JOM 23563

X-ray diffraction studies of polymeric lithiobenzotriazole · DMSO and lithiotetrazole · DMSO: from β-sheet to wash-board structures

Christoph Lambert, Frank Hampel and Paul von Ragué Schleyer

Institut für Organische Chemie der Friedrich-Alexander Universität Erlangen-Nürnberg, Henkestrasse 42. W-8520 Erlangen, (Germany)

(Received January 18, 1993)

Abstract

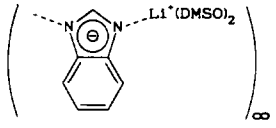
Two lithiated aromatic amines, lithiobenzotriazole · DMSO (3) and lithiotetrazole · DMSO (4) have polymeric (X-ray) structures in the solid state. While lithiobenzotriazole · DMSO exhibits a ribbon structure, lithiotetrazole prefers a two dimensional network. Generally, the structures of lithioamines are the result of competition between electrostatic and steric effects. Since aromatic lithioamines with more than one nitrogen atom form Li–N bonds in the heterocyclic ring plane, additional ligands (*e.g.* DMSO) do not interfere with the amide moiety, and the electrostatically preferred polymer arrangement is observed in 3 and 4.

1. Introduction

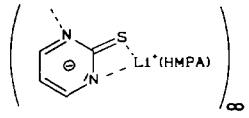
Owing to the importance of lithioamines as nonnucleophilic bases in organic synthesis [1], the structures of such species have been studied extensively in both the solid state and in solution [2]. This paper reports the X-ray structures of two lithiated aromatic amines containing more than one nitrogen atom, namely lithiobenzotriazole · DMSO (3) and lithiotetrazole · DMSO (4).

Lithiated amines exhibit great structural variety [2]. However, most of the lithiated amines studied have alkyl or aryl substituents and a single nitrogen. Monomers, dimers, trimers, tetramers, hexamers and higher oligomers (formed by ring stacking or laddering of smaller aggregated units [2]) are quite common. Aromatic heterocyclic amines with only one nitrogen behave similarly, *e.g.* lithiated carbazole is a monomer in THF solution [3] and a dimer with each Li^+ coordinated to two THF molecules in the solid state [4]. Lithioindole · TMEDA is a dimer both in THF solution and in the solid state [5]. Lithiopyrrole · TMEDA is also a dimer in the solid state [6].

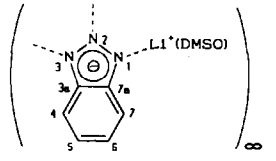
The structural preference is different when two nitrogen atoms are involved. Both lithiobenzimidazole (1) [7] and lithiomercaptopyrimidine (2) [8] are polymeric; these preferences were attributed to a gain in electrostatic stabilization [7].



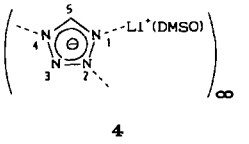
1



2



3



4

We have now investigated the influence of three and four nitrogen atoms on the structure of lithiated aromatic amines, choosing benzotriazole, the isoelectronic counterpart of benzimidazole, and tetrazole as the substrates. New one dimensional ribbon and two dimensional lattice arrangements are revealed by the X-ray structures of lithiobenzotriazole · DMSO (3) and lithiotetrazole · DMSO (4) respectively.

2. Experimental section

All manipulations were carried out with conventional Schlenk tube, syringe, and septum tech-

Correspondence to: Prof. Dr. P. von R. Schleyer.

0022-328X/93/$6.00

niques with argon as inert gas. Solvents were distilled from potassium-benzophenoneketyl (THF) or CaH_2 (DMSO).

2.1. Synthesis of [lithiobenzotriazole · DMSO]$_\infty$ (3)

Benzotriazole (2.383 g, 20 mmol) was dissolved in 40 ml of THF. To this solution, 12.5 ml (20 mmol) of 1.6 M ^{n}BuLi/hexane was added at −15°C. The resulting white suspension was stirred for *ca.* 1 h at room temperature; 50 ml of hexane was added, the precipitate filtered off and dried *in vacuo*. The white powder (lithiobenzotriazole · THF; the THF content was determined by integration of the ^{1}H-NMR spectrum) was dissolved in hot DMSO. The solution was allowed to cool to room temperature and colourless needles separated out. These were filtered off and washed with toluene and then with hexane and dried *in vacuo* (1.910 g, 47%). Anal. Calcd. for $C_8H_{10}LiN_3OS$: C, 47.28; H, 4.96; N, 20.68. Found: C, 46.91; H, 4.90; N, 20.24%. ^{1}H-NMR (400 MHz, d_6-DMSO, RT, numbering according to formula **3**) δ 2.62 (s, 6H, DMSO), 6.98 (m, 3 Hz, 2H, H 5,6), 7.73 (m, 3 Hz, 2H, H 4,7). ^{13}C-NMR (100.6 MHz, d_6-DMSO, RT) δ 145.3 (C 3a,7a), 119.2 (C 5,6), 116.0 (C 4,7), 40.4 (DMSO).

