188. $^2H/^1H$ Isotope Shifts for ^6Li-NMR: First Experimental Detection and Applications to Structural Problems in the Field of Organolithium Compounds[1])[2])

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Dedicated to Professor *P. von Ragué Schleyer* on the occasion of his 60th birthday

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Deuterium-induced isotope effects on ^6Li chemical shifts, transmitted over two bonds, $^2\Delta(^6Li)(^2H/^1H)$, have been measured for the first time for methyllithium and the system methyllithium/lithium iodide. The observed shifts are to low field and range from 15 to 20 ppb per CD_3 group. The multiplicity and intensity distribution of the ^6Li signals resulting for mixtures of CH_3- and CD_3-containing samples in the limit of slow *inter*- as well as *intra*-aggregate exchange yield information about the size of the various clusters present in diethylether solution. It is expected that these isotope shifts can facilitate structural investigations of organolithium compounds. In some cases, the results of such measurements are expected to be less ambiguous then the conclusions based on *multiplets* that arise from scalar $^{13}C,^6Li$ spin-spin coupling.

Introduction. – Intrinsic NMR isotope effects [2] – to be distinguished from equilibrium isotope effects detected by NMR methods [3] – have found increasing attention in recent years, and in particular $^2H/^1H$ isotope shifts for ^{13}C-NMR signals emerged as important parameters in the area of organic and physical organic chemistry [2a]. In general, the substitution of ^1H by ^2H induces high-field shifts for ^{13}C resonances of C-atoms which are up to three bonds away, but four-bond effects are also found quite frequently, and, in certain cases, isotope effects transmitted even over twelve bonds have been reported [4]. In saturated systems, where one-bond effects are in the order of 0.4 ppm, the magnitude of the isotope shift is attenuated with the number of bonds separating the heavy isotope and the ^{13}C nucleus by a factor of $^1/_3$ per bond. In a few instances, low-field isotope shifts have been found. So far, additivity for intrinsic isotope shifts was observed in all cases of multiple $^2H/^1H$ substitution in equivalent positions (for example CH_2D, CHD_2, CD_3).

In connection with NMR studies of organolithium compounds [1], we became interested to investigate the occurrence of ^2H-induced NMR isotope shifts for ^6Li resonances of alkyllithium systems. If such parameters can indeed be measured, they are expected to yield new informations on structure and bonding for these important species. Until now, a theoretical study on lithium hydride had predicted that $^2H/^1H$ isotope shifts for ^6Li resonances should exist, and that the heavier isotope should cause a downfield shift as a

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[1]) NMR Spectroscopy of Organolithium Compounds, XI; earlier papers in this series: [1].

[2]) Presented in part at the '10th European Experimental NMR Conference', Veldhoven, Netherlands, 28.5.–1.6.1990.

consequence of a negative shift derivative upon bond shortening [5]. This situation is observed less frequently, since the majority of isotope shifts induced by heavier isotopes are, as in the case of ^{13}C mentioned above, to high-field. Experimentally, *Loewenstein et al.* [6] had tried to detect solvent isotope shifts on the ^{7}Li resonance of lithium chloride dissolved in H_2O and D_2O, but no effect was observed within the error limits of their measurements. Today, higher magnetic fields are available, and the chances to uncover small isotope shifts have considerably improved. A detailed investigation of the problem of ^{6}Li-NMR isotope shifts was, therefore, of interest.

Methyllithium in Et_2O. It is well known that organolithium compounds dissolved in ethereal solvents form various aggregates, and that oligomerization of simple alkyllithium compounds can be monitored by the multiplicities of the ^{13}C resonances of the lithiated C-atoms and the size of the one-bond $^{6,7}Li,^{13}C$ scalar spin-spin coupling constants [7] [8]. For methyllithium, early X-ray investigations [9] revealed a tetrameric structure for the solid, consisting of a tetrahedral arrangement of four Li-atoms with the organic ligands associated with the four faces of the metal cluster (*Fig. 1*). Recent neutron diffraction measurements [10] fully support these findings which are also corroborated by theoretical calculations at the *ab initio* level [11]. This work also showed on the basis of MNDO calculations that, in donor solvents, the tetramer is the most stable aggregate in solution, with the dimer as high-energy structure.

