High-field Lithium-7 Nuclear Magnetic Resonance Spectroscopic and Cryoscopic Relative Molecular Mass Studies on Solutions of Amido- and Imido-lithium Compounds

David Reed *
Department of Chemistry, University of Edinburgh, West Mains Road, Edinburgh EH9 3JJ
Donald Barr, Robert E. Mulvey, and Ronald Snaith *
Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL

High-field lithium-7 n.m.r. spectroscopy and molecular mass measurements are shown to provide an important guideline into the nature of the species present in benzene and toluene solutions of a representative selection of amido- and imido-lithium derivatives. The compounds have solid-state structures ranging from hexameric to tetrameric clusters {$[Ph(Bu^t)C{=}NLi]_6$ (**3**), $[(Me_2N)_2C{=}NLi]_6$ (**4**), $[Ph(Me_2N)C{=}NLi]_6$ (**5**), to $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$ (**2**) (NC_5H_5 = pyridine)}, to trimeric and dimeric rings {$[(PhCH_2)_2NLi]_3$ (**6**) and $(Bu^t_2C{=}NLi{\cdot}hmpa)_2$ (**1**) (hmpa = hexamethylphosphoramide), $[(PhCH_2)_2NLi{\cdot}OEt_2]_2$ (**7**), with probably $n = 2$ for $[PhN(H)Li{\cdot}hmpa]_n$ (**8**), and $[(C_6H_{11})_2NLi{\cdot}hmpa]_n$ (**10**)}, and to a likely monomer {$[(Bu^n)(C_5H_5N)Li{\cdot}2(NC_5H_5)]_n$ (**9**)}, yet even more diverse behaviour has been detected in solution. Thus while some of the compounds essentially retain their solid association states [hexameric (**3**), (**4**), (**5**), dimeric (**8**), and monomeric (**9**)], others engage in concentration-dependent equilibria also involving monomeric species [tetrameric (**2**), trimeric (**6**), dimeric (**1**) and (**10**)], and one complex [dimeric (**7**)] loses donor on dissolution before rearranging to a trimer and a monomer.

Recently, considerable advances have been made in the understanding of the chemistry of organonitrogen–lithium species such as amidolithiums, $[RR'NLi(donor)_x]_n$, and imidolithiums, $[RR'C{=}NLi(donor)_x]_n$, particularly regarding their solid-state structures.[1–15] While such compounds have long been reagents for the transfer of nitrogen ligands to other metals and metalloids,[16] they are currently increasingly finding use as selective proton abstraction agents in numerous organic syntheses.[17] However, despite the advances noted above, there has been very little work reported on the solution states of association of these species.[13,15,18] Given that most reactions of the types just mentioned are carried out in solution and often at around room temperature, some knowledge of the nature of these compounds under these conditions would be invaluable.

In this work, we present mainly the results of linked high-field ^7Li n.m.r. spectroscopic and cryoscopic relative molecular mass (c.r.m.m.) measurements, at near room temperatures, on aromatic hydrocarbon solutions of ten amido- and imido-lithium compounds both with and without additional donors; of these, seven have been structurally characterised in the solid state. In the past, relatively low-field ^7Li n.m.r. spectroscopy has been but briefly used in the study of solutions of organolithium compounds (*i.e.*, those with Li–C bonds) and even then usually at low temperature; for example, the solution equilibria of $LiPr^n$ were so investigated in conjunction with ^{13}C n.m.r. spectroscopy.[19] More successful experiments on such organolithium systems required the use of ^6Li-enriched materials; these allowed assignments of solution species responsible, at various temperatures, for ^6Li resonances *via* observation of ^6Li–^{13}C couplings.[20,21] Independently, cryoscopic measurements have also led to similar assignments; for example, the amidolithium compound 3,6-diethoxy-1-lithio-2,5-dimethyl-1,2-dihydropyrazine–tetrahydrofuran (1/1.5),[13] a dimer as a solid, has recently been shown to have, in thf solution at −108 °C, a molecular weight of 1.5 times the formula weight thus implying a 5:1 monomer:dimer ratio under such conditions. The major feature of our present study is that we have been able to link both cryoscopic and n.m.r. spectroscopic solution techniques, at around room temperature and in non-interacting solvents; the latter high-field studies do not require isotopic enrichment.

Experimental

Of the ten compounds discussed in this paper, five were prepared by methods described in earlier preliminary reports of their crystal structures, these being $(Bu^t_2C{=}NLi{\cdot}hmpa)_2$ (**1**) (hmpa = hexamethylphosphoramide),[15] $(Ph_2C{=}NLi{\cdot}NC_5H_5)_4$ (**2**) (NC_5H_5 = pyridine),[5] $[(Me_2N)_2C{=}NLi]_6$ (**4**),[3] $[(PhCH_2)_2NLi]_3$ (**6**),[8,18] and $[(PhCH_2)_2NLi{\cdot}OEt_2]_2$ (**7**).[8,18] Preparative details and analytical results are now given for the other five hitherto unreported derivatives. As many of the reagents used, and all the compounds isolated, are moisture-sensitive, standard inert atmosphere techniques were employed throughout.

Synthesis of $[Ph(Bu^t)C{=}NLi]_n$ (**3**).—t-Butyl cyanide (0.83 g, 10 mmol) in hexane (5 cm^3) was added to a frozen solution of phenyl-lithium [5.0 cm^3 of a 2.0 mol dm^{-3} solution in diethyl ether–benzene (1:3), 10 mmol]. Warming to room temperature produced a pale yellow solid, which dissolved on addition of warm toluene (3 cm^3). Slow cooling then afforded large, pale yellow hexagonal plates of compound (**3**); yield 90%, decomp. 119—121 °C (Found: C, 79.0; H, 8.6; Li, 4.4; N, 8.2. $C_{11}H_{14}LiN$ requires C, 79.0; H, 8.4; Li, 4.2; N, 8.4%).

Synthesis of $[Ph(Me_2N)C{=}NLi]_n$ (**5**).—Dimethylamine (0.45 g, 10 mmol) in pentane (8 cm^3) was added by syringe to a frozen solution of n-butyl-lithium (5.0 cm^3 of a 2.0 mol dm^{-3} solution in pentane, 10 mmol). Warming to room temperature gave a white precipitate. The mixture was slightly re-chilled and benzonitrile (1.03 g, 10 mmol) added dropwise, producing a yellow solid which was dissolved in warm toluene (6 cm^3). Cooling of the deep yellow solution at 0 °C resulted in deep yellow hexagonal plates of the product, (**5**); yield 78%, decomp. 129—131 °C (Found: C, 70.4; H, 7.4; Li, 4.3; N, 17.8. $C_9H_{11}LiN_2$ requires C, 70.1; H, 7.1; Li, 4.5; N, 18.1%).

