185. Vicinal ^{2}H/^{1}H Isotope Shifts for ^{6}Li-NMR and the Aggregation Behavior of Phenyllithium[1])[2])

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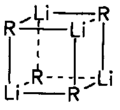
Dedicated to Professor *Emanuel Vogel* on the occasion of his 65th birthday

(1.X.92)

Vicinal deuterium-induced ^{6}Li-NMR isotope shifts have been found for (D_5)phenyllithium. These shifts are to low field, and their magnitude varies from 7 to 19 ppb with different solvents and donor molecules. On the basis of the *isotopic fingerprints* observed in the ^{6}Li-NMR spectra of $C_6H_5{}^6Li/C_6D_5{}^6Li$ mixtures, the aggregation behaviour of phenyllithium under different solvent conditions and in the presence of amines as donor ligands (TMEDA, PMDTA) was studied. Tetramers and dimers are observed in Et_2O, dimers as well as momomers in Et_2O/TMEDA and in THF, and momomers in THF/PMDTA. The hitherto unidentified species in Et_2O/TMEDA was shown to be a monomer.

Introduction. – With the observation of deuterium-induced isotope shifts for ^{6}Li-NMR spectra of various (D_3)methyllithium aggregates, a new approach for the analysis of aggregation phenomena in the field of organolithium compounds was initiated which produced promising results especially for mixed aggregates [2].

The principle of the methods is best explained with an example. Given a tetrameric structure of type **1**, like that of methyl- or butyllithium [3] [4] ($R = CH_3$ and C_4H_9, respectively), and a 1:1 mixture of deuterated and non-deuterated ligands (d and h, respectively), the environments **2**–**5** for ^{6}Li exist, if only next neighbours are taken into account. According to straightforward statistical considerations a ^{6}Li *quartet* with an intensity distribution of 1:3:3:1 should then result in the case of slow *intra*- as well as *inter*-aggregate exchange, if a ^{2}H/^{1}H isotope effect for $\delta({}^6Li)$ exists. Each line of this *multiplet*[3]) is characteristic for a differnt ^{6}Li environment. In turn, for a dimer (**6**) we expect a 1:2:1 *triplet* and for a monomer (**7**) a 1:1 *doublet*. Thus, clusters of different size are characterized by *isotopic fingerprints*. An attractive feature of this method as com-



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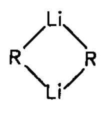
[h,h,h] **2**

[h,h,d] **3**

[h,d,d] **4**

[d,d,d] **5**



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R — Li

7

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[1]) 'NMR Spectroscopy of Organolithium Compounds', Part XIV; Part XIII: [1].

[2]) Part of the Ph. D. thesis of *O. E.*, University of Siegen, 1991.

[3]) It must be emphasized that the *multiplets* discussed here are based on chemical shifts. They should not be mistaken as *multiplets* that result from scalar spin-spin coupling.

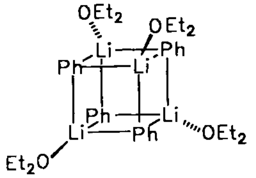
pared to the determination of the aggregation number from scalar ^{13}C,^{6,7}Li spin-spin coupling constants [5] [6] is its sensitivity which is achieved by twofold isotopic enrichment (^{2}H and ^{6}Li).

If only the *inter*-aggregate exchange is slow and the *intra*-aggregate exchange still fast on the NMR time scale, the situation changes for clusters with aggregation numbers > 2. The ^{6}Li nucleus then interacts with all ligands of the particular cluster, including the remote ones. Consequently, for a dynamic tetramer of structure **1** the environments **8–12** result, and a 1:4:6:4:1 ^{6}Li *quintet* is expected. Now, each line of the *multiplet* corresponds to a different aggregate[4]).

[h,h,h,h]	[h,h,h,d]	[h,h,d,d,]	[h,d,d,d]	[d,d,d,d]
8	**9**	**10**	**11**	**12**

After the detection of *geminal* ^{2}H-induced ^{6}Li-isotope shifts over two bonds in (D$_3$)methyllithium and the verification of *isotopic fingerprints* [2], it was of interest to search for *vicinal* effects, $^3\Delta(^6\text{Li})(^2\text{H}/^1\text{H})$, which are transmitted over three bonds. If they can be measured, the investigation of phenyllithium clusters becomes possible. We, thus, initiated the present study which deals with the aggregation behaviour of phenyllithium under different solvent and donor conditions.

