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The solution and solid state structure of {[1-(dimethylamino)-8-naphthyl]lithium·THF}$_2$ †

Jürgen Betz, Frank Hampel and Walter Bauer *

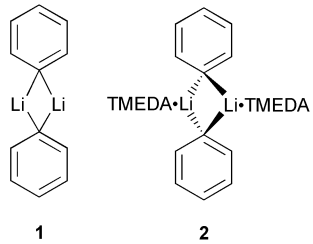
Institut für Organische Chemie, Universität Erlangen-Nürnberg, Henkestrasse 42,
D-91054 Erlangen, Germany. E-mail: bauer@organik.uni-erlangen.de

Received 13th November 2000, Accepted 26th April 2001
First published as an Advance Article on the web 29th May 2001

The reaction of *N*,*N*-dimethyl-1-naphthylamine with butyllithium agents is known to yield the *peri* lithiated product (**3**). The now reported structure of dimeric [1-(dimethylamino)-8-naphthyl]lithium with two molecules of THF (**3**·THF)$_2$ shows a twist angle between the naphthyl-rings and the Li–C$_{ipso}$–Li plane of *ca.* 38°. The magnitude of the $^1J(^{13}C,^7Li)$ coupling constant as well as the line splitting pattern of the lithiated carbon atom in the ^{13}C spectrum (THF-d_8) demonstrate the existence of a dimeric species at −90 °C in solution. A previously published single crystal X-ray structure of dimeric [1-(dimethylamino)-8-naphthyl]lithium with two coordinating molecules of diethyl ether (**3**·Et$_2$O)$_2$ shows a smaller twist angle between the naphthyl-rings and the Li–C$_{ipso}$–Li plane of *ca.* 11°. We assign this reduction of the twist angle to the weaker solvation properties of Et$_2$O.

Introduction

According to computational studies carbon atoms attached to two lithium atoms should be stabilized in a planar tetracoordinated ($R^1R^2CLi_2$) arrangement.[1,2] Although calculations on the unsolvated phenyllithium dimer (**1**, see Scheme 1) show the planar $R^1R^2CLi_2$ to be energetically favorable,[3] solvation of the lithium atoms results in a preferred formation of the "perpendicular" structure [*e.g.* (phenyllithium·TMEDA)$_2$ (**2**),[4] see Scheme 1]. Hence, Chandrasekhar and Schleyer proposed intramolecular solvation (chelation) to lead toward planar tetracoordinated carbon atoms.[3]



Scheme 1 Drawings of planar coordinated unsolvated phenyllithium dimer (**1**) and perpendicular coordinated (phenyllithium·TMEDA)$_2$ (**2**).

The first observed nearly planar C$_{ipso}$ arrangement (twist angle *ca.* 11°) was observed within the dimeric [1-(dimethylamino)-8-naphthyl]lithium·Et$_2$O (**3**·Et$_2$O)$_2$.[5,6] During our investigations on the lithiation of 1-methoxynaphthalene with butyllithium agents we were able to isolate and characterize crystals of (1-methoxy-8-naphthyllithium·THF)$_2$ (**4**·THF)$_2$[7] (Fig. 1). Although this compound is quite similar to **3**·Et$_2$O the twist angle between the naphthyl skeleton and the Li–C$_{ipso}$–Li plane of about 63° is remarkably high. Thus replacement of the NMe$_2$-group by OMe and replacement of Et$_2$O by THF as coordinating solvent leads to a much more pronounced perpendicular arrangement. In order to separate the influence of the intramolecular solvation group (OMe and NMe$_2$, respectively) from the influence of the intermolecular solvation group (Et$_2$O and THF, respectively), we became interested in crystals of [1-(dimethylamino)-8-naphthyl]lithium (**3**) with THF as coordinating solvent. Treatment of *N*,*N*-dimethyl-1-naphthylamine with *n*-BuLi in THF at room temperature yields [1-(dimethylamino)-8-naphthyl]lithium. Crystals of dimeric [1-(dimethylamino)-8-naphthyl]lithium·THF (**3**·THF)$_2$ are formed upon cooling of this solution. This compound allows us to gain information on the influence of the intramolecular solvation group [comparison of (**3**·THF)$_2$ with (**4**·THF)$_2$ since these compounds differ only in the nature of their substituents]. Additional information on the influence of the coordinating solvent can be gained by comparison of (**3**·THF)$_2$ with (**3**·Et$_2$O)$_2$, here only the solvent molecules are interchanged.