Table 1. Degrees of association of imidolithium compounds, $[RR'C{=}NLi(donor)_x]_n$ (x = 0 or 1), in solution and in the solid state

Compound	Value of n in solid[a]	Value of n in C_6H_6 solution[b] conc.	dilute	Ref.
(**1**) $(Bu^t{}_2C{=}NLi{\cdot}hmpa)_n$	2	1.33 (3.3)	1.12 (1.7)	15
(**2**) $(Ph_2C{=}NLi{\cdot}NC_5H_5)_n$	4	2.21 (7.0)	1.40 (3.0)	5
(**3**) $[Ph(Bu^t)C{=}NLi]_n$	6	6.1 (8.5)		*c*
(**4**) $[(Me_2N)_2C{=}NLi]_n$	6	6.1 (4.5)	5.9 (3.1)	3,14
(**5**) $[Ph(Me_2N)C{=}NLi]_n$	6	6.0 (7.9)		*c*

[a] By *X*-ray diffraction. [b] By cryoscopy. Relatively concentrated and dilute solutions respectively, with molarities ($\times 10^2$) calculated on the basis of empirical formulae (*i.e.*, n = 1) shown in parentheses; centred values indicate that only one molecular mass determination has been carried out. [c] This work.

Table 2. Degrees of association of amidolithium compounds, $[RR'NLi(donor)_x]_n$ (x = 0—2), in solution and in the solid state

Compound	Value of n in solid[a]	Value of n in C_6H_6 solution[b] conc.	dilute	Ref.
(**6**) $[(PhCH_2)_2NLi]_n$	3	2.87 (3.3)	2.66 (2.5)	8,18
(**7**) $[(PhCH_2)_2NLi{\cdot}OEt_2]_n$	2	1.20 (3.1)	1.07 (1.8)	8,18
(**8**) $[PhN(H)Li{\cdot}hmpa]_n$	2[c]	2.07 (2.8)	2.05 (1.7)	*d*
(**9**) $[(Bu^n)(C_5H_5N)\text{-}Li{\cdot}2(NC_5H_5)]_n$	1[c]	1.04 (4.5)	0.99 (3.0)	*d*
(**10**) $[(C_6H_{11})_2NLi{\cdot}hmpa]_n$	2[c]	1.60 (4.0)	1.10 (1.0)	*d*

[a] By *X*-ray diffraction. [b] By cryoscopy. Relatively concentrated and dilute solutions respectively, with molarities ($\times 10^2$) calculated on the basis of empirical formulae (*i.e.*, n = 1) shown in parentheses. [c] Assumed states of association by analogy with known crystal structures of similar compounds, see text. [d] This work.

Synthesis of $[PhN(H)Li{\cdot}hmpa]_n$ (**8**).—n-Butyl lithium (7.1 cm^3 of a 1.40 mol dm^{-3} solution in hexane, 10 mmol) was slowly added by syringe to a stirred, chilled solution of freshly-distilled aniline (0.93 g, 10 mmol) and hexamethylphosphoramide (1.79 g, 10 mmol) in diethyl ether–hexane (1:2, 15 cm^3). A cloudy solution was produced which cleared to pale yellow on warming to 30 °C. Cooling in dry-ice for 3 d gave a crop of colourless crystals which were filtered off, washed with hexane and dried, and identified as the title compound, (**8**); yield 73%, m.p. 64—66 °C (Found: C, 51.5; H, 8.4; Li, 2.5; N, 20.6; P, 11.5. $C_{12}H_{24}LiN_4OP$ requires C, 51.8; H, 8.6; Li, 2.5; N, 20.1; P, 11.2%).

Synthesis of $[(Bu^n)(C_5H_5N)Li{\cdot}2(NC_5H_5)]_n$ (**9**).—A mixture of pyridine (2.77 g, 35 mmol) and n-butyl-lithium (6.4 cm^3 of a 1.56 mol dm^{-3} solution in hexane, 10 mmol) at −80 °C was allowed to warm to room temperature, producing a deep red solution. Refrigeration rapidly produced large orange crystals of compound (**9**); yield 80%, m.p. 78—79 °C (Found: C, 75.6; H, 8.2; Li, 2.5; N, 13.1. $C_{19}H_{24}LiN_3$ requires C, 75.7; H, 8.0; Li, 2.3; N, 14.0%).

Synthesis of $[(C_6H_{11})_2NLi{\cdot}hmpa]_n$ (**10**).—Reaction of n-butyl-lithium (5.9 cm^3 of a 1.70 mol dm^{-3} solution in hexane, 10 mmol) with a cooled mixture of dicyclohexylamine, $NH(C_6H_{11})_2$ (1.81 g, 10 mmol), and hmpa (1.79 g, 10 mmol) in hexane (15 cm^3) produced a white, microcrystalline solid. This was dissolved by dropwise addition of warm toluene (3 cm^3) to give a pale yellow solution, refrigeration of which for 2 d afforded a batch of colourless hexagonal plates shown to be compound (**10**); yield 67%, m.p. 106 °C (Found: C, 58.0; H, 11.0; Li, 1.8; N, 15.1; P, 8.3. $C_{18}H_{40}LiN_4OP$ requires C, 59.0; H, 10.9; Li, 1.9; N, 15.3; P, 8.5%).

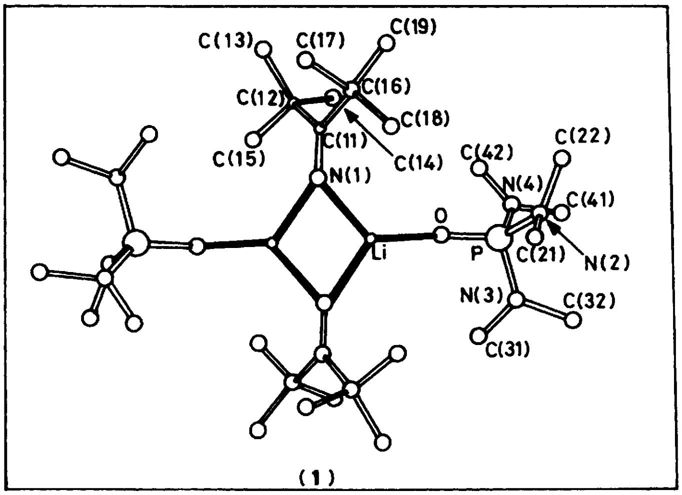
Fuller accounts of the characterisation of these compounds (*e.g.*, by i.r. and ^1H and ^{13}C n.m.r. spectroscopy) will appear in future papers more concerned with detailed studies of specific classes of compound (imido- and amido-lithiums, parent and complexed) rather than, as here, with solution techniques applicable to all such classes.