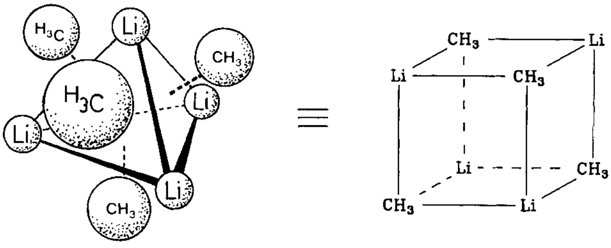


Fig. 1. *Structure of methyllithium tetramer*

On the basis of these results, the tetramer is also expected to dominate in solution, and measurements of colligative properties provided the first experimental verification [12]. Later, the tetramer was detected in a ^{7}Li-NMR study that used a sample 50% enriched in ^{13}C [13] [14]. The observed $^{7}Li,^{13}C$ scalar spin-spin coupling constant of 14.5 Hz, measured at $-70°$ in the slow exchange limit in Et_2O and THF solution, where *inter*- as well as *intra*-aggregate exchange processes are negligible on the NMR time scale, is typical for the local ^{7}Li environment in a tetrameric structure, where the metal is surrounded by three Me groups (*Fig. 1*). Similarily, each C-atom in the tetramer is surrounded by three equivalent Li-atoms, and a ^{13}C *septet* is expected for a $(^{6}LiCH_3)_4$ species with a coupling of *ca.* 5.5 Hz ($I(^{6}Li) = 1$), but this measurement has so far, to the best of our knowledge, not been reported.

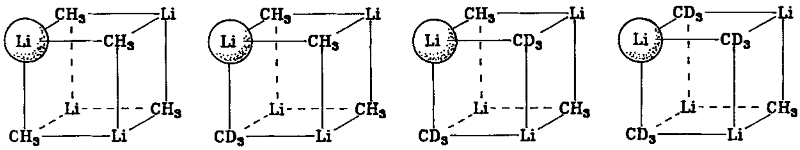
In the meantime, $^{6,7}Li$- and ^{13}C-NMR methods have developed into the most powerful tools for structure elucidations of organolithium compounds in solution [1c] [1h] [15]. While the natural abundance of ^{6}Li is only 7.6%, full enrichment is easily achieved, and a variety of 1D- and 2D-NMR experiments can be performed for $^{6}Li,^{13}C$ as well as $^{7}Li,^{13}C$ spin systems. As far as scalar spin-spin interactions are concerned, the multiplicity *m* of

^{13}C signals in oligomers of organolithium compounds corresponds to the general rule $m = 2nI + 1$, where n is the number of equivalent ^{6,7}Li neighbours and I the spin quantum number (I = 1 for ^{6}Li, I = $\frac{3}{2}$ for ^{7}Li). On the other hand, ^{13}C enrichment is less feasable, and there is usually only one ^{13}C that causes detectable splittings of ^{6,7}Li signals, which leads to weak (0.5% rel. intensity) satellite lines in the ^{6,7}Li-NMR spectra [16].

Related rules with respect to signal multiplicity and intensity distributions may be developed, if the possibility of isotope shifts for ^{6,7}Li resonances is considered. Here, however, only ^{2}H/^{1}H-induced isotope shifts are expected to yield an observable effect, because, as a consequence of the smaller mass ratio and the relatively small shift scale of both lithium nuclides, ^{13}C/^{12}C isotope effects should be difficult to detect. Furthermore, the restrictions due to low natural abundance is much easier lifted in practice through deuteriation than through ^{13}C labelling. Thus, in methyllithium, for a ^{2}H/^{1}H-NMR isotope effect over two formal bonds, we may expect, on the basis of the structure shown in *Fig. 1* and the selected aggregates drawn in *Fig. 2*, different resonances for the following local Li environments:

$[CH_3,CH_3,CH_3]$	$[CH_3,CH_3,CD_3]$	$[CH_3,CD_3,CD_3]$	$[CD_3,CD_3,CD_3]$
1a	**1b**	**1c**	**1d**

If the effect of the 'remote' neighbour is neglected, a 1:1 mixture of labelled and unlabelled methyllithium should then show, according to straightforward statistics, four resonances in the ratio 1:3:3:1. This is indeed found, as the experiments described below demonstrate.



1a 1b 1c 1d

Fig. 2. *Selected tetramer structures for an equimolar mixture of CH_3Li and CD_3Li*

Results and Discussion. – ^{2}H-labelled and non-labelled methyllithium was prepared from CD_3Cl and CH_3Cl, respectively, in Et_2O. ^{6}Li metal was used in order to take advantage of the better resolution attainable for the NMR spectra of this spin-1 nucleus with its very small quadrupole moment, even if the smaller shift range compared to ^{7}Li should lead to smaller isotope effects [17]. The solvent was removed under reduced pressure and replaced by a mixture of $Et_2O/(D_{10})Et_2O$ 7:3 in order to produce 0.1 to 0.2M solutions. A sample with a molar ratio CH_3Li/CD_3Li 1:1 was prepared by mixing appropriate amounts of the two solutions and used for NMR spectroscopy at low temperature. The ^{13}C{^{1}H}-NMR spectrum was observed at –77° (*Fig. 3(a)*) and showed, under ^{1}H as well as ^{2}H decoupling (*Fig. 3(b)*) the expected high-field '*doublet*' for the $^{13}CH_3$ and $^{13}CD_3$ resonance at –13.26 and –14.56 ppm relative to TMS, respectively. The shift difference of 1.30 ppm or 0.43 ppm per ^{2}H is in the right order for a one-bond ^{2}H/^{1}H ^{13}C isotope shift [2]. Moreover, in a separate measurement with improved resolution, the ^{13}C *septet* due to ^{13}C,^{6}Li coupling was observed (*Fig. 3(c)*). The signal multiplicity as well as the coupling constant of 5.7 ± 0.2 Hz prove the presence of the methyllithium tetramer in the slow exchange limit, and the latter compares well with the ^{7}Li,^{13}C coupling reported earlier [13] [14] (*cf.* above), if the different γ factors for ^{6}Li and ^{7}Li are taken into account.

