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Structural investigation of aryllithium clusters in solution

I. A ^{13}C and ^{7}Li NMR study of phenyllithium and some methyl-substituted phenyllithium derivatives

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Abstract

^{13}C and ^{7}Li NMR spectra of phenyllithium and several methyl substituted phenyllithium derivatives have been recorded in the presence of known amounts of coordinating solvents such as monodentate diethyl ether and THF and the potentially bidentate TMEDA (tetramethylethylenediamine). The relative amounts of the tetrameric and dimeric aggregates identified in these spectra depend on the donor strength, on the amount and denticity of added donor, and the presence or absence of *ortho* substituents in the phenyl group. Discrete solvated tetrameric aggregates were formed upon addition of exactly one equivalent of the monodentate donor solvent to an aryllithium compound having no *ortho* substituents; the addition of either two equivalents or excess of monodentate donor solvent or one equivalent of bidentate donor ligand afforded dimeric species. When one or two methyl substituents were present *ortho* to the lithium–carbon bond, either a mixture of dimeric and tetrameric species was formed (one methyl group) or the dimeric species was exclusively formed (two methyl groups).

Introduction

Recent X-ray [1–19], NMR [20–39] and colligative [40] studies have shown that alkyl-, aryl- and alkynyl-lithium compounds can exist in a variety of structural forms. In particular carbon–lithium interactions of two main types have been

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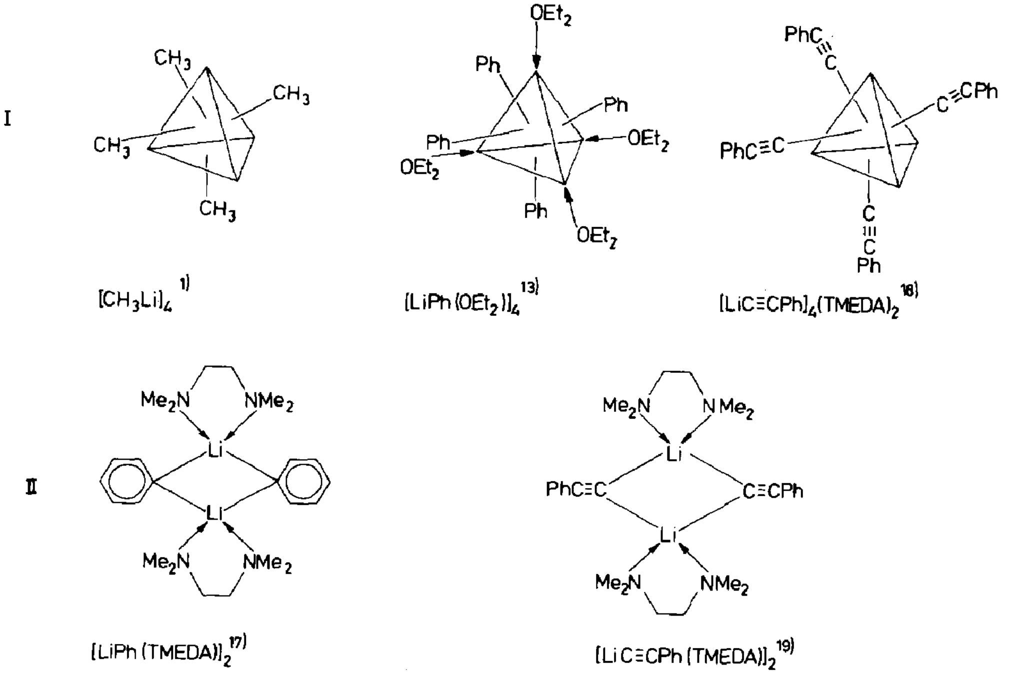


Fig. 1. Some representative organolithium structures showing the two different types of carbon–lithium interaction.

found: type I is found in clusters in which the organic group (R) is four-centre, two-electron bonded to three lithium atoms, and type II is found in dimers, in which this group is three-centre, two-electron bonded to two lithium atoms.

Figure 1 shows representative structures, established by single crystal X-ray studies, of lithium species containing methyl, phenyl and phenylethynyl groups.

Each structure of an organolithium compound with a type I interaction contains a CLi_3 unit. The tetrameric species involve a regular Li_4 tetrahedron, and the hexamers have a folded chair conformation. The open coordination positions at the lithium atoms in these clusters are occupied either by an additional nucleophile, which in some cases is a Lewis base (e.g. Et_2O in $[LiPh(Et_2O)]_4$ [13]), or by a H–Li interaction (e.g. $[LiMe]_4$ [1] or $[LiC_6H_{11}]_6$ [6]), although the existence of the latter is a subject of discussion [3].