2.2. Synthesis of [lithiotetrazole · DMSO]$_\infty$ (4)

Tetrazole (0.200 g, 2.85 mmol) and 0.068 g (2.85 mmol) of LiOH were dissolved in 1 ml of hot DMSO. The solution was filtered and the filtrate allowed to cool to room temperature. After a few days, colourless plates had formed (0.144 g, 33%). Anal. Calcd. for $C_3H_7LiN_4OS$: C, 23.38; H, 4.58; N, 36.36. Found: C, 23.54; H, 4.59; N, 36.14%. ^{1}H-NMR (400 MHz, d_6-DMSO, RT, the numbering is given in formula **4**) δ 8.21 (s, 1H, H 5), 2.62 (s, 6H, DMSO). ^{13}C-NMR (100.6 MHz, d_6-DMSO, RT) δ 149.1 (C 5), 40.4 (DMSO).

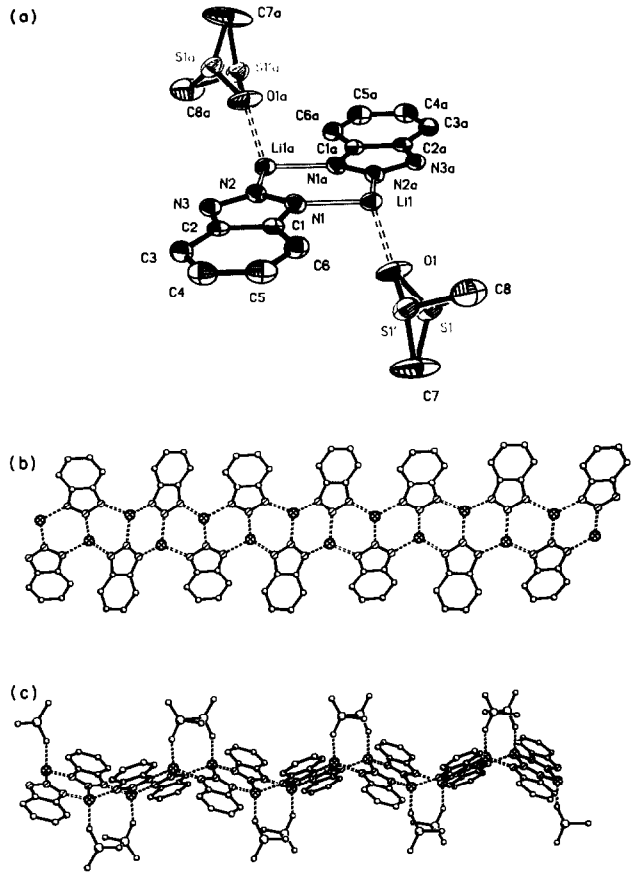


Fig. 1. Solid state structure of **3**. (a) ORTEP plot (50% probability ellipsoids) of two asymmetric units. The DMSO sulphur atoms exhibit disorder; the hydrogen atoms are omitted for clarity. (b) View of the polymer, perpendicular to the plane of the ribbon. The hydrogen atoms and the DMSO molecules are omitted. (c) Side view of the polymer; hydrogen atoms are omitted.

TABLE 1. Crystallographic details for **3** and **4**

	3	**4**
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$
a, Å	22.205(8)	10.463(4)
b, Å	8.227(3)	9.824(4)
c, Å	11.273(6)	14.637(5)
β, deg	104.19(4)	91.95(3)
V, Å^3	1996.4(15)	1512(2)
Z	8	8
d_{calcd}, Mg m^{-3}	1.352	1.354
Cryst. size, mm	0.2×0.4×0.6	0.2×0.4×0.4
Absorption coeff., mm^{-1}	0.277	0.362
Scan method	ω, 0.70° range	ω, 1.40° range
2θ range, deg	3.0–55.0	3.0–54.0
Reflections collected	4954	5101
Observed refl. ($F > 4.0\sigma(F)$)	1620	1348
Refined parameters	139	203
R, %	5.30	5.20
wR, %	5.34	5.13
GOF	1.72	1.86
Largest diff. peak, eÅ^{-3}	0.34	0.32
Largest diff. hole, eÅ^{-3}	−0.41	−0.35

2.3. X-Ray diffraction analysis

Single crystals of **3** and **4** were sealed in Lindemann capillaries under argon and mounted on a four circle diffractometer (Nicolet R3m/V). All data were collected at 200 K using Mo Kα radiation with a graphite monochromator. Further details concerning the data collection and the cell parameters are given in Table 1. The structures were solved by direct methods (SHELXTL + 4.11/v). All non-hydrogen atoms were refined anisotropically and the hydrogen atoms isotropically in