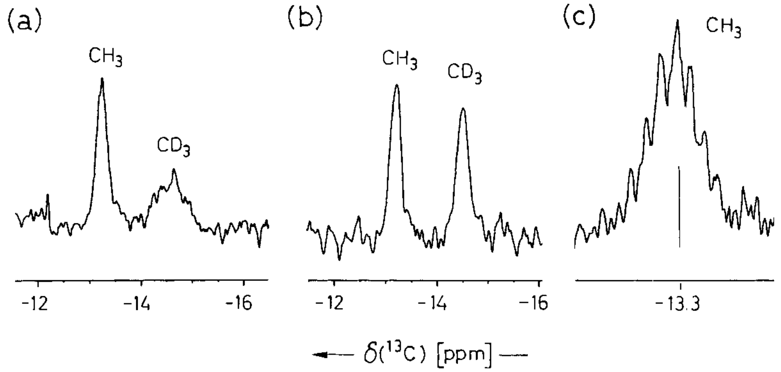


Fig. 3. *100-MHz ^{13}C-NMR spectra of an equimolar mixture of CH_3Li and CD_3Li in the slow-exchange limit at −77°;* a) *with ^{1}H decoupling;* b) *with ^{1}H and ^{2}H decoupling;* c) *^{1}H-decoupled ^{13}C* multiplet *of CH_3Li tetramer*

The ^{6}Li-NMR spectrum of the same sample (*Fig. 4(a)*), recorded at −92°, showed the methyllithium tetramer as the main signal at 2.48 ppm (relative to external 0.1M LiBr in THF), besides some smaller signals most probably due to mixed aggregates which were formed as a consequence of the presence of small amounts (*ca.* 10%) of LiCl or to decomposition products. The important finding is the fine-structure of the tetramer signal, which is revealed from the broadened signal (*Fig. 4(c)*) as the expected *quartet*, if

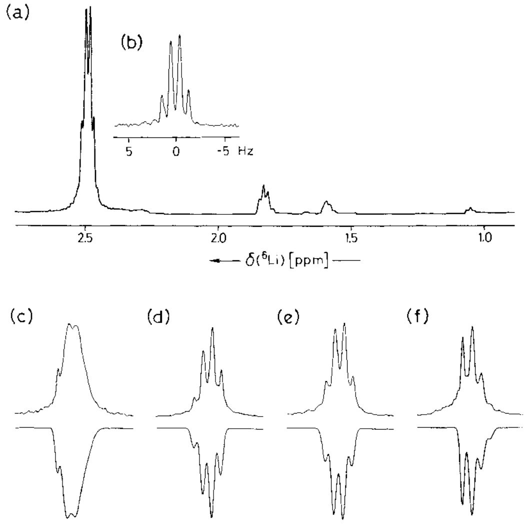


Fig. 4. *58.885-MHz ^{6}Li-NMR spectra of an equimolar mixture of CH_3Li and CD_3Li in the slow-exchange limit at −92°;* a) *total shift range with inverse-gated ^{1}H decoupling;* b) *tetramer signal as in* e) *with resolution enhancement;* c) *^{1}H-coupled tetramer signal;* d) *^{1}H-decoupled tetramer signal;* e) *tetramer signal with inverse-gated ^{1}H decoupling;* f) *tetramer signal of a 3:7 mixture of CH_3Li and CD_3Li*

^1H decoupling is used (*Fig. 4(d)*). The distorted intensity ratio, which is due to the well-known $\{^1H\}^6Li$ nuclear *Overhauser* effect [18], is removed through inverse-gated decoupling (*Fig. 4(e,b)*), where the decoupler is on during data acquisition. The isotope effect measured amounts to -15.6 ± 0.3 ppb and observes additivity within the error limits. The sign can be inferred from the partial broadening seen in the ^1H-coupled ^6Li signal (*Fig. 4(c)*), which must clearly be attributed to the high-field signals. It disappears with ^1H decoupling and is, thus, due to unresolved $^6Li,^1H$ scalar spin-spin coupling. Consequently, the high-field lines, which also show heteronuclear $\{^1H\}^6Li$ *Overhauser* enhancement (*Fig. 4(d)*) correspond to local ^6Li environments of type **1a**, **1b**, and **1c** (*Fig. 2*), and the observed isotope shift is a down-field shift. Independent support for this assignment comes from a spectrum with a CH_3Li/CD_3Li mixture of molar ratio of 3:7, which is shown in *Fig. 4(f)*. Here, the low-field lines gain in intensity relative to those at high field.