A change of the four-centre, two-electron CLi_3 building block into a three-centre two-electron CLi_2 unit usually occurs when two monodentate donor solvents (S) such as Et_2O [10] and THF, or one bidentate ligand like TMEDA [17] coordinate to the lithium centre. In both type I and type II interactions a common feature of the organic groups is their bonding to the lithium core with a molecular orbital that has axial symmetry. For the aryllithium compounds it is noteworthy that the type of interaction (I or II) does not affect the ability of the phenyl ring to rotate about the C(1)–C(4) axis, since the overlap in the $C–Li_n$ MO is the same for all rotamers. However, steric effects caused by an *ortho* substituent can give rise to various rotamers having different populations. An additional contribution to the three-centre, two-electron bonding can be expected in aryllithium dimers with type II interactions where the aryl rings are perpendicular to the Li–Li vector (see, for example, ref. 49).

For compounds having either type I or type II interactions, it can be concluded that (i) a lithium atom tends to maximise the number of contacts with the negatively charged carbon atoms, and, (ii) a lithium atom strongly prefers a tetrahedral coordination environment (vide infra).

From the point of view of organic synthesis, it is of interest to study the implications of the different structural possibilities for the reactivity of the organolithium compounds, and so many groups have put considerable effort into elucidating structural aspects of organolithium reagents [41–43].

Up to now solution studies have almost always been carried out either in non-coordinating solvents (benzene or toluene) or in the presence of an excess of coordinating molecules. For example, the elegant ^{13}C and ^{6}Li NMR measurements on ^{13}C enriched organolithium compounds by Seebach et al. were carried out in pure THF [31]. These approaches were also used by Snaith et al. in their recent investigation of the structures of amido- and imido-lithium compounds [44a,b].

We have chosen a different approach in our study of the influence of coordinating molecules on the structure of organolithium compounds. In the present work, the structures of pure organolithium compounds in non-coordinating solvents have been investigated by ^{13}C and ^{7}Li NMR spectroscopy. The structural changes caused by subsequent addition of stoichiometric amounts of coordinating molecules were then studied.

In our previous research on the structures of organolithium compounds containing a built-in potentially-coordinating ligand we studied the formation and presence of aryllithium dimers in solution by ^{13}C NMR spectroscopy [9]; for both $[Li\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}]_2$ and $[Li\{C_6H_4(CH_2NMe_2)\text{-}2\}(THF)_2]_2$ the ^{13}C resonance of the aryl C(1) nucleus is observed as a seven-line pattern resulting from its coupling to two equivalent lithium atoms ($^{1}J(^{13}C,^{7}Li)$ 20 Hz). Furthermore, the ^{7}Li NMR spectra show that $[Li(C_{10}H_6NMe_2\text{-}8)(Et_2O)]_2$ exists in solution in equilibrium with an unsolvated organolithium species $[Li(C_{10}H_6NMe_2\text{-}8)]_n$ [10].

The present study was initiated by the striking similarity between solid state structures of $[Li\{C_6H_4(CH_2NMe_2)\text{-}2\}]_4$ and $[LiPh(Et_2O)]_4$ that both contain a regular Li tetrahedron with four-centre, two-electron bonded aryl groups. In $[LiPh(Et_2O)]_4$ the fourth coordination site of each lithium is occupied by a solvent molecule, whereas in $[Li\{C_6H_4(CH_2NMe_2)\text{-}2\}]_4$ this site is occupied by the internal amino ligand that can be regarded as a suitably placed solvent molecule. The presence of this built-in ligand gives $[Li\{C_6H_4(CH_2NMe_2)\text{-}2\}]_4$ the special property that its structure is retained in diethyl ether.

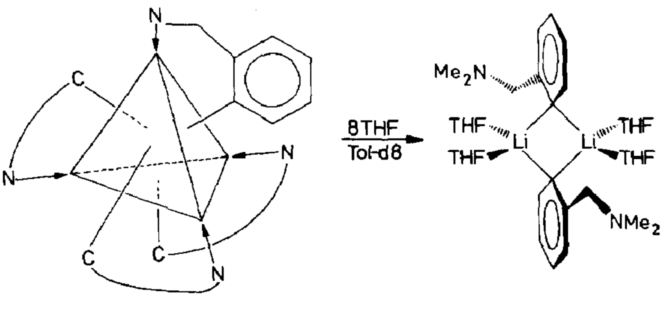


Fig. 2. Cluster break-down of $[Li\{C_6H_4(CH_2NMe_2)\text{-}2\}]_4$ in the presence of THF.