High-field ^7Li (139.96 MHz) and ^1H (360.13 MHz) n.m.r. spectroscopic measurements were obtained on a Bruker WH360 n.m.r. spectrometer. All such experiments were carried out at 20 °C on either [$^2H_6$]benzene or [$^2H_8$]toluene solutions prepared in a glove-box with tubes subsequently being sealed under nitrogen. Lithium-7 chemical shifts (δ) are quoted relative to external phenyl-lithium in the appropriate solvent (Ξ values for LiPh in [$^2H_6$]benzene and [$^2H_8$]toluene being 38.863 883 and 38.863 882 MHz respectively). Proton chemical shifts are given relative to external $SiMe_4$. All shifts are positive to high frequency of these standards. At least two solutions of each compound, at different concentrations, were examined. As checks of sample purity, the i.r. and ^1H n.m.r. spectra of the particular batch of freshly prepared crystalline material being used for ^7Li n.m.r. experiments were recorded, and correlated with those obtained during original compound characterisation. The same batch was used for the cryoscopic measurements described below.

Relative molecular mass (r.m.m.) measurements were carried out cryoscopically on variable-concentration benzene solutions of the organonitrogen–lithium compounds. The modified Beckmann-type apparatus was fitted with vacuum tubing and stopcocks to allow prior repeated evacuation/nitrogen-filling and passage of a slow N_2 stream through it during the determination; several successive near-constant (±0.002 °C) freezing-point depression readings were required to give confidence that slow hydrolysis was not occurring, while the final mass of benzene was measured to guard against the possibility of excessive solvent loss by evaporation. Results are given as the average solution state of aggregation, n, for $[RR'NLi(donor)_x]_n$ (x = 0—2) and $[RR'C{=}NLi(donor)_x]_n$ (x = 0 or 1) systems. It is, however, important to stress at this point that a good match cannot always be achieved between the concentrations of solutions used for n.m.r. work and those of solutions used in cryoscopy. For the latter, the range of concentrations spanned (typically between 80 and 400 mg in 15—20 cm^3 of benzene) is restricted at one end by the need to obtain meaningfully measurable freezing point depressions (a minimum ΔT of 0.050 °C) and at the other by colligative property laws. In the ^7Li n.m.r. work, although there is considerable overlap within the range of concentrations just noted, the most dilute solution for cryoscopy is sometimes difficult to match given the need to obtain good quality spectra and in a reasonable time. Typically, as a minimum, 10 mg of sample in 1 cm^3 of solvent were taken (*i.e.*, now equivalent to 150—200 mg in 15—20 cm^3 of benzene); using pulse repetition times of up to 0.5 s, the number of transients then required was usually of the order of 7 000. The slight experimental temperature difference (20 °C *cf. ca.* 6 °C) between the two techniques also of course prevents a perfect match. Account has been taken of these factors in the interpretations given in this paper.

Results and Discussion

The results are presented in Tables 1 and 2 (for imido- and amido-lithiums respectively) and in Figures 1—6. The Tables



(1)

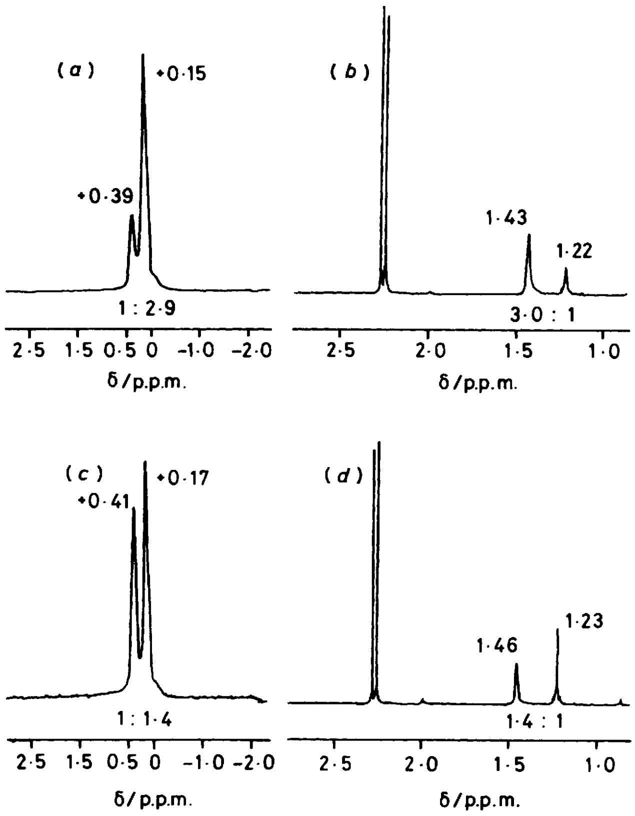


Figure 1. The solid-state structure of $(Bu^t{}_2C{=}NLi{\cdot}hmpa)_2$ (**1**), with the n.m.r. spectra of a relatively concentrated solution (0.25 mol dm^{-3}), (*a*) ^{7}Li, (*b*) ^{1}H; and of a relatively dilute solution (0.05 mol dm^{-3}), (*c*) ^{7}Li, (*d*) ^{1}H of (**1**) in [$^2H_8$]toluene

note the solid-state structures where available and give cryoscopically-determined solution aggregation values, *n*, usually for two solutions of different molarities. The Figures show the variable-concentration n.m.r. spectra of the compounds studied and are labelled with δ values and, where appropriate, with integration ratios; in cases where *X*-ray results are known, the solid-state structure is included.

For complexes, account has been taken of the possibility that where at least two ^{7}Li resonances arise, one of these could in principle be due to the uncomplexed species. In all but one case, such possible donor loss on dissolution has been eliminated, either on the basis that the uncomplexed compound is known to be hydrocarbon-insoluble, or that, where soluble, its measured ^{7}Li n.m.r. spectrum (in the same solvent) shows no resonances co-incident with those here. Specific details of such considerations are given in the text.

Imidolithium Compounds.—Complex (**1**) affords a good preliminary example of how ^{7}Li (along with in this case ^{1}H) n.m.r. spectroscopy and cryoscopic r.m.m. results can be linked to provide firm evidence for species engaging in solution equilibria. In the solid state, the complex is dimeric ($n = 2$) with an N_2Li_2-ring structure[15] (see Figure 1), while in benzene solution *n* ranges from only 1.33 decreasing further to 1.12 on dilution (Table 1); such results suggest an approximately 2:1 monomer:dimer ratio in the more concentrated solution, this becoming about 6:1 on dilution. The ^{7}Li and ^{1}H n.m.r. spectra of a relatively concentrated [$^2H_6$]benzene solution of (**1**) are shown in Figure 1(*a*) and (*b*) respectively, while (*c*) and (*d*) are analogous spectra for a more dilute solution. In both cases, the lithium spectra [(*a*) and (*c*)] consist of two distinct signals, with the high-frequency one being proportionately larger in the dilute solution, (*c*), thus suggesting, given the r.m.m. results above, that it is due to a monomeric species, while the low-frequency one corresponds to a dimer. Such conclusions are fully supported by the ^{1}H n.m.r. spectra [Figure 1(*b*) and (*d*)] which comprise three sets of signals, the highest frequency one (a doublet centred at *ca.* δ 2.25) being due to hmpa protons. Those at around δ 1.4 and 1.2 can be assigned to the Bu^t groups in the dimeric and monomeric species respectively, their separate appearance presumably being due to relatively slow exchange of $Bu^t{}_2C{=}N$ ligands between the two. Both types of spectra do, in fact, closely agree on the relative molar ratios of dimer:monomer in each solution, being around 1.45:1 in the more concentrated solution, thus giving a relative integration of *ca.* 2.9:1 [Figure 1(*a*) and (*b*)] and implying an *n* value close to 1.6, and around 0.7:1 in the more dilute one [Figure 1(*c*) and (*d*)] with *n* then about 1.4. The possibility of either of the two ^{7}Li resonances observed being due to an uncomplexed species can be discounted as neither corresponds with those found in the ^{7}Li n.m.r. spectra of solutions of $(Bu^t{}_2C{=}NLi)_6$ where the ^{7}Li signal appears as a broad singlet at δ +0.62 to δ +0.64 depending on concentration.