Our results, thus, demonstrate that $^2H/^1H$ isotope shifts for ^6Li resonances of organolithium compounds indeed exist, and that the observed multiplicity correlates with the size of the particular aggregate. The isotope shift over two bonds is negative[3]) and amounts to -5.2 ppb per ^2H. Using a curve-fitting procedure (*cf. Experimental*), a signal intensity ratio of 1.14:2.71:2.90:1.26 was determined for the *multiplet* recorded with inverse-gated ^1H decoupling (*Fig. 4(e)*). This result deviates from the statistical 1:3:3:1 ratio, but we doubt that this can be attributed to an equilibrium isotope effect. Various reasons for experimental errors must be considered, the two main sources being the *Gilman* titration of the methyllithium solutions and the error in the line fitting procedure. For both aspects, a rigorous error analysis is not feasable. In any case, the resulting errors are certainly much larger than intensity changes caused by a possible equilibrium isotope effect, and we believe that the ratio found experimentally can be taken as strong indication for a situation which is identical with or close to the statistical distribution. This view is also supported by the fact that the data yield intensities for the two small lines at highest and lowest field which are too high. An equilibrium isotope effect, however, should lead to a large intensity difference in particular for these lines and to an intensity of < 1 for one of these signals.

From a comparison of the line intensities determined for the tetramer signal recorded with standard ^1H decoupling (1.14:3.76:5.16:2.70) and with inverse-gated ^1H decoupling (see above), an estimation of the $\{^1H\}^6Li$ nuclear *Overhauser* effect was possible. The low-field line, which corresponds to environment **1d**, where NOE effects from a CH_3 group as a possible remote neighbour due to their r^{-6} dependence are small[4]), was taken as reference. With the relation $\eta = (I - I_0)/I_0$ dimensionless values of 0.39, 0.78, and 1.15 resulted for the NOE of the lines at higher field corresponding to environments **1c**, **1b**, and **1a**. This yields a constant enhancement of 38% per CH_3 group. *Wehrli* [18] found at room temperature 70% as an overall effect, which is 20% of the theoretical value.

It is interesting to note that the ^6Li isotope shift, as the scalar $^{13}C,^6Li$ and $^1H,^6Li$ spin-spin coupling, is also transmitted through the multiple-center Li–C bond which is

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

[4]) For a cube of edge a, the distance to the remote CH_3 group is $a\sqrt{3}$. Compared to the next neighbour, the NOE effect is thus attenuated by $1/(\sqrt{3})^6$ or 1/27.

believed to be highly ionic [19]. From a line shape simulation of the ^{1}H-coupled ^{6}Li resonance (*Fig. 4(c)*), we derive 0.34 ± 0.07 Hz as an estimate for the geminal ^{1}H,^{6}Li coupling in the present case. An independent measurement with non-labelled material yielded 0.34 ± 0.02 Hz. The existence of scalar ^{1}H coupling to ^{6}Li and ^{7}Li was derived earlier by *Brown* and *Ladd* [20] from line-width considerations for ethyllithium, but a line splitting due to $J(^7\mathrm{Li},^1\mathrm{H})$ was observed only recently in the case of an iridium lithium hydride complex [21].

Furthermore, there is no indication of a ^{13}C isotope shift over more than one bond, which should lead to additional signals. While small line splittings could be hidden in the rather broad signals of *Fig. 3(b)*, the resolution of the *septet* in *Fig. 3(c)* clearly speaks against overlapping resonances for different C environments. Thus, ^{2}H/^{1}H isotope shifts on ^{13}C resonances are apparently not transmitted through the C–Li multiple-center bond.

Another important aspect of the present finding is the fact that the observed multiplicity of the ^{6}Li signal is only compatible with a static structure of the tetramer, where both *intra*- and *inter*-aggregate exchange is slow. Thus, the signals observed correspond to individual Li environments and not to individual aggregates. If only *inter*-aggregate exchange were slow (dynamic structure), the 'remote' neighbours could contribute to the isotope effect, and an average value over all Li positions in one particular aggregate should result. In this case, five lines with an intensity distribution of 1:4:6:4:1 must be found. This situation is easily distinguished from the observed 1:3:3:1 *multiplet*. ^{6}Li isotope shifts are, thus, better suited to decide between a static and a dynamic structure with *intra*-aggregate exchange than the ^{6}Li,^{13}C spin-spin coupling constants, because the ^{13}C spin *multiplets* for these two situations have intensity distributions of 1:3:6:7:6:3:1 and 1:4:10:16:19:16:10:4:1, respectively, which, for reasons of sensitivity, are difficult to discriminate.

