(2-lithiophenyl)-1-phenylpent-1-ene (**2**), are available. Both form monomers and dimers; **1** is obtained by the reaction of diphenylacetylene with 2 mol of BuLi [5], while **2** results from the reaction of 1-methylidene-2,3-diphenylcyclobutane with Li *via* the short-lived intermediate **3** [27]. Compound **1** is prepared in hexane in the presence of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). After replacing hexane by THF, a mixture of the monomer and the dimer is formed [5]. The structure of both species can be represented by (**1**)₁ and (**1**)₂, respectively, as shown by extensive NMR and X-ray investigations [5]. In the case of **2**, the reaction is carried out in Et₂O in the absence of TMEDA and the dimer results [28]. The monomer, however, can be obtained, if the dimer is dissolved in THF in the presence of the diamine. Both species possess structures (**2**)₁ and (**2**)₂, respectively, as derived from a detailed NMR study [28]. Since the C/Li



skeleton of both dimers lacks cubic symmetry due to the structure of the ligands, the ${}^6\text{Li}$ spin systems expected are more complex than A_2X_2 systems. They rather constitute $AA'XX'$ systems, which may, however, in view of the minute differences expected for the various ${}^6\text{Li}$, ${}^6\text{Li}$ interactions savelly be classified as A_2X_2 systems. As noted before [1], the resulting *quintet* structure of the ${}^6\text{Li}$ resonances yields INADEQUATE spectra which are identical to those predicted above for the AX system, as far as the three inner lines of the *quintet* are concerned. For a total evolution period of $1/4J$, the outer lines evolve twice as fast as the inner ones. At the end of this evolution period, their magnetization points along the $-y$ axis of the rotating frame and is eliminated by the phase cycle as is the center line which lies along the $+y$ axis.

The ${}^6\text{Li}$ -NMR spectra of the monomer/dimer mixtures of both systems, **1** and **2**, are shown in Fig. 1, *a, b*. The 1D-INADEQUATE experiments (Fig. 1, *c, d*) select the dimer signals and allow the determination of the homonuclear ${}^6\text{Li}$, ${}^6\text{Li}$ -coupling constant. Because the splitting of the two *anti*-phase components of the INADEQUATE signals was found to depend slightly on the parameters used for resolution enhancement by *Gaussian* multiplication of the time domain signal, the observed frequency difference was calibrated by the value for $J({}^6\text{Li}, {}^6\text{Li})$ measured directly from the 1D- ${}^6\text{Li}$ -NMR spectrum of $(\mathbf{2})_2$ [1]. With this procedure, we find a coupling of 0.30 Hz for $(\mathbf{1})_2$, while the value for $(\mathbf{2})_2$ was 0.16 Hz. Despite of this difference, a direct observation of the larger coupling in the case of $(\mathbf{1})_2$ was until now not possible.

A more stringent test for the ${}^6\text{Li}$, ${}^6\text{Li}$ -INADEQUATE experiment as an instrument to establish ${}^6\text{Li}$, ${}^6\text{Li}$ correlations may be envisaged in cases where several AX or spin systems of higher order overlap. This situation was simulated by the superposition of the spectra