The pyridine complex (**2**) presented a more difficult problem as it has a tetrameric ($n = 4$) pseudo-cubane structure in the solid state[5] (Figure 2) and so inherently gives wider possibilities for solution equilibria. Molecular mass measurements (Table 1) gave *n* values ranging from *ca.* 2.2 to 1.4 on increasing dilution, this implying rather drastic dissociation of the tetramer in solution. Figure 2 shows the ^{7}Li n.m.r. spectra of three [$^2H_8$]toluene solutions of (**2**), of increasing dilution from (*a*) to (*c*). All show two main areas of resonance at around δ 1.7 and 1.5, though successive dilutions result in progressive increases in the relative proportions of the latter, lower frequency signal. Given the reasonable assumption that the resonance at δ 1.7 is due to the intact tetramer, then clearly the lower frequency one can be assigned to a lower association species. That this is almost certainly a monomer can be ascertained from the fact that the molarity of the most dilute solution used for ^{7}Li n.m.r. recordings [0.05 mol dm^{-3}, Figure 2(*c*)] was the same as one of a solution examined cryoscopically. The latter gave a value of *n* around 1.7 which is in reasonable agreement, given the slightly different temperatures of the two experiments (*ca.* +6 °C for cryoscopy, +20 °C for n.m.r. spectroscopy), with $n = 1.5$ derived from the n.m.r. integration values [Figure 2(*c*)] assuming that the lower-frequency signal does indeed relate to a monomer (and ignoring all minor resonances visible); if, for example, a tetramer $\rightleftharpoons$ dimer equilibrium was assumed, the *n*

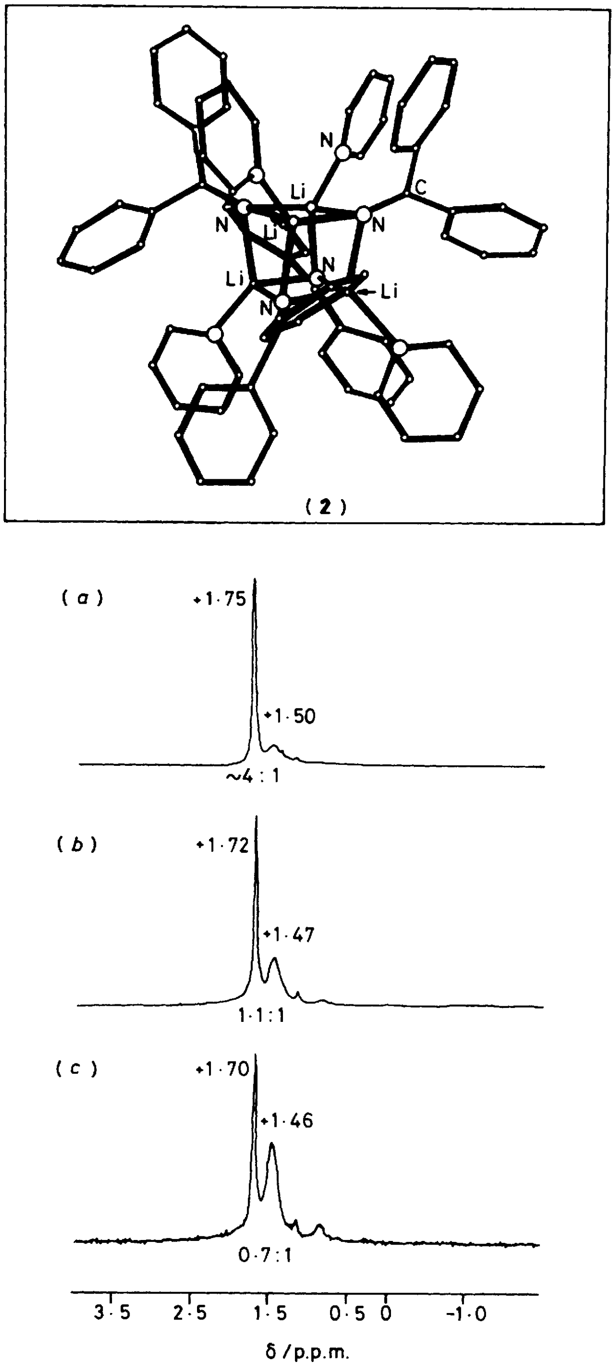


Figure 2. The solid-state structure of $(\text{Ph}_2\text{C=NLi}\cdot\text{NC}_5\text{H}_5)_4$ (**2**), with the ^{7}Li n.m.r. spectra of (*a*) a relatively concentrated (0.41 mol dm^{-3}), (*b*) an intermediate (0.12 mol dm^{-3}), and (*c*) a dilute [0.05 mol dm^{-3}] solution of (**2**) in [$^2\text{H}_8$]toluene

value would be 2.5 in this solution, while dissociation of pyridine can be discounted as the parent imidolithium, $(\text{Ph}_2\text{C=NLi})_n$, is polymeric and almost totally insoluble in aromatic solvents.

The three uncomplexed imidolithiums studied, $(\text{RR'C=NLi})_n$ [R = Ph, R′ = Bu^t (**3**); R = R′ = Me_2N (**4**); and R = Ph, R′ = Me_2N (**5**)], exist as hexamers (n = 6) in the solid state[3,14] (see Figure 3) and cryoscopic measurements suggest that these hexamers are largely retained in benzene solutions (Table 1), reflecting the relatively high stability of such clusters. In this context, addition of common donors of various denticities, *e.g.*, thf, pyridine, NEt_3, and *NNN′N′*-tetramethylethylenediamine (tmen) to such solutions pointedly fails to give complexed species of lower association, the only exception being hmpa which, for example, as already noted converts $(\text{Bu}^t_2\text{C=NLi})_6$[3] to $(\text{Bu}^t_2\text{C=NLi}\cdot\text{hmpa})_2$ (**1**).[15] In the ordinary ^{7}Li n.m.r. spectra of solutions of these species [*e.g.*, for compound (**3**), Figure 3(*a*)], only single, but broad and slightly asymmetric, signals are observed so, linking this with cryoscopic results, it can be assumed that these major resonances are due to the lithium atoms in hexameric clusters. Resolution enhancement of ^{7}Li spectra demonstrated that distortion of the broad peaks was due to the presence of some minor signals (relative integrals approximately 1:8); compounds (**3**) and (**4**) each showed one minor peak to low frequency of the main one [Figure 3, (*a*) (inset) and (*b*) respectively], while the line-narrowed spectrum of (**5**) exhibited two minor signals, one to low frequency and one to high frequency of the dominant signal [Figure 3(*c*)]. However, in contrast to other studies so far reported in this paper, no significant differences in integration ratios of specified resonances were observed on recording ^{7}Li n.m.r. spectra of solutions of widely differing concentration, so that these minor signals may well be due to impurities; there are certainly no significant solution equilibria occurring.