The System CH_3Li/LiI. The structure of mixed aggregates between organolithium compounds and lithium halides bears on the reactivity of organolithium reagents [22] and was investigated by NMR some years ago by *Novak* and *Brown* [23]. These authors measured 38.863-MHz ^{7}Li- and 220-MHz ^{1}H-NMR spectra of mixed complexes between methyllithium and LiI in Et_2O and found at −70° low-field from the ^{7}LiI signal three broadened lines which they attributed, on the basis of a tetrameric structure, to the local environment [CH_3,$CH_3$$CH_3$] of the aggregate $Li_4(CH_3)_3I$, to the same local environment of $Li_4(CH_3)_4$, and to the local environment [CH_3,CH_3,I] in the aggregate $Li_4(CH_3)_3I$ (from low to high magnetic field).

The present results for the same system are shown in *Fig. 5(a)*. For reasons of resolution, we used again ^{6}Li species. In addition to the main peaks at 2.18, 2.06, 1.33, and 0.22 ppm relative to 0.1M LiBr in THF already described for the ^{7}Li-NMR spectrum [23], we find, aside from some minor lines due to impurities and/or higher aggregates[5]), an additional absorbtion at 0.62 ppm. This signal was not seen in the earlier work, because, as one can infer from the broadened spectrum, the system was still under exchange. Since our measurements were performed at lower temperature (−95°), and the higher field strength (58 MHz) nearly sets off the disadvantage of the lower $\gamma(^6\mathrm{Li})$ factor, conditions for slow exchange were better met in our case. Thus, an additional Li site must be present.

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[5]) According to *McGarrity* and *Ogle*, aggregates of organolithium compounds easily incorporate hydrolysis products or basic impurities [24].

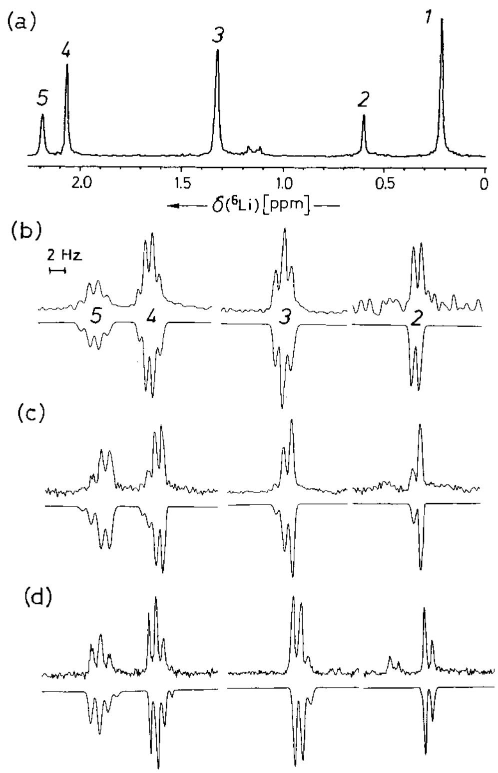

Fig. 5. *58.38-MHz* ^{6}*Li-NMR spectrum of* CH_3Li/*LiI mixtures in the slow-exchange limit at* –95°; a) *total shift range, external reference 0.1*M *LiBr in THF;* ^{1}*H-coupled;* b) – d) *fine structure of signals 2–5 for samples with partial* ^{2}*H labelling observed under conditions of inverse-gated* ^{1}*H decoupling to avoid NOE effects* (molar ratio CH_3Li/CD_3Li 1:1, 7:3, and 3:7, respectively)

For the assignment of the various absorptions to individual ^{6}Li environments, we consider first for simplicity without proof tetrameric structures as in the case of methyllithium (see above) with the next neighbour arrangements **2a–d**:

[I,I,I]	[I,I,CH_3]	[I,CH_3,CH_3]	[CH_3,CH_3,CH_3]
2a	**2b**	**2c**	**2d**

While *Novak* and *Brown* [23] used the intensity changes observed by changing the concentration of LiI – which by itself provide direct evidence for the formation of mixed aggregates –, we tried first to derive an independent assignment on the basis of the NOE factors obtained from a comparison of the ^{1}H-decoupled and ^{1}H-coupled ^{6}Li spectra. The results are given in *Table 1*.

