Evidence for CH · · Li Interactions in the Solid State Structure of Dibenzylamidolithium, and in Solutions of It and Its Complexes: Coloured Species due to Benzyl → Lithium Charge Transfer

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While CH · · Li interactions are implicated in the solid-state structure of trimeric dibenzylamidolithium, in contrast to those of its dimeric complexes, spectroscopic studies on their coloured solutions, linked to predictive MO calculations, provide firm evidence for such interactions, with colours being due to benzyl → Li charge transfer in low-association species.

In the preceding communication,[1] we reported the preparation, properties, and crystal structures of dibenzylamidolithium, $[(PhCH_2)_2NLi]_3$, (**1**), and two of its complexes, $[(PhCH_2)_2NLi{\cdot}OEt_2]_2$, (**2**), and $[(PhCH_2)_2NLi{\cdot}O{=}P(NMe_2)_3]_2$ (**3**). Here, we show how certain structural features in (**1**) implicate C–H · · Li interactions in the solid state, and, more importantly, how the unexpected solution colours of these species provide more definitive evidence for such interactions and for a monomeric $(PhCH_2)_2NLi$ in solution.

$[(PhCH_2)_2NLi]_3$
(**1**)

$[(PhCH_2)_2NLi{\cdot}OEt_2]_2$
(**2**)

$[(PhCH_2)_2NLi{\cdot}O{=}P(NMe_2)_3]_2$
(**3**)

Comparing trimeric (**1**) with its dimeric complexes (**2**) and (**3**), we believe that Li · · benzyl interactions may be responsible for the changed state of association, in that the decrease in formal Li co-ordination number from 3 [in (**2**), (**3**)] to 2 [in (**1**)] may cause the much closer approach of the benzyl units to the Li atoms in (**1**), which in turn sterically necessitates expansion to a larger ring system. Thus, in (**1**), Figure 1, each Li atom has contacts of <3.05 Å to $4CH_2$ units (to C, av. 2.81, shortest 2.69 Å; to H, av 2.80, shortest 2.67 Å), to 2 α-C ring carbon atoms of benzyl units on separate N atoms (av. 2.80, shortest 2.60 Å), and to 2 *ortho*-CH units (to C, av. 2.80, shortest 2.70 Å; to H, av. 2.66, shortest 2.32 Å). Although the Li · · CH_2 distances are necessarily short for a reasonable co-ordination geometry of the N atoms, the Li · · phenyl

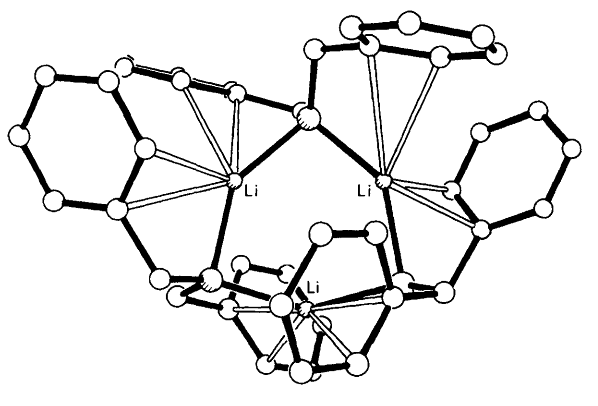
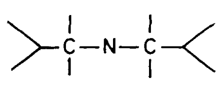


Figure 1. Lithium · · carbon interactions (shown as open bonds) in the crystal structure of $[(PhCH_2)_2NLi]_3$.

interactions represent a genuine bending of the benzyl groups towards the Li atoms, not imposed by steric restrictions. Corresponding distances in (**2**) and (**3**) all exceed 3 Å. Such Li · · CH interactions have been proposed to contribute significantly to the stereochemistry and bonding of alkyl-lithiums [notably (cyclohexyl-lithium)$_6$[2]] and of certain 'ate species [*e.g.* $LiBMe_4$[3]], where short Li · · CH contacts may aid co-ordinative saturation of electron-deficient Li atoms; however, such proposals remain contentious.[4] Calculations on (**1**), (**2**), and (**3**) using the established molecular orbital bond index method,[5] show that in (**1**), although most individual interactions are small, expectedly so, as the Li · · C distances are long [*cf.* 'direct' Li · · C bonds in *e.g.*, $(EtLi)_4$ 2.28,[6] with intermolecular contacts, 2.50 Å], cumulatively they contribute significantly to the Li valency. Thus, Li valencies in (**1**) and (**2**) are remarkably similar (1.44 and 1.42, respectively), despite each Li in (**1**) having two weaker Li–N bonds [bond index 0.24; *cf.* 0.30 in (**2**)], and no donor bonding; part compensation in (**1**) comes from two Li · · Li interactions (instead of only one), but most is provided by increased Li · · CH covalent interaction (cumulatively, 0.57, *ca.* 40% of total Li valency). Where larger individual interactions occur, there is consequential weakening of C–H bonds (typically, an 'interacting' *ortho* C–H index 0.89 *cf.* 0.97 for *ortho* CH unit distant from all Li). In this context, i.r. spectra of alkyl-[7] and aryl-Li[8] compounds show aliphatic α-CH and aromatic *o*-CH stretching modes at lower frequency relative to those in parent hydrocarbons, and this has been interpreted[2] in terms of bond weakening, possibly due to Li · · CH interactions. However, here such shifts occur for (**1**), *and* for (**2**) and (**3**), and for *both* the CH_2 and aromatic CH bands, and this, plus the uniformity of shifts [*e.g.* $\Delta\nu(CH_2)$ for (**1**) -140, for (**3**) -120 cm^{-1}; $\Delta\nu(CH)$ for (**1**) and for (**2**), -45 cm^{-1}] argues against this interpretation.