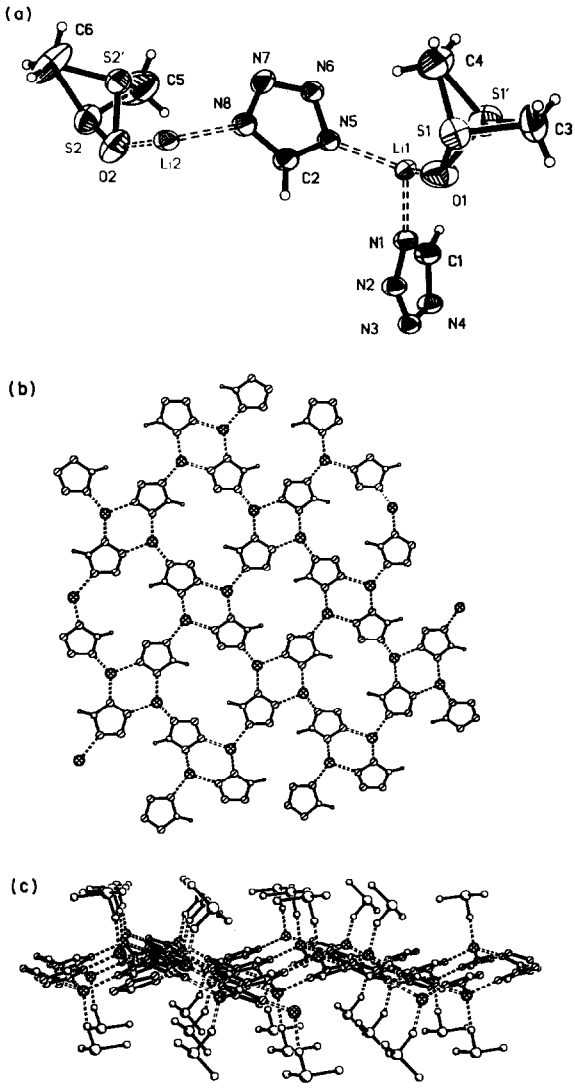


Fig. 2. Solid state structure of **4**. (a) ORTEP plot (50% probability ellipsoids) of the asymmetric unit. The sulphur atoms of DMSO are disordered. (b) View of the polymeric network perpendicular to the plane. The DMSO molecules are omitted for clarity, (c) Side view of the network. The hydrogen atoms are omitted.

fixed idealized positions (riding model) with different thermal parameters for the alkyl and aryl hydrogen atoms. In both structures, the DMSO molecules exhibited disorder involving the inversion at the sulphur atom. The disorder was refined with different occupation probabilities of the sulphur atoms in both positions. **3**: S1, 43; S1', 57%. **4**: S1, 88; S1', 12%; S2, 68, S2', 32% (see Figs. 1(a) and 2(a)). *

2.4. Colligative properties of 3 and 4

Cryoscopic measurements in DMSO were carried out with a modified apparatus described elsewhere [9]. The cryoscopic constant was found to be 5.107 K Kg mol^{-1} in the concentration range 0.04–0.17 mol/Kg by use of freshly sublimed biphenyl, triphenylmethane, and naphthalene, which were assumed to be monomeric in the solution.

3. Results and discussion

The lithiation of benzotriazole in THF resulted in a white precipitate of lithiobenzotriazole · THF. This complex is also insoluble in hydrocarbons and ethers but DMSO proved to be an excellent solvent. When a hot saturated DMSO solution was cooled, small needles of lithiobenzotriazole · DMSO (**3**) formed. The THF had been replaced by the stronger ligand, DMSO.

The X-ray analysis of **3** revealed a polymeric ribbon structure (see Fig. 1a,b; atomic parameters are given in Table 2, and bond distances and angles in Table 3). The structure is built up from two infinite [benzotriazolide$^-$Li$^+$] chains similar to those in [lithiobenzimidazole · DMSO]$_\infty$ (**1**) [7]. The lithium cations bridge the benzotriazole anions at the N(1) and N(3) nitrogen atoms of different benzotriazole moieties. The two [benzotriazolide$^-$Li$^+$] chains are fused together by additional Li–N bondings from the Li$^+$ of one chain to the N(2) atoms of the other chain. While Li$^+$ in lithiobenzimidazole is coordinated by two DMSO molecules, one DMSO is replaced in lithiobenzotriazole (**3**) by the additional Li–N(2) contact to the second chain. Hence, in **3** only one DMSO molecule is needed to complete the fourfold Li$^+$ coordination sphere. The DMSO ligands are located above and below the ribbon. Alternatively, the structure can be described in terms of a ladder [2]: dimeric subunits with a central planar Li–N–N–Li–N–N-six membered ring (shown in Fig. 1(a)) are connected via a folded six membered Li–N–N–Li–N–N-ring to form the polymeric arrangement of **3**. Since Li$^+$ prefers a tetrahedral coordination sphere [10] *, the ribbon folds. The resulting arrangement is very similar to the β-sheet structure of proteins [11] (see Fig. 1(c)). Interestingly, the solid state helix of ligand-free lithiodiisopropylamine (**5**) which Mulvey [12] reported recently, is analogous to the helical structures of proteins [11].

* Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, W-7514 Eggenstein Leopoldshafen 2 (Germany), on quoting the depository number CSD-57195, the names of the authors, and the journal citation.

* Reference number with an asterisk indicates a note in the list of references.

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) of **3**

	x	y	z	U_{eq} [a]
C(1)	1354(1)	4029(3)	6524(2)	25(1)
C(2)	1374(1)	4527(3)	7716(2)	24(1)
C(3)	1886(1)	4171(3)	8691(2)	32(1)
C(4)	2365(1)	3320(3)	8421(2)	38(1)
C(5)	2346(1)	2801(3)	7220(2)	38(1)
C(6)	1851(1)	3138(3)	6267(2)	33(1)
N(1)	801(1)	4521(2)	5788(2)	28(1)
N(2)	503(1)	5289(2)	6525(2)	27(1)
N(3)	828(1)	5322(2)	7689(2)	27(1)
Li(1)	398(2)	3818(5)	4017(4)	28(1)
O(1)	422(1)	1469(2)	4092(2)	62(1)
S(1)	507(1)	−57(2)	3630(2)	41(1)
S(1′)	908(1)	258(2)	4250(1)	42(1)
C(7)	694(3)	−1600(4)	4449(4)	128(3)
C(8)	1150(2)	131(4)	2891(3)	76(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

The asymmetric unit of **3** contains one lithiobenzotriazole · DMSO molecule (see Fig. 1(a)). The benzotriazolide unit possesses C_{2v} symmetry within experimental error. The geometrical parameters for the benzotriazolide moiety are similar to those for the tridentate benzotriazolide of thalium(I)benzotriazolide [13]. The sums of the angles around the N1, N2, and N3 atoms in **3** are 358.6, 359.8, and 359.4°, respectively. Thus, Li–N bonds are formed exclusively in the σ-plane of the benzotriazole ring system. The three different Li–N lengths range only from 2.06 to 2.09 Å, and are similar to those in lithiobenzimidazole · $DMSO_2$ (**1**) [7].

TABLE 3. Bond lengths (Å) and angles (deg) in **3**

C(1)–C(2)	1.396(3)	C(1)–C(6)	1.411(4)
C(1)–N(1)	1.364(3)	C(2)–C(3)	1.404(3)
C(2)–N(3)	1.371(3)	C(3)–C(4)	1.368(4)
C(4)–C(5)	1.411(4)	C(5)–C(6)	1.364(3)
N(1)–N(2)	1.341(3)	N(1)–Li(1)	2.061(4)
N(2)–N(3)	1.334(3)	N(2)–Li(1A)	2.077(4)
N(3)–Li(1C)	2.086(5)	Li(1)–O(1)	1.935(4)
Li(1)–N(2A)	2.077(4)	Li(1)–N(3A)	2.086(5)
Li(1)–Li(1B)	3.443(8)	O(1)–S(1)	1.389(3)
O(1)–S(1′)	1.448(3)	S(1)–S(1′)	1.022(2)
S(1)–C(7)	1.565(4)	S(1)–C(8)	1.828(5)
S(1′)–C(7)	1.633(4)	S(1′)–C(8)	1.746(5)
C(2)–C(1)–C(6)	120.6(2)	C(3)–C(2)–N(3)	131.2(2)
C(6)–C(1)–N(1)	131.4(2)	C(3)–C(4)–C(5)	121.8(2)
C(1)–C(2)–N(3)	107.4(2)	C(1)–C(6)–C(5)	117.6(2)
C(2)–C(3)–C(4)	117.2(2)	C(1)–N(1)–Li(1)	128.2(2)
C(4)–C(5)–C(6)	121.5(2)	N(1)–N(2)–N(3)	112.8(2)
C(1)–N(1)–N(2)	105.7(2)	N(3)–N(2)–Li(1A)	122.2(2)
N(2)–N(1)–Li(1)	124.7(2)	C(2)–N(3)–Li(1C)	134.7(2)
N(1)–N(2)–Li(1A)	124.8(2)	N(1)–Li(1)–O(1)	103.7(2)
C(2)–N(3)–N(2)	106.0(2)	O(1)–Li(1)–N(2A)	112.3(2)
N(2)–N(3)–Li(1C)	118.7(2)	O(1)–Li(1)–N(3A)	111.0(2)
N(1)–Li(1)–N(2A)	110.1(2)	Li(1)–O(1)–S(1)	153.0(2)
N(1)–Li(1)–N(3A)	115.7(2)	O(1)–S(1)–C(7)	123.6(2)
N(2A)–Li(1)–N(3A)	104.3(2)	O(1)–S(1)–C(8)	106.7(2)
Li(1)–O(1)–S(1′)	134.7(2)	C(7)–S(1)–C(8)	102.3(3)
C(2)–C(1)–N(1)	108.0(2)	O(1)–S(1′)–C(7)	115.3(2)
C(1)–C(2)–C(3)	121.4(2)	O(1)–S(1′)–C(8)	108.3(2)
		C(7)–S(1′)–C(8)	103.1(2)