These data show increasing NOE effects from high to low field which clearly demonstrate the increasing number of CH_3 neighbours and lead to the indicated assignment. Clearly, the two absorptions at lowest field both correspond to local environments of type **2d** and must, therefore, arise from aggregates with different remote neighbours as in **2e** and **2f**:

[CH_3,CH_3,CH_3]CH_3	[CH_3,CH_3,CH_3]I
2e	**2f**

Table 1. *Nuclear* Overhauser *Enhancement* (NOE) *Measured for Local ^{6}Li Environments in Aggregates of CH_3Li and LiI From the ^{6}Li-NMR Spectrum of* Fig. 5(a)

Signal	*1*	*2*	*3*	*4*	*5*
δ [ppm][a])	0.22	0.62	1.33	2.06	2.18
Relative intensity[b])	1.0	0.284	0.638	0.299	0.186
NOE	0[c])	0.17	0.37	0.74	0.69
Number of next CH_3 neighbour	0	1	2	3	3
NOE/CH_3		0.17	0.18	0.25	0.23
Assignment of ^{6}Li environment	**2a**	**2b**	**2c**	**2d** **2e**	**2d** **2f**

[a]) Relative to 0.1M LiBr in THF.
[b]) Without NOE effect.
[c]) Reference signal of ^{6}LiI.

The high-field signal apparently shows an additional small NOE contribution and can, thus, be assigned to environment **2e**, where a remote CH_3 group can contribute to the signal enhancement. Additional arguments result from the isotope shift and the relative intensity of these signals as discussed below.

If a 1:1 mixture of CH_3Li/CD_3Li and LiI is now investigated, the interesting aspect of the spectrum lies in the fine structure of the individual absorptions (*Fig. 5(b)*). Again, as in the case of the methyllithium experiment described above, each multiplet component corresponds to a different local environment. However, three species are now in competition: CH_3, CD_3, and I. Accordingly, the spectrum of labelled material (*Fig. 5(b)*), measured with the inverse-gated ^{1}H-decoupling technique in order to avoid line broadening due to ^{6}Li,^{1}H spin-spin coupling and intensity distortions due to $\{^1H\}^6Li$ NOE effects, shows a 1:1 *doublet* for environment **2b**, a 1:2:1 *triplet* for environment **2c**, and two 1:3:3:1 *quartets* corresponding to an environment of type **2d**. The individual isotope shifts are given in *Table 2*.

Table 2. *$^2H/^1H$ Isotope Shifts for ^{6}Li-NMR, $^2\Delta(^6Li)$* (in ppb, upper limit of exper. error ± 0.2 ppb) *Measured for Mixed Aggregates of CH_3Li/CD_3Li and LiI from the Spectrum Shown in* Fig. 5(b)

Signal	*2*	*3*	*4*	*5*
$^2\Delta(^6Li)$	15.0	20.0/19.3	15.9/16.0/16.2	19.2/19.6/20.0

The observation of *two quartets* at lowest field again requires the presence of two species with a nearest neighbour arrangement [CH_3,CH_3,CH_3] but with a different remote neighbour. Therefore, environments **2e** and **2f** with either CH_3/CD_3 or I as remote neighbours have a different ^{6}Li shift, as already suggested by *Novak* and *Brown* from their ^{7}Li study, and the assignment given in [23] is verified by our results. Apart from the NOE results discussed above and from the analysis of the intensity distribution to be given below, the isotope effect measured for the high-field *quartet*, which is identical with the isotope shift found for CH_3Li/CD_3Li (see above), strongly supports this conclusion.

Let us now ask which aggregates must be present to explain the experimental findings. *Novak* and *Brown* concluded from their results that besides LiI, for which a dimerization was indicated by differential vapor-pressure measurements [23], only the tetramers $Li_4(CH_3)_4$ and $Li_4(CH_3)_3I$ are present. Our findings verify the presence of both aggregates, reproduced as **A** and **B**, respectively, in *Fig. 6*, since the local environment **2d** secured for signals *4* and *5* can only arise from a tetrameric structure. Signal *3* arises from the neighbour arrangement **2c**. If this signal originates entirely from aggregate **B**, its intensity *I*(*3*) should not exceed three times the intensity of signal *5*. Contrary to *Novak* and *Brown*, we find *I*(*3*) > 3 × *I*(*5*) (*Table 1*), and an additional aggregate must be present. In principle, a methyllithium dimer could account for this intensity increase on the basis of the observed multiplet for the CH_3Li/CD_3Li mixture (*Fig. 5(b)*), but such a structure is not stable, and a mixed tetramer of structure **C** (*Fig. 6*) must exist.