Amidolithium Compounds.—As with the imido-derivatives discussed above, the solution natures of amidolithiums, complexed and otherwise, were readily examined using cryoscopy (Table 2) and ^{7}Li n.m.r. spectroscopy (Figures 4—6). For a first illustration of this, dibenzylamidolithium, $[(\text{PhCH}_2)_2\text{NLi}]_n$ (**6**), and its diethyl ether adduct, $[(\text{PhCH}_2)_2\text{NLi}\cdot\text{OEt}_2]_n$ (**7**), which have been alluded to in prior communications,[8,18] have trimeric N_3Li_3 and dimeric N_2Li_2 ring structures respectively in the solid state (see Figure 4). Variable-concentration relative molecular mass studies were carried out on their pink solutions in benzene (Table 2). For (**6**), n values somewhat less than 3 indicate that, while the trimeric structure largely persists in solution, dimeric and/or monomeric species are also present, their relative amounts expectedly increasing on dilution. In contrast, aggregation values found for solutions of (**7**) are much less than 2, pointing either to extensive dissociation of the crystalline dimer into an etherate monomer, $(\text{PhCH}_2)_2\text{NLi}\cdot\text{OEt}_2$, or to loss of ether in solution to give uncomplexed $[(\text{PhCH}_2)_2\text{NLi}]_n$, formally and directly with n = 2 {and such an uncomplexed dimer is not without precedent, as solid $[(\text{Me}_3\text{Si})_2\text{NLi}]_3$[1] has been shown by electron diffraction studies to exist as $[(\text{Me}_3\text{Si})_2\text{NLi}]_2$ in the vapour phase[12]}, though this might then engage in the same solution equilibria as noted for (**6**) above, *viz.* trimer $\rightleftharpoons$ dimer/monomer; this latter possibility is given some credence by the observation that the etherate (**7**) first loses ether on heating, before melting at the same temperature (146—148 °C) as uncomplexed (**6**). Clarification of these points was obtained *via* the ^{7}Li n.m.r. spectra of concentrated and dilute [$^2\text{H}_6$]benzene solutions of (**6**) [Figure 4(*a*) and (*b*) respectively] and (**7**) [Figure 4(*c*), a line-narrowed spectrum, and (*d*), an ordinary spectrum, with a vertically-expanded version inset, respectively]. The spectra of the relatively concentrated solutions [(*a*) and (*c*)] each show only single resonances and at essentially the same frequency in both, while on dilution [(*b*) and (*d*)], second, smaller signals appear at the same, now very low frequency (δ −2.9) for both compounds. These spectra, in conjunction with the cryoscopic results above, thus strongly suggest that the same (therefore uncomplexed) species are present in solutions of (**6**) and (**7**), namely trimeric $[(\text{PhCH}_2)_2\text{NLi}]_3$ as the major one [responsible for the ^{7}Li signals at *ca.* δ −0.7 and for the n value approaching