More conclusive evidence for Li · · benzyl interactions comes from solution studies. Colours of organolithium species, $(RLi)_n$,[9] are normally associated with charge delocalisation from the carbanionic carbon atom into an unsaturated system *e.g.*, red when R = Ph, green when R = naphthyl; the pink–red solution colours of (**1**) and (**2**) cannot be so explained, however, as such delocalisation from the bridging N atom is blocked by methylene groups. The u.v.–visible spectra (800—280 nm) of (**1**) and (**2**) [C_6H_6 solution] were recorded under nitrogen, and both showed a similar band in the visible spectrum (λ_{max}, 525 and 520 nm respectively) of weak absorptivity (a cm^{-1} mol^{-1} dm^3). However, the intensity *increased* on dilution [*e.g.*, for (**1**), *a ca.* 100 in 5.3×10^{-3} M solution (relative to a monomeric species); 10-fold dilution gave *a ca.* 300], implying that a lower association species, possibly common to both, is responsible for the colour. Cryoscopic measurements (C_6H_6 solutions) consistently confirmed the expected increased dissociation on dilution, *e.g.* for (**2**), $[(PhCH_2)_2NLi{\cdot}OEt_2]_n$, at 3.0×10^{-2} M, M_r 320, $n = 1.16$ and at 1.8×10^{-2} M, M_r 294, $n = 1.06$; values for (**1**) $[(PhCH_2)_2NLi]_n$, ranged n = 2.87—2.74. High field (139.96 MHz) ^7Li n.m.r. spectra were recorded in C_6D_6 for relatively dilute and concentrated solutions. The latter for (**1**) showed a broad resonance (-0.69 p.p.m.) and a much smaller singlet (relative intensity *ca.* 16:1) to high field (-2.90 p.p.m.); dilution caused the intensity of this latter signal to increase (now *ca.* 6:1). For (**2**), the more concentrated solution spectrum had a large asymmetric singlet (-0.65 p.p.m.), and again a small singlet to high field, essentially coincident with that in (**1**) (-2.86 p.p.m.); as for (**1**), its relative intensity increased on dilution.



(A)

Such results imply that the solution colours of (**1**) and (**2**) are due to a common, therefore uncomplexed, low association species. To identify it, the excited states of (**1**) and (**2**), and of fragments taken from them, were calculated by a configuration interaction method which has proved successful in predicting electronic spectra of main group species.[10] In both cases, only the calculations on uncomplexed monomeric $(PhCH_2)_2NLi$ led to the predicted highest wavelength transition (HOMO→LUMO) being in the visible, *e.g.*, for this species derived from (**2**)'s co-ordinates, at 546 nm, *cf.* experimental 520 nm. This calculated transition invariably shifted into the u.v. on complexation, *e.g.*, to 396 nm for monomeric $(PhCH_2)_2NLi{\cdot}OEt_2$, or on association, *e.g.*, for dimeric (**2**), with and without an ether, to 294 and 320 nm, respectively, and for trimeric (**1**), to 255 nm. The same applies for other conceivable solution species, *e.g.*, the dibenzylamine hydrolysis product (predicted λ 290 *cf.* experimental 277 nm) or amide ion (λ 316 nm). From these calculations for the lithium species, the HOMO is a combination of ligand backbone atomic orbitals [see (A)] and the LUMO of Li orbitals; *i.e.*, this transition is of the charge transfer type.

Bond index calculations on monomeric $(PhCH_2)_2NLi$ species show that benzyl · · Li interactions are much greater, despite the same assumed distances, than in the parent associated species (**1**), (**2**) *e.g.*, in $(PhCH_2)_2NLi$ (fragment of the trimer geometry), they account for 50% of the Li valency as they now need to compensate the formally only 1-co-ordinate Li for dissociation. Although the detailed solution structure of monomeric $(PhCH_2)_2NLi$ is obviously unknown, the implication is that the $PhCH_2$ groups are here much closer to the Li, giving large benzyl · · Li interactions which thus allow the charge transfer mechanism to operate efficiently, producing the HOMO → LUMO bathochromic shift into the visible.

The solution behaviour of (**3**) is more complex, involving several dissociation equilibria, and will be discussed in a more detailed account of this work.

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