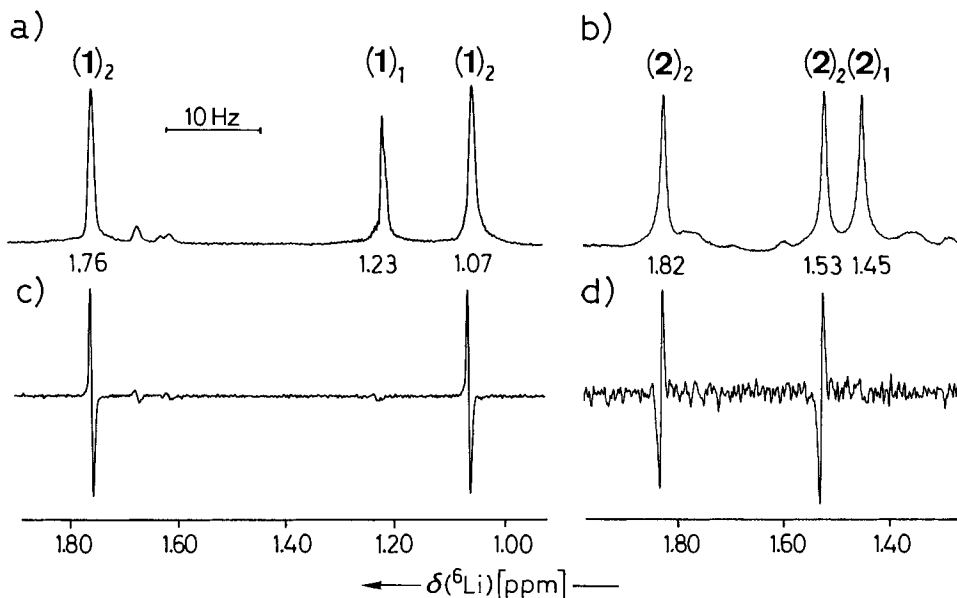


Fig. 1. 58.88-MHz ${}^6\text{Li}$ -NMR spectra of the mixtures $(\mathbf{1})_1/(\mathbf{1})_2$ (a) and $(\mathbf{2})_1/(\mathbf{2})_2$ (b) in $\text{THF}/(D_8)\text{THF}$ (1:1) at -73° and their ${}^6\text{Li}$, ${}^6\text{Li}$ -1D-INADEQUATE spectra (c, d). δ Values relative to 0.1M LiBr in THF as external reference.

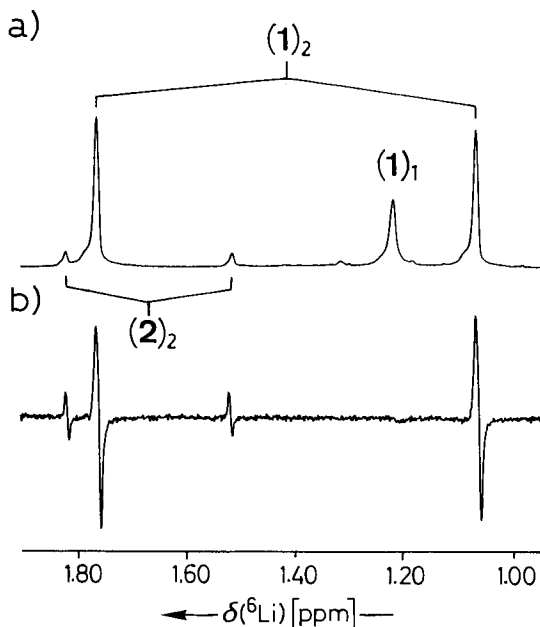


Fig. 2. a) 58.88-MHz ${}^6\text{Li}$ -NMR spectrum of a sample with co-axial 5-mm and 10-mm o. d. NMR tubes. Inner tube $(2)_2$, outer tube $(1)_1$ and $(1)_2$; solvent THF/ (D_8) THF (sample A); temp. -70° . b) 1D- ${}^6\text{Li}$, ${}^6\text{Li}$ -INADEQUATE spectrum of sample A. Note that the singlet of $(1)_1$ and signals of minor components and/or decomposition products are eliminated.

of $(1)_1$, $(1)_2$, and $(2)_2$. To avoid unexpected reactions, co-axial NMR tubes with separate solutions of both systems, **1** and **2**, were used. The recorded spectrum (Fig. 2, a) now displays, apart from some minor components or decomposition products, five signals, and their connectivity is clearly established by a 1D-INADEQUATE experiment. The result demonstrates again the elimination of single-quantum magnetization and the detection of the spin systems belonging to $(1)_2$ and $(2)_2$, respectively (Fig. 2, b).

In cases where signal intensities do not allow to distinguish individual spin systems, the 2D version of the INADEQUATE experiment is to be preferred. As a 2D experiment, however, it requires appreciable more experimental time, but yields an unequivocal result (Fig. 3, a).

It was also of interest to compare the INADEQUATE spectrum with the result of a COSY-45-LR experiment [29] (Eqn. 11) which provides a reduction of diagonal peak intensity relative to the intensity of the cross peaks and, in addition, emphasizes cross peaks due to long range or generally small coupling constants:

$$90^\circ - - t_1 - - \Delta, 45^\circ, \Delta, \text{FID}(t_2) \quad (11)$$

As expected, within the same experimental time, the COSY experiment is more sensitive as the double-quantum-based INADEQUATE sequence, and the results, even for the less intense lines of $(2)_2$, are very satisfactory (Fig. 3, b). Thus, both approaches, the INADEQUATE as well as the COSY experiment, are established as valuable tools for the detection of ${}^6\text{Li}$ spin systems.

