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Preliminary communication

SYNTHESIS OF 8-(DIMETHYLAMINO)-1-NAPHTHYLLITHIUM ETHERATE: ITS STRUCTURE IN THE SOLID (X-RAY) AND IN SOLUTION (^{7}Li AND ^{1}H NMR)*

JOHANN T.B.H. JASTRZEBSKI, GERARD VAN KOTEN**,

Anorganisch Chemisch Laboratorium, J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

KEES GOUBITZ,

Laboratorium voor Kristallografie, J.H. van 't Hoff Instituut, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam (The Netherlands)

CRISTIAN ARLEN and MICHEL PFEFFER

Laboratoire de Chimie de Coordination, Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cedex (France)

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Summary

The reaction of Bu_4Li_4 with 4 molar equivalents of 1-(dimethylamino)naphthalene in diethyl ether affords novel 8-(dimethylamino)-1-naphthyllithium. Its molecular structure (X-ray) consists of two 8-(dimethylamino)-1-naphthyl groups each 3 center-2 electron bonded via C(1) to two lithium atoms and via the nitrogen lone pair to one of these lithium atoms. Diethyl ether coordination completes the pseudo tetrahedral lithium coordination sphere. Variable temperature ^{7}Li and ^{1}H NMR spectroscopy reveals an equilibrium between the $[8\text{-}Me_2NC_{10}H_6Li\cdot OEt_2]_2$ species and the ether-free $[8\text{-}Me_2NC_{10}H_6Li]_n$. A tetranuclear structure is proposed for the latter species.

Heteroatom-facilitated *ortho*-lithiation is a valuable tool in organic and organometallic synthesis [1]. However, little is known about either the detail of the sequence of this reaction or the importance of the lithium-heteroatom interaction and its influence on the structures of organolithium species in various solvents.

*Dedicated to Professor G.J.M. van der Kerk, on the occasion of his 70th birthday on March 21, 1983.

**To whom correspondence should be addressed.

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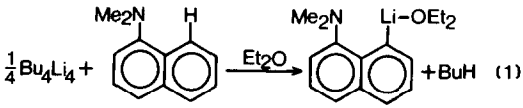
We recently described the structure of $2\text{-}Me_2NCH_2C_6H_4Li$ (I) which exists both in the solid state and in diethyl ether as a tetranuclear species having each aryl moiety 4 center-2 electron bonded (via C(1)) to one Li_3 face of a Li_4 tetrahedron [2]. The remaining free coordination site on each Li atom is occupied by the heteroatom-containing substituent $CH_2(Me_2)N$. It is probably this Li—N coordination which stabilizes the tetranuclear structure in Et_2O. In the more strongly coordinating solvent THF the tetranuclear structure of I breaks down into a dinuclear one involving $2\text{-}Me_2NCH_2C_6H_4$ groups which are 3 center-2 electron bonded via C(1) and free $2\text{-}Me_2NCH_2$ substituents. In order to find out whether the flexibility of the five-membered chelate ring formed on Li—N coordination is an important factor affecting the structural features of these organolithium compounds we have studied the structure of 8-(dimethylamino)-1-naphthyllithium (II). In contrast to the flexible, puckered C(1)CCN moiety present in I, the naphthyllithium compound II should have a rigid, flat C(1)CC(8)N arrangement.

The 1/1 molar reaction of 1-(dimethylamino)naphthalene with n-butyllithium in diethyl ether affords quantitatively 8-(dimethylamino)-1-naphthyllithium etherate (II) by the H/Li exchange reaction shown in eq. 1. Crystals



of II, grown from Et_2O are monoclinic with space group $P2_1/c$ with two molecules in a unit cell of dimensions a 10.669(2), b 12.647(5), c 11.592(3) Å and β 102.95(2)°. 2102 Reflections with intensities above the 2.5 σ level were measured on a Nonius-CAD4 diffractometer using graphite monochromated Cu-K_α radiation. No absorption correction was applied. The structure was solved by means of the new version of the symbolic addition program set SIMPEL [3]. Block-diagonal least-squares refinement anisotropic for Li, C, N and O, isotropic for H, converged to an R value of 0.070. A weighting scheme $w = (5.86 + F_o + 0.0068\,F_o^2)^{-1/2}$ was applied. The calculations were performed with the XRAY system and PLUTO.