Results. – Because of its importance as a synthetic reagent, numerous efforts have been made to uncover the structure of phenyllithium in the solid as well as in solution. X-Ray investigations have characterized the tetramer **13**, crystallized from Et$_2$O [7], the dimer **14** which crystallizes as a complex with tetramethylethylenediamine (TMEDA) from the same solvent in the presence of the donor ligand [8], and the monomer **15**, stabilized through complexation with the tridentate ligand pentamethyldiethylenetriamine (PMDTA) [9].



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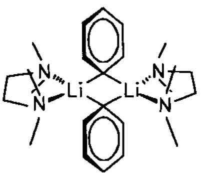

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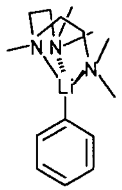

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In solution, aside from early ebullioscopic measurements [10], NMR investigations dominate. Here, the aggregation number can be derived from chemical-shift considerations but more clearly from the multiplicity of the ^{13}C-NMR signal of the lithiated C-atom and the magnitude of the ^{13}C,^{6}Li scalar spin-spin coupling [5] [6]. Published results are summarized in *Table 1*. They lead to the conclusion that phenyllithium forms a tetramer in Et$_2$O. Only at low concentration [11] and in the presence of toluene [12], indications for the coexistence of dimers are found. In none of these cases, a ^{13}C,^{6}Li or ^{13}C,^{7}Li coupling could be observed.

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[4] So far, cyclic oligomers have not been studied by the isotopic-labelling technique, but appropriate experiments are under way, and the results will be reported in due course.

Table 1. *Survey of Available NMR Information about the Aggregation States of Phenyllithium Under Different Solvent Conditions*

Solvent	Donor	c[a])	T[K]	$n(^{13}C)$[b])	M[c])	$n(^6Li)$[d])	N[e])	Lit.
Et_2O		0.2	299	1			2/4	[11]
Et_2O		6	299	1			4	[11]
Et_2O		3	213	1		1	4	[12]
Et_2O		0.08	168	2		2	2/4	[14]
Et_2O	TMEDA	1	198	1	q	2	2/4	[13]
THF		0.3	155	1	q		2	[5c]
THF		1	299	1			2	[11]
THF		0.26	170	2			1/2	[15]
THF	PMDTA	1.6	170	1	t		1	[15]
THF		0.04	173	2		2	1/2	[14]

[a]) Concentration, mol/l.

[b]) Number of detected ^{13}C-NMR signals.

[c]) Multiplicity of ^{13}C-NMR signals due to $^{13}C,^6Li$ spin-spin coupling, if resolved (*t* = *triplet*, *q* = *quintet*).

[d]) Number of detected ^6Li-NMR signals.

[e]) Aggregation number (1 = monomer, 2 = dimer, 4 = tetramer).

The dimer is stabilized in the presence of equimolar amounts of TMEDA and yields a ^{13}C *quintet* at 187.7 ppm with $J(^{13}C,^6Li) = 8$ Hz [13] [14]. An additional signal at 184.4 ppm showed no splitting and was tentatively assigned to a tetramer [13].

In THF, two aggregates are present, presumably the monomer and the dimer [15], but scalar $^{13}C,^6Li$ coupling was resolved only for the dimer [5c]. At low concentrations and in the presence of strong donor ligands like PMDTA, hexamethylphophoric-acid-triamide (HMPA), or 12-crown-4 the formation of the monomer is preferred [14] [15], and the observed ^{13}C *triplet* showed a splitting of 15.6 Hz [15].

To investigate the situations described above with the *isotopic fingerprint* method, a salt-free 1:1 mixture of phenyllithium and (D_5)phenyllithium was prepared and studied under different solvent conditions.

