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Solution and Solid-State Structure of (1-Methoxy-8-naphthyllithium·THF)$_2$

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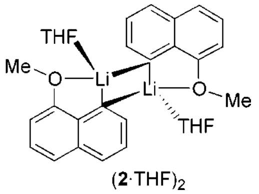
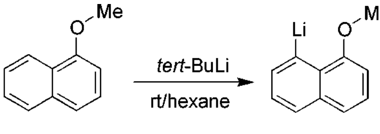
ABSTRACT



The structure of (1-methoxy-8-naphthyllithium·THF)$_2$, (2·THF)$_2$, determined by single-crystal X-ray diffraction (crystal data: monoclinic, a = 8.1816 (5), b = 21.9649 (14), and c = 8.2345 (3) Å, β = 117.969 (3)°; V = 1306.97 (12) Å^3; space group $P2_1/n$; Z = 4) reveals a centrosymmetrical dimer with a twist angle of about 63° between the naphthyl rings and the Li–C$_{ipso}$–Li plane, representing an intermediate between perpendicular and planar tetracoordinated C$_{ipso}$. NMR studies at low temperature indicate that 2 is dimeric in THF-d_8 solution under these conditions.

Investigations on the reaction of 1-methoxynaphthalene (**1**) with n-BuLi by Graybill and Shirley[1] showed the lithium agent to metalate the aromatic compound either in the ortho (2) or in the peri position (8), respectively. According to Shirley and Cheng,[2] the regioselectivity of this metalation can be controlled very effectively. Thus, reacting **1** with an equimolar *n*-BuLi/*N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) mixture and quenching with solid CO$_2$ results in more than 99% carboxylation in position 2 (59% overall yield), whereas treatment with *tert*-BuLi and subsequent quenching leads to more than 98% carboxylation in position 8 (20−35% overall yield) (Scheme 1).

Scheme 1



1 **2**

During our investigations on the mechanisms of these lithiation reactions, we were able to isolate crystals of **2**·THF. The lithium compound was synthesized by metalation of **1** with 1 equiv of *tert*-BuLi and crystallization of the product in THF at low temperatures.

The structure of dimeric **2**·THF is shown in Figure 1. Selected bond lengths and bond angles are listed in Table 1.

The “anionic” carbon atom is bonded to two lithium atoms. One of these lithium atoms is part of a nearly planar O(10)−

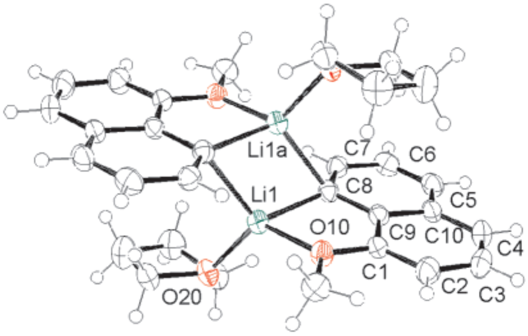


Figure 1. ORTEP drawing of dimeric (1-methoxy-8-naphthyllithium·THF)$_2$, (**2**·THF)$_2$ (symmetry operation: $-x + 1, -y, -z$).

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Table 1. Selected Bond Lengths (Å) and Angles (deg) of (1-Methoxy-8-naphthyllithium·THF)$_2$, (**2**·THF)$_2$

atoms	bond length	atoms	bond length
Li(1)−O(20)	1.949 (4)	Li(1)−Li(1a)[a]	2.391 (8)
Li(1)−O(10)	2.020 (4)	C(1)−O(10)	1.385 (3)
Li(1)−C(8)	2.162 (5)	C(8)−Li(1a)[a]	2.232 (4)
Li(1)−C(8a)[a]	2.232 (4)	C(9)−C(10)	1.430 (3)

atoms	
C(1)−C(2)−C(3)	119.7 (2)
C(2)−C(1)−C(9)	122.3 (2)
C(10)−C(9)−C(1)	116.2 (2)
C(2)−C(1)−O(10)	123.0 (2)
C(8)−C(7)−C(6)	124.8 (2)
C(7)−C(8)−C(9)	113.5 (2)
C(10)−C(9)−C(8)	123.1 (2)
C(7)−C(8)−Li(1)	139.2 (2)
O(20)−Li(1)−O(10)	120.1 (2)
O(10)−Li(1)−C(8)	82.14 (16)
C(8)−Li(1)−Li(1a)[a]	58.45 (17)
Li(1)−C(8)−Li(1a)[a]	65.89 (18)

[a] Symmetry transformation used to generate equivalents atoms: $-x + 1, -y, -z$.

C(1)−C(9)−C(8)−Li(1) five-membered ring which is coplanar with the naphthyl backbone (Figure 2).

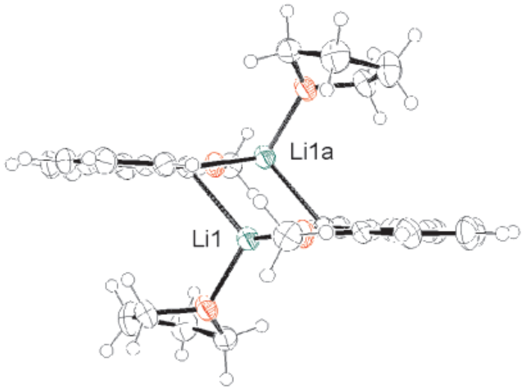
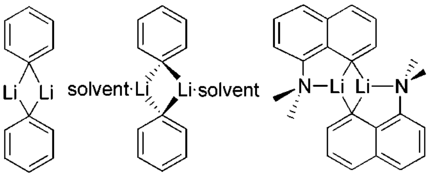


Figure 2. ORTEP drawing of (**2**·THF)$_2$ to demonstrate the nearly in plane coordination of the lithium atoms.