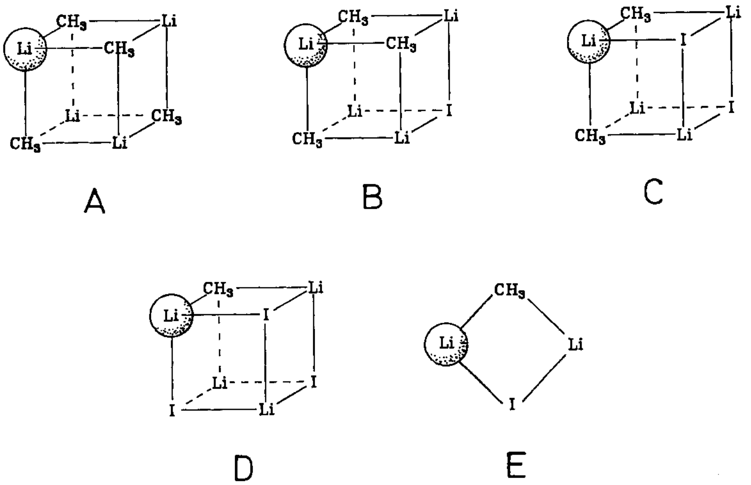

Fig. 6. *Aggregates present in a mixture of $CH_3Li/CD_3Li/LiI$ 1:1:2 in Et_2O at −95° with selected ^6Li sites*

Considering next signal *2* (environment **2b**), a mixed dimer of structure **E** would explain the *doublet* for the corresponding ^6Li signal in *Fig. 5(b)* equally well, but the observed high-field shift supports the tetrameric structure **D**. For the selected ^6Li site in *Fig. 6*, we find a shift increment of −0.85 ppm in going from aggregate **B** to **C**. The shift difference between signal *3* and *2* is −0.71 ppm, compatible with the transition from aggregate **C** to **D**. In contrast, the final step to signal *1*, which is presumably due to $(LiI)_2$, yields only −0.40 ppm.

On the basis of the integrated signal intensity given in *Table 1* and the origin of the observed ^6Li signals, we can also derive mole fractions for aggregates **A**–**D** and LiI. Evidently, signal *4* can only come from aggregate **A**. Similarily, signal *5* is due only to environment **2d** in aggregate **B**, which, however, also contains environment **2c** (signal *3*) in a ratio fo 3:1 relative to **2d**. Thus, if we substract three times the intensity of signal *5* from the intensity of signal *3*, we are left with the contribution of the environment **2c** which stems from aggregate **C**. Aggregate **C**, in turn, contains two Li sites with environment **2b** which gives rise to signal *2*. The additional intensity of signal *2* originates from aggregate **D**. Finally, the Li site of **D** corresponding to environment **2a** contributes to signal *1*, which also arises from LiI. The mole fractions (in %) for aggregates **A**–**D** and LiI derived in this way are **A**:**B**:**C**:**D**:LiI 12.4:30.9:6.7:11.3:38.7. This result is compared in *Fig. 7* with the expectation based on statistical considerations [23] alone. It shows relatively large differences for the mole fractions of LiI and aggregate **C**. A closer inspection of our sample revealed a pronounced temperature dependence of the signal intensities. While the data given in *Table 1* and *Fig. 7(a)* were obtained *ca.* 5 min after inserting the sample into the precooled spectrometer probe, a new measurement after 60 min yielded the results shown in *Fig. 7(b)*. It shows that aggregate **C** nearly disappeared by crystallization, suggested by the precipitate observed in the sample tube. This might be the reason for the failure of the earlier work [23] to detect aggregate **C**. At the same time, it prevents us to derive relative energies for the various aggregates from the present results.

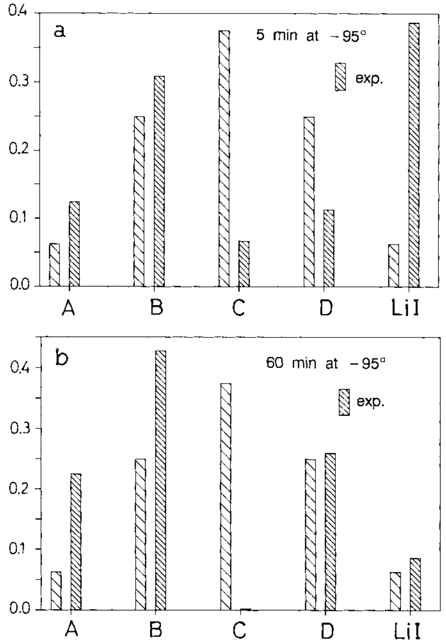

Fig. 7. *Mole fractions of aggregates* **A**–**D** *and LiI as determined from the integration of the* ^{6}*Li-NMR spectrum* (left bar statistical ratio, right bar experimental). *a)* After *ca.* 5 min at –95°: **A**/**B**/**C**/**D**/LiI=12.4/30.9/6.7/11.3/38.7 (in mol-%, integrals see *Table 1*); *b)* after *ca.* 60 min at –95°; **A**/**B**/**C**/**D**/LiI = 22.5/42.8/0.2/26.0/8.6. (in mol-%, rel. integrals *1*/*2*/*3*/*4*/*5* = 0.15/0.19/0.32/0.23/0.11); the statistical ratio is in both cases 6.25/25.0/37.5/25.0/6.25.