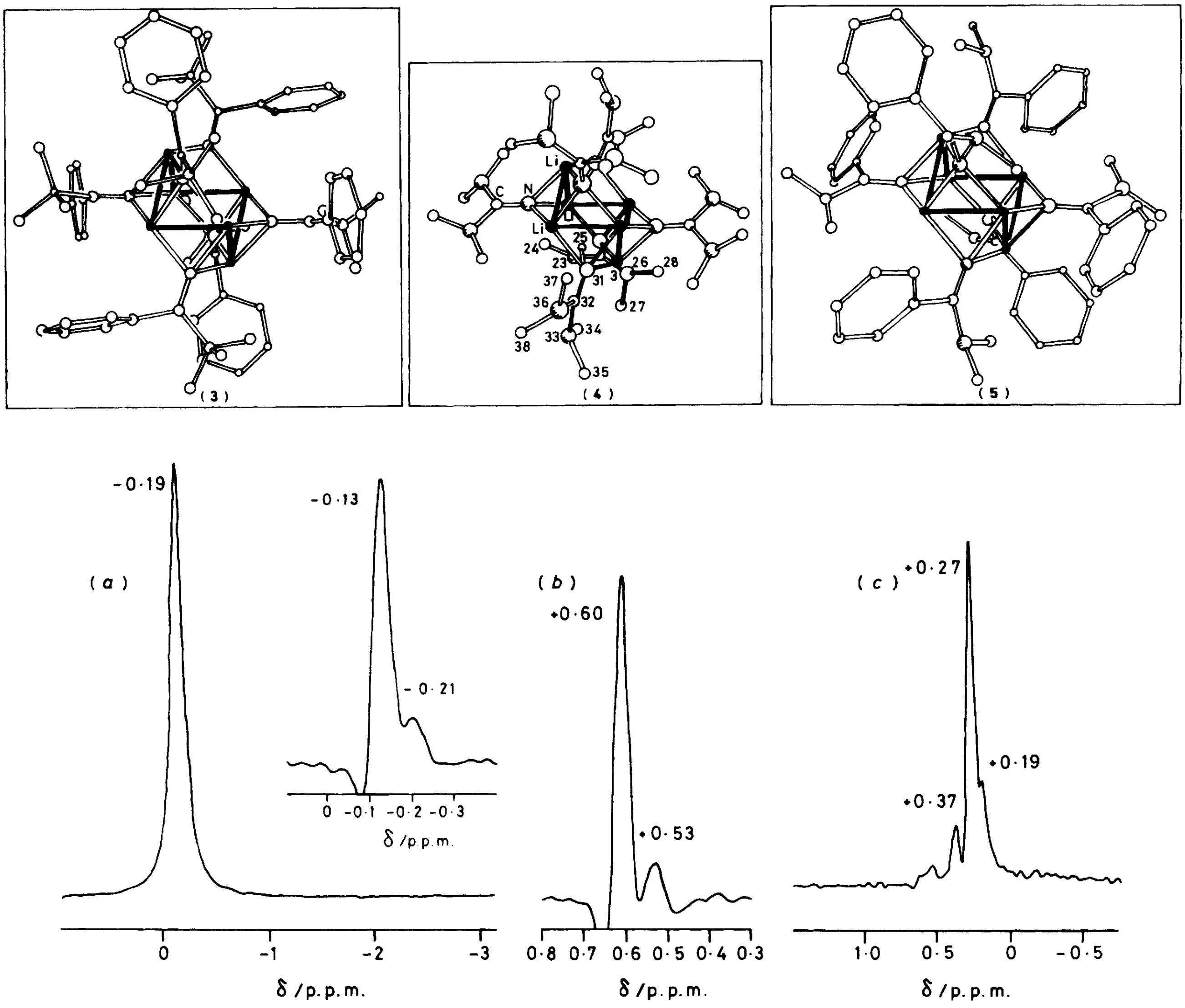


Figure 3. The solid-state structures of $[Ph(Bu^t)C{=}NLi]_6$ (3), $[(Me_2N)_2C{=}NLi]_6$ (4), and $[Ph(Me_2N)C{=}NLi]_6$ (5), with the ^7Li n.m.r. spectra of $[^2H_8]$toluene solutions of (*a*) compound (3), line-narrowed version as inset, (*b*) compound (4), line-narrowed, and (*c*) compound (5), line-narrowed

3 for (**6**)], with, on dilution, monomeric $(PhCH_2)_2NLi$ (responsible for ^7Li signals at δ *ca.* −2.9).

In fact, experimental u.v.–visible spectroscopy, together with configuration–interaction m.o. calculations capable of predicting the positions of electronic transitions for molecular species, have been used to reinforce such conclusions by showing that the pink solution colours of (**6**) and (**7**) must be due to such a monomeric $(PhCH_2)_2NLi$ species.[18] Our results on two other as yet structurally uncharacterised amidolithium complexes, $[PhN(H)Li{\cdot}hmpa]_n$ (**8**), and $[(Bu^n)(C_5H_5N)Li{\cdot}2(NC_5H_5)]_n$ (**9**), provide an interesting contrast with earlier examples in that they seemingly pointedly fail to engage in solution equilibria. Complex (**8**), prepared by the monolithiation of aniline in the presence of hmpa, is believed to be dimeric ($n = 2$) in the solid state by analogy with several characterised species of type $(RR'NLi{\cdot}L)_2$, *viz.* R = R′ = $SiMe_3$, L = Et_2O,[2,4] R = H, R′ = $C_6H_2Bu^t{}_3$-2,4,6, L = Et_2O,[6] R = R′ = $PhCH_2$, L = Et_2O [(**7**)] or hmpa,[8] and R = Ph, R′ = 2-pyridyl (C_5H_4N), L = hmpa,[11] and cryoscopic measurements imply the same, and only the one, state of aggregation in benzene solutions of varying concentrations (Table 2). In agreement with the presence of just one (dimeric) species, the ^7Li n.m.r. spectra of both concentrated and dilute $[^2H_6]$benzene solutions of (**8**) show only one very sharp signal [Figure 5(*a*), dilute solution] in each case at *ca.* δ −0.60; resolution enhancement fails to reveal any other distinct signal [Figure 5(*b*)]. Inclusion of results on complex (**9**), isolated from the reaction of $LiBu^n$ with excess pyridine, allows us to emphasise the above arguments. It seems sterically inconceivable, given the proximity of the Bu^n group to the Li and the attachment of *two* neutral pyridine molecules, that this complex could be other than monomeric, *cf.* the known structurally-characterised solid-state amidolithium monomers, $Ph(C_5H_4N)NLi{\cdot}hmpa{\cdot}Ph(C_5H_4N)NH$,[10] $(Me_3Si)_2NLi{\cdot}12$-crown-4 (12-crown-4 = 1,4,7,10-tetra-oxacyclododecane),[9] and $(C_6H_2Bu^t{}_3$-2,4,6)N(H)Li·tmen[12] which perhaps rely particularly on steric factors (*i.e.* attachment of two unidentate ligands or of one large multidentate one, combined with the presence of bulky groups within the amide moiety) to prevent association. In accord with this, molecular mass measurements indicate that only a monomer

