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Synthesis and characterization of novel chelated dimethylamino lithium arylamide dimers: molecular structure of [1-LiNPhCHPhCH$_2$-2-NMe$_2$C$_6$H$_4$]$_2$

Harbi Tomah Al-Masri, Joachim Sieler and Evamarie Hey-Hawkins*

Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany

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The reaction of 1-NHPhCHPh-2-NMe$_2$C$_6$H$_4$ (1) and 1-NHPhCHPhCH$_2$-2-NMe$_2$C$_6$H$_4$ (2) with *n*-BuLi in diethyl ether gave the solvent-free chelated dimethylamino lithium amides [1-LiNPhCHPh-2-NMe$_2$C$_6$H$_4$]$_2$ (3) and [1-LiNPhCHPhCH$_2$-2-NMe$_2$C$_6$H$_4$]$_2$ (4). The lithium amides 3 and 4 were characterized by ^{1}H, ^{7}Li, and ^{13}C NMR spectroscopy. A crystal structure determination was carried out on 4, which is the first example of a structurally characterized solvent-free dimeric chelated dimethylamino lithium arylamide with three-coordinate lithium centers that contains a seven-membered chelate ring. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: lithium arylamide; molecular structure; seven-membered chelate ring

INTRODUCTION

Amidolithium compounds (LiNRR′)$_n$ and their adducts [Li(L)$_x$NRR′]$_n$ (L = Lewis base) are valuable reagents in organic and organometallic synthesis.[1] Titherley presented the first preparation of lithium amides as early as 1894,[2] and a large number of different oligomers and structural motifs for lithium amides have been revealed by X-ray crystallography,[3–6] such as: monomers; dimers, trimers, and tetramers with planar Li–N rings; lithium amides solvated by the corresponding amine; solvent-bridged aggregates; ladders; mixed-metal ladders; and cage compounds. Crystal structures of dimeric lithium amides with three-coordinate lithium centers are known.[7–62] However, no crystal structures of solvent-free dimeric arylamides with three-coordinate lithium centers that contain a seven-membered chelate ring have been reported to date. A related alkylamido compound with three-coordinate lithium centers and a seven-membered chelate ring has been reported.[63]

We previously reported the synthesis and spectroscopic properties of the solvent-free chelated dimethylamino lithium alkoxide dimers [1-LiOCPh$_2$-2-NMe$_2$C$_6$H$_4$]$_2$, [1-LiOC(C$_6$H$_{11}$)$_2$-2-NMe$_2$C$_6$H$_4$]$_2$ and [1-LiOCPh$_2$CH$_2$-2-NMe$_2$C$_6$H$_4$]$_2$,[64] and the X-ray structural characterization of the solvent-free chelated dimethylamino lithium alkoxide dimers [1-LiOC(C$_6$H$_{11}$)$_2$-2-NMe$_2$C$_6$H$_4$]$_2$ and [1-LiOCPh$_2$CH$_2$-2-NMe$_2$C$_6$H$_4$]$_2$.[64]

We now report the high-yield synthesis and spectroscopic properties of the novel chelated dimethylamino lithium arylamides **3** and **4**, the latter being the first example of a structurally characterized solvent-free dimeric chelated dimethylamino lithium arylamide that contains a seven-membered chelate ring. Compounds **3** and **4** are of interest as chelating ligands for transition metals[65] and main group elements such as boron,[66–69] whereby intramolecular coordination by a tertiary amino group is possible.

SYNTHESIS AND SPECTROSCOPIC PROPERTIES

Synthesis

The dimeric lithium amides **3** and **4** can be readily prepared by addition of *n*-butyllithium in hexane to equimolar amounts of the organic ligands **1** and **2**[70] in diethyl ether at −15 °C (Scheme 1).

When the reaction was conducted in tetrahydrofuran, the temperature had to be maintained at −15 °C to obtain **3** and **4**. When the temperature was allowed to rise to 20 °C, a dark red solution was obtained, but the products that had formed were not characterized. However, when diethyl ether was employed as the solvent, the solvent-free chelated lithium