Et_2O as Solvent. A 0.5M sample of the above mixture in Et_2O showed at 170.6 K a strong ^6Li-NMR signal at 2.26 ppm (relative to external 0.1M LiBr in THF), besides a smaller absorption at 1.52 ppm (*Fig. 1, a*). The fine structure of the main signal was identified under ^1H decoupling as a *quintet* (*Fig. 1, b*), while the smaller absorption revealed a *triplet* (*Fig. 1, d*). *Thus, $^2H/^1H$ substitution at the Ph ring indeed leads to vicinal isotope shifts for ^6Li resonances and paves the way for aggregation studies on phenyllithium and related compounds.*

From the observed multiplicity of the ^6Li-NMR signals, we can conclude that a dynamic tetramer and a dimer co-exist under the experimental conditions used. The isotopic fingerprints thus yield the *first direct experimental evidence* for the existence of these clusters. Support for the presence of the dimer, which was proposed by *Jackman* and *Scarmoutzos* [11] and *Green* [14] for samples with low C_5H_6Li concentrations (0.2M), came from the results obtained for a 0.05M solution, which yielded ^6Li resonances at 2.25 and 1.69 ppm with a strong increase of the highfield signal (*Fig. 1, e*). Finally, the spectrum of a 5:3 mixture of non-deuterated and deuterated material shows an intensity

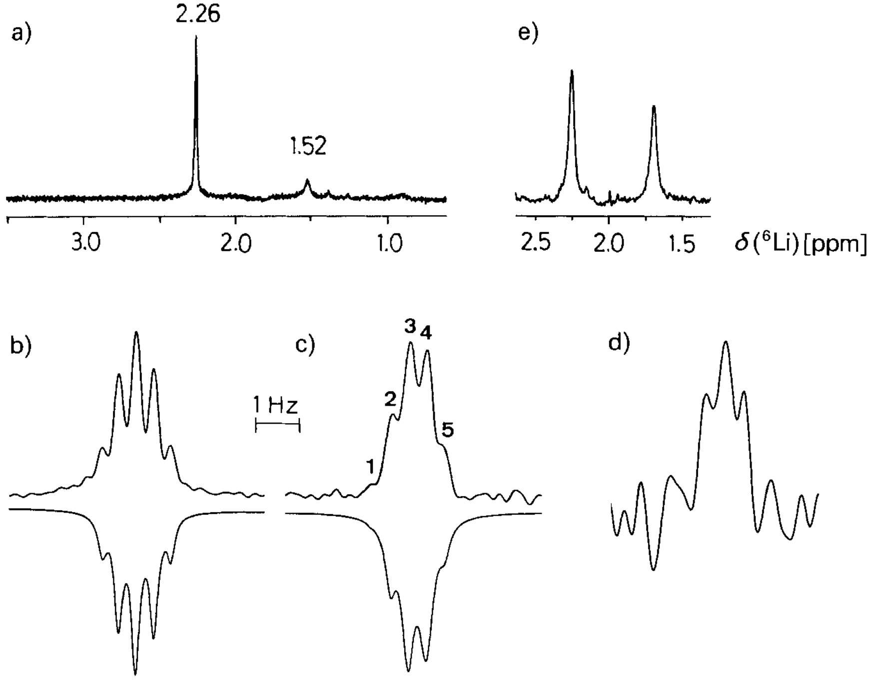

Fig. 1. *^{6}Li-NMR Spectrum* (58.88 MHz) *of an equimolar mixture of C_6H_5Li and C_6D_5Li 0.5M in $Et_2O/(D_{10})Et_2O$ 7:3 at 170.6 K.* δ Scale relative to exernal 0.1M LiBr in THF. *a*) Total shift range with ^{1}H decoupling; *b*) fine structure of the signal at 2.26 ppm with gated ^{1}H decoupling for NOE supression: experimental (*above*) and simulated (*below*); *c*) the tetramer signal as in *b* for a 5:3 mixture at 177.5 K; *d*) fine structure of the signal at 1.52 ppm; *e*) spectrum of an equimolar C_6H_6Li/C_6D_5Li mixture 0.05M in $Et_2O/(D_{10})Et_2O$ 7:3.

increase for the highfield components of the *quintet* (*Fig. 1, c*). The ^{2}H/^{1}H isotope shift is, thus, negative[5]) as is the shift over two bonds [2].

