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Preliminary communication

ISOLATION AND SOLUTION STRUCTURES OF {PhCH₂NLiCH₂CH₂NMe₂}_n AND OF THE TOTALLY RIGID DILITHIUM COMPOUND, {*o*-LiC₆H₄CH₂NLiCH₂CH₂NMe₂}_n; EVIDENCE FOR Li...*o*-HC INTERACTIONS *

DONALD BARR, RONALD SNAITH*, DOMINIC S. WRIGHT,
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

ROBERT E. MULVEY, KATHLEEN JEFFREY,
Department of Pure and Applied Chemistry, University of Strathclyde, Glasgow G1 1XL (Great Britain)

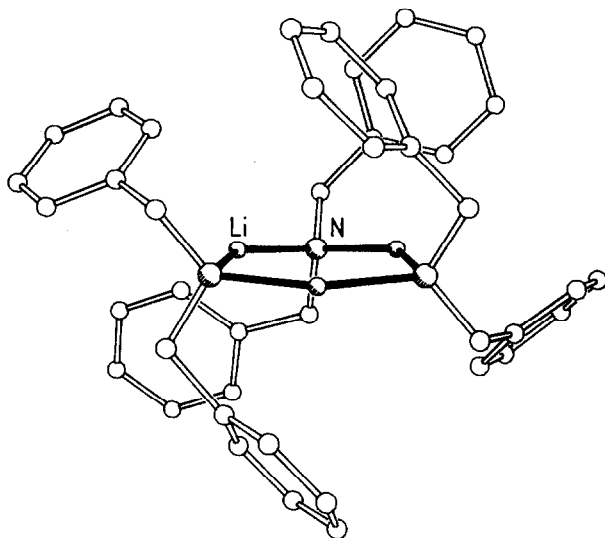
and DAVID REED
Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ (Great Britain)
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Summary

Monolithiation of *N'*-benzyl-*N,N*-dimethylethylenediamine produces {PhCH₂NLiCH₂CH₂NMe₂}_n, believed to have a trimeric (NLi)₃ ring structure in arene solutions. Lithium...*o*-HC interactions are implicated within this monolithiated compound since further lithiation proceeds smoothly and regiospecifically to give {*o*-LiC₆H₄CH₂NLiCH₂CH₂NMe₂}_n. High-field ¹H and ⁷Li NMR spectra show that this dilithium derivative (probably tetrameric) has a totally rigid solution structure brought about by intra- and inter-molecular N → Li coordinations.

Recently we described the solid-state structure of dibenzylamidolithium, ((PhCH₂)₂NLi)₃ (1), whose benzyl groups bend towards the merely 2-coordinate Li atoms of the (NLi)₃ ring, so giving numerous relatively short Li...H₂C, ...α-C, and ...*o*-HC distances [1]. These contacts imply substantial Li...HC interactions, in turn hinting at possible concomitant C–H bond activation. Distances apart, evidence has been presented that the second lithiations of aromatic ring compounds such as naphthalene are regiospecifically directed by Li...*peri*-H interactions existing within the monolithiated derivatives [2]. Here we describe preliminary results from a follow-up study involving the lithiations of the related mono-benzyl-

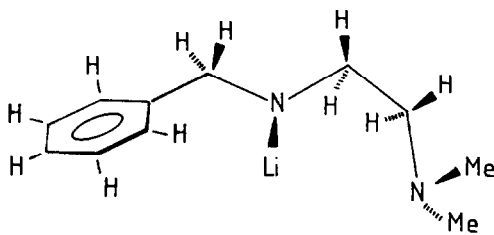
* Dedicated to Professor G.E. Coates on the occasion of his 70th birthday. R.S. remembers with gratitude many enjoyable lectures and tutorials given by G.E.C. in Durham.



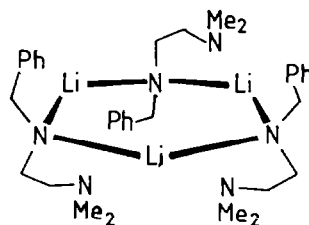
(1)

amine, $\text{PhCH}_2\text{NHCH}_2\text{CH}_2\text{NMe}_2$. In particular, we were interested in probing the structural effect of replacing one benzyl group in each monomeric unit of **1** by a dimethylamino side-arm, itself also capable of coordinating to Li centres, and to seek NMR spectroscopic and reactivity evidence for $\text{Li}\dots\text{HC}$ interactions within the *N*-monolithiated derivative.

