X-Ray Crystal Structures of some Lithium Aryl Thiolates: Monomeric [o-MeC$_6$H$_4$SLi·(NC$_5$H$_5$)$_3$], Chain [PhSLi·(NC$_5$H$_5$)$_2$]$_\infty$, and the Unique Folded Ladder of [PhCH$_2$SLi·NC$_5$H$_5$]$_\infty$ with Li–S Rungs

Arthur J. Banister,*[a] William Clegg,[b] and Wendy R. Gill[a]

[a] *Department of Chemistry, University of Durham, South Road, Durham DH1 3LE, U.K.*
[b] *Department of Inorganic Chemistry, The University, Newcastle upon Tyne NE1 7RU, U.K.*

The *X*-ray crystallographic study of the title compounds has shown a remarkable structural variation induced by minor changes in the anion, [PhCH$_2$SLi·NC$_5$H$_5$]$_\infty$ forming an infinite folded ladder polymer with Li–S rungs, removal of the CH$_2$ group to give [PhSLi·(NC$_5$H$_5$)$_2$]$_\infty$ resulting in a polymer containing an infinite Li–S chain, while the introduction of an Me group into the *ortho*-position in [o-MeC$_6$H$_4$SLi·(NC$_5$H$_5$)$_3$] prevents association; all three structures have tetrahedral lithium whereas the co-ordination around sulphur varies from 2 to 4.

We recently[1] reported the structure of a complexed lithium derivative of monothiobenzoic acid. This is one of only a few reported structures where lithium is bonded to sulphur. The majority of these compounds, *e.g.* 2-lithio-2-methyl-1,3-dithiane,[2] phenylthiomethyl-lithium·(TMEDA),[3] two lithium alkyl thiolates,[4] and lithium monothiobenzoate·(TMEDA)[1] exist as dimers in the solid state (TMEDA = tetramethylethylenediamine).

We now report the preparation and crystal structures of a series of simple aryl thiolates where the structure in the solid state is considerably modified by small changes in the groups attached to the benzene ring.

