

A Li₈ Cluster of Three Edge-connected Li₄ Tetrahedra Held by Li–N, Li ··· C, and Li ··· Li Interactions: Crystal Structure of (o-LiC₆H₄CH₂NLi·CH₂CH₂NMe₂)₄ and Detection of Metal ··· Metal Coupling within it by ⁷Li COSY N.M.R. Spectroscopy

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The compound (o-LiC₆H₄CH₂NLi·CH₂CH₂NMe₂)_n (**1**) is tetrameric (*n* = 4) in the crystal, with a core of three edge-connected Li₄ tetrahedra bonded by ~N(Me₂)Li, μ₃-N-amido-Li, o-C-Li, η²-o-C-*m*-CH-Li, and η³-CH₂-α-C-o-C-Li interactions; in addition, the Li₈ array displays some extremely short Li ··· Li contact distances and coupling of Li atoms in solutions of (**1**) has been detected by homonuclear ⁷Li COSY n.m.r. spectroscopy.

Within organolithium aggregates (RLi)_{*n*}, *e.g.*, R = alkyl, alkoxy, or imino and *n* = 6 or 4, it has often been proposed that, aside from the direct E–Li bonds (*e.g.*, E = C, O or N), secondary Li ··· HC and Li ··· Li interactions may be electronically important, and especially so when the metal atoms are formally co-ordinatively unsaturated.^{1–4} Evidence for such interactions has relied mainly on quite short Li ··· HC and Li ··· Li distances found in certain crystal structures, *e.g.*, for the former type, in dibenzylamidolithium [(PhCH₂)₂NLi]₃, benzyl groups orientate themselves closely over the merely two-co-ordinate Li atoms of the (NLi)₃ ring.³ Here we describe more conclusive evidence for both types of interaction in the previously isolated⁴ dilithiated monobenzylamine (o-LiC₆H₄CH₂NLi·CH₂CH₂NMe₂)_n (**1**). An X-ray diffraction study has shown that (**1**) is tetrameric, with a centralised Li₈ core of three edge-connected Li₄ tetrahedra held together by Li–N, Li–o-C, η²-Li–o-C-*m*-CH, and η³-Li–CH₂-α-C-o-C co-ordinations, and possibly, in view of some strikingly short contacts, by direct Li–Li bonding. Crucially, the central [(o-C)Li]₄ portion of (**1**) could not exist without Li ··· hydrocarbon and/or Li ··· Li interactions (*i.e.*, no direct o-C–Li or N–Li bonds are involved), while, in solution [where (**1**) is also tetrameric⁴], Li ··· Li coupling, probably involving the metal atoms at the ends of the array and those in

the centre, has been detected for the first time by ⁷Li COSY n.m.r. spectroscopy.

Although the complicated structure of (**1**) is held together by delocalised bonding, it can conveniently be described in terms of formal monomeric units. Figure 1 shows one such unit with its Li(11)–amido-N(12) and Li(12)–o-C(101) bonds, but also including the other three Li atoms to which this unit is attached. Key distances involving the metal atoms are given in

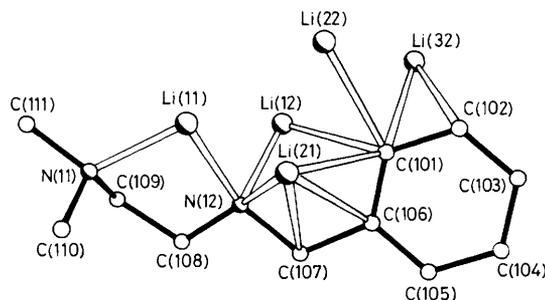


Figure 1. One Me₂NCH₂CH₂NCH₂C₆H₄ ligand of (**1**), together with the five Li atoms to which it is bonded in the tetrameric molecule.

Table 1. Key Li-N and Li-C bond distances in (1).