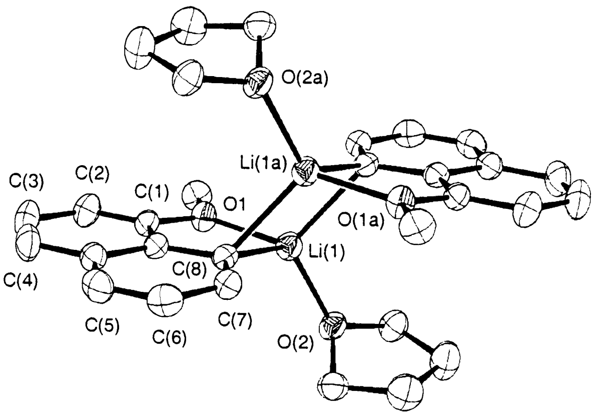


Fig. 1 ORTEP[17] drawing of (1-methoxy-8-naphthyllithium·THF)$_2$ (**4**·THF)$_2$. For clarity, hydrogen atoms are omitted.

Results

The structure of dimeric **3**·THF is shown in Fig. 2. Selected bond lengths and bond angles are listed in Table 1. Each naphthyl group is attached (*via* C8) to two lithium atoms. The C(8)–Li(1) and C(8)–Li(1a) bond lengths [2.207(4) and 2.223(4) Å, respectively] are nearly identical. These numbers lie within the normal range of lithium–carbon distances. Due to the attached substituents the naphthyl skeleton is distorted. Appointed bond angles, as well as dihedral angles, differ from the numbers in

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† Dedicated to the memory of Dr Ron Snaith.

Electronic supplementary information (ESI) available: ^1H and COSY NMR spectra of [1-(dimethylamino)-8-naphthyl]lithium; PM3 calculations on **3** and **4**. See http://www.rsc.org/suppdata/dt/b0/b009077h/

Table 1 Selected bond lengths (Å) and angles (°) of [1-(dimethylamino)-8-naphthyl]lithium·THF

Li(1)–N(1a)[a]	2.102(4)	Li(1)–C(1a)[a]	2.761(4)
Li(1)–C(8)	2.207(4)	Li(1)–C(7)	2.740(4)
Li(1)–C(8a)[a]	2.223(4)	N(1)–C(1)	1.446(3)
Li(1)–Li(1a)[a]	2.335(7)		
N(1a)–Li(1)–C(8)	116.14(17)	C(2)–C(1)–C(9)	121.1(2)
N(1a)–Li(1)–C(8a)[a]	82.04(14)	C(1)–C(9)–C(10)	116.58(19)
C(8)–Li(1)–C(8a)[a]	116.38(15)	C(10)–C(9)–C(8)	122.54(19)
C(8)–Li(1)–Li(1a)	58.53(15)	C(7)–C(8)–C(9)	113.35(18)
C(8a)–Li(1)–Li(1a)[a]	57.86(15)	C(8)–C(7)–C(6)	125.4(2)
C(1)–C(2)–C(3)	120.8(2)		

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

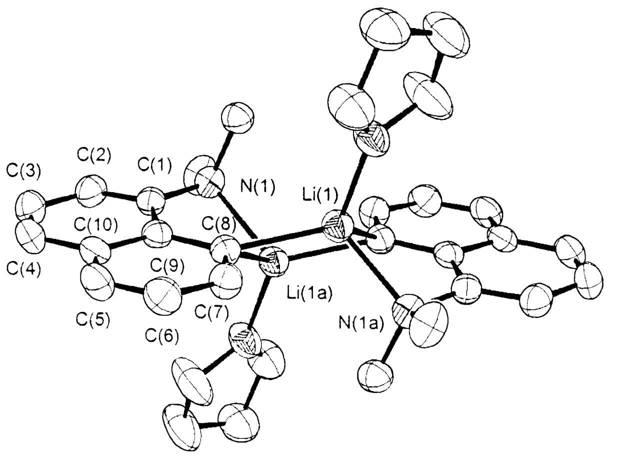


Fig. 2 ORTEP drawing of dimeric [1-(dimethylamino)-8-naphthyl]lithium·THF (**3**·THF)$_2$. For clarity, hydrogen atoms are omitted.