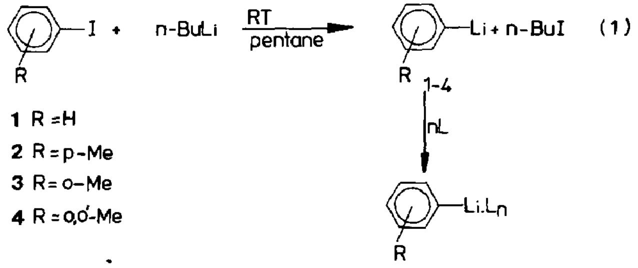
It is only in the presence of strongly coordinating solvents such as THF that the intra-aggregate solvation in $[Li\{C_6H_4(CH_2NMe_2)\text{-}2\}]_4$ is replaced by external solvent coordination. Concomitant break-down of the tetranuclear structure then occurs, to afford a dinuclear structure with uncoordinated $\text{-}CH_2NMe_2$ substituents. Since in this latter case the uncoordinated $\text{-}CH_2NMe_2$ group is a bulky *ortho* substituent whose influence on the relative stability of the tetra- and di-nuclear species is unknown, we studied the structural aspects of a series of selected *ortho*-methyl substituted phenyllithium compounds following the approach outlined above.

Results and discussion

Synthesis of the compounds

In order to study the structures and reactivities of the pure organolithium compounds it was necessary to prepare and isolate them free from lithium halide and solvent. This is essential, since it is known that lithium halides can equilibrate with organolithium compounds [45] and that Et_2O and LiBr can form complexes with these compounds. This latter aspect is clearly shown in the crystal structures of $[LiPh(Et_2O)]_4$ and $[Li_4Ph_3Br(Et_2O)_4]$ [13]. Halide- and solvent-free aryllithium compounds were obtained from the reaction of n-BuLi with an aryl halide as shown in eq. 1; a method similar to that described by Schlosser et al. [51].

When carried out using a pentane solution of the aryl iodide this reaction resulted in an almost immediate precipitation of the corresponding aryllithium compound, and the butyl iodide formed could be removed by washing the precipitate with pentane.



NMR solutions of about 3 *M* concentration were prepared by suspending the lithium compound in toluene-d_8 and adding precise amounts of the coordinating solvent, sufficient to give a clear solution. It should be noted that rather high concentrations of the organolithium compounds were used in order to minimise the dimer–tetramer equilibria that can be significant in dilute solutions. Jackman et al. have found that phenyllithium exists in solution mainly as a tetramer, with dimeric species also present at low concentrations [34].

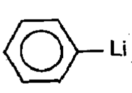
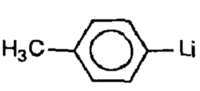
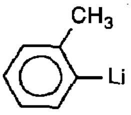
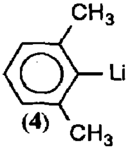
In the following sections, because of the originally unknown state of aggregation of the $[LiR]_n$ species, the equivalency given is always based on the monomeric aryllithium unit unless otherwise stated.

Phenyllithium

Addition of one equivalent of diethyl ether to a suspension of phenyllithium (**1a**) in toluene-d_8 resulted in complete dissolution of the solid. The ^{13}C NMR spectrum

Table 1

Relevant ^{13}C [a] and ^{7}Li [b] NMR data for aryllithium compounds 1–4

Compound	Solvent	Added ligand	Complex [c]	Temp. [d] (°C)	C(1)	C(2)	C(6)	$^{1}J(^{13}C,^{7}Li)$ (Hz)	$\delta(^{7}Li)$
 (1)	tol-d_8	1 Et_2O	B	−50	174.6	143.1	143.1	[11] [f]	2.03
	Et_2O		B	−60	174.7	142.9	142.9	[11] [f]	1.90
	tol-d_8	1 THF	B	−60	175.9	144.4	144.4	[11] [f]	2.01
	tol-d_8	2 THF	C	−60	188.7	146.8	146.8	19.5	1.47
	tol-d_8	1 TMEDA	C	−40 [e]	186.8	145.1	145.8	19.5	1.83
 (2)	tol-d_8	1 Et_2O	B	−50	170.2	142.0	142.0	[11] [f]	1.90
	Et_2O		B	−50	170.9	142.7	142.7	[11] [f]	1.90
	tol-d_8	1 THF	B	−50	171.3	142.9	142.9	[11] [f]	2.17
	tol-d_8	2 THF	C	−50	178.6	144.4	144.4	20	1.82
	THF-d_8		C	−50	178.7	144.5	144.5	20	[g]
	tol-d_8	1 TMEDA	C	−40 [e]	182.8	145.8	145.8	20	1.89
 (3)	tol-d_8	6 Et_2O	B	−80	182.8	151.1	143.7	[11] [f]	1.98
	tol-d_8	1.5 THF	B/C	−70	185.5	151.4	144.4	[h]	1.70
	tol-d_8	2.1 THF	C	−70	188.1	151.5	144.5	20	1.38
	THF-d_8		C	−70	189.0	151.5	144.5	20	[g]
	tol-d_8	1 TMEDA	C	−40	189.3	150.8	143.0	20	1.72
 (4)	tol-d_8	2 THF	C	−60	183.0	150.9	150.9	20	1.18
	THF-d_8		C	−60	183.9	151.2	151.2	20	[g]