Bond type	Example (see Figure 1)	Range of distances/Å	Average distance/Å
(amido-N)Li-N			
-amido-N, intra-monomer	Li(11)-N(12)	2.01(1)-2.07(1)	2.04
-amido-N, inter-monomer	Li(21)-N(12)	2.04(1)-2.13(1)	2.08
-(Me ₂)N, intra-monomer	Li(11)-N(11)	1.98(1)-2.01(1)	2.00
(amido-N)Li-η ³ -CH ₂ -α-C-o-C, inter-monomer			
-(H ₂)C	Li(21)-C(107)	2.42(1)-2.53(1)	2.47
-α-C	Li(21)-C(106)	2.36(1)-2.44(1)	2.40
-o-C	Li(21)-C(101)	2.23(1)-2.35(1)	2.28
(o-C)Li-N			
-amido-N, intra-monomer	Li(12)-N(12)	1.98(1)-2.03(1)	2.01
(o-C)Li-o-C			
-o-C, intra-monomer	Li(12)-C(101)	2.43(1)-2.46(1)	2.45
-o-C, inter-monomer	Li(22)-C(101)	2.33(1)-2.37(1)	2.35
(o-C)Li-η ² -o-C-m-CH, inter-monomer			
-o-C	Li(32)-C(101)	2.43(1)-2.48(1)	2.46
-m-C	Li(32)-C(102)	2.37(1)-2.47(1)	2.42

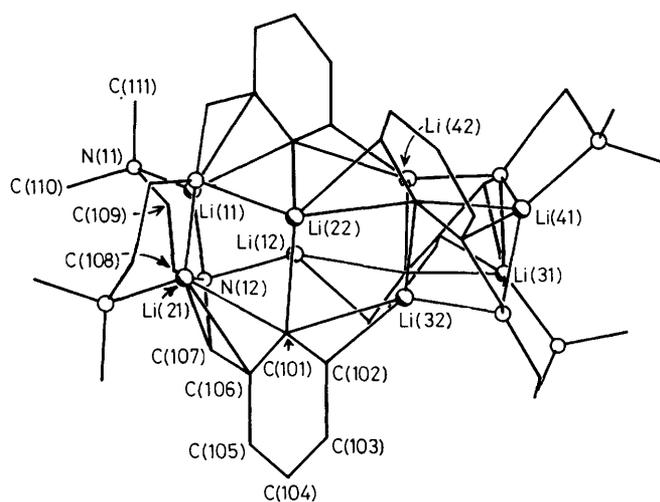


Figure 2. The molecular structure of (1). One ligand and all eight Li atoms are labelled; H atoms omitted. Orthorhombic, space group *Pbca*, *a* = 26.139(1), *b* = 19.700(1), *c* = 18.496(1) Å, *U* = 9524.3 Å³, *Z* = 8 tetramers. *R* = 0.135, *R_w* = (Σ*w*Δ²/Σ*wF_o*²)^{1/2} = 0.042⁶ for 2983 reflections with *F* > 3σ(*F*) and 2θ ≤ 110° (Cu-*K*_α radiation, λ = 1.54184 Å). SHELXTL (G. M. Sheldrick, University of Göttingen) and local computer programs were used. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

Table 1. Each Li forming a bond with its 'intra-monomer' amido-N atom [e.g., Li(11)-N(12)] is also bonded, slightly more distantly, to an amido-N of another monomer [e.g., Li(21)-N(12) or Li(11)-N(22)] and, more closely, to its own Me₂N side arm [Li(11)-N(11)]. In addition, each such metal atom has, as shown for Li(21), an 'inter-monomer' η³-interaction with the CH₂-α-C-o-C portion of a neighbouring phenyl

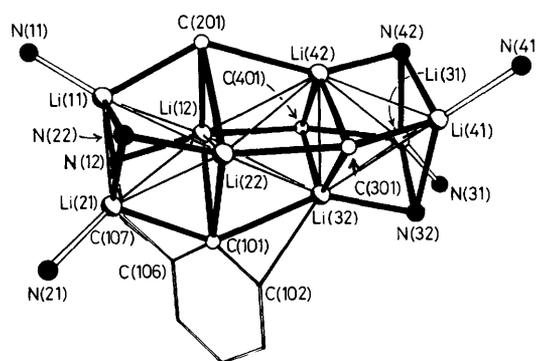


Figure 3. The central core of (1), view slightly rotated from that of Figure 2. Atoms (Li shaded, N filled, C open) are labelled by their numbers only. Li ··· Li interactions are shown as thin lines, giving edge-linked Li₄ tetrahedra. Li-N and Li-C bonds in the central core are filled and thick. Other Li-C interactions are shown for one ligand only.