*Correspondence to: Evamarie Hey-Hawkins, Institut für Anorganische Chemie der Universität Leipzig, Johannisallee 29, D-04103 Leipzig, Germany.
E-mail: hey@rz.uni-leipzig.de

$$\underset{(\mathbf{1})}{\text{1-NHPhCHPh-2-NMe}_2\text{C}_6\text{H}_4} + n\text{-BuLi} \longrightarrow \underset{(\mathbf{3})}{1/2\ [\text{1-LiNPhCHPh-2-NMe}_2\text{C}_6\text{H}_4]_2}$$

$$\underset{(\mathbf{2})}{\text{1-NHPhCHPhCH}_2\text{-2-NMe}_2\text{C}_6\text{H}_4} + n\text{-BuLi} \longrightarrow \underset{(\mathbf{4})}{1/2\ [\text{1-LiNPhCHPhCH}_2\text{-2-NMe}_2\text{C}_6\text{H}_4]_2}$$

Scheme 1. Preparation of **3** and **4**.

amides **3** and **4** were obtained in 90–95% yield at −15 °C. Even when the solution was allowed to warm to 20 °C, the yields were still as high as 85–90%. Hence, the introduction of an NMe_2 substituent in the ortho position results in intramolecular coordination to lithium and formation of solvent-free lithium amides.

^{1}H, ^{13}C and ^{7}Li NMR

In the ^{1}H NMR spectrum, the most noticeable signal is that due to the $N(CH_3)_2$ protons, which give rise to a singlet at about 2.40 (**3**) and 2.39 ppm (**4**). These signals are at higher field than those of the precursors **1** (2.63 ppm) and **2** (2.73 ppm). The CH proton gives a singlet at 4.10 (**3**) and 2.90 ppm (**4**). In **4**, the signal of the methylene protons is observed at 4.2 ppm. The ^{1}H NMR signals of the aromatic rings of **3** and **4** are in the expected chemical shift range (6.5–7.4 ppm), as is also observed for **1** and **2**.[70]

The ^{13}C NMR spectrum shows one signal for the $N(CH_3)_2$ carbon atoms at 46.1 (**3**) and 45.8 ppm (**4**). For **3** and **4**, the signals of the CH proton are observed at 57.3 ppm and 62.2 ppm respectively. The methylene carbon atom of **4** gives a singlet at 42.2 ppm. The signals of the aromatic carbon atoms (114–153.5 ppm) are in the expected range, as observed for **1** and **2**.[70]

Both the ^{1}H and ^{13}C NMR spectra indicate that Li–N coordination and dimeric structures are present (on the NMR time scale) for **3** and **4** in solution.

The ^{7}Li NMR spectrum of the lithium amides **3** and **4** in C_6D_6 consists of a broad signal at about 2.2 ppm. As the ^{1}H and ^{13}C NMR spectra indicate that **3** and **4** do not dissociate into monomers but exist as dimers in solution, the two lithium atoms are isochronic.[64]

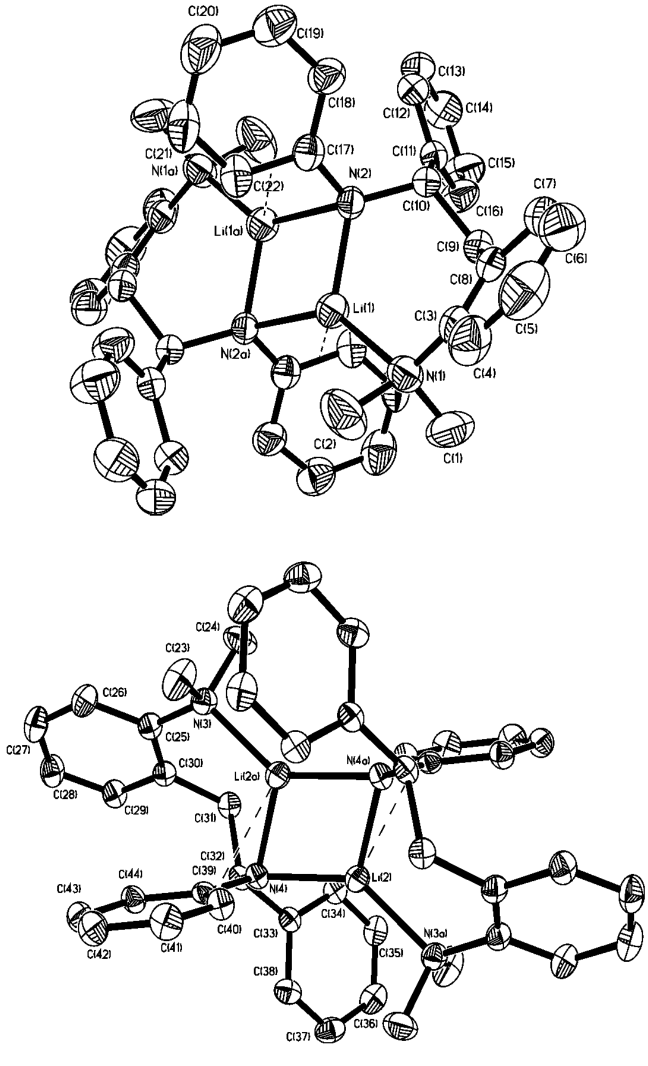


Figure 1. Molecular structure of the two independent molecules **4a** and **4b** showing the atom numbering scheme employed (ORTEP plot, 50% probability, SHELXTL-PLUS, XP).[71] Hydrogen atoms omitted for clarity.