[a] Chemical shift values are in ppm relative to internal TMS. [b] Chemical shift values are relative to external 70% LiCl in D_2O. [c] B = tetramer, C = dimer; see Fig. 3. [d] At higher temperatures $^{1}J(^{13}C,^{7}Li)$ was not observed, unless stated otherwise. [e] $^{1}J(^{13}C,^{7}Li)$ observed up to ca. 0 °C. [f] Calculated value, based on the linewidth. [g] Not measured. [h] Could not be observed.

at room temperature showed one resonance pattern for the aryl carbon nuclei with C(*ipso*) as a sharp singlet at 174.6 ppm (see Table 1). Below −50 °C C(*ipso*) appeared at the same chemical shift as a broad line without structure. This chemical shift is similar to that found by Jackman et al. for 6 *M* solutions of phenyllithium in cyclohexane/Et_2O (2/1) [34]. The internuclear Li–C(1) distance of 2.27 Å, which they calculated from the experimentally determined ^{7}Li contribution to the spin lattice relaxation of C(*ipso*), was interpreted as pointing to a tetrameric etherate structure $[LiPh(Et_2O)]_4$ (see Fig. 3B). Moreover, the linewidth of 110 Hz we observed for the toluene-d_8 solution of **1a** with one equivalent of Et_2O at −50 °C is compatible with coupling of the ^{13}C nucleus to three ^{7}Li nuclei with $^{1}J(^{13}C,^{7}Li)$ of about 12 Hz. This value falls in the range calculated for a four-centre, two-electron Li_3–C interaction based on studies of the dependence of $^{1}J(^{13}C,^{7}Li)$ on the aggregation of organolithium compounds [46] (cf. $^{1}J(^{13}C,^{7}Li)$ values of 14 and 11 Hz for $[Li(n\text{-}Bu)(Et_2O)]_4$ and $[Li(t\text{-}Bu)]_4$, respectively [22]). Accordingly, the most likely assignment for the signal at 174.6 ppm is to the etherate of tetrameric phenyllithium, i.e. $[LiPh(Et_2O)]_4$ (**1b**), with a structure similar to that found by Hope and Power for this compound in the solid state [13]. Addition of an excess of diethyl ether to this solution of **1b** leaves the spectrum unaffected, and it is essentially the same as that obtained for **1a** in pure diethyl ether. This indicates that

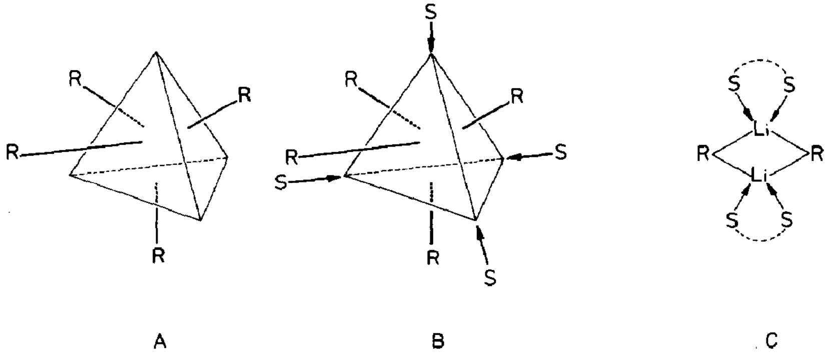


Fig. 3. Aggregate types for aryllithium compounds; S is monodentate donor solvent.

the $[LiPh(Et_2O)]_4$ aggregate is retained in weakly coordinating solvents such as diethyl ether.

When a toluene-d_8 suspension of pure phenyllithium (**1a**) is titrated with THF, one equivalent of THF is needed to give a clear solution. The ^{13}C NMR spectrum of this solution at −60 °C is similar to that observed for $[LiPh(Et_2O)]_4$ (see also Table 1) and shows the C(*ipso*) resonance as an unresolved broad signal at 175.9 ppm with a linewidth of 110 Hz, the same as that observed for **1b**. This points to a tetrameric etherate structure $[LiPh(THF)]_4$ (**1c**) (Fig. 3B) with THF coordinated to each lithium atom (cf. the structure found for $[(o\text{-}FC_6H_4)Li(THF)]_4$) [47]. Further support for the similarity of the $[LiPh]_4$-etherates **1b** and **1c** comes from the almost identical ^7Li NMR shifts for these compounds in toluene-d_8 (2.03 and 2.01 ppm for **1b** (Et_2O) and **1c** (THF), respectively). Addition of another two equivalents of THF (relative to $[LiPh(THF)]_4$) resulted in the appearance of a second aryl resonance pattern, with C(*ipso*) at 188.7 ppm. Below −60 °C, this second C-*ipso* resonance showed a characteristic seven-line pattern resulting from coupling to two ^7Li nuclei ($^1J(^{13}C,^7Li)$ 19.5 Hz), and these data are consistent with a dimeric structure $[LiPh(THF)_2]_2$ (see Fig. 3C).