Addition of an equimolar amount of *n*-butyllithium to a chilled solution of *N'*-benzyl-*N,N*-dimethylethylenediamine, $\text{PhCH}_2\text{NHCH}_2\text{CH}_2\text{NMe}_2$, in hexane produces a red powder in a red solution. Warming to 60°C effects complete dissolution, slow cooling of the solution then giving red crystals of the *N*-lithiated derivative, $\{\text{PhCH}_2\text{NLiCH}_2\text{CH}_2\text{NMe}_2\}_n$ (**2**) [3]. Although incorporation of a potential intramolecular Me_2N donor might have been expected to produce a dimeric species, cf. $\{(\text{PhCH}_2)_2\text{NLi}\}_3$ becomes $\{(\text{PhCH}_2)_2\text{NLi}\cdot\text{OEt}_2\}_2$ [1], in fact **2** seems trimeric (**2a**), in benzene solutions at just below room temperatures (by cryoscopy, $n = 2.92\text{--}3.00$ for $0.035\text{--}0.070\text{ mol dm}^{-3}$ solutions with molarities expressed relative to a monomer, $n = 1$). Further, the room temperature high-field (139.96 MHz) ^7Li NMR spectra of solutions of differing concentrations (0.08 and



(2)



(2a)

0.40 mol dm⁻³) in {²H₈}-toluene consist of sharp single resonances (at δ -0.19 ppm in both, relative to external PhLi in the same solvent, Ξ value 38.863882 MHz). Such apparent simplicity is reflected also in the 25°C 360 MHz ¹H NMR spectra of **2**, that of the more concentrated solution for example consisting of just three aromatic resonances (d, centred at 7.28, 2H; t, 7.17, 2H; t, 7.00 ppm, 1H), one singlet due to the benzyl CH₂ (4.05 ppm), two multiplets assigned to the two CH₂ units of the amine side-arm (centred at 2.83 and 2.17 ppm), and a single resonance for its NMe₂ protons (1.77 ppm). The spectrum of the parent amine shows these protons at 7.28, 7.20, and 7.14, at 3.69, at 2.58 and 2.36, and at 2.07 ppm, respectively, with the NH resonance at 1.68 ppm. Nonetheless, at low temperatures a far more complicated solution behaviour occurs (or, perhaps more accurately, can

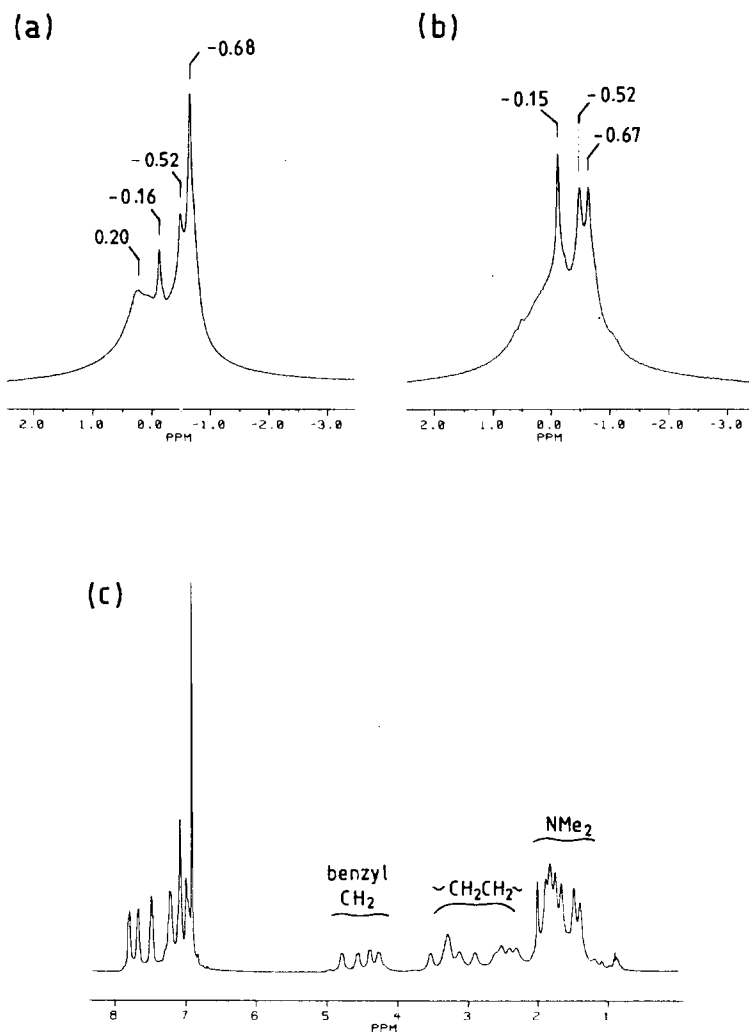
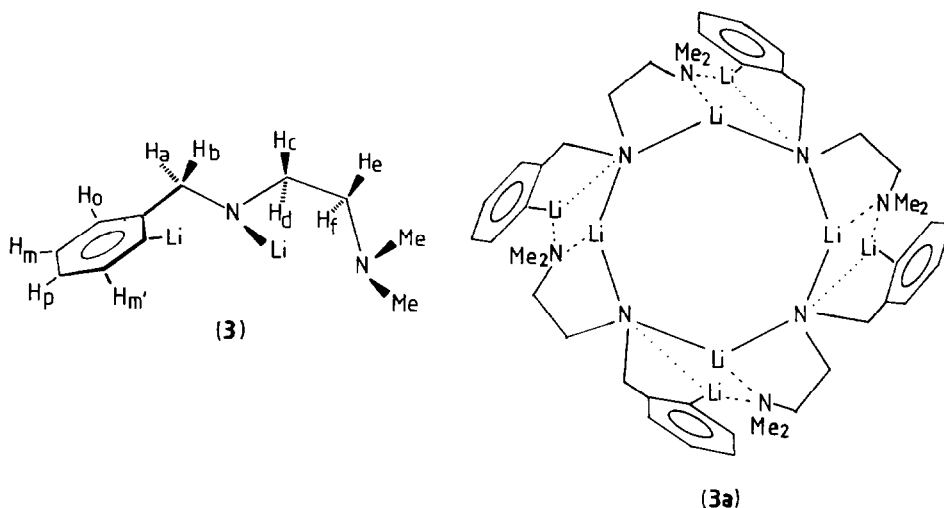