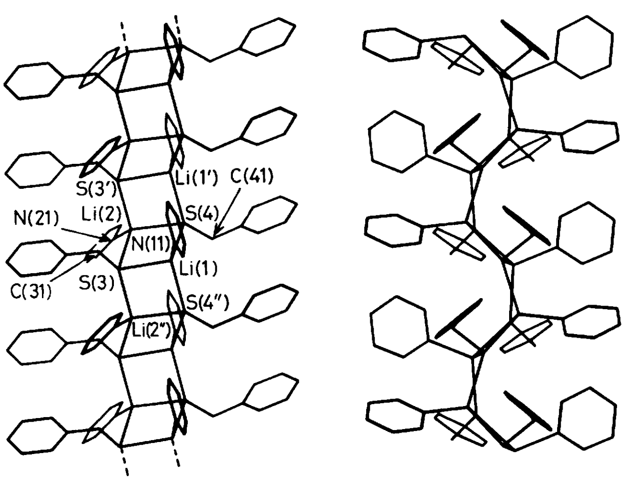

Figure 1. Two views of the buckled infinite ladder of $[PhCH_2SLi{\cdot}NC_5H_5]_\infty$ (**2**). *Crystal data:* $C_{12}H_{12}LiSN$ monomeric unit, M_r = 209.23, monoclinic, space group *Cc*, *a* = 16.8292(8), *b* = 17.4783(10), *c* = 8.2787(4) Å, β = 104.494(6)°, *U* = 2357.6 Å^3, *Z* = 8; *R* = 0.037 for 3182 reflections with $F > 4\sigma(F)$ and $2\theta \leq 130°$ (Cu-K_α radiation, λ = 1.54184 Å). Key dimensions: Li(1)–S(3) 2.508(2), Li(2)–S(3') 2.454(5), Li(2)–S(3) 2.477(5), Li(1)–S(4) 2.473(4), Li(1)–S(4'') 2.470(1), Li(2)–S(4) 2.498(5), Li(1)–N(11) 2.045(5), Li(2)–N(21) 2.068(6), S(3)–C(31) 1.837(3), S(4)–C(41) 1.813(3) Å; N(11)–Li(1)–S(3) 108.8(1), N(11)–Li(1)–S(4) 106.9(1), N(11)–Li(1)–S(4'') 115.4(2), S(3)–Li(1)–S(4) 103.0(1), S(3)–Li(1)–S(4'') 94.5(1), S(4)–Li(1)–S(4'') 125.4(2), N(21)–Li(2)–S(3) 107.4(2), N(21)–Li(2)–S(4) 122.5(2), N(21)–Li(2)–S(3') 111.3(2), S(3)–Li(2)–S(4) 103.1(2), S(3)–Li(2)–S(3') 117.6(2), S(4)–Li(2)–S(3') 95.2(2), Li(1)–S(3)–Li(2) 76.7(1), Li(1)–S(3)–Li(2'') 81.6(1), Li(2)–S(3)–Li(2'') 144.9(2), C(31)–S(3)–Li(1) 106.0(1), C(31)–S(3)–Li(2) 102.3(2), C(31)–S(3)–Li(2'') 110.1(2), Li(1)–S(4)–Li(2) 76.9(1), Li(1')–S(4)–Li(1) 131.6(1), Li(1')–S(4)–Li(2) 81.5(1), C(41)–S(4)–Li(1) 105.3(1), C(41)–S(4)–Li(1') 122.6(1), C(41)–S(4)–Li(2) 123.7(2)°. Symmetry transformation for primed (') atoms, *x*, −*y*, ½ + *z*; for double-primed ('') atoms, *x*, −*y*, −½ + *z*.†

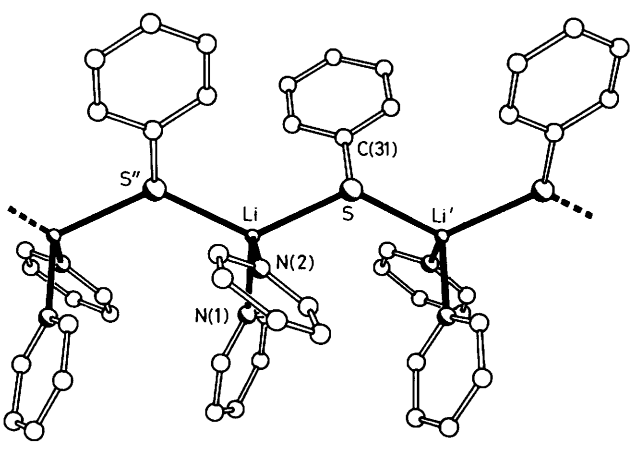

Figure 2. The chain structure of $[PhSLi{\cdot}(NC_5H_5)_2]_\infty$ (**1**). *Crystal data:* $C_{16}H_{15}LiN_2S$ monomeric unit, M_r = 274.31, monoclinic, space group $P2_1/c$, *a* = 9.8032(7), *b* = 18.0044(12), *c* = 8.8064(4) Å, β = 100.172(5)°, *U* = 1529.9 Å^3, *Z* = 4; *R* = 0.059 for 1477 reflections with $F > 3\sigma(F)$ and $2\theta \leq 115°$. Key dimensions: Li–S 2.513(6), Li–S'' 2.459(7), Li–N(1) 2.063(6), Li–N(2) 2.085(6), S–C(31) 1.752(3) Å; S–Li–S'' 124.7(2), N(1)–Li–N(2) 100.2(3), S–Li–N(1) 108.0(3), S–Li–N(2) 106.0(3), S''–Li–N(1) 104.4(2), S''–Li–N(2) 110.9(3), Li–S–Li' 129.8(2), Li–S–C(31) 113.6(2), Li'–S–C(31) 100.7(2)°. Symmetry transformation for primed (') atoms, *x*, $\frac{3}{2}$ − *y*, ½ + *z*; for doubled-primed ('') atoms, *x*, $\frac{3}{2}$ − *y*, −½ + *z*.†