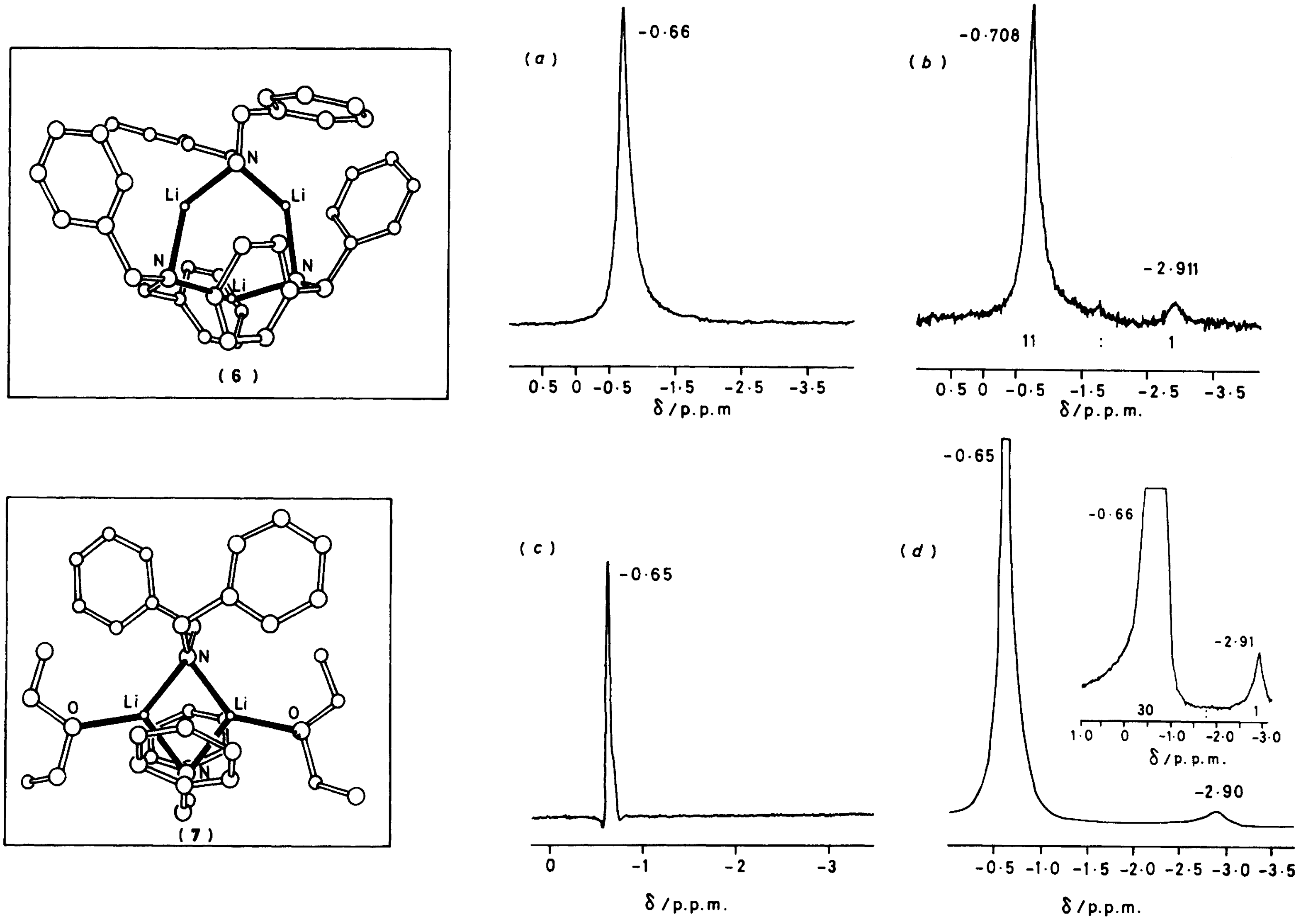


Figure 4. The solid-state structures of $[(PhCH_2)_2NLi]_3$ (**6**) and $[(PhCH_2)_2NLi{\cdot}OEt_2]_2$ (**7**), with the ^7Li n.m.r. spectra of (*a*) a relatively concentrated (0.17 mol dm^{-3}) and (*b*) a dilute solution (0.06 mol dm^{-3}) of (**6**), and (*c*) a relatively concentrated (0.26 mol dm^{-3}) (line-narrowed spectrum) and (*d*) a dilute solution (0.05 mol dm^{-3}) of (**7**) (inset: vertically expanded version); all are $[^2H_6]$benzene solutions

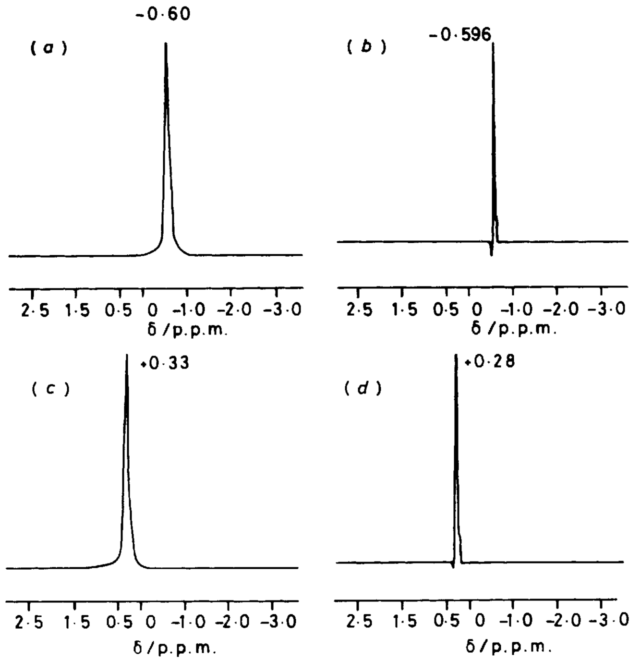


Figure 5. The ^{7}Li n.m.r. spectra of [$^2H_6$]benzene solutions of $[PhN(H)Li{\cdot}hmpa]_n$ (**8**), (*a*) ordinary spectrum, (*b*) line-narrowed spectrum; and $[(Bu^n)(C_5H_5N)Li{\cdot}2(NC_5H_5)]_n$ (**9**), (*c*) ordinary spectrum, (*d*) line-narrowed spectrum

occurs in benzene solutions of (**9**), despite varying concentrations (Table 2), and once again [as for (**8**)], only one sharp Li signal at *ca.* δ +0.30 can be detected in the variable-concentration spectra of [$^2H_6$]benzene solutions. Figure 5(*c*) and (*d*) show the ordinary and line-narrowed spectra respectively of a relatively concentrated solution of (**9**), *i.e.*, one in which association would be most likely.

The results on the final complex, $[(C_6H_{11})_2NLi{\cdot}hmpa]_n$ (**10**), illustrate how the work reported in this paper could be of value to the study, and thereby the development, of the application of organonitrogen–lithium compounds as selective, often asymmetric, proton abstraction reagents in many key organic syntheses.[17] Thus it is common practice not to isolate such reagents as pure crystalline materials but rather to prepare them in solution immediately prior to use; the precise nature of the lithiating species therefore remains unknown, yet such basic information is a vital preliminary to the proper understanding of how they work. A good example of such practice is the parent of (**10**), dicyclohexylamidolithium itself, $[(C_6H_{11})_2NLi]_n$, which has been used over recent years[22] as a bulky lithium amide base, of somewhat greater basicity than the more familiar lithium diisopropylamide (lda). However, many reported reactions apparently using this base, which we find to be only sparingly soluble in aromatic hydrocarbons, have actually been carried out in donor solvents such as Et_2O and thf, so that in reality the 'active' lithiating species may well be a complex. Supporting these arguments, such a complex, (**10**), can be isolated in good yield from lithiation of dicyclohexylamine in the presence of hmpa. Solid-state identity having been established, cryoscopic and ^{7}Li n.m.r. spectroscopic measurements can then pinpoint the exact nature of the lithium species in solution.

Although the solid-state structure of (**10**) is as yet unknown, it almost certainly has a dimeric N_2Li_2 ring structure, *cf.* the structurally characterised dimers of type $(RR'NLi{\cdot}L)_2$ (L = unidentate donor, see above) noted earlier with reference to complex (**8**). It is highly soluble in aromatic hydrocarbons and,