Fig. 1. NMR spectra of {²H₈}-toluene solutions of **2** at -95°C: ⁷Li spectra of (a) concentrated (0.40 mol dm⁻³), (b) dilute (0.08 mol dm⁻³) solutions; (c) ¹H spectrum of concentrated solution.



now be detected spectroscopically). In the -95°C ^7Li NMR spectra of the concentrated and dilute solutions of **2** (Fig. 1, (a) and (b), respectively) at least four lithium environments are observed, three of them (at δ ca. -0.67 , -0.52 , and -0.16 ppm) being common to both even though the relative amounts vary dramatically with concentration. As the temperature is raised, these signals merge until, at -45°C , just one extremely broad resonance (δ -0.36 ppm) is seen. The above complexity is mirrored in the ^1H NMR spectra of these solutions at -95°C (Fig. 1(c), more concentrated solution) with in particular several sets of resonances being apparent for the benzyl CH_2 protons, and for the side-arm CH_2CH_2 and NMe_2 protons. Whether these solution equilibria relate to different association states of **2** and/or to different conformations of just one association state, e.g., varieties of a trimer **2a** perhaps with and without coordinative involvement of the benzyl and dimethylamino side-arms, remains to be determined.

Dilithiation of $\text{PhCH}_2\text{NHCH}_2\text{CH}_2\text{NMe}_2$ proceeds surprisingly smoothly, room-temperature reaction of the amine with two molar equivalents of Bu^nLi in hexane giving a high yield of yellow crystals shown to be $\{o\text{-LiC}_6\text{H}_4\text{CH}_2\text{-NLiCH}_2\text{CH}_2\text{NMe}_2\}_n$ (**3**) [4]. Even in the room-temperature ^7Li NMR spectra of solutions of **3**, two very distinct 1/1 signals are observed, as shown in Fig. 2(a) for a 0.40 mol dm^{-3} solution; the low-frequency resonance can be assigned to the amido-N-Li atom since it appears at precisely the same position as in the 25°C spectra of **2**. These two resonances, and their 1/1 relative integration, are maintained on cooling and over numerous solution concentrations, e.g., as shown in Fig. 2(b) for a 0.08 mol dm^{-3} solution at -95°C , so they are not due to equilibria between different association states. The ^1H NMR spectrum of a $\{^2\text{H}_8\}$ -toluene solution of **3** at 25°C proves conclusively that further lithiation has taken place at the phenyl *ortho* position (Fig. 3). Just four distinct aromatic proton resonances, each equivalent to 1H, are observed, the pattern being two doublets and two triplets. Furthermore, every other proton or Me group has its own individual signal: the benzyl CH_2 protons appear as two mutually-coupled doublets (J 17.4 Hz), the four CH_2CH_2 side arm ones as two doublets and two triplets (J 12.0 Hz), and the