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients (Å$^2 \times 10^3$) of **4**

	x	y	z	U_{eq} [a]
Li(1)	10835(6)	1344(8)	4377(6)	33(3)
N(1)	12265(3)	2584(5)	4848(3)	36(2)
N(2)	12296(3)	3903(5)	4622(3)	36(2)
N(3)	13445(3)	4375(4)	4821(3)	34(2)
N(4)	14183(3)	3396(5)	5175(3)	37(2)
C(1)	13434(4)	2295(6)	5180(4)	41(2)
N(5)	9160(3)	1590(4)	5059(3)	33(1)
N(6)	8480(3)	588(5)	5437(3)	40(2)
N(7)	7375(3)	1073(5)	5682(4)	51(2)
N(8)	7312(3)	2410(5)	5486(3)	39(2)
C(2)	8420(4)	2682(6)	5116(4)	41(2)
Li(2)	5966(5)	3821(8)	5761(6)	35(3)
O(1)	10420(3)	1712(5)	3133(3)	66(2)
S(1)	9507(1)	1150(2)	2413(1)	47(1)
S(1′)	10360(11)	189(18)	2631(12)	62(7)
C(3)	10473(6)	197(8)	1663(5)	88(3)
C(4)	8730(5)	−298(7)	2894(5)	68(3)
O(2)	5803(3)	4133(5)	7041(3)	62(2)
S(2)	5444(2)	3554(3)	7948(2)	54(1)
S(2′)	5238(3)	2549(6)	7320(4)	46(2)
C(5)	6209(6)	1993(9)	8037(7)	109(4)
C(6)	3828(5)	3002(10)	7792(6)	104(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

Lithiotetrazole · DMSO (**4**) made by lithiation of tetrazole with solid LiOH in DMSO, is insoluble both in ethers and in hydrocarbons. This behaviour is consistent with a polymeric network structure in the solid state. Indeed, the X-ray analysis of a crystal of **4** revealed a two dimensional lattice (see Fig. 2(a), (b), atomic parameters are listed in Table 4, and bond distances and angles in Table 5). Like that of **3**, the structure of **4** contains planar dimeric subunits with a six membered Li–N–N–Li–N–N-ring. These dimers are connected by Li–N contacts to form a two dimensional network. Only three of the four nitrogen atoms in each tetrazolide moiety are involved in lithium bonding. Hence, it is not necessary to have four nitrogen atoms to form a two dimensional network; three nitrogen atoms in a more suitable (Li–N(1,2,4)) arrangement are sufficient.

Owing to an approximately tetrahedral Li^+ surrounding, the entire network is folded like a wash-board

(see Fig. 2c). The fourfold coordination sphere of the lithium cations is completed by DMSO ligands placed above and below the network. As in **3**, the tetrazolide ions display approximately C_{2v} symmetry. The tetrazolide geometries resemble those reported for [natriotetrazole · H_2O]$_\infty$ [14]. The asymmetric unit contains two lithiotetrazole · DMSO molecules, but these have nearly identical atomic distances and angles. The sums of angles around the lithiated nitrogen atoms range between 357.1 and 359.9°. Once again, Li–N bonding is favoured in the σ-plane of the heterocycle, whereas mixed σ- and π-interactions are present in the dimeric structures of lithioindole · TMEDA [5] and of lithiocarbazole · $(THF)_2$ [4]. The Li–N bond lengths in **4** are all similar (2.03–2.07 Å), but are slightly shorter than those in **3**.