The molecular geometry of the dimeric $[8\text{-}Me_2NC_{10}H_6Li\cdot OEt_2]_2$ units as well as relevant bond distances and bond angles are given in Fig. 1a.

Each of the 8-(dimethylamino)-1-naphthyl groups is bonded to two Li atoms via C(1), with almost equal C(1)—Li distances (2.224(4) and 2.232(4) Å) and via the lone pair of the NMe_2-nitrogen atom to one of these Li atoms, N—Li 2.136(4) Å*. The fourth coordination site of each Li atom is occupied by a coordinated diethyl ether molecule, with a Li—O distance of 1.969(4) Å: thus giving distorted tetragonal coordination geometry for each Li atom.

Complex II is to our knowledge the first example for which X-ray crystallography has revealed how an ether molecule coordinates to lithium in an organolithium-ether complex. The Li—O (diethyl ether) distance in II is comparable to previously reported Li—O (THF) distances (1.97 Å [4,5]).

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*The Li—Li distance of 2.366(5) Å is the shortest observed so far.

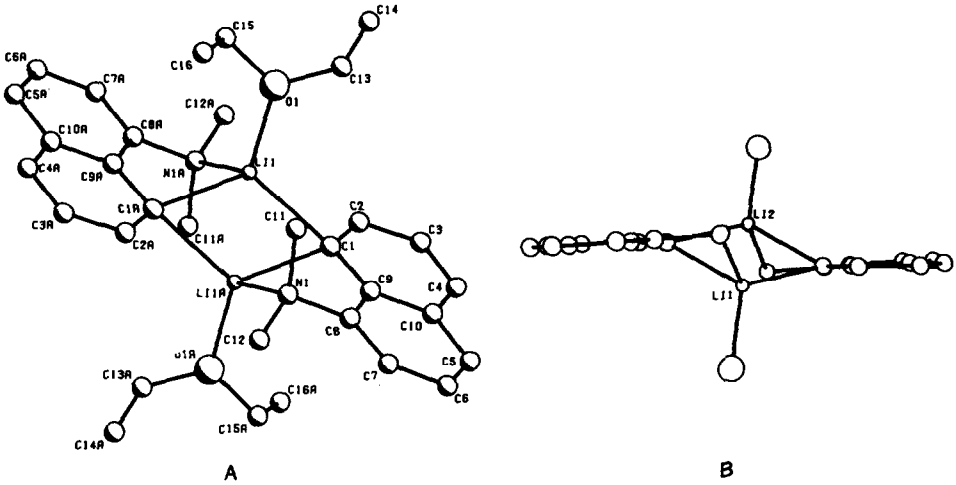
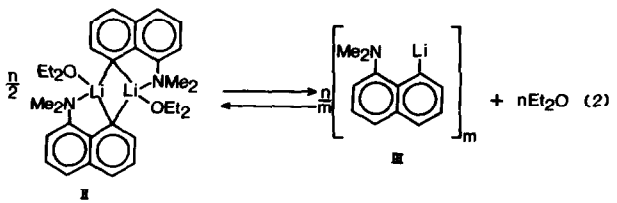


Fig. 1. (A) Overall structure of dimeric 8-(dimethylamino)-1-naphthyllithium etherate (II): Li(1)—Li(1A) 2.366 (5), C(1)—Li(1) 2.232 (4), C(1)—Li(1A) 2.224 (4), N(1)—Li(1A) 2.136 (4), O(1)—Li(1) 1.969 (4) Å; Li(1)—C(1)—Li(1A) 64.2 (1), C(1)—Li(1)—O(1) 114.3 (2), C(1)—Li(1)—C(1A) 115.8 (2), C(1)—Li(1)—N(1A) 116.7 (2)°. (B) Projection of molecule II perpendicular to the plane of the naphthalene rings. (The alkyl groups on both nitrogen and oxygen atoms are not shown).

As shown in Fig. 1b the orientation of the naphthyl skeleton with respect to the $C(1)Li_2C(1)'$ unit deviates markedly from the arrangement expected for an electron deficient (3 center-2 electron) CLi_2 bond (cf. structures of Ph_6Al_2 [6], $Me_4Ph_2Al_2$ [7], $Ph_2Li_2 \circ 2TMEDA$ [8]). This may be due to the fact that, in contrast to the distorted naphthyl skeletons found in other 1,8-disubstituted naphthyl compounds [9], the C(1)CC(8)N arrangement in II remains essentially flat (see Fig. 1b) when C(1) binds to two Li atoms. A further factor may be Li—N coordination, leading to a Li—N distance of 2.136(4) Å*.