These data, and the conclusions reached, are in agreement with those reported by Seebach et al., who worked with ^6Li labelled phenyllithium dissolved in THF-d_8 [31]. The view that the $[LiPh(THF)_2]_2$ dimer is formed has recently gained further support from the results of colligative experiments in THF [40]. However, below −60 °C we observed that the resonance pattern of the dimer was accompanied by that of $[LiPh(THF)]_4$ even up to a $[LiPh]_4$/THF ratio of 1/12, indicating that an equilibrium exists between the dimer and tetramer (eq. 2).

$$\underset{\mathbf{(1d)}}{2\,[LiPh(THF)_2]_2} \rightleftharpoons \underset{\mathbf{(1c)}}{[LiPh(THF)]_4} + 4\ THF \qquad (2)$$

Above −50 °C, as the reactions involved in the equilibrium process become faster, the signals for these compounds coalesce to a new resonance pattern at averaged positions of the dimer and tetramer resonances. The new resonance of the C(*ipso*) nucleus does not show coupling to ^7Li, and this is consistent with the occurrence of intermolecular aryl group exchange, which is known to be fast on the NMR timescale at these temperatures [39]. Because the signal for C(*ipso*) is broad, no NMR line shape analyses, such as those made by Fraenkel et al. [39] were carried out to study the dynamics of the C–Li bond.

A solution of $[LiPh(TMEDA)]_2$ (**1e**) (prepared by Weiss's method [19]) in toluene-d_8 showed one resonance pattern for the aryl group, with C(*ipso*) as a seven line resonance at 186.8 ppm; $^1J(^{13}C,^7Li)$ is 19.5 Hz. These data are in line with the presence of phenyl groups involved in a three-centre, two-electron Li_2C interaction in a dimeric structure similar to that found in the solid state [17].

From the above NMR studies it can be concluded that phenyllithium in solution forms complexes with polar solvent molecules that closely resemble the isolated complexes structurally characterized by X-ray crystallography. We believe that the insolubility of phenyllithium in apolar solvents is best attributed to the formation of flat $(phenylLi)_2$ rings that stack [44b] continuously to give polymers with central 4-coordinate lithium atoms. An interesting example of this is represented by the structure recently determined for $[Li\{C_6H_3(OMe)_2\text{-}2,6\}]_4$ [44c]. Addition of monodentate donor species such as ethers or bidentate TMEDA to this polymer can result in its disruption and formation of discrete, solvent (S) coordinated $[LiR(S)]_4$ clusters (Fig. 3B). Monodentate donor molecules with a strong coordinating ability can then react further to give $[LiR(S)_2]_2$ species (Fig. 3C). However, upon further addition of weakly coordinating solvents (e.g. diethyl ether) the tetrameric oligomer persists in solution.

To study the influence of substituents on the structure of aryllithium compounds some methyl-substituted phenyllithium compounds were also investigated.

Methyl-substituted phenyllithium derivatives

Treatment of a suspension of *p*-tolyllithium, $[Li(p\text{-Tol})]_n$ (**2a**), in toluene-d_8 with exactly one equivalent of either diethyl ether or THF resulted in both cases in the formation of clear solutions whose ^{13}C and ^7Li NMR spectra showed features similar to those described above for phenyllithium in the presence of these donor molecules. It is thus likely that similar tetranuclear structures i.e. $[Li(p\text{-Tol})(S)]_4$ ($S = Et_2O$, **2b**; THF, **2c**) are formed.

In contrast to the ready solubility of phenyl- and *p*-tolyllithium in ethers, dissolution of *o*-tolyllithium (**3a**) suspended in toluene-d_8 requires addition of an excess of Et_2O (>1.5 molar equivalents). The ^{13}C NMR spectrum of the resulting solution shows one temperature-independent resonance pattern for the aryl group. Below $-60\,°C$ the signal for C(*ipso*) is a broad line at 182.8 ppm with a linewidth of ca. 110 Hz resulting from a $^1J(^{13}C,^7Li)$ coupling consistent with the formation of a tetrameric species $[Li(p\text{-Tol})(Et_2O)]_4$.