TABLE 5. Bond lengths (Å) and angles (deg) in **4**

Li(1)–N(1)	2.031(8)	Li(1)–N(5)	2.061(7)
Li(1)–O(1)	1.892(9)	Li(1)–S(1′)	2.825(19)
Li(1)–N(6A)	2.044(9)	N(1)–N(2)	1.338(7)
N(1)–C(1)	1.332(5)	N(2)–N(3)	1.312(5)
N(3)–N(4)	1.329(6)	N(3)–Li(2B)	2.069(9)
N(4)–C(1)	1.336(7)	N(4)–Li(2A)	2.069(7)
N(5)–N(6)	1.344(6)	N(5)–C(2)	1.327(7)
N(6)–N(7)	1.312(5)	N(6)–Li(1A)	2.044(9)
N(7)–N(8)	1.347(7)	N(8)–C(2)	1.323(6)
N(8)–Li(2)	2.026(8)	Li(2)–O(2)	1.912(10)
Li(2)–S(2′)	2.732(10)	Li(2)–N(3A)	2.069(9)
Li(2)–N(4A)	2.069(7)	O(1)–S(1)	1.503(4)
O(1)–S(1′)	1.667(18)	S(1)–S(1′)	1.330(15)
S(1)–C(3)	1.783(8)	S(1)–C(4)	1.793(7)
S(1′)–C(3)	1.425(19)	S(1′)–C(4)	1.825(13)
O(2)–S(2)	1.503(5)	O(2)–S(2′)	1.718(7)
S(2)–S(2′)	1.362(6)	S(2)–C(5)	1.733(9)
S(2)–C(6)	1.783(6)	S(2′)–C(5)	1.537(10)
S(2′)–C6	1.709(8)		
N(1)–Li(1)–N(5)	113.2(4)	N(1)–Li(1)–O(1)	110.8(4)
N(5)–Li(1)–O(1)	105.8(3)	N(1)–Li(1)–S(1′)	130.7(4)
N(5)–Li(1)–S(1′)	111.1(4)	N(5)–Li(1)–N(6A)	110.1(4)
N(1)–Li(1)–N(6A)	105.1(3)	S(1′)–Li(1)–N(6A)	78.3(4)
O(1)–Li(1)–N(6A)	111.9(4)	Li(1)–N(1)–C(1)	130.8(5)
Li(1)–N(1)–N(2)	121.3(4)	N(1)–N(2)–N(3)	108.5(3)
N(2)–N(1)–C(1)	105.5(4)	N(2)–N(3)–Li(2B)	119.7(4)
N(2)–N(3)–N(4)	110.3(4)	N(3)–N(4)–C(1)	104.8(3)
N(4)–N(3)–Li(2B)	127.1(3)	C(1)–N(4)–Li(2A)	133.0(4)
N(3)–N(4)–Li(2A)	121.3(4)	Li(1)–N(5)–N(6)	125.8(4)
N(1)–C(1)–N(4)	110.9(5)	N(6)–N(5)–C(2)	104.4(4)
Li(1)–N(5)–C(2)	129.2(4)	N(5)–N(6)–Li(1A)	123.1(3)
N(5)–N(6)–N(7)	109.3(4)	N(6)–N(7)–N(8)	109.4(4)
N(7)–N(6)–Li(1A)	127.5(4)	N(7)–N(8)–Li(2)	130.8(4)
N(7)–N(8)–C(2)	104.3(4)	N(5)–C(2)–N(8)	112.6(5)
C(2)–N(8)–Li(2)	124.6(5)	N(8)–Li(2)–S(2′)	94.0(3)
N(8)–Li(2)–O(2)	113.0(4)	N(8)–Li(2)–N(3A)	106.6(3)
O(2)–Li(2)–N(3A)	107.7(4)	S(2′)–Li(2)–N(3A)	146.2(4)
N(8)–Li(2)–N(4A)	113.7(4)	O(2)–Li(2)–N(4A)	109.2(3)
S(2′)–Li(2)–N(4A)	88.9(3)	N(3A)–Li(2)–N(4A)	106.2(4)
Li(1)–O(1)–S(1)	136.4(4)	Li(1)–O(1)–S(1′)	104.9(7)
O(1)–S(1)–C(3)	105.3(3)	O(1)–S(1′)–C(3)	115.5(11)
O(1)–S(1)–C(4)	107.6(3)	Li(1)–S(1′)–C(4)	92.9(7)
C(3)–S(1)–C(4)	95.7(3)	Li(2)–O(2)–S(2)	146.9(4)
Li(1)–S(1′)–C(3)	151.5(10)	O(2)–S(2)–C(5)	105.8(4)
O(1)–S(1′)–C(4)	99.4(8)	O(2)–S(2)–C(6)	105.4(3)
C(3)–S(1′)–C(4)	108.7(9)	C(5)–S(2)–C(6)	100.0(4)
Li(2)–O(2)–S(2′)	97.5(4)	Li(2)–S(2′)–C(5)	122.5(4)
O(2)–S(2′)–C(5)	105.1(4)	O(2)–S(2′)–C(6)	99.7(4)
Li(2)–S(2′)–C(6)	119.2(4)	C(5)–S(2′)–C(6)	112.1(5)