MOLECULAR STRUCTURE

Colorless crystals of **4** were obtained from toluene at 20 °C. Compound **4** crystallizes in the triclinic space group $P\bar{1}$ with two independent molecules in the asymmetric unit (**4a** and **4b**, Fig. 1). Selected interatomic distances and angles are collected in Table 1.

The two independent molecules differ in the conformations of their seven-membered rings (Fig. 2), as indicated by the different puckering parameters,[72] in particular for the parameter ϕ (Table 2).

As in solution, **4** forms a centrosymmetric dimer in the solid state (Table 1, Fig. 1). Owing to the presence of an inversion center, only the *meso* isomer (*R*,*S*) is observed in the solid state. In **4a** and **4b**, the central four-membered Li_2N_2 ring is planar with smaller Li–N–Li and larger N–Li–N bond angles. The Li–N–Li and N–Li–N angles in **4a** and **4b** are similar to those in **5**–**8** (Table 3). In addition, the Li–N–Li angles in **4a** and **4b** are larger than those in **9**–**15** and smaller than those in **16**–**25** (Table 3), whereas the situation is reversed

Table 1. Selected bond lengths (Å) and bond angles (deg) for **4a** and **4b**

4a		4b	
Li(1)–N(2)	2.001(4)	Li(2)–N(4)	2.044(4)
Li(1)–N(2a)	2.102(4)	Li(2)–N(4a)	2.047(4)
Li(1)–N(1)	2.089(4)	Li(2)–N(3a)	2.071(4)
Li–η^2-Ph	2.510(4), 2.573(4)	Li–η^2-Ph	2.530(4), 2.593(4)
Sum of angles at Li(1)	359.99	Sum of angles at Li(2)	355.82
Li(1)–N(2)–Li(1a)	73.41(16)	Li(2)–N(4)–Li(2a)	72.71(16)
N(2)–Li(1)–N(2a)	106.59(16)	N(4)–Li(2)–N(4a)	107.29(16)
C(17)–N(2)–C(10)	116.64(16)	C(39)–N(4)–C(32)	115.96(16)
C(17)–N(2)–Li(1)	121.16(16)	C(39)–N(4)–Li(2)	120.43(16)
C(17)–N(2)–Li(1a)	89.79(15)	C(39)–N(4)–Li(2a)	92.92(14)

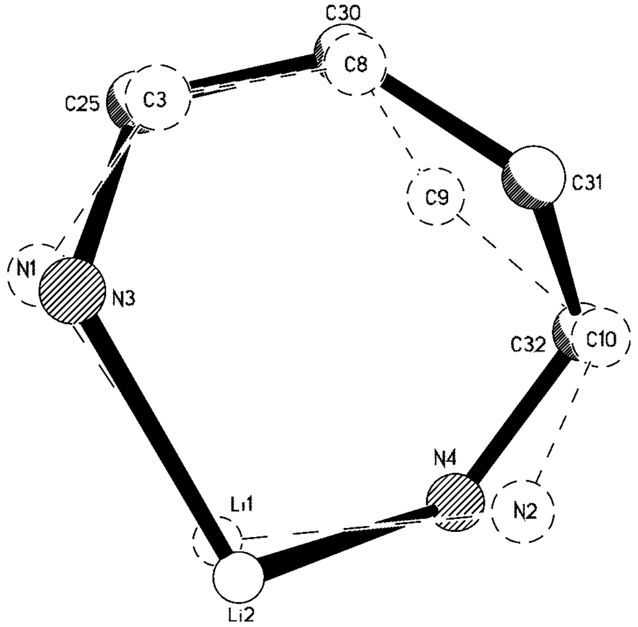


Figure 2. Conformations of the seven-membered rings for the independent molecules **4a** and **4b**.