group: the distances involved are much less than those found in [(PhCH₂)₂NLi]₃, [Li ··· C(H₂) 2.69, Li ··· α-C 2.60, Li ··· o-C(H) 2.70 Å],³ and indeed some are comparable with those in 'true' organolithium compounds, whose C-Li bond lengths average around 2.29 Å.¹ Each of the lithium atoms present formally by substitution of o-C-H bonds in the precursor amine [e.g., Li(12) in Figure 1] bonds to just one N atom, the amido one within its own monomeric unit [e.g., Li(12)-N(12)], but to no fewer than four C atoms: obviously to its o-C [e.g., Li(12)-C(101)], even more closely to an o-C in another unit [e.g., Li(22)-C(101)], and, in an η²-mode previously only observed in the 'loose dimer' [Ph(naphthyl)N-Li-TMEDA]₂ (TMEDA = tetramethylethylenediamine),⁵ [Li ··· o-C(H) 3.12, ··· m-C(H) 3.15 Å], to an o-C-m-C(H) segment of a neighbouring phenyl ring [e.g., Li(32)-C(101)·C(102)H].

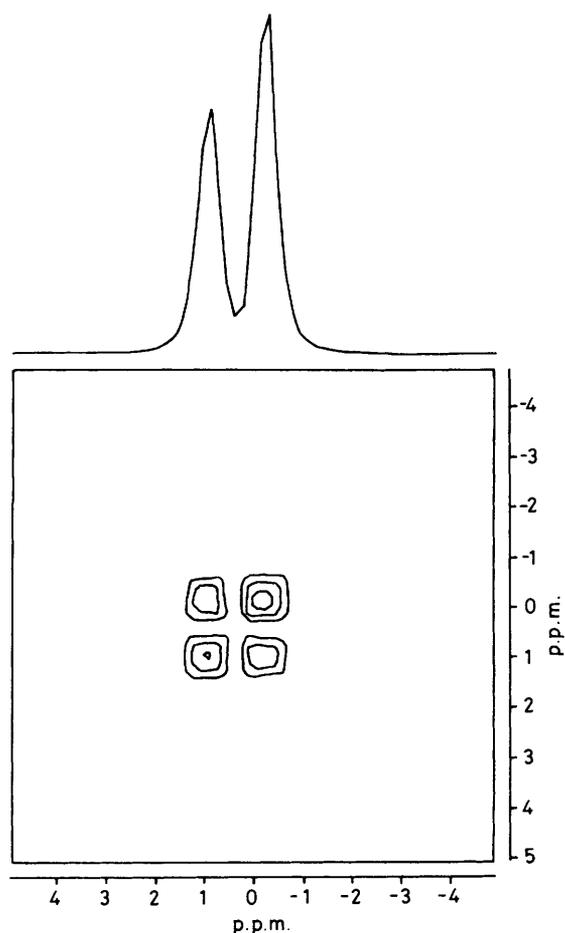


Figure 4. ${}^7\text{Li}$ n.m.r. spectra (139.96 MHz) of a solution of (1) in $[\text{}^2\text{H}_8]\text{toluene}$ at 25°C : top, normal spectrum; bottom, COSY spectrum.

The multifarious interactions described above allow association of four monomeric units, as shown in Figure 2. Noteworthy features are, firstly, that the $\sim\text{NMe}_2$ side-arms play no direct part in this association, being constrained to the ends of the Li_8 array and leading to merely an 'intra-monomer' chelating mode [e.g., $\text{N}(11)\text{--Li}(11)\text{--N}(12)$]. Secondly, the $o\text{-C}$ -phenyl ring atoms are particularly crucial in holding together the metal array since each bridges two Li atoms [e.g., $\text{Li}(12)$, $\text{Li}(22)$ in Figures 1, 2], forms part of an $\eta^3\text{-Li-CH}_2\text{-}\alpha\text{-C-}o\text{-C}$ moiety [e.g., $\text{C}(101)\text{--Li}(21)$], and contributes to an $\eta^2\text{-Li-}o\text{-C-}m\text{-CH}$ moiety [e.g., $\text{C}(101)\text{--Li}(32)$]. Clearly, replacement of three benzyl units of $[(\text{PhCH}_2)_2\text{NLi}]_3$ by three dimethylamino-containing side-arms has, abetted by second lithiation, in fact greatly enhanced $\text{Li}\cdots\text{benzyl}$ interactions.