TABLE 6. Dissociation constants of **3** and **4** in DMSO from cryoscopic measurements

Compound	Concentration (mol Kg^{-1})	Degree of dissociation (%)	K^a (mol l^{-1})
3	0.0347	74.9	0.086
3	0.0779	63.7	0.096
3	0.1260	55.2	0.095
			$\bar{K} = 0.092 \pm 0.004$
4	0.0267	77.8	0.080

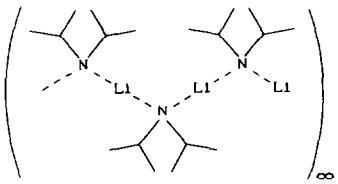
[a] $K = [A^-][Li^+]/[ALi]$.

Variable temperature NMR studies were not possible owing to the high melting point of DMSO and fast lithium exchange at room temperature. However, cryoscopic measurements in DMSO showed both **3** and **4** to be dissociated significantly (*ca.* 70 to 80%) into free ions in *ca.* 0.03 mol Kg^{-1} concentrations (see Table 6). Thus, DMSO not only causes deaggregation of the polymeric structures to monomers, but solvates the cation sufficiently to bring about ion separation [15].

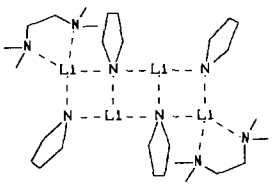
Comparisons between the "hydrogen bond" and the "lithium bond" have been reviewed recently [16]. Lithium bonds in LiX species ($X = CR_3$, NR_2, OR) are predominantly ionic [16,17]. *Ab initio* calculations as well as simple electrostatic point charge models show that the polymeric nature of lithiobenzimidazole · DMSO (**1**) is due to an increase in electrostatic stabilization. This stabilization is less in oligomeric alternatives [7]. Similar arguments for polymeric structures *vs.* smaller aggregates also hold for both **3** and **4**. Thus, in general lithiated amines should polymerize. In most cases, this tendency is counteracted by steric hindrance of bulky amine substituents and the additional (fourth) Li-ligand. The result is lower aggregation of the lithioamines.

Only three crystal structures involving lithioamine ladder arrangements have been reported. The lithiopyrrolidines $\{[H_2C(CH_2)_3NLi]_3 \cdot PMDTA\}_2$ and $\{[H_2C(CH_2)_3NLi]_2 \cdot TMEDA\}_2$ (**6**) [18], and a piperidine

solvated lithiumpiperidide $\{[H_2C(CH_2)_4NLi]_2 \cdot [H_2C(CH_2)_4NH]_2\}_2$ [19] can be regarded as intermediates during the formation of polymers.



5



6

However, the substituents are all quite small. Since the substituents are nearly perpendicular to the ladder, the lithium cations are only threefold coordinated owing to steric constraints. The ladder is terminated by TMEDA, PMDTA, or piperidine ligands. Completely ligand-free lithiopyrrolidine is thought to be polymeric in the solid state [18]. Moreover, in the polymeric solid state structure of **5** with bulkier substituents, the Li^+ only is twofold coordinated [12]. The reduction in the Li^+ coordination is clearly destabilizing [20].

In lithioamines with one nitrogen, stabilization due to polymer formation competes with destabilization due to the concomitant loss of Li^+ solvation. This is not so with lithiated heterocyclic amines with more than one nitrogen atom. In these amides, the negative charge is delocalized over more than one nitrogen atom in the anion. Two lithium cations do not need to bind to one nitrogen atom in order to form an infinite chain, but can bridge two different negatively charged nitrogen atoms in the anionic heterocycle. As a result, the lithium cations are further apart. Since the Li–N interactions are formed exclusively within the heterocycle plane, the polymeric chain is formed in **1**, the polymeric ribbon in **3**, and the polymeric network in **4**. In these polymers, the heterocyclic rings are more or less in plane with the ribbon (**3**) or the lattice (**4**). Hence, fourfold Li^+ solvation can easily be achieved since the fourth ligand (DMSO) can "stick out" from the ribbon or the lattice (see Figs. 1c and 2c, respectively). Both electrostatic stabilization by polymerization and good Li^+ coordination are achieved.

As Snaith *et al.* have noted [18], the preferred structure of a lithioamine results from a competition between electrostatic and steric effects. The difference between the polymeric preferences of both the lithiated aromatic heterocycles lithiobenzotriazole · DMSO (**3**) and lithiotetrazole · DMSO (**4**) over the oligomeric ladder arrangements of lithiopyrrolidine and lithiopiperidine, as well as the polymeric nature of lithiodiisopropyamine (**5**) may be interpreted on the secondary structure of peptides and those of this basis. Moreover, the analogy between **3** and **5** emphasizes the "supramolecular" [21] nature of organolithium aggregates. Noncovalent attractions rather than conventional covalent bonds hold such species together [22].