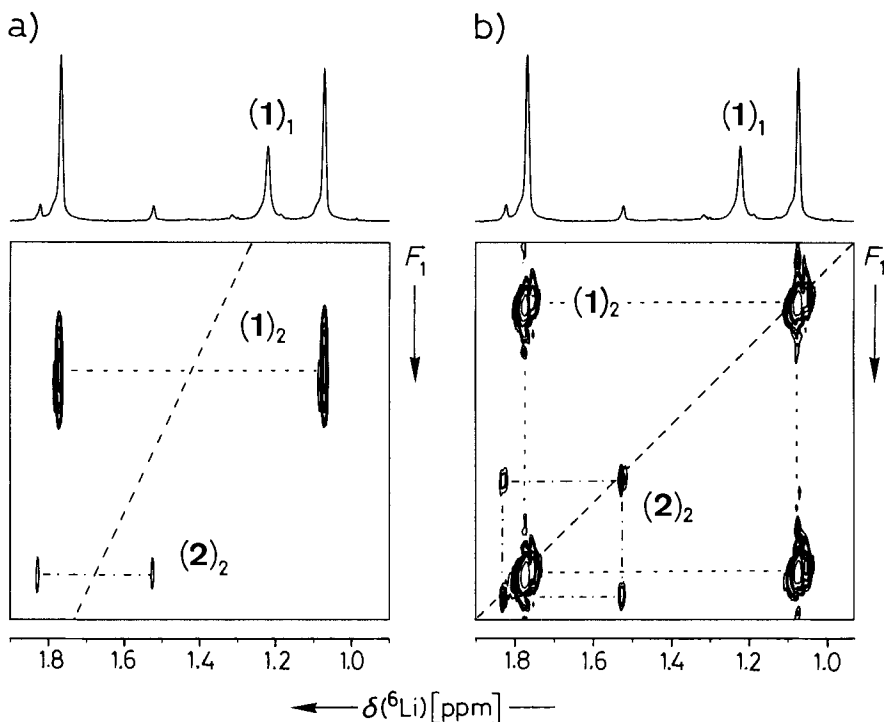


Fig. 3. $2D\text{-}^6\text{Li},^6\text{Li}\text{-INADEQUATE}$ spectrum of sample A (cf. legend to Fig. 2) (a) and $^6\text{Li},^6\text{Li}\text{-COSY-45-LR}$ spectrum of sample A (b). For exper. details, see *Experimental*.

An additional interesting aspect of the COSY experiment is the fact that the diagonal signal for the monomer $(1)_1$ was not detected. The introduction of the fixed delay Δ for the emphasis of small couplings apparently causes transverse relaxation of this magnetization prior to detection. A similar observation has been reported for a COSY-LR experiment of 2-nitroaniline that gives rise to a broadened NH_2 resonance [30], and a method for the selective elimination of the H_2O signal was based on this effect [31]. Thus, in case of fast transverse relaxation for *singlet* resonances, the COSY-LR experiment can replace a COSY-DQF experiment, which uses a double-quantum filter for the elimination of single-quantum magnetization, but suffers from the sensitivity loss that is characteristic for double-quantum experiments. However, if, in a first analysis of an experimental ^6Li -NMR spectrum, homonuclear coupled ^6Li resonances are to be distinguished from uncoupled ^6Li *singlets*, the 1D-INADEQUATE experiment is by far the fastest and most efficient way to achieve this. Also, impurities that might overlap with resonances belonging to an AX or A_2X_2 spin system can in this way be eliminated. Both aspects are evident from the spectrum shown in Fig. 2, b.

C. Chemical Shifts. The ppm scale for ^6Li chemical shifts is remarkable small [32] and except for diamagnetic shielding effects observed for poly- η -bound Li in anions of cyclic π -systems [33] only moderate changes are induced by structural changes in the ligands. The influence of the latter is further reduced by the importance of solvation effects not

present in ^1H - or ^{13}C -NMR. Nevertheless, in comparing the results for the monomers and dimers of **1** and **2**, compounds that differ with respect to the position of the alkyl and one Ph group, a systematic trend for the ^6Li shifts is obvious.