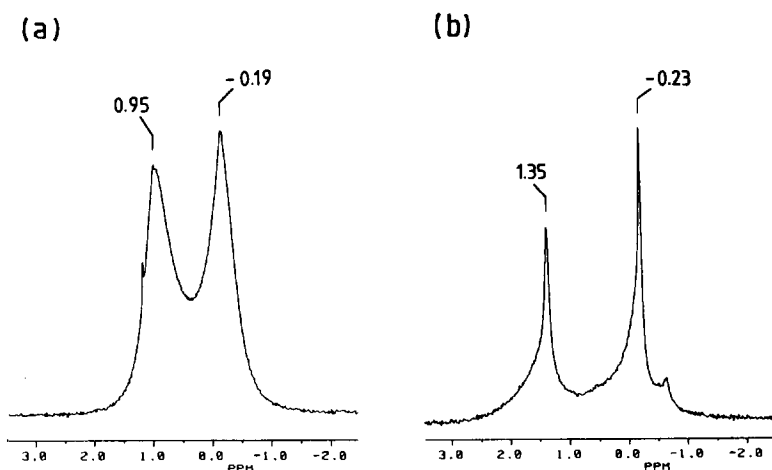


Fig. 2. ^7Li NMR spectra of $\{^2\text{H}_8\}$ -toluene solutions of **3**, (a) concentrated solution (0.40 mol dm^{-3}) at 25°C , (b) dilute solution (0.08 mol dm^{-3}) at -95°C .

two Me–N groups as two distinct and well-separated singlets (δ 1.60 and 0.93 ppm). Clearly, therefore, the structure of **3** is totally rigid even in solution and even at ambient temperatures. Details await further NMR experiments and X-ray determination of the solid-state structure, but cryoscopic measurements imply that **3** is in fact tetrameric in solution ($n = 3.88\text{--}3.97$ for $0.040\text{--}0.080 \text{ mol dm}^{-3}$ benzene solutions), so that such rigidity of $\text{LiC}_6\text{H}_4\text{CH}_2$ and $\text{Me}_2\text{NCH}_2\text{CH}_2$ side arms must be due to combinations of amide-N/ $\text{Me}_2\text{N} \rightarrow$ amide-Li/phenyl-Li coordinations both within and between monomeric units of **3**, e.g., as in **3a**. Furthermore, the regioselective and near-quantitative further lithiation of **2** at the *ortho*-phenyl position suggests that $\text{Li}\dots o\text{-HC}$ interactions occur in **2**, and so help direct this second lithiation.

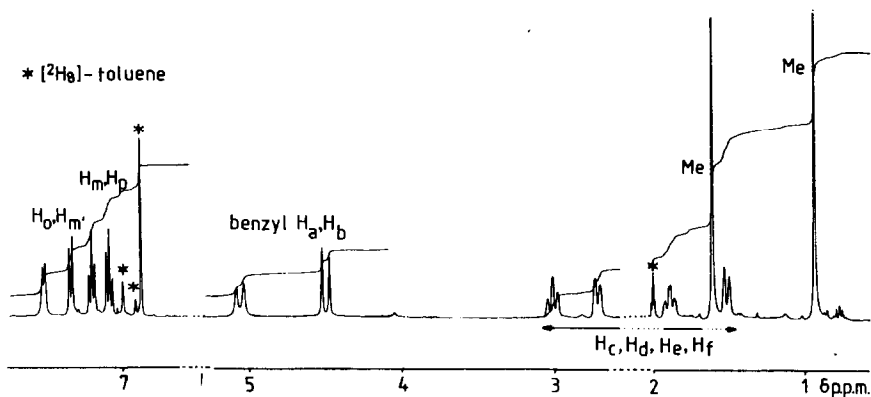


Fig. 3. ^1H NMR spectrum of a $\{^2\text{H}_8\}$ -toluene solution of **3** at 25°C .

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- 3 For compound 2. Yield 85%, m.p. 100–101° C. Anal. Found: C, 69.60; H, 9.21; Li, 3.80; N, 14.88. $C_{11}H_{17}LiN_2$ calcd.: C, 71.74; H, 9.24; Li, 3.80; N, 15.22%.
- 4 For compound 3. Yield 82%, m.p. 145° C. Anal. Found: C, 68.66; H, 8.45; Li, 6.89; N, 14.53. $C_{11}H_{16}Li_2N_2$ calcd.: C, 67.47; H, 8.42; Li, 7.37; N, 14.74%.