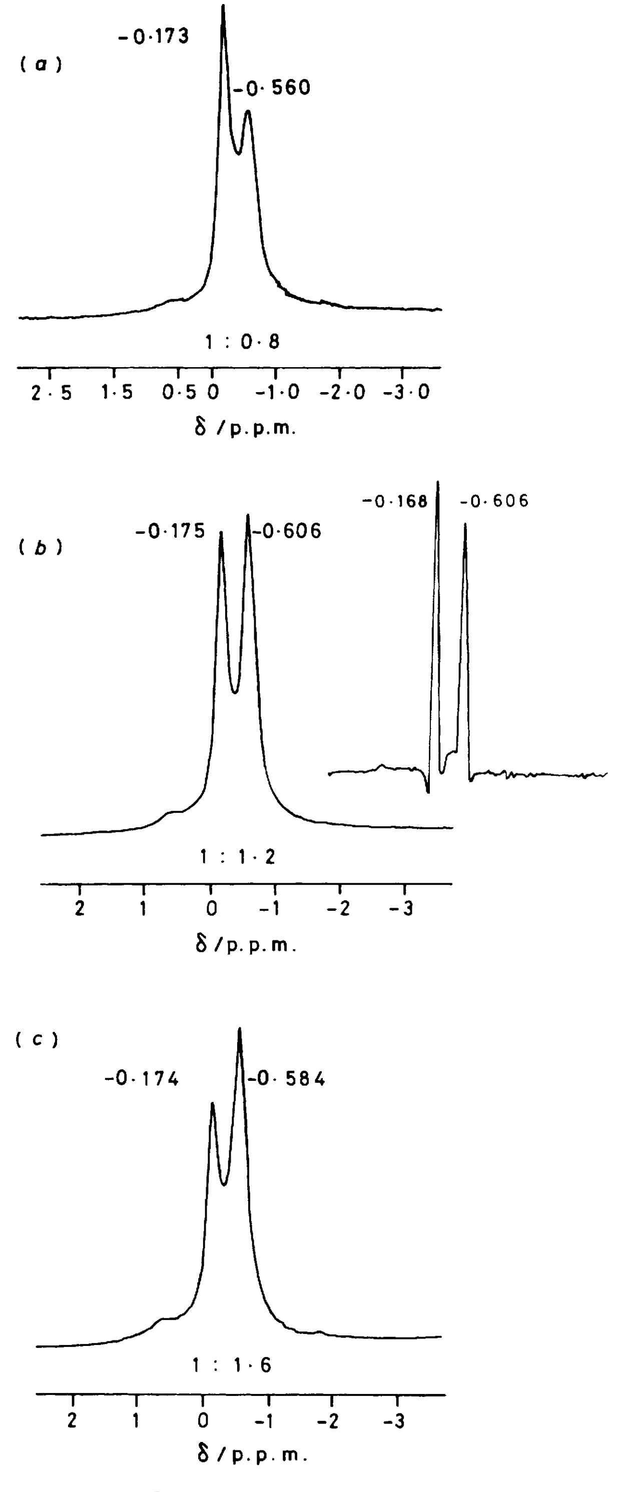


Figure 6. The ^{7}Li n.m.r. spectra of [$^2H_6$]benzene solutions of $[(C_6H_{11})_2NLi{\cdot}hmpa]_n$ (**10**), (*a*) concentrated (0.20 mol dm^{-3}), (*b*) intermediate (0.10 mol dm^{-3}) (with line-narrowed spectrum as inset), and (*c*) dilute (0.02 mol dm^{-3}) solutions

unlike (**8**) which dissolves as a dimer only, cryoscopic experiments indicate complexed monomer $\rightleftharpoons$ dimer equilibria, with more of the former on dilution (Table 2). Figure 6 shows the ^{7}Li n.m.r. spectra (139.96 MHz) of three [$^2H_6$]benzene solutions of (**10**), of decreasing concentrations from (*a*) to (*c*). At this high field strength, two signals are readily apparent in each, without recourse to low-temperature work, or even to resolution-enhancement techniques; indeed, the line-narrowed spectrum of the solution of intermediate concentration [shown as an inset to Figure 6(*b*)] merely helps to emphasise the presence of only two solution species. It is also clear that the low-frequency signal becomes proportionately more intense on dilution [Figure 6(*a*)—(*c*)] and, given the c.r.m.m. results (*i.e.*, n varies from 1.6 to 1.1 on dilution), this feature essentially proves a slow complexed monomer $\rightleftharpoons$ dimer equilibrium, with this low-frequency signal being due to the monomeric species. To substantiate this, the very low value of n (1.1) must be due to a complexed monomer and cannot correspond to an anomalous result caused by loss of hmpa ligands on dissolution, since the ^{7}Li n.m.r. spectrum of a solution of $[(C_6H_{11})_2NLi]_n$ itself[14] consists of a much broader signal at very different chemical shift (δ +0.75) to those observed here (around δ −0.17 and −0.60) for solutions of (**10**). The other species giving rise to the higher frequency resonance (δ −0.17), is most likely to be a dimer, first on the basis of its probable solid-state structure and secondly from consideration of n values then calculated from the observed integration ratios; thus, those for the most dilute solution [Figure 6(*c*)] would lead to n = 1.24, in fair agreement, given temperature differences and the obvious difficulty of precise integration, with n = 1.10 found by cryoscopy on a solution of similar concentration, while assumption of monomer $\rightleftharpoons$ trimer or tetramer equilibria, structurally unlikely anyway, would afford n = 1.35 or n = 1.41 respectively.

Acknowledgements

We thank the S.E.R.C. for provision of n.m.r. facilities and for research grants (to D. B., R. E. M., and R. S.), Dr. W. Clegg for his *X*-ray diffraction work on the compounds described here, and Dr. I. H. Sadler for useful advice and discussion.

References

1 R. D. Rogers, J. L. Atwood, and R. Grüning, *J. Organomet. Chem.*, 1978, **157**, 229.
2 M. F. Lappert, M. J. Slade, A. Singh, J. L. Atwood, R. D. Rogers, and R. Shakir, *J. Am. Chem. Soc.*, 1983, **105**, 302.
3 W. Clegg, R. Snaith, H. M. M. Shearer, K. Wade, and G. Whitehead, *J. Chem. Soc., Dalton Trans.*, 1983, 1309.
4 L. M. Engelhardt, A. S. May, C. L. Raston, and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1983, 1671.
5 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 79.
6 B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, M. C. Misra, and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1984, 148.
7 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 226.
8 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 285.
9 P. P. Power and X. Xiaojie, *J. Chem. Soc., Chem. Commun.*, 1984, 358.
10 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 469.
11 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem Commun.*, 1984, 700.
12 T. Fjeldberg, P. B. Hitchcock, M. F. Lappert, and A. J. Thorne, *J. Chem. Soc., Chem. Commun.*, 1984, 822.
13 D. Seebach, W. Bauer, J. Hansen, T. Laube, W. B. Schweizer, and J. D. Dunitz, *J. Chem. Soc., Chem. Commun.*, 1984, 853.
14 D. Barr, W. Clegg, R. E. Mulvey, D. Reed, and R. Snaith, unpublished work.
15 D. Barr, W. Clegg, R. E. Mulvey, D. Reed, and R. Snaith, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 328.
16 M. F. Lappert, P. P. Power, A. R. Sanger, and R. C. Srivastava, 'Metal and Metalloid Amides,' Ellis Horwood and John Wiley, Chichester, 1980.
17 M. Fieser, 'Fieser's Reagents for Organic Synthesis,' Wiley-Interscience, New York, 1982, vol. 10.
18 D. Barr, W. Clegg, R. E. Mulvey, and R. Snaith, *J. Chem. Soc., Chem. Commun.*, 1984, 287.
19 G. Fraenkel, A. M. Fraenkel, M. J. Geckle, and F. Schloss, *J. Am. Chem. Soc.*, 1979, **101**, 4745.
20 G. Fraenkel, M. Henrichs, J. M. Hewitt, B. M. Su, and M. J. Geckle, *J. Am. Chem. Soc.*, 1980, **102**, 3345.
21 G. Fraenkel, M. Henrichs, M. Hewitt, and B. M. Su, *J. Am. Chem. Soc.*, 1984, **106**, 255.
22 See ref. 17, 1969, vol. 2, p. 247; 1975, vol. 5, p. 397.

Received 12*th December* 1984; *Paper* 4/2108