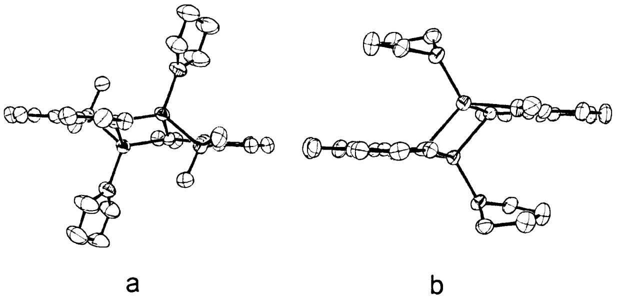
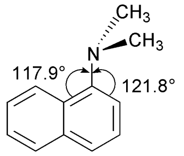


Fig. 3 ORTEP drawing of a) dimeric [1-(dimethylamino)-8-naphthyl]lithium·THF (**3**·THF)$_2$ and b) dimeric 1-methoxy-8-naphthyllithium·THF (**4**·THF)$_2$, view along the naphthyl planes to demonstrate the different distances between the naphthyl planes. Furthermore, the different arrangement of the THF molecules—"perpendicular" to the naphthyl plane for (**4**·THF)$_2$ and "parallel" to the naphthyl plane for (**3**·THF)$_2$—are observable. For clarity, hydrogen atoms are omitted.

unsubstituted naphthalene. The distance between the (parallel) averaged main planes of the two naphthyl skeletons (0.68 Å) is remarkably small (Fig. 3). In (**4**·THF)$_2$ this distance is distinctly larger (1.4 Å).

The lithium atoms in (**3**·THF)$_2$ are located *ca.* 0.37 Å above and 1.05 Å beneath the naphthyl planes. It is not possible to assign a particular lithium atom to one specific naphthyl ring. The distance between Li(1) and C(8) is slightly shorter than the distance between Li(1) and C(8a). Also, Li(1) is closer to the naphthyl plane involving C(8) but is coordinated to the nitrogen atom N(1a) of the second monomeric unit. This indicates a strong linkage between the two monomeric units. In contrast, in (**4**·THF)$_2$ the lithium atom Li(1) lies nearly in between the naphthyl plane involving C8. The Li(1)–C(8) bond length in (**3**·THF)$_2$ is by 0.07 Å shorter than the corresponding Li(1)–C(8a) distance, and Li(1) is coordinated to the oxygen atom of the same plane. Here, the monomeric units seem to be more loosely bound. In (**4**·THF)$_2$, as well as in most *ortho*-lithiated compounds, the hetero-substituent is significantly directed toward the lithium atom. Due to the intersected arrangement in (**3**·THF)$_2$, the amino groups are only slightly distorted [C(2)–C(1)–N(1) 121.6(2)° and C(9)–C(1)–N(1) 117.27(17)°, respectively] from the idealized 120° angle. These numbers are nearly identical with the calculated (PM3) N-C–C angles of *N*,*N*-dimethyl-1-naphthylamine (121.8° and 117.9°, respectively, Scheme 2). As discussed for (1-methoxy-8-naphthyllithium·THF)$_2$, a pronounced distortion within the naphthyl skeleton is observable.[7] The C(7)–C_{ipso}–C(9) angle (113.3°) is significantly reduced as compared to the idealized 120° angle.



Scheme 2 *N*,*N*-Dimethyl-1-naphthylamine with selected bond angles (PM3 calculation).

Similar deformations of the benzene geometry due to substitution are described.[8–11] Such distortions are directly related to the Pauling electronegativity of the substituents.[10,12] Thus, an electron-withdrawing substituent increases the angle around the substituent-bearing carbon atom, and *vice versa.* The replacement of a ring bound hydrogen atom by a stronger electronegative substituent (*e.g.* by NMe_2 in *N*,*N*-dimethyl-1-naphthylamine) results in a concentration of the p-character into the hybrid orbital directed toward the more electronegative substituent (Walsh's rule).[13,14] This is quite reasonable, since the p-electrons are held more loosely than the s-electrons and therefore shift more easily toward the more electronegative substituent. This electron shift of p-electrons causes an increased s-character in the neighboring C–C bonds and consequently an increased C–C–C angle around the substituted carbon atom.

The opposite effect occurs when replacing a hydrogen atom with an electropositive substituent (*e.g.* lithium). For aryllithium compounds numerous examples with remarkably distorted geometries can be found.[11,15] In contrast to *ortho*-substituted benzene derivatives, in {[1-(dimethylamino)-8-naphthyl]lithium·THF}$_2$, (**3**·THF)$_2$, the electronegative and the electropositive substituents are spatially separated. Therefore, both effects are observable. The C(7)–C_{ipso}–C(9) angle is decreased to 113.35(18)°, and the C(2)–C(NMe_2)–C(9) angle is slightly increased to 121.1(2)°. Despite these interferences the naphthyl plane remains comparatively flat. This is only possible due to the fact that the endocyclic angles (around the substituted carbon atoms) partly compensate these distortions. Thus the angles C(6)–C(7)–C(8) 125.4(2)° and C(8)–C(9)–C(10) 122.54(19)° are noticeably enlarged whereas the angles C(1)–C(2)–C(3) 120.8(2)° and C(10)–C(9)–C(1) 116.58(19)° are—at least in the latter case—minimized. The smaller distortions for the angle neighboring the nitrogen substituted carbon atom are due to the overall smaller effect evoked by the dimethylamino group compared to the lithium cation.