The data of *Fig. 1* show that from the two resonances of the dimers those at low field practically have identical chemical shifts (δ 1.76, 1.82). It is, therefore, reasonable to assign these resonances to the ^6Li with environment $[\text{C}_y, \text{C}_x, \text{C}_x]$ (see *Formulae*). Experimental proof for this assumption comes from ^1H , ^6Li nuclear *Overhauser* measurements [28]. The other resonances, than due to ^6Li in environment $[\text{C}_x, \text{C}_x, \text{C}_y]$, are more shielded than the first ones and a low field shift of 0.46 ppm results when going from $(\mathbf{1})_2$ to $(\mathbf{2})_2$. A similar low-field shift is found by comparing the monomer signals of **1** and **2** ($\Delta\delta$ 0.22 ppm), where ^6Li has the environment $[\text{C}_x, \text{C}_y]$. Thus, changing C_x from a $=\text{C}$ -aryl to a $=\text{C}$ -alkyl unit induces a downfield shift of *ca.* 0.2 ppm. At least three different factors may be discussed as possible sources of this effect: 1) charge-density changes, 2) ring-current effects of the Ph group, and 3) differences in Li solvation due to steric effects. The second factor seems less important, because the structure of $(\mathbf{2})_2$ [5] indicates that the Li nuclei most probably reside in or close the zero-shielding region of the Ph rings. From the remaining points, changes in solvation effects due to different steric constraints can hardly be estimated, but charge-density changes may also be reflected in the ^{13}C chemical shifts. Here, we find indeed a deshielding for C_x in going from $(\mathbf{1})_1$ to $(\mathbf{2})_1$ ($\Delta\delta$ +2.1 ppm [28]) which parallels the deshielding for the ^6Li signals described above. On the other hand, for the dimers the trend is opposite ($\Delta\delta$ -3.3 ppm) and in the case of C_y , shielding results for both pairs of aggregates ($\Delta\delta$ -3.2 and -1.9 ppm, respectively). These trends are, however, at variance with the observations for the ^6Li shifts, and a simple rationalization of the experimental findings seems at present not available.

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Experimental. – The synthesis of $(\mathbf{1})_1$, $(\mathbf{1})_2$, and $(\mathbf{2})_2$ followed published procedures [5] [27]. For the preparation of $(\mathbf{2})_1$, the solvent was removed from an ethereal soln. of the dimer and replaced by THF with 2 mol-equiv. of TMEDA with respect to the concentration of **2**. A mixture of the dimer and the monomer resulted (*Fig. 1, b*). Samples for NMR measurements were transferred under Ar in sealed NMR tubes.

^6Li -NMR spectra were obtained at 58.88 MHz on a *Bruker 400 MHz AMX* spectrometer, equipped with an ASPECT 32 computer and the *Bruker* variable-temp. unit. Broad-band multinuclear probe heads with ^2H locksystem were used. Temp. measurements were performed with the MeOH thermometer [34]; δ values given in the *Figs.* are relative to 0.1M LiBr in THF as external reference.

The sample used for the spectrum shown in *Fig. 1, a* was *ca.* 0.3M. The following spectral parameters for the 1D-INADEQUATE experiment were used: sweep width 471 Hz (8 ppm), $A = 1/(8J) = 0.625$ s ($J = 0.2$ Hz), 1170 transients, acquisition time 4.34 s, relaxation delay 2 s, total experiment time 2.46 h. A 135° read pulse was used in this and all subsequent INADEQUATE experiments. For the spectrum of *Fig. 1, b* a 0.4M soln. was measured with the following spectral parameters: sweep widths 110 Hz (1.87 ppm), $A = 0.735$ (for $J = 0.17$ Hz), 64 transients, acquisition time 4.67 s, relaxation delay 1 s, total experiment time 7.6 min.

Sample *A*, used in the experiments shown in *Figs. 2* and *3*, was a co-axial NMR tube assembly with $(\mathbf{2})_2$ 0.2M in THF/(D₈)THF (1:1) in the inner 5-mm o. d. tube and $(\mathbf{1})_1$ / $(\mathbf{1})_2$ 0.8M in the same solvent mixture in the 10-mm o. d. outer tube. The 1D- ^6Li , ^6Li -INADEQUATE experiment (*Fig. 2*) used a sweep width of 1238 Hz (21 ppm), $A = 0.4$ s (for $J = 0.3$ Hz) 152 transients, 6.62-s acquisition time and a relaxation delay of 1 s. The total experiment time was 21 min. For the 2D-INADEQUATE experiment (*Fig. 3, a*) a sweep width of 158 Hz (2.68 ppm) was used in both dimensions, 64 t_1 experiments, with 64 transients each, were performed; A was 0.66 s (for $J = 0.2$ Hz), the t_1 increment 6.3 ms, and the total experiment time 6.9 h. The same sweep width and the same number of t_1 experiments, and transients were applied in the COSY-45-LR experiment (*Fig. 3, b*). The delay for emphasizing small couplings (A in pulse sequence *Eqn. 11*) was 0.834 s, the total experiment time 8.1 h.

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