Titration of an *o*-tolyllithium suspension in toluene-d_8 with THF also requires addition of somewhat more than one mole equivalent for complete dissolution. The ^{13}C NMR spectrum of this solution shows one resonance pattern in the temperature range $+30$ to $-90\,°C$. However, increasing the concentration of THF to an ArLi/THF ratio of 1/2 resulted in a downfield shift for the signal of C(*ipso*) from 185.5 to 188.1 ppm. This value is close to that of 189.0 ppm found for C(*ipso*) when *o*-tolyllithium is dissolved in pure THF-d_8. In the light of these results and by analogy with the phenyllithium system [40], we suggest that *o*-tolyllithium also forms a dimer $[LiR(THF)_2]_2$ in the presence of an excess of THF. The downfield shift of C(*ipso*) with increasing THF concentrations can consequently be accounted for in terms of a fast equilibrium between tetranuclear and dinuclear species that in the presence of excess THF lies predominantly to the side of the dimer. The ^7Li NMR spectra of solutions of *o*-tolyllithium in toluene-d_8 with 1.5 equivalents of

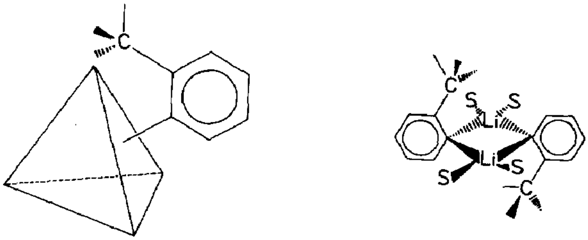


Fig. 4. Schematic representation of the interaction between lithium atoms and the *ortho*-methyl groups or monodentate solvent (S) molecules (see text) in tetrameric (a) and dimeric (b) aggregates.

THF show a signal at 1.70 ppm that shifts downfield to 1.38 ppm as the amount of THF is increased to 2.1 equivalents. Such a shift appears to be characteristic of a conversion of tetramer to dimer for aryllithium compounds [10,49].

The preference for formation of dimers observed for *o*-tolyllithium is even more pronounced for 2,6-dimethylphenyllithium (**4a**). The insolubility of this compound in diethyl ether indicates that the donor ability of this solvent is insufficient to break down the coordination polymers to give solvated tetramers or dimers. However, a treatment of a suspension of **4a** in toluene-d_8 with at least two equivalents of THF for each ArLi unit affords a clear solution whose ^{13}C NMR spectrum is similar to that obtained when pure **4a** is directly dissolved in THF-d_8. The spectrum is temperature-independent, and shows a seven line pattern for C-*ipso* at 183.0 ppm with $^1J(^{13}C,^7Li)$ 20 Hz. These observations indicate that 2,6-dimethylphenyllithium in THF solution exists only in its dimeric solvated form $[Li(C_6H_3Me_2\text{-}2,6)(THF)_2]_2$ (**4b**). This conclusion gains support from the recent X-ray crystal structure determination on $[(\text{mesityl})Li(THF)_2]_2$ [15] that shows it to be a dimeric species which, apparently as a result of the steric requirements of the *ortho*-methyl groups, is prevented from forming a tetrameric aggregate.

The insolubility of *o*-tolyllithium and 2,6-dimethylphenyllithium in diethyl ether is probably attributable to the fact that the initial formation of $[LiR(S)]_4$ clusters (S is a monodentate donor solvent) is energetically unfavourable. In these solvated tetrameric aryllithium clusters (see Fig. 4) there would be a severe steric repulsion between the *ortho* methyl groups and the solvent molecule. With Et_2O the various equilibria possible (see eq. 3) lie mainly to the side of unsolvated $[LiR]_4$ tetramers.

$$Li_4R_4 + 8R'_2O \rightleftharpoons R_4Li_4(R'_2O)_4 + 4\,R'_2O \rightleftharpoons 2\,R_2Li_2(R'_2O)_4 \qquad (3)$$

However, in the case of the tetramer $[LiR]_4$, strong donor molecules such as THF or TMEDA can form the tetrameric species $[LiR(S)]_4$, which breaks down to form dimeric $[LiR(S)_2]_2$ species. In the structure of the latter species the aryl groups are preferably positioned perpendicular to the Li ··· Li axis, and consequently the steric interactions between the coordinated donor solvents and the *ortho*-methyl groups will be minimised [48].

Concluding remarks

In organolithium compounds the lithium atoms have a strong tendency to adopt a tetrahedral coordination geometry, in the solid state and in solution. A polymeric network for phenyllithium could account for its insolubility, and that of related compounds, in apolar solvents. In the presence of monodentate donor molecules the aryllithium species studied form discrete solvated clusters. When no *ortho*-substituents are present a tetramer is formed, e.g. $[LiPh(Et_2O)]_4$ [13]. In the presence of an excess of molecules of sufficient donor strength, dimers can be formed in which the aryl groups are three-centre, two-electron bonded to two lithium atoms and in which additionally two donor molecules are coordinated to each lithium atom. However, when an *ortho*-methyl substituent is present the formation of a solvated tetramer is hindered for steric reasons, and the more favourable dimeric structure then predominates. The chelating TMEDA ligand also stabilizes the dimeric form for both phenyllithium, i.e. $[LiPh(TMEDA)]_2$, and aryl-methyl substituted derivatives. The ready formation of solvated aggregates of unsubstituted phenyllithium by coordinating molecules contrasts with the behaviour of aryllithium compounds containing *ortho* heteroatom-containing substituents, e.g. $[Li\{C_6H_4(CH_2NMe_2)\text{-}2\}]_4$. In these latter compounds solvation is not observed with weakly coordinating molecules [50], since in the tetramers this would lead to a sterically unfavourable interaction with an uncoordinated bulky *ortho*-substituent. Consequently, species such as *o*-tolyllithium and 2,6-dimethylphenyllithium dissolve only in the presence of strong donors (e.g. two THF molecules or one bidentate TMEDA ligand), to form discrete dimeric species.