In connection with the observation of the *quintet* (*Fig. 1, b*) it is worthwhile to note that this is the *first documentation of a dynamic ligand exchange within an aggregate by the isotopic fingerprint method.* The multiplicity of the signal immediately tells us that the tetramer shows *intra*-aggregate exchange that is still fast on the NMR time scale at the temperature of our measurements.

The ^{2}H-induced isotope shifts found in the present case are *ca.* −7 ppb (0.4 Hz at our measuring frequency of 58.88 MHz) for the *quintet* of the tetramer (*cf. Table 2*) and −8.3 ppb (0.49 Hz) for the *triplet* of the dimer. Because pentadeuterated material was used, the measured effect also contains contributions from the deuterons in *meta*- and *para*-position which are 4 and 5 bonds, respectively, away from the ^{6}Li nucleus. Even if the magnitude of these contributions must be considered, it is reasonable to assume that due to the usual attenuation of isotope shifts with the number of intervening bonds [16] (in the case of ^{2}H/^{1}H effects on ^{13}C-NMR by a factor of 1/3 per bond), the vicinal effects

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[5]) A unique sign convention for NMR isotope shifts does not exist. We use negative signs for low-field shifts, which correspond to the observed decrease in shielding constant σ.

Table 2. *Comparison of Experimental and Theoretical Relative Intensities* I *for the* ^{6}*Li-NMR* Quintets *of* Fig. 1b,c, *and Measured* $^2H/^1H$ *Isotope Shift*

$T = 170.6$ K; C_6H_5Li/C_6D_5Li 1:1									
ν/Hz[a])	0.83		0.42		0		–0.41		–0.81
$I_{exp.}$	0.073		0.259		0.337		0.241		0.089
$I_{theor.}$	0.0625		0.250		0.375		0.250		0.0625
$^3\Delta(^6Li)$/ppb[b])		–7.0		–7.1		–7.0		–6.8	
$T = 177.5$ K; C_6H_5Li/C_6D_5Li 5:3									
ν/Hz[a])	0.88		0.43		0		–0.44		–0.87
$I_{exp.}$	0.006		0.172		0.379		0.370		0.072
$I_{theor.}$	0.020		0.132		0.330		0.366		0.153
$^3\Delta(^6Li)$/ppb[b])		–7.6		–7.3		–7.5		–7.3	

[a]) Relative line frequencies; digital resolution ● 0.03 Hz. [b]) Upper limit of experimental error ± 0.2 ppb.

dominate. From our findings, an upper limit for $^3\Delta(^6Li)(^2H/^1H)$ of *ca.* −4 ppb per deuteron results, while for methyllithium and mixed aggregates from methyllithium and lithium iodide the geminal effect amounts to −5 to −7 ppb/^2H [2].

The symmetry of the *quintet* in *Fig. 1, b*, which was recorded under ^1H decoupling, shows that $\{^1H\}^6Li$ nuclear *Overhauser* effects are, within experimental error, absent. Otherwise, the high-field lines which are due to environments where protons dominate should show an intensity increase [2]. If ^1H decoupling is removed, the line-width does not change which indicates negligible scalar $^1H,^6Li$ spin-spin coupling, even if one remembers that the *intra*-aggregate exchange process averages possible spin-spin interactions between ^6Li and next neighbours on one side and between ^6Li and remote neighbours on the other.

Et_2O and TMEDA. As mentioned above, *Fraenkel et al.* [13] reported the observation of two ^{13}C-NMR signals in the spectral region of lithiated C-atoms for 1.0 and 0.7M samples of phenyllithium/TMEDA 1:1 in Et_2O at −75° and two signals in the corresponding ^6Li-NMR spectrum. The low-field ^{13}C signal at 187.7 ppm was identified as belonging to a dimer by its *quintet* structure and a $^{13}C,^6Li$ coupling of 8 Hz. The high-field signal at 184.5 ppm showed no coupling and was tentatively assigned to a tetramer.