Figure 3 focuses on the central core of (1) consisting of eight Li, four *amido-N*, and four *o-C* atoms, but also including the four dimethylamino-N atoms and one benzyl unit (that shown in Figure 1). It can be seen that the Li centres form three edge-connected tetrahedra and that the $\mu_3\text{-N-amido}$ atoms (N-Li distances, 1.98–2.13, av. 2.04 Å) help to hold together the two end Li_4 tetrahedra. However the central tetrahedron exists solely due to $\text{Li}\cdots\text{benzyl}$ interactions, specifically the $\eta^2\text{-Li-}o\text{-C-}m\text{-CH}$ ones, aided, possibly, by direct $\text{Li}\cdots\text{Li}$ bonds (all $\text{Li}\cdots\text{Li}$ contacts shown as thin lines). Figure 3 also demonstrates that this $\text{Li}_8\text{N}_4\text{C}_4$ core could be seen as arising from the stacking of two $(\text{NLi})_2$ rings onto the outer faces of

two already-stacked ($o\text{-CLi})_2$ rings (bold N-Li and C-Li bonds). This would explain the alternation of successive pairs of Li atoms to give tetrahedra (as would electrostatics, since these are $\text{Li}^{\delta+}\cdots\text{Li}^{\delta+}$ pairs within a highly polarised molecule), but suffers from undue emphasis on $o\text{-C-Li}$ interactions, e.g., those involving $\text{C}(101)$, while ignoring others which are of similar length, or even shorter, e.g., those involving $\text{C}(102)$, $\text{C}(106)$, $\text{C}(107)$ in Figure 3. Of more significance is the distortion of such a simple array to produce some very short $\text{Li}\cdots\text{Li}$ contacts in (1). Thus, each end-Li [formally an *N(amido)-attached* one] contacts three other Li atoms, viz. an $o\text{-C-Li}$ one within its own monomer, e.g., $\text{Li}(11)\cdots\text{Li}(12)$ [range of distances, 2.50(1)–2.60(1), av. 2.54 Å], and neighbouring $o\text{-C-Li}$ and *N(amido)-Li* ones, e.g., $\text{Li}(11)\cdots\text{Li}(22)$ [2.83(1)–2.91(1), av. 2.87 Å] and $\text{Li}(11)\cdots\text{Li}(21)$ [2.20(1)–2.25(1), av. 2.22 Å], respectively. Each central, formally $o\text{-C-attached}$ Li engages no fewer than five other metal atoms: two amido ones as detailed above, and three $o\text{-C-metal}$ atoms of other monomers, one being close e.g., $\text{Li}(12)\cdots\text{Li}(22)$ [2.50(1)–2.54(1), av. 2.52 Å] and two more distant [2.80(1)–2.91(1), av. 2.86 Å]. Although comparisons with distances in, for example, the Li_2 molecule (2.74 Å) and metallic lithium (3.04 Å) must have limited value, the fact remains that some of these metal \cdots metal distances in (1) are exceedingly short. Indeed, some of those at the ends of the Li_8 cluster [$\text{Li}(11)\text{--Li}(21)$ 2.20(1), $\text{Li}(31)\text{--Li}(41)$ 2.25(1) Å] are, even allowing for e.s.d.'s, significantly less than the shortest observed hitherto, i.e., 2.30(1) Å in $[\text{Li}(\mu\text{-OCBu}_2\text{CH}_2\text{PMe}_2)]_2$.⁷

In arene solutions, (1) is also tetrameric (by cryoscopy in benzene, $n = 3.88\text{--}3.97$ for $0.040\text{--}0.080$ mol dm^{-3} solutions), and even at 25°C , just two 1:1 ${}^7\text{Li}$ n.m.r. resonances are observed (top, Figure 4); the lower-frequency one can be assigned to the (*amido-N*)Li atoms since a signal at the same frequency constitutes the analogous spectrum of the monolithiated amine $(\text{PhCH}_2\text{NLi-CH}_2\text{CH}_2\text{NMe}_2)_n$.⁴ The homonuclear ${}^7\text{Li}$ COSY n.m.r. spectrum of (1) (bottom, Figure 4) represents these two signals as the diagonal, bottom left to top right: the two signals off this diagonal prove the presence of coupling between the central ($o\text{-C}$) Li_4 portion of the cluster and the end pairs of (*amido-N*)Li atoms.

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