Experimental

Preparation of the compounds

All the syntheses were carried out under purified nitrogen by standard Schlenk techniques. The solvents were distilled prior to use. The syntheses of the organolithium compounds are exemplified by the preparation of phenyllithium [51].

Phenyllithium

A 1.5 *M* solution of n-butyllithium in hexane (15 ml) was added to a solution of phenyl iodide (4.1 g, 20 mmole) in pentane (15 ml). The suspension was stirred for a further 15 min and then filtered. The white phenyllithium collected was washed several times with pentane and subsequently dried in vacuo.

The other aryllithium species were prepared similarly from the appropriate aryl halide.

Preparation of the NMR solutions

In a Braun glovebox, about 1.5 g of the organolithium compound was transferred to a pre-weighed 10 mm o.d. NMR tube, which was capped and then, after removal from the glovebox, reweighed to give the amount of Li compound present. The NMR tube was placed under nitrogen in a modified Schlenk tube with a B24 neck, the cap removed, and toluene-d_8 (3 ml) added. To the white suspension, the deoxygenated donor species (Et_2O, THF or TMEDA) was added from a microsyringe and the cap was replaced.

^{13}C NMR measurements

The ^{13}C NMR measurements were carried out on a Bruker WP-80 spectrometer in the temperature range -80 to $+30$ °C with steps of 10 °C. The ^7Li NMR spectra were obtained similarly on a Bruker WM-250 spectrometer in the temperature range -80 to $+40$ °C with a 70% solution of LiCl in D_2O as external standard ($\delta(Li) = 0.0$

ppm). Checks showed that the same NMR spectra (^{13}C and ^{7}Li) were obtained again at − 80 °C upon recooling of the solution after it had been warmed from − 80 to 30 or 40 °C.