Our results for the ^6Li-NMR spectrum of a 0.22M sample of C_6H_5Li/C_6D_5Li/TMEDA 1:1:2 are shown in *Fig. 2*. A *triplet* and a *doublet* is observed at 2.32 and 2.07 ppm, respectively (*Fig. 2, a*), identifing the two organolithium species as a dimer and a monomer rather than a dimer and a tetramer, respectively. The spectrum of a 2:1:3 mixture (*Fig. 2, b*) shows increasing intensities for the high-field components and establishes again a negative (low-field) $^2H/^1H$ isotope shift for the ^6Li resonance. It amounts to – 10.4 ppb for the dimer and to −6.8 ppb for the monomer. The complete data as well as the comparison between calculated and observed intensity distributions are given in *Table 3*. The sample used for the spectrum of *Fig. 2, b*, showed $\delta(^{13}C)$ values identical to those reported by *Fraenkel et al.* [13] (see *Experimental*). In addition, for a 0.5M sample of C_6H_6Li/TMEDA 1:1, we were able to resolve a 1:1:1 *triplet* structure for the high-field ^{13}C signal (*Fig. 2, c*) which yielded with $^1J(^{13}C,^6Li) = 16.0 \pm 0.2$ Hz a coupling typical for a monomer [6] [15].

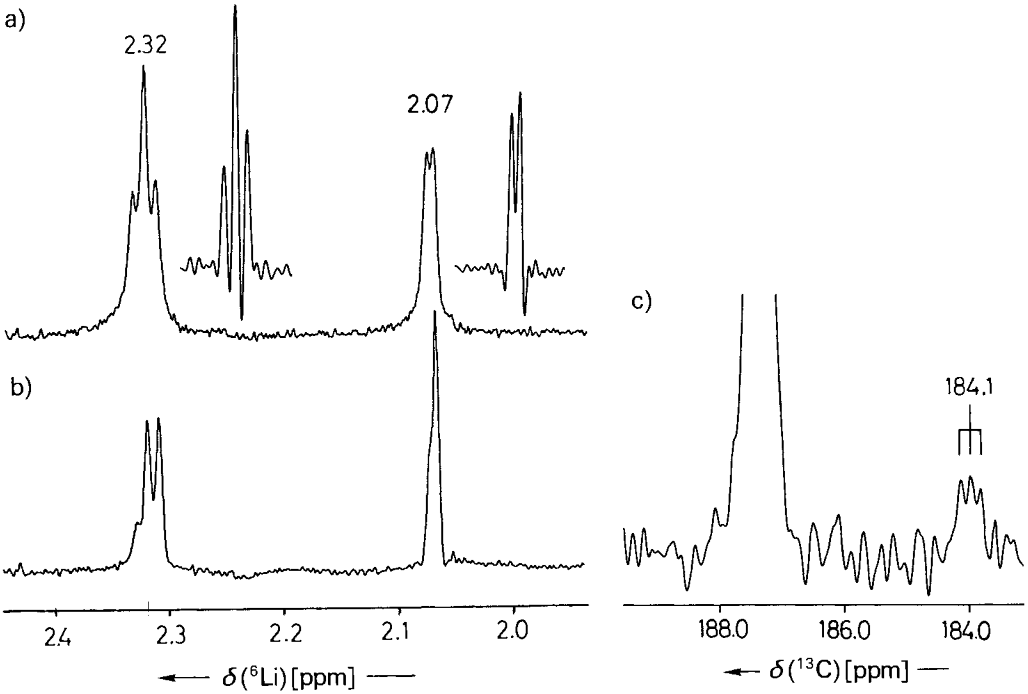

Fig. 2. a) *⁶Li-NMR Spectrum* (58.88 MHz) *of a mixture of C_6H_5Li/C_6D_5Li and TMEDA 1:1:2 in $Et_2O/(D_{10})Et_2O$ 7:3 at 162 K with gated ¹H decoupling.* At the right signals after resolution enhancement using *Gaussian* multiplication; δ scale relative to external 0.1M LiBr in THF. b) *The same spectrum for a 2:1:3 mixture.* c) *¹³C-NMR Spectrum* (100 MHz) *of C_6H_5Li/TMEDA 1:1 0.5M in $(D_{10})Et_2O$ at 173 K.* δ Scale relative to TMS.