Table 2. Puckering parameters for the seven-membered rings in **4a** (Li1–N2–C10–C9–C8–N1–C3) and **4b** (Li2–N4–C32–C31–C30–C25–N3)

Puckering parameter	4a	4b
q_2 (Å)	1.114(2)	1.110(2)
q_3 (Å)	0.128(2)	0.265(1)
ϕ_2 (deg)	−120.5(1)	−134.5(1)
ϕ_3 (deg)	109.6(11)	142.5(2)
QT (Å)	1.121(2)	1.141(2)
θ_2 (deg)	83.4(1)	76.6(1)

for the N–Li–N angles. Apparently, the presence of the N–Ph group increases the N–Li–N bond angle, presumably as a result of steric effects. The dimethylamino groups are coordinated to the lithium atoms [**4a**: Li(1)–N(1) 2.089(4) Å; **4b**: Li(2)–N(3a) 2.071(4) Å]. The Li–NMe_2 bond lengths are shorter than those in [$LiN(SiMe_3)_2(NMe_2CH_2Ph)$] (av. 2.22 Å).[33] The bond lengths and angles of the organic fragment of **4** are similar to those observed for the corresponding organic compound **2**.[70]

A planar environment would be expected for the three-coordinate lithium atoms in **4a** and **4b**, and the sums of bond angles in **4a** and **4b** are indeed close to 360°. The *anti* arrangement of the two NMe_2 methyl groups with respect to the Li_2N_2 core in **4a** and **4b** is similar to the *anti* alignment of the two NMe_2 methyl groups with respect to the Li_2O_2 core in [1-$LiOC(C_6H_{11})_2$-2-$NMe_2C_6H_4]_2$ and [1-$LiOCPh_2CH_2$-2-$NMe_2C_6H_4]_2$.[64] The Li–N amide bond lengths in **4a** [Li(1)–N(2) 2.001(4) Å, Li(1)–N(2a) 2.102(4) Å] and **4b** [Li(2)–N(4) 2.044(4) Å, Li(2)–N(4a) 2.047(4) Å] are comparable to those in **5**–**25**, which also contain a three-coordinate lithium atom. The distorted tetrahedral geometry at the amide nitrogen centers [**4a**: C(17)–N(2)–C(10) 116.64(16) Å, C(17)–N(2)–Li(1) 121.16(16) Å; **4b**: C(39)–N(4)–C(32) 115.96(16) Å, C(39)–N(4)–Li(2) 120.43(16) Å] dictates that the Ph groups lie above and below the Li_2N_2 plane, and ring stacking (face to face association) is thus prevented. Coordination of a donor solvent and achievement of a higher degree of association by ring-laddering[4] are prevented for steric reasons, as the relatively bulky Ph groups occupy much of the lateral space surrounding the Li_2N_2 rings. Each Ph group is arranged so that it is close to one lithium atom [**4a**: C(17)–N(2)–Li(1a) 89.79(15) Å; **4b**: C(39)–N(4)–Li(2a) 92.92(16) Å]. This allows each formally three-coordinate lithium atom to interact intramolecularly with the *ipso* and an *ortho* carbon atom of the *N*-phenyl rings [**4a**: Li(1)–C(17) 2.510(4) Å, Li(1)–C(22) 2.573(4) Å; **4b**: Li(2)–C(39) 2.530(4) Å, Li(2)–C(23) 2.593(4) Å]. The interaction of the phenyl ring with lithium in [Li(TMEDA)NPh(naphthyl)]$_2$ [Li$\cdots$C(Ph) 3.12–3.15 Å][73] and in the trimer [$LiN(CH_2Ph)_2]_3$ [Li$\cdots$C(benzyl) av. 2.80 Å][61] are weaker than those observed in **4a** and **4b**.