The C(8)−Li(1) distance within this ring (2.162 (5) Å) is about 0.07 Å shorter than the distance of C(8) to the lithium atom (Li(1a)) of the second monomeric unit.

Scheme 2



3 **4** **5**

An interesting aspect of the dimer is the coordination of the lithium-bound carbon atom (C8). According to computational studies, carbon atoms attached to two lithium atoms are stabilized in a planar tetracoordinated ($R^1R^2CLi_2$) arrangement.[3,4] For example, calculations on the unsolvated phenyllithium dimer **3** (Scheme 2) show the planar R^1R^2-CLi_2 coordination to be more stable then the analogous "perpendicular" structure.[5] However, solvation of the lithium results in a preferred formation of the "perpendicular" structure [e.g., (phenyllithium·TMEDA)$_2$ (**4**)].[6]

Therefore, Schleyer et al. suggested intramolecular solvation (chelation) to favor a planar tetracoordinated carbon atom.[5] In (**2**·THF)$_2$ both inter- and intramolecular solvation are present. In agreement with the existence of both solvation possibilities, the value of the twist angle between the Li(1)−C(8)−Li(1a) plane and the naphthyl ring (ca. 63°) lies between the perpendicular (90°) and the planar (0°) arrangement (Figure 3).

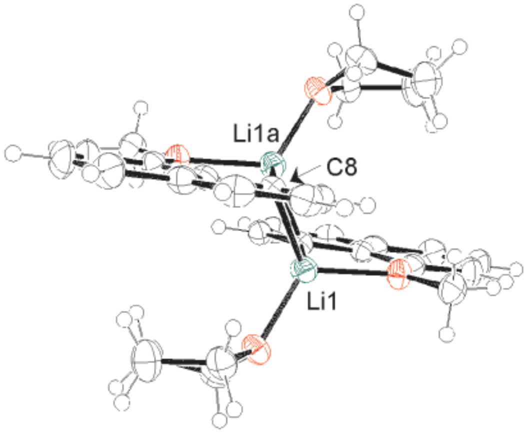


Figure 3. ORTEP drawing of (**2**·THF)$_2$ to demonstrate the twist angle between the Li(1)−C(8)−Li(1a) plane and the naphthyl backbone.

Interestingly, the first observed nearly planar C_{ipso} arrangement (twist angle ca. 11°) was observed within the dimer (1-(dimethylamino)-8-naphthyllithium·Et_2O)$_2$[7,8] (**5**·Et_2O)$_2$. This compound—quite similar to (**2**·THF)$_2$—indicates that increasing intramolecular and decreasing intermolecular

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solvation—the transition from **2**·THF to **5**·Et_2O—actually leads to planar tetracoordinated C_{ipso} atoms. In this context, the structure of **2**·THF can be viewed as a link between perpendicular and planar coordination.

The geometries of the two nearly regular hexagons within the 1-methoxynaphthalene skeleton in $(\mathbf{2}\cdot THF)_2$ are distinctly distorted. The angle around the lithiated carbon atom (C(7)−C(8)−C(9)) is remarkably small (113.5°). To preserve the planarity of the ring, the neighboring endocyclic angles are comparatively high (124.8° and 123.1°, respectively).[7] The same effect, although smaller and with reversed sign, can be observed in the second ring. The CCC angle around the methoxy-substituted carbon (C(9)−C(1)−C(2)) atom is increased (122.3°), and the endocyclic angles alongside are decreased (119.7 and 116.2°, respectively).

According to Domenicano et al.,[9,10] there is a linear correlation between the angle around the substituted carbon and the Pauling electronegativity of the ring-bound substituent. As discussed by Harder et al.,[11] the p character tends to concentrate in the hybrid orbital directed toward the most electronegative substituent (Walsh's rule).[12] Thus, the decrease of the C−C(Li)−C angle is due to the electropositive effect of the lithium cation increasing the p character in the C−C(Li) bonds.[11]

These pronounced deformations can be found in numerous aryllithium crystal structures.[11,13] In general, the large distortions caused by the lithium ions dominate the weaker distortions caused by other substituents which may be present in these molecules,[11] e.g., methoxy or dimethylamino groups ortho to lithium. In **2**·THF, the lithium and the methoxy group are attached to different rings of the naphthyl skeleton. Because of this structural separation, it is possible to distinguish the weak distortion caused by the methoxy group from the stronger one originating from the lithium atom (see above).

NMR studies to determine the aggregation state of **2** in solution were successful at very low temperatures. The ^{13}C spectrum of **2** in THF-d_8 at −105 °C shows a septet ($^1J(^{13}C,^7Li) = 19.3$ Hz) for the *ipso* carbon atom. Since commercial *tert*-BuLi (92.5% ^7Li, $I = ^3/_2$) was employed for the metalation, this line splitting pattern indicates a static dimer. Measurements at higher temperatures gave no further information; the C_{ipso} signal broadens and no line splitting is observable.

This structure nicely demonstrates the influence of electron-donating solvents and ligands on the arrangement of the lithiated carbon atoms. Because of the separation of the lithium atom in the peri position and the methoxy ether (in contrast to ortho-lithiated compounds), the influence on the naphthyl skeleton of both groups is observable.

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Supporting Information Available: ^{13}C NMR spectrum and X-ray data for $(\mathbf{2}\cdot THF)_2$. This material is available free of charge via the Internet at http://pubs.acs.org.

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