The intensity considerations discussed above also yield an additional support for the assignment of environments **2e** and **2f** to signal *4* and *5*, respectively, since the intensity of signal *4* is too large to match the intensity of signal *3*. Thus, only those aggregates with direct Li,I contact lead to a high-field shift and a heavy-atom effect for the ^{6}Li resonance.

It has to be emphazised, that the aggregate structures of *Fig. 6* are only schematic representations. Clearly, the different size of the CH_3 and I particles (*Pauling van-der-Waals* radii for the neutral systems are 200 and 215 pm, respectively [25]) will introduce strong deformations. Even the substitution of CH_3 by CD_3 might slightly change the nuclear distances. It is thus not surprising that $^2\Delta$(^{6}Li) differs for arrangement **A** and **B** (signal *4* and *5*, *Table 2*). The data for the **B** *multiplet* also indicate a small but steady increase of $^2\Delta$(^{6}Li) with the number of CD_3 groups. Thus, the additivity observed for methyllithium (see above) and aggregate **A** seems violated. This might be attributed to structural distortions arising for **B** as a consequence of the presence of the large iodine ion.

The intensity ratios for the individual *multiplets* observed for the 1:1, 7:3, and 3:7 mixture of CH_3 and CD_3 containing material shown in *Fig. 5(b–d)* were again determined by curve analysis. In *Table 3*, the results are compared with the theoretical predictions derived on the basis of the statistical factor and the relative intensity of the various absorptions.

Table 3. *Relative Intensities of Components of Cluster Multiplets for Mixtures of $CH_3Li/CD_3Li/LiI$ Shown in* Fig. 5(b–d)

		Signals			
CH_3Li/CD_3Li		*2*	*3*	*4*	*5*
1:1	Exper.	0.46/0.54	0.23/0.46/0.32	0.09/0.34/0.38/0.19	0.11/0.30/0.39/0.20
	Theor.	0.5/0.5	0.25/0.50/0.25	0.125/0.375/0.375/0.125	0.125/0.375/0.375/0.125
7:3	Exper.	0.27/0.73	0.09/0.38/0.54	0.06/0.18/0.38/0.37	0.0/0.17/0.42/0.41
	Theor.	0.3/0.7	0.09/0.42/0.49	0.03/0.19/0.44/0.34	0.03/0.19/0.44/0.34
3:7	Exper.	0.67/0.33	0.49/0.43/0.09	0.32/0.45/0.21/0.02	0.36/0.42/0.19/0.03
	Theor.	0.7/0.3	0.49/0.42/0.09	0.34/0.44/0.19/0.03	0.34/0.44/0.19/0.03

In conclusion, the ^2H-labelling technique introduced here, which is in a way related to the SIMPLE-NMR method used for ^{13}C assignment in carbohydrates and polyalcohols [26] [27] and to the observation of spin *multiplets* caused for ^{59}Co resonances by H/D exchange in ethylenediamine ligands [28], constitutes a new tool for structure elucidations in the field of organolithium compounds. The relatively small line-width of ^6Li-NMR signals is favourable for the observation of small isotope shifts, and a number of promising applications, especially in the field of mixed aggregates, can be envisaged. A major advantage of the present approach as compared to the use of $^6Li,^{13}C$ spin-spin coupling must be seen in the ease of isotopic double-labelling (^6Li and ^2H) which reduces the sensitivity problem of the NMR method considerably.

Experimental. – *Compounds.* A soln. of MeLi in Et_2O with a low LiCl content was prepared from CH_3Cl by reaction with ^6Li powder as described in [29]. For the deuterated sample, CD_3Cl was synthezised from CD_3OD and $AlCl_3$ [30]. The MeLi concentrations were determined by the *Gilman* procedure [31]. The mixed aggregates $CH_3Li/CD_3Li/LiI$ were prepared in the NMR tube by direct reaction of the appropriate amounts of CH_3I/CD_3I with ^6Li powder in $Et_2O/(D_{10})Et_2O$ 7:3. All sample cells were degassed and sealed. The solvents were carefully degassed and dried over Na/K alloy. All operations were performed under Ar.

Spectra. NMR spectra were recorded with *Bruker WH-400* and *AMX-400* spectrometers, equipped with an *ASPECT 2000* and an *X32* computer, respectively. The ^6Li frequency was 58.38 and 58.885 MHz, respectively. Temp. control was achieved with the *Bruker* unit and measured with the methanol thermometer [32]. For lineshape simulations, the program GLINFIT (ABACUS library of *Spectrospin AG*, Zürich, author *A.D. Bain*) was used.

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