Table 3. Selected dimeric lithium amides

Dimer	No.	CN of Li[a]	Li–N(amido) (Å)	N–Li–N av. (°)	Li–N–Li av. (°)	Ref.
$[Li\{N,N\text{-}N(SiMe_3)N(SiMe_3)_2\}]_2$	**5**	3	1.917–1.970	107.8	72.2	30
$[Li(py)N(SiMe_3)_2]_2$	**6**	3	2.02–2.06	106.2	73.8	40
$[Li\{N,N\text{-}N(SiMe_3)SiMe_2NMe_2\}]_2$	**7**	3	2.013–2.029	106.3	73.1	35
$[Li\{N,N\text{-}N(^tBu)S(Et)N(^tBu)\}]_2$	**8**	3	1.914–2.247	105.65	73.65	42
cis-$[Li\{N,N\text{-}N(^tBu)CH_2CH_2N(H)(^tBu)\}]_2$	**9**	3	1.973–2.017	109.0	70.6	44
cis-$[Li\{N,N\text{-}N(^tBu)CH(^tBu)CH{=}N^tBu\}]_2$	**10**	3	1.974–2.125	113.3	66.4	59
$[Li\{N,N\text{-}N(SiMe_3)N(SiMe_3)(CH_2Ph)\}]_2$	**11**	3	1.922–2.001	109.0	71.0	45
$[Li\{N,N\text{-}N(^tBu)SiMe_2\text{-}2\text{-}NMe_2C_6H_4\}]_2$	**12**	3	2.003–2.064	109.0	70.85	63
$[Li\{N,N\text{-}N(Cy)S(^tBu)N(SiMe_3)\}]_2$	**13**	3	1.994–2.169	108.22	71.78	54
$[Li\{N,N\text{-}N(SiMe_3)S(Me)N(SiMe_3)\}]_2$	**14**	3	1.916–1.965	112.8	67.10	49
$[Li\{N,N\text{-}N(^tBu)SiMe_2\text{-}2\text{-}NMe_2CH_2C_6H_4\}]_2$	**15**	3	2.052–2.102	109.2	70.8	63
$[LiN(SiMe_3)_2(^tBuCN)]_2$	**16**	3	2.021–2.036	105.36	74.61	53
$[Li\{N,N\text{-}N(SiMe_3){=}C(Ph)\text{–}C(H){=}C(Ph)\text{–}N(SiMe_3)\}]_2$	**17**	3	1.965–2.095	105.0	75.0	26
$[Li\{N,N\text{-}8\text{-}N(SiMe_3)\text{–quinoline}\}]_2$	**18**	3	2.033–2.087	103.5	76.5	23
$[Li(py)N(CH_2Ph)_2]_2$	**19**	3	1.983–1.988	105.29	74.71	27
$[LiN(SiMe_3)_2(N\text{-}NH_2CH_2CMe_2CH_2NMe_2)]_2$	**20**	3	2.009–2.060	105.75	74.2	57
$[LiN(SiMe_3)_2(N\text{-}NH_2CH_2CH_2CH_2NMe_2)]_2$	**21**	3	2.029–2.073	105.5	74.5	57
$[LiN(SiMe_3)_2(NMe_2CH_2Ph)]_2$	**22**	3	2.037–2.095	104.2	75.55	33
$[Li\{N,N\text{-}N(SiMe_3)C(Ph)C(H)C(^tBu)N(SiMe_3)\}]_2$	**23**	3	2.04	103.8	76.2	39
$[Li\{N,N\text{-}N(SiMe_3)C(^tBu)C(H)C_5H_4N\text{-}2\}]_2$	**24**	3	1.968–2.032	105.3	74.7	43
$[Li\{N,N\text{-}N(SiMe_3)C(Ph)C(SiMe_3)C_5H_4N\text{-}2\}]_2$	**25**	3	1.998–2.026	104.6	75.4	43

[a] CN: coordination number.

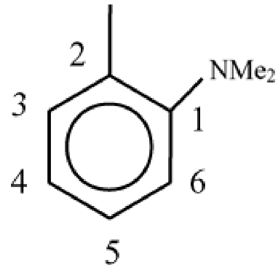
EXPERIMENTAL DETAILS

All experiments were carried out under purified dry nitrogen. Solvents were dried and freshly distilled under nitrogen. The NMR spectra (in C_6D_6, δ/ppm) were recorded with an AVANCE DRX 400 spectrometer (Bruker); ^1H NMR (400 MHz): internal standard trace amount of protonated solvent, C_6D_6; ^{13}C NMR (100 MHz): internal standard solvent; ^7Li NMR (155 MHz): external standard 1 M LiCl. Elemental analyses were obtained with a VARIO EL (Heraeus) apparatus; the melting points were determined in sealed capillaries under nitrogen and are uncorrected; 1-NHPhCHPh-2-$NMe_2C_6H_4$ (**1**) and 1-NHPhCHPhCH_2-2-$NMe_2C_6H_4$ (**2**) were prepared by literature procedures.[70]

Preparation of [1-LiNPhCHPh-2-$NMe_2C_6H_4]_2$ (3)