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References

1 E. Weiss and E.A.C. Lucken, J. Organomet. Chem., 2 (1964) 197.
2 H. Köster, D. Thoennes and E. Weiss, J. Organomet. Chem., 160 (1978) 1.
3 (a) H. Dietrich, Acta Cryst., 16 (1963) 681; (b) H. Dietrich, J. Organomet. Chem., 205 (1981) 291.
4 H. Köster and E. Weiss, Chem. Ber., 115 (1982) 3422.
5 R. Zerger, W. Rhine and G. Stucky, J. Am. Chem. Soc., 96 (1974) 6048.
6 W.H. Ilsley, T.F. Schaaf, M.D. Glick and J.P. Oliver, J. Am. Chem. Soc., 102 (1980) 3769.
7 H. Schmidbaur, A. Schier and U. Schubert, Chem. Ber., 116 (1983) 1938.
8 M.F. Lappert, L.M. Engelhardt, C.L. Raston and A.H. White, J. Chem. Soc., Chem. Commun., (1982) 1323.
9 J.T.B.H. Jastrzebski, G. van Koten, M. Konijn and C.H. Stam, J. Am. Chem. Soc., 104 (1982) 5490.
10 J.T.B.H. Jastrzebski, G. van Koten, K. Goubitz, C. Arlen and M. Pfeffer, J. Organomet. Chem., 246 (1983) C75.
11 G.W. Klumpp, P.J.A. Geurink, A.L. Spek and A.J.M. Duisenberg, J. Chem. Soc., Chem. Commun., (1983) 814.
12 K.S. Lee, P.G. Williard and J.W. Suggs, J. Organomet. Chem., 299 (1986) 311.
13 H. Hope and P.P. Power, J. Am. Chem. Soc., 105 (1983) 5320.
14 L.M. Engelhardt, W-P. Leung, C.L. Raston, P. Twiss and A.H. White, J. Chem. Soc., Dalton Trans., (1984) 321.
15 M.A. Beno, H. Hope, M.M. Olmstead and P.P. Power, Organometallics, 4 (1985) 2117.
16 R.I. Papasergio, C.L. Raston and A.H. White, J. Chem. Soc., Chem. Commun., (1983) 1419.
17 D. Thoennes and E. Weiss, Chem. Ber., 111 (1978) 3157.
18 B. Schubert and E. Weiss, Angew. Chem., 95 (1983) 499.
19 B. Schubert and E. Weiss, Chem. Ber., 116 (1983) 3212.
20 M. Witanowski and J.D. Roberts, J. Am. Chem. Soc., 88 (1966) 737.
21 S. Toppet, G. Slinckx and G. Smets, J. Organomet. Chem., 9 (1967) 205.
22 L.D. McKeever and R. Waack, J. Chem. Soc., Chem. Commun., (1969) 750.
23 L.D. McKeever, R. Waack, M.A. Doran and E.B. Baker, J. Am. Chem. Soc., 90 (1968) 3244.
24 L.D. McKeever, R. Waack, M.A. Doran and E.B. Baker, J. Am. Chem. Soc., 91 (1969) 1057.
25 T.L. Brown, L.M. Seitz and B.Y. Kimura, J. Am. Chem. Soc., 90 (1968) 3245.
26 D.P. Novak and T.L. Brown, J. Am. Chem. Soc., 94 (1972) 3793.
27 P.A. Scherrer, R.J. Hogan and J.P. Oliver, J. Am. Chem. Soc., 96 (1974) 6055.
28 J.P.C.M. van Dongen, H.W.D. van Dijkman and M.J.A. de Bie, Recl. Trav. Chim. Pays-Bas, 93 (1974) 29.
29 S. Bywater, P. Lachance and D.J.W. Worsfold, J. Phys. Chem., 79 (1975) 2148.
30 D. Seebach, H. Siegel, J. Gabriel and R. Hässig, Helv. Chim. Acta, 63 (1980) 2046.
31 D. Seebach, R. Hässig and J. Gabriel, Helv. Chim. Acta, 66 (1983) 308.
32 R. Hässig and D. Seebach, Helv. Chim. Acta, 66 (1983) 2269.
33 J. Heinzer, J.F.M. Oth and D. Seebach, Helv. Chim. Acta, 68 (1985) 1848.
34 L.M. Jackman and L.M. Scarmoutzos, J. Am. Chem. Soc., 106 (1984) 4627.
35 G. Fraenkel, W.E. Beckenbaugh and P.P. Yang, J. Am. Chem. Soc., 98 (1976) 6878.
36 G. Fraenkel, A.M. Fraenkel, M.J. Geckle and F. Schloss, J. Am. Chem. Soc., 101 (1979) 4745.
37 G. Fraenkel, M. Henrichs, J.M. Hewitt, B.M. Su and M.J. Geckle, J. Am. Chem. Soc., 102 (1980) 3345.
38 G. Fraenkel and P. Pramnik, J. Chem. Soc., Chem. Commun., (1983) 1527.
39 G. Fraenkel, M. Henrichs, M. Hewitt and B.M. Su, J. Am. Chem. Soc., 106 (1984) 255.

40 W. Bauer and D. Seebach, Helv. Chim. Acta, 67 (1984) 1972.

41 B.J. Wakefield, The Chemistry of Organolithium Compounds, Pergamon, Oxford, 1974 and references cited herein.

42 J.L. Wardell, in G. Wilkinson, F.G.A. Stone and E.W. Abel (Eds.), Comprehensive Organometallic Chemistry, Vol. 1, Chap. 2, Pergamon Press, Oxford, 1982.

43 W. Setzer and P. von R. Schleyer, Adv. Organomet. Chem., 24 (1985) 39.

44 (a) D. Reed, D. Barr, R.E. Mulvey and R. Snaith, J. Chem. Soc., Dalton Trans., (1986) 557; (b) D.R. Armstrong, R. Snaith, W. Clegg, R.E. Mulvey, K. Wade, D. Reed, J. Chem. Soc., Dalton Trans., (1987) 1071; S. Harder, J. Boersma, L. Brandsma and J.A. Kanters, J. Organomet. Chem., 339 (1988) 7.

45 (a) H.J.S. Winkler and H. Winkler, J. Am. Chem. Soc., 88 (1966) 964; (b) H.J.S. Winkler and H. Winkler, J. Am. Chem. Soc., 88 (1966) 969.

46 T. Clark, J. Chandrasekhar and P. von R. Schleyer, J. Chem. Soc., Chem. Commun., (1980) 672.

47 O.M. Nefedov, A.I. D'yachenko and A.Ya. Shteinshneider, Izv. Akad. Nauk SSSR, Ser. Khim., (1975) 320.

48 The crystal structure of dimeric $[(\text{mesityl})\text{Li}(\text{THF})_2]_2$ also showed very short contacts between the methyl groups and the solvent molecules [15].

49 G. van Koten, J.T.B.H. Jastrzebski, C.H. Stam and C. Brevard, in K.D. Karlin and J. Zubieta (Eds.), Biological & Inorganic Copper Chemistry, Adenine Press, New York, 1985.

50 E. Wehman, J.T.B.H. Jastrzebski, J.M. Ernsting, D.M. Grove and G. van Koten, J. Organomet. Chem., 353 (1988) 145.

51 M. Schlosser and V. Ladenberger, J. Organomet. Chem., 8 (1967) 193.