Table 3. *Comparison of Experimental and Theoretical Relative Intensities* I *for the ⁶Li-NMR* Triplet *and* Doublet *of* Fig. 2a,b, *Measured at* T = *162 K*

a) C_6H_5Li/C_6D_5Li/TMEDA 1:1:2

	Triplet					*Doublet*		
ν/Hz[a])	0.61		0		–0.61	0.40		0
$I_{exp.}$	0.24		0.51		0.25	0.49		0.51
$I_{theor.}$	0.25		0.50		0.25	0.50		0.50
$^3\Delta$(⁶Li)/ppb[b])		–10.4		–10.4			–6.8	

b) C_6H_5Li/C_6D_5Li/TMEDA 2:1:3

	Triplet					*Doublet*		
ν/Hz[a])	0.62		0		–0.62	0.37		0
$I_{exp.}$	0.12		0.43		0.45	0.31		0.69
$I_{theor.}$	0.111		0.444		0.444	0.333		0.667
$^3\Delta$(⁶Li)/ppb[b])		–10.5		–10.5			–6.3	

[a]) Relative line frequencies; digital resolution ± 0.03 Hz.
[b]) Upper limit of experimental error ± 0.02 ppb.

THF as Solvent. Two additional ^{6}Li-NMR measurements with the $C_6H_5{}^6Li/C_6D_5{}^6Li$ mixture were made in THF as solvent. As *Fig. 3, a,* demonstrates, at 151 K, besides a broad signal at higher field, a *singlet* can be observed which shows after *Gaussian* multiplication the expected *triplet* structure for the dimer (*Fig. 3, b*). Since a dimer-monomer equilibrium was established by ^{13}C-NMR in THF by *Bauer et al.* [15] and by ^{13}C- as well as ^{7}Li-NMR by *Green* [14], the broad adsorption can be assigned to the monomer, especially since *Green* reports two broad ^{6}Li-NMR signals at 163 K and, from his ^{7}Li-NMR studies at 168 K, chemical shifts of 1.415 and 0.95 ppm (relative to external LiCl in MeOH) for the dimer and monomer, respectively. Under our conditions and due to the smaller shift difference in Hz for ^{6}Li as compared to ^{7}Li resonances, the ^{6}Li-NMR spectrum is, thus, still affected by chemical exchange between the monomer and the dimer which also explains the difficulties to resolve the *triplet* structure for the large signal.

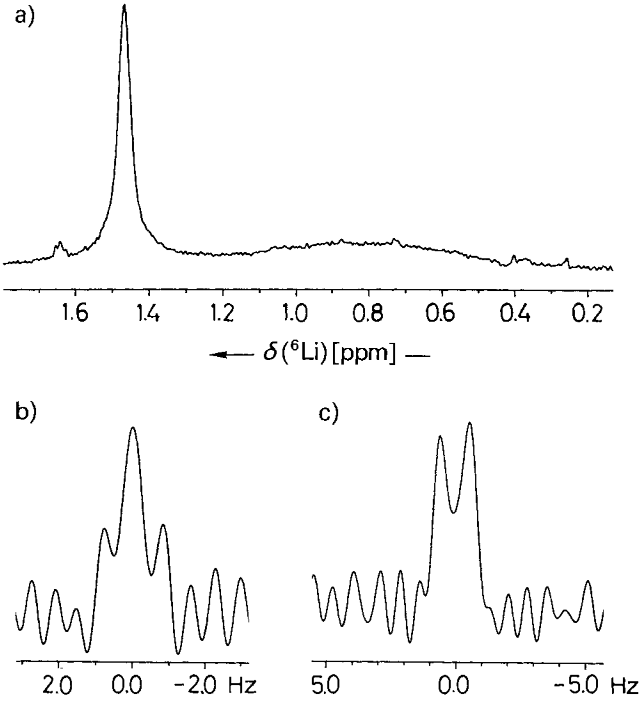

Fig. 3. *^{6}Li-NMR Spectrum* (58.88 MHz) *of an equimolar mixture of C_6H_5Li and C_6D_5Li in (D_8)THF at 151 K.* δ Scale relative to external 0.1M LiBr in THF. *a*) Total shift range; *b*) the signal at 1.46 ppm with resolution enhancement by *Gaussian* multiplication; *c*) ^{6}Li-NMR signal for a mixture of C_6H_5Li/C_6D_5Li and PMDTA 1:1:2 at 151 K with resolution enhancement as for *b*), δ(^{6}Li) = 1.96 ppm.