As mentioned before, one of the main interests concerns the twist angle between the naphthyl skeleton and the Li(1)–C_{ipso}–Li(1a) plane in order to gain information on a route toward a planar tetracoordinated carbon atom. Within (**3**·THF)$_2$ the angle between the naphthyl skeleton and the Li(1)–C_{ipso}–Li(1a) plane (in the text this angle will be termed "twist angle") is about 38°. This means that replacement of Et_2O by THF as solvation agent for the [1-(dimethylamino)-8-naphthyl]lithium leads—in the solid state—to a dramatically increased twist angle [in (**3**·Et_2O)$_2$ this angle is about 11°]. Substitution of the stronger electron-donating THF by Et_2O therefore tends to result in an increased planar (less perpendicular) arrangement.

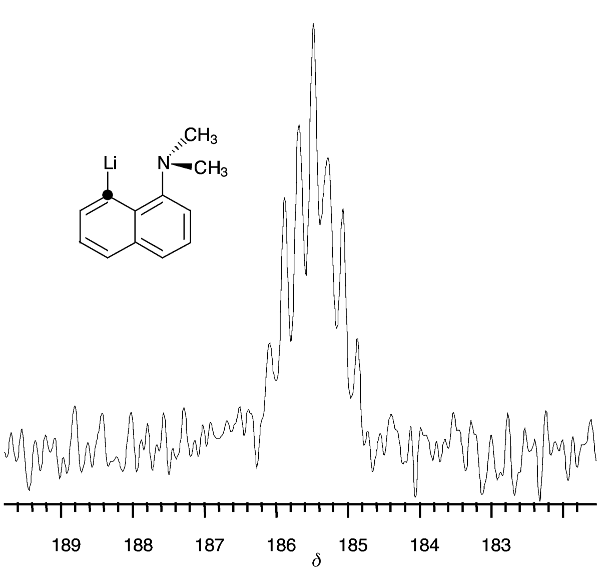


Fig. 4 ^{13}C spectrum of [1-(dimethylamino)-8-naphthyl]lithium (**3**) in THF-d_8 at −90 °C. Only the zoomed region of the lithiated carbon atom C8 (marked with a ●) is reproduced.

Semiempirical (PM3) calculations on (**3**·THF)$_2$ and (**3**·Et$_2$O)$_2$ confirm this tendency. Additional calculations on unsolvated dimeric **3** show a further minimized twist angle: the numbers for the twist angles decrease from 47.6° for (**3**·THF)$_2$ and 41.7° for (**3**·Et$_2$O)$_2$ to 26.2° for unsolvated dimeric [1-(dimethylamino)-8-naphthyl]lithium. PM3 calculations on unsolvated dimeric 1-naphthyllithium (no intra- nor inter-molecular solvation is present) even results in a planar coordination (twist angle = 0.8°).

The single crystal X-ray structure of (**4**·THF)$_2$ shows—compared to (**3**·THF)$_2$—a further increased twist angle (about 63°). Thus, replacement of the NMe$_2$ group in (**4**·THF)$_2$ by OMe in (**3**·THF)$_2$ leads to an almost perpendicular arrangement. Comparison of the PM3 calculations on (**3**·THF)$_2$ with those of (**4**·THF)$_2$ (45.1°) show a reversed result. The calculated twist angle of (**4**·THF)$_2$ is 2.5° smaller than the twist angle of (**3**·THF)$_2$. This difference between calculated and experimental data is probably due to intermolecuar interactions in the solid state (such as packing effects). PM3 calculations on (**4**·Et$_2$O)$_2$ show a minimal reduced twist angle for (**4**·Et$_2$O)$_2$ (45.0°) compared to (**4**·THF)$_2$ (45.1°), calculations on solvent free dimeric 1-methoxy-8-naphthyllithium resulted in a nearly planar tetracoordinated carbon atom with a twist angle of only 4.4°.