Unlike I, which is a tetramer both in benzene and in diethyl ether, II exists in diethyl ether as a dimeric monoetherate and can only be isolated as such from this solvent. The ether molecule cannot be removed from solid II in vacuo. It was therefore surprising to observe that diethyl ether free, crystalline



$[8\text{-}Me_2NC_{10}H_6Li]_n$ (III), can be isolated by dissolution of the etherate complex, II, in benzene and subsequent evaporation of the solvent. Solutions of II and III studied by ^1H, ^{13}C and ^7Li NMR at different temperatures point to the existence of equilibrium 2.

*C(1)···C(8) is about 2.4 Å.

The ^1H NMR spectrum of III in toluene-d_8, below 0°C, shows two resonances for the NMe_2 CH_3 groups (δ 1.80 and 2.45) which coalesce to one singlet (δ 2.10) at 24°C. (See below for a proposed structure). The ^1H NMR spectrum of pure II (or the solution obtained by adding Et_2O in a 1/1 molar ratio to III) in toluene-d_8 at room temperature revealed the same resonance pattern (e.g. δ(H(2)) 8.45). In addition to this pattern the CH_3 (δ 1.05 t) and CH_2O (δ 3.25 q) resonances of free diethyl ether were present. This indicates that equilibrium 2 lies to the right at room temperature. On cooling this solution the ^1H resonance pattern of a second organolithium species, tentatively assigned to II, appears (0°C; δ(NMe_2) 3.25 and δ(H(2)) 8.85). The proton resonances of Et_2O start to shift upfield reaching at −70°C the position of coordinated Et_2O [10] (δ(CH_3) 0.60 and δ(CH_2O) 2.80). The II/III molar ratio is then 4/1. This process is fully reversible with temperature.

More direct evidence for such an equilibrium comes from the ^7Li NMR spectra at different temperatures (See Fig. 2) with the ^7Li resonance at 4.72 ppm being ascribed to III. At −90°C this resonance has almost disappeared and a new resonance belonging to the etherate is present at 3.45 ppm.

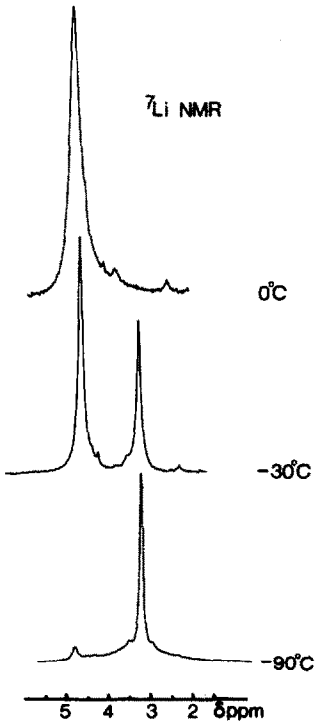


Fig. 2. ^7Li NMR spectra of II in toluene-d_8 at 0, −30 and −90°C respectively. Shifts are in ppm relative to 1 *M* LiCl in D_2O external.

The structure of III is now being studied in detail. The available data (^1H and ^{13}C NMR: diastereotopic NMe_2 resonances, δ($^{13}C(1)$) 177 which are characteristic for 4 center-2 electron bonded $sp^2C(1)$ [2]) suggest a structure similar to that established for tetrameric I. This implies that as a

result of the rigid, flat C(1)CC(8)N arrangement, polynuclear III and the dinuclear etherate II have comparable stabilities. In the presence of even a weakly coordinating solvent, such as Et_2O, 8-$Me_2NC_{10}H_6Li$ exists as (at least) two species (having entirely different structures), the relative concentration of which depends on the temperature (See Fig. 2). These species probably (cf. also the $I/R_2Li_2 \cdot 4$ THF system [2]) also have different reactivities, which makes these findings important for a better understanding of the structure (solvent)/reactivity relationship of *ortho*-lithiated reagents in organic and organometallic synthesis [1].

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