In a further experiment, the monomer was stabilized as described in [14] [15] by the addition of PMDTA, and the *doublet* shown in *Fig. 3, c,* was observed at δ(^{6}Li) = 1.96 ppm.

The isotope shifts measured in these two experiments were −13.2 ppb for the dimer and −19.2 ppb for the monomer. Due to the higher viscosity of THF and the effect of chemical exchange, the resolution of the small line splittings caused by the ${}^{2}H$-induced isotope shift turned ou to be more difficult than in Et_2O.

Discussion. – Our results show that ${}^{2}H$-induced isotope shifts for ${}^{6}Li$-NMR signals transmitted over three bonds can be resolved, and that valuable conclusions regarding the aggregation state of phenyllithium can be drawn from the ${}^{6}Li$-NMR fingerprints observed. All ${}^{2}H$-isotope shifts measured sofar are low-field shifts. The present results show that the magnitude of the effects varies with solvent and cluster size, but apparently not in a systematic manner. In Et_2O, we find 7.0 ppb for the tetramer and 8.3 ppb for the dimer. In the presence of TMEDA, the values are 10.4 ppb for the dimer and 6.8 ppb for the monomer. In THF, however, the isotope shift for the dimer is 13.2 ppb and for the monomer 19.2 ppb, which is surprisingly large. An interpretation of these values is difficult, because the observed effects are transmitted over three bonds, and a simple correlation with one-bond properties of the respective C–Li bonds is not possible. In addition, the influence of complexation with different solvent molecules and/or amines cannot be neglected. Nevertheless, since the structural features at the site of deuteration are kept constant, the observed variation of the isotope shift must be caused by changes in the C–Li bond.

Naively, we could expect a decrease for the total isotope shift observed in going from the static tetramer to the monomer, because in the multicenter C–Li bonds of the aggregates three ligands interact with one ${}^{6}Li$ nucleus in the tetramer, two in the dimer, and only one in the monomer. The corresponding values are obtained from the shift differences between the outer lines of the observed *multiplets*: 27.9 ppb for the tetramer, 16.3, 20.8, and 26.4 ppb for the dimer, and 6.8 and 19.2 ppb for the monomer. Due to the fast *intra*-aggregate exchange, the value for the tetramer is an average of three large effects by direct neigbours and a small or even non-existing effect of the remote neighbour. An isotope shift of *ca.* −10 ppb per C_6D_5 group then holds for all clusters as a crude estimate, if we exclude the data for the PMDTA-complexed monomer from our consideration.

Considering the three aggregates **13**–**15** where X-ray data are available for the solid – the tetramer coordinated with Et_2O [7], the dimer complexed with TMEDA [8], and the monomer complexed with PMDTA [9] – the magnitude of the observed isotope shift per neighbouring Ph group shows an inverse correlation with the average C–Li distance found in the solid: 7.0, 10.4, and 19.2 ppb *vs.* 231, 224, and 214 pm, respectively. This behaviour has been reported for one-bond isotope shifts like ${}^{1}\Delta({}^{19}F)({}^{34}S/{}^{32}S)$, ${}^{1}\Delta({}^{31}P)({}^{18}O/{}^{16}O)$, ${}^{1}\Delta({}^{31}P)({}^{15}N/{}^{14}N)$, or ${}^{1}\Delta({}^{77}Se)({}^{13}C/{}^{12}C)$ and attributed to bond order changes [16a]. The variation in ${}^{3}\Delta({}^{6}Li)({}^{2}H/({}^{1}H)$ is then due to the electronic factor, an interpretation supported by the increase of the direct ${}^{13}C,{}^{6}Li$ coupling constant in these systems, which changes from 8 Hz in the dimer [13] to 15.6 Hz in the monomer [14]. For the tetramer the coupling was never resolved, but according to the empirical correlation between aggregate size and the magnitude of ${}^{1}J({}^{13}C,{}^{6}Li)$ [6] [15], a value of *ca.* 5–6 Hz is expected. The linewidth observed for the ${}^{13}C$ resonance in our experiments at 178 K was *ca.* 30 Hz and is compatible with this value because of the expected ${}^{13}C$ *septet* (four equivalent ${}^{6}Li$ neighbours in case of fast *intra*-aggregate exchange).