NMR investigations of [1-(dimethylamino)-8-naphthyl]lithium in THF-d_8 at −90 °C reveals a resolved septet in the ^{13}C spectrum for the lithiated carbon atom (Fig. 4). Since commercial *t*-BuLi (92.5% ^{7}Li, $I = 3/2$) was employed for the metalation, this line splitting pattern indicates a static dimer with a coupling constant $^{1}J(^{13}\mathrm{C},^{7}\mathrm{Li})$ of 20.5 Hz. The ^{13}C spectrum of 1-methoxy-8-naphthyllithium in THF-d_8 at −105 °C also revealed a septet for the lithiated carbon atom [$^{1}J(^{13}\mathrm{C},^{7}\mathrm{Li})$ = 19.3 Hz].[7] Apart from the line splitting pattern, the magnitude of the coupling constant also indicates a dimeric structure in solution. The numbers of the detected $^{1}J(^{13}\mathrm{C},^{7}\mathrm{Li})$ coupling constants (20.5 Hz and 19.3 Hz, respectively) lie within the normal range of dimeric organolithium compounds.[16]

Conclusions

The single crystal X-ray structure of dimeric [1-(dimethylamino)-8-naphthyl]lithium·THF (**3**·THF)$_2$ fills the gap between the known structures of dimeric [1-(dimethylamino)-8-naphthyl]lithium·Et$_2$O (**3**·Et$_2$O)$_2$ and the likewise dimeric 1-methoxy-8-naphthyllithium·THF (**4**·THF)$_2$. Here, the replacement of Et$_2$O by THF [transition from (**3**·Et$_2$O)$_2$ to (**3**·THF)$_2$] leads—due to the enhanced intermolecular solvation—to the expected increased twist angle between the naphthyl-plane and the Li(1)–C$_{ipso}$–Li(1a) plane. A further enlargement of this twist angle is observable within the structure of (**4**·THF)$_2$ (transition from *N*,*N*-dimethyl-1-naphthylamine to 1-methoxynaphthalene). In the ^{13}C spectrum, both the line splitting pattern as well as the coupling constants are indicative of a dimeric structure of [1-(dimethylamino)-8-naphthyl]lithium·THF in solution at low temperatures (−90 °C).

Experimental

[1-(Dimethylamino)-8-naphthyl]lithium (3)

In a flame dried Schlenk flask 0.25 ml (6.3 mmol) n-BuLi (2.5 M in hexane) was added to 1 g (5.8 mmol) *N*,*N*-dimethyl-1-naphthylamine (Aldrich). The solvent was removed *in vacuo* and 10 ml dry THF were added. The formation of [1-(dimethylamino)-8-naphthyl]lithium (**4**) is completed after *ca.* 12 hours at room temperature. Crystals of dimeric [1-(dimethylamino)-8-naphthyl]lithium·THF (**3**·THF)$_2$ are formed upon cooling of this solution to −78 °C. Once the crystals are formed, they remain stable at room temperature. The crystals were mounted in inert oil and transferred to the cold gas stream of the diffractometer. NMR spectra for **3** are provided as ESI.†

Crystal data

$C_{16}H_{20}LiNO$, $M = 249.17$, monoclinic, $a = 11.5897(6)$, $b = 11.7592(8)$, and $c = 11.3237(7)$ Å, $\beta = 109.222(3)°$, $U = 1457.22(15)$ Å^3, space group $P2_1/c$, $Z = 4$, μ(Mo-K$_\alpha$) = 1.9 mm^{-1}, $T = 173(2)$ K, 4266 reflections measured, 2559 unique ($R_{\mathrm{int}} = 0.0298$). The final $wR(F^2)$ was 0.1709 (all data). X-Ray data of these crystals were collected on a Nonius Kappa CCD diffractometer.

CCDC reference number 161688.

See http://www.rsc.org/suppdata/dt/b0/b009077h/ for crystallographic data in CIF or other electronic format.

^{13}C NMR measurement

The ^{13}C spectrum was obtained on a JEOL GX400 spectrometer (100.5 MHz for ^{13}C). Resolution enhancement (Gaussian window) was applied. The moisture sensitive lithium compound was handled in a glove bag. Crystals of [1-(dimethylamino)-8-naphthyl]lithium·THF (**3**·THF) were transferred into an NMR tube which was sealed with a serum cap and *ca.* 0.7 ml of dry THF-d_8 were added *via* syringe.

Acknowledgements

This work was supported by the Fonds der Chemischen Industrie and the Deutsche Forschungsgemeinschaft.

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