4. Acknowledgments

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and the latter for a scholarship to C.L.

References and notes

1 (a) L. Brandsma and H. Verkruijsse, *Preparative Polar Organometallic Chemistry 1*, Springer, Berlin, 1987; (b) L. Brandsma, *Preparative Polar Organometallic Chemistry 2*, Springer, Berlin, 1990.
2 (a) R.E. Mulvey, *Chem. Soc. Rev., 20* (1991) 167; (b) K. Gregory, P.v.R. Schleyer and R. Snaith, *Adv. Inorg. Chem., 37* (1991) 47.
3 C. Lambert, W. Bauer and P.v.R. Schleyer, unpublished work.
4 R. Hacker, E. Kaufmann, P.v.R. Schleyer, W. Mahdi and H. Dietrich, *Chem. Ber., 120* (1987) 1533.
5 K. Gregory, M. Bremer, W. Bauer and P.v.R. Schleyer, *Organometallics, 9* (1990) 1485.
6 K. Gregory, Dissertation, Universität Erlangen-Nürnberg, 1991.
7 C. Lambert, P.v.R. Schleyer, G.M. Newton, P. Schreiner and P. Otto, *Z. Naturforsch., 47b* (1992) 869.
8 D.R. Armstrong, R.E. Mulvey, D. Barr, R.W. Porter, P.R. Raithby, T.R.E. Simpson, R. Snaith, D.S. Wright, K. Gregory and P. Mukulcik, *J. Chem. Soc., Dalton Trans.*, (1991) 765.
9 D.R. Armstrong, R.E. Mulvey, G.T. Walker, D. Barr, R. Snaith, W. Clegg and D. Reed, *J. Chem. Soc., Dalton Trans.*, (1988) 617.
10 The coordination number of lithium ranges from 2 to 8. However fourfold coordination is by far the most common. See ref. 2 and W.N. Setzer and P.v.R. Schleyer, *Adv. Organomet. Chem., 24* (1985) 353; C. Schade and P.v.R. Schleyer, *Adv. Organomet. Chem., 27* (1987) 169.
11 J.A. McCammon and S.C. Harvey, *Dynamics of Proteins and Nucleic Acids*, Cambridge University Press, Cambridge, 1987; W. Hoppe, W. Lohmann, H. Markl and H. Ziegler (Eds.), *Biophysik*, Springer, Berlin, 1982.
12 N.D.R. Barnett, R.E. Mulvey, W. Clegg and P.A. O'Neil, *J. Am. Chem. Soc., 113* (1991) 8187.
13 J. Reedijk, G. Roelofsen, A.R. Siedle and A.L. Spek, *Inorg. Chem., 18* (1979) 1947.
14 G.J. Palenik, *Acta Crystallogr., 16* (1963) 596.
15 For further investigations on ion pairing effects in DMSO, see J.H. Exner and E.C. Steiner, *J. Am. Chem. Soc., 96* (1974) 1782; V.M. DePalma and E.M. Arnett, *J. Am. Chem. Soc., 100* (1978) 3514.
16 A.B. Sannigrahi, T. Kar, B. Guha Niyogi, P. Hobza and P.v.R. Schleyer, *Chem. Rev., 90* (1990) 1061.
17 C. Lambert and P.v.R. Schleyer, in M. Hanack (Ed.), *Methoden der Organischen Chemie (Houben-Weyl)*, Vol. E19d, Thieme, Stuttgart, in press, and references therein.
18 (a) D.R. Armstrong, D. Barr, W. Clegg, R.E. Mulvey, D. Reed, R. Snaith and K. Wade, *J. Chem. Soc., Chem. Commun.*, (1986) 869; (b) D.R. Armstrong, D. Barr, W. Clegg, S.M. Hodgson, R.E. Mulvey, D. Reed, R. Snaith and D.S. Wright, *J. Am. Chem. Soc., 111* (1989) 4719.

19 G. Boche, I. Langlotz, M. Marsch, K. Harms and N.E.S. Nudelman, *Angew. Chem., 104* (1992) 1239.
20 (a) E. Kaufmann, J. Gose and P.v.R. Schleyer, *Organometallics, 8* (1989) 2577; (b) F.E. Romesberg and D.B. Collum, *J. Am. Chem. Soc., 114* (1992) 2112.
21 F. Vögtle, *Supramolekulare Chemie*, Teubner, Stuttgart, 1989.
22 J.-M. Lehn, in A.F. Williams, C. Floriani and A.E. Merbach (Eds.), *Perspectives in Coordination Chemistry*, VCH and VHCA, Weinheim and Basel, 1992, p. 447.