If this correlation between isotope shift and scalar coupling also holds for the monomer found in Et_2O/TMEDA, the small isotope effect observed in this case (−6.8

ppb) would require a strongly reduced $^1J(^{13}C,^6Li)$ value. The experimental value of 16 Hz (see above) does not meet this expectation. Thus, a simple correlation between isotope shift and spin-spin coupling including all clusters does not exist. Two findings must remain unexplained at present: *i*) the strong difference found between the isotope shifts in the two monomers and *ii*) the shielding observed for the lithiated C-atom (C(1)) of the phenyllithium monomer in Et_2O/TMEDA, which falls with $\delta(^{13}C) = 184.1$ ppm in the region where normally, according to literature data [11–15], the C(1) resonances of dimers are found.

Experimental Part

Compounds. (D_5)Bromobenzene was synthesized from (D_6)benzene following a standard procedure [17]. (^{6}Li)Phenyllithium and (D_5,^{6}Li)phenyllithium were prepared from bromobenzene and (D_5)bromobenzene, respectively, with (^{6}Li)butyllithium in hexane as described in [9] [13] [15]. The solid precipitate formed was washed with hexane and dried under Ar. Appropriate amounts of the solid material were used to prepare the solns. for the NMR measurements. The mixtures of deuterated and non-deuterated material were either prepared by mixing appropriate solns. of the isotopically pure compounds or by carrying out the complete preparation sequence with a mixture of bromobenzene and (D_5)bromobenzene. Both procedures gave identical results. Concentrations were determined by *Gilman* titration [18] or HCl titration of a hydrolyzed sample. The solvents Et_2O and THF, mixed with 30% (D_{10})Et_2O and (D_8)THF, respectively, as lock substances were carefully degassed and dried over Na/K alloy. All operations were performed under Ar and the NMR sample cells degassed and sealed. For the spectra shown the phenyllithium concentrations are given in the legends.

Spectra. NMR Spectra were recorded with *Bruker AMX-400* spectrometer, equipped with an *ASPECT X32* computer. The ^{6}Li frequency was 58.885 MHz. To achieve high resolution, the sweep width did not exceed 100 Hz; 1-K data points were stored to avoid truncation effects (acquisition time up to 8 s) and zero-filled to 64 K. Temp. control was achieved with the *Bruker* variable-temperature unit and measured with the methanol thermometer [19]. ^{6}Li Chemical shifts were measured in a coaxial tube arrangements against external 0.1M LiBr in THF. No volume susceptibility corrections were made. For the determination of signal intensities through lineshape simulations by visual comparison between calculated and observed *multiplets*, the program GAUSSIM, written for the simulation of *Gaussian* lineshapes, was employed. It was found that this gave an improved curve fit as compared to the use of *Lorentzian* lineshapes. The theoretical intensities were calculated by the expression $(a + b)^n$, where a and b are the mole fractions of deuterated and non-deuterated material and n is the number of ligands surrounding one Li-atom ($n = 1$ for the monomer, $n = 2$ for the dimer, $n = 3$ for the static tetramer, and $n = 4$ for the dynamic tetramer).

The $\delta(^{13}C)$ values found in EtO_2/TMEDA for the two species (dimer and monomer) were as follows:

	C(1)	C(2,6)	C(3,5)	C(4)	
dimer	187.3	144.9	124.9	123.4	
dimer	187.7	145.2	125.6	124.7	[13]
monomer	184.1	144.1	125.3	124.3	
‘tetramer’	184.5	144.5	125.3	123.8	[13]

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