A 150 ml Schlenk flask was charged with 1-NHPhCHPh-2-$NMe_2C_6H_4$ (**1**; 0.48 g, 1.6 mmol) and diethyl ether (50 ml). Then *n*-butyllithium (one equivalent) was added dropwise at −15 °C. The solution was warmed to room temperature and stirred for about 1 h. The solvent was then removed, and the remaining solid was washed with pentane to give the product in 90% yield. Mp: 120–127 °C. Anal. Found: C, 81.60; H, 6.80; N, 9.06. Calc. for $C_{42}H_{42}Li_2N_4$: C, 81.80; H, 6.82; N, 9.1%. ^1H NMR: 2.40 (s, 12H, $N(CH_3)_2$), 4.10 (d, 2H, CH), 6.50–7.20 (br., 28H, C_6H_4 and C_6H_5). ^{13}C NMR: 46.1 (s, $N(CH_3)_2$), 57.3 (s, CH), 114.3 (s, C6 in C_6H_4), 121.5 (s, C4 in C_6H_4), 125.0 (s, C3 in C_6H_4), 127.4 (s, C5 in C_6H_4), 145.2 (s, C2 in C_6H_4), 148.7 (s, C1 in C_6H_4), 130.2 (s, *p*-C in C_6H_5), 138.0 (s, *o*-C in C_6H_5), 140.0 (s, *m*-C in C_6H_5), 153.5 (s, *ipso*-C in C_6H_5). ^7Li NMR: 2.2.

Phenyl ring numbering scheme:



Preparation of [1-LiNPhCHPhCH_2-2-$NMe_2C_6H_4]_2$ (4)

A similar procedure to that described for **3** was used here, except 1-NHPhCHPhCH_2-2-$NMe_2C_6H_4$ (**2**; 1.03 g, 1.6 mmol) was employed instead of **1**, and colorless crystals were obtained from toluene at 20 °C in 85% yield. Mp: 130–135 °C. Anal. Found: C, 82.10; H, 7.12; N, 8.67. Calc. for $C_{44}H_{46}Li_2N_4$: C, 81.96; H, 7.13; N, 8.69%. ^1H NMR: 2.39 (s, 12H, $N(CH_3)_2$), 2.90 (t, 2H, CH), 4.20 (d, 4H, CH_2), 6.50–7.40 (br., 28H, C_6H_4 and C_6H_5). ^{13}C NMR: 42.2 (s, CH_2), 45.8 (s, $N(CH_3)_2$), 62.2 (s,

Table 4. Crystal data and structure refinement for **4**

Formula	$C_{44}H_{46}Li_2N_4$
Formula weight	644.73
Temperature (K)	223(2)
Crystal system	Triclinic
Space group	$P\bar{1}$
a (Å)	10.2173(12)
b (Å)	10.9757(12)
c (Å)	18.411(2)
α (°)	81.199(2)
β (°)	76.204(2)
γ (°)	65.909(2)
V (Å^3)	1826.8(4)
Z	2
D_{calcd} (g cm^{-3})	1.172
F(000)	688
Crystal size (mm^3)	0.20 × 0.20 × 0.10
Abs coefficient (mm^{-1})	0.068
No. of reflections collected	10 783
No. of independent reflections	7120
R_{int}	0.0291
No. of params	604
$R_1(I > 2\sigma(I))$	0.0507
wR_2 (all data)	0.1460
$(\Delta/\rho)_{min}$ (e$^-$ Å^{-3})	0.192
$(\Delta/\rho)_{max}$ (e$^-$ Å^{-3})	−0.184
Deposition number	CCDC 186420

CH), 114.2 (s, C6 in C_6H_4), 116.5 (s, C4 in C_6H_4), 120.9 (s, C3 in C_6H_4), 127.0 (s, C5 in C_6H_4), 145.7 (s, C2 in C_6H_4), 149.1 (s, C1 in C_6H_4), 132.2 (s, *p*-C in C_6H_5), 139.0 (s, *o*-C in C_6H_5), 140.0 (s, *m*-C in C_6H_5), 153.4 (s, *ipso*-C in C_6H_5). ^{7}Li NMR: 2.2.

Data collection and structural refinement of 4

Crystallographic data are given in Table 4. Data [λ(Mo Kα) = 0.710 73 Å] were collected with a Siemens CCD (SMART) diffractometer. All observed reflections were used for determination of the unit cell parameters. Empirical absorption correction with SADABS.[74] The structure was solved by direct methods (SHELXTL PLUS[71]). Restrictions for **4**: lithium, nitrogen and carbon atoms anisotropic. Hydrogen atoms located by difference maps and refined isotropically.

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