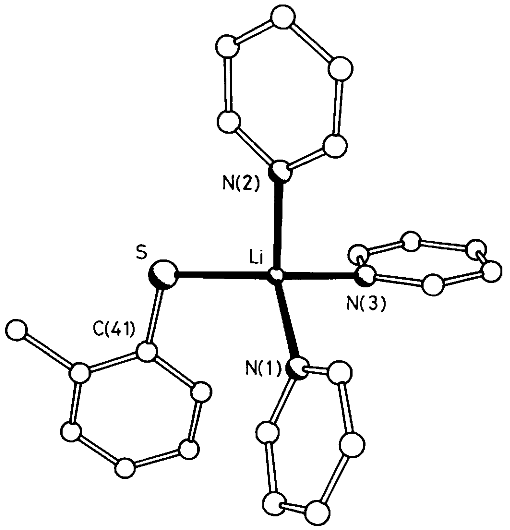

Figure 3. Molecular structure of $[o\text{-}MeC_6H_4SLi{\cdot}(NC_5H_5)_3]$ (**3**). *Crystal data:* $C_{22}H_{22}LiN_3S$, M_r = 367.44, orthorhombic, space group $Pna2_1$, *a* = 15.3020(9), *b* = 9.6656(7), *c* = 14.2885(5) Å, *U* = 2113.3 Å^3, *Z* = 4; *R* = 0.055 for 2461 reflections with $F > 3\sigma(F)$ and $2\theta \leq 115°$. Key dimensions: Li–S 2.412(6), Li–N(1) 2.081(7), Li–N(2) 2.083(6), Li–N(3) 2.081(7), S–C(41) 1.751(3) Å; S–Li–N(1) 117.4(2), S–Li–N(2) 104.8(3), S–Li–N(3) 115.4(3), N(1)–Li–N(2) 112.6(3), N(1)–Li–N(3) 101.7(3), N(2)–Li–N(3) 104.5(3), Li–S–C(41) 114.0(2)°.†

$[PhSLi{\cdot}(NC_5H_5)_2]_\infty$ (**1**), $[PhCH_2SLi{\cdot}NC_5H_5]_\infty$ (**2**), and $[o\text{-}MeC_6H_4SLi{\cdot}(NC_5H_5)_3]$ (**3**) were synthesized by the addition of n-butyl-lithium solution in hexane to chilled (−20 °C) toluene solutions of the thiol and pyridine. Warming slowly to room temperature produced white precipitates. Complexes (**1**) and (**2**) were dissolved in hot pyridine–toluene (40 : 60) at *ca.* 80 °C and colourless crystals appeared on cooling: (**1**), m.p. 115 °C; (**2**), m.p. 147 °C. The precipitate from the reaction of *o*-thiocresol was dissolved in pyridine–toluene (15 : 85) at *ca.* 30 °C and overnight cooling to −10 °C produced white needle-like crystals of (**4**); cooling the filtrate to 0 °C over several hours allowed a second crop of crystals (**3**) to be collected. These were transparent, colourless platelets, m.p. 82 °C.

As illustrated in Figure 1 the lithium benzylthiolate units in complex (**2**) are compactly arranged in an infinite wave-shaped ladder composed of alternative planar and buckled Li_2S_2 rhombs. The compound could be regarded as two $(LiS)_\infty$ infinite chains clipped together, in which the possible bonding benefit of a second co-ordinating pyridine at lithium is over-ridden by the additional Li–S interaction. The structure could also be viewed as a distorted zig-zag chain of lithium atoms. However, the Li–Li distance in lithium metal is 3.04 Å and covalency reduces it still further (Li–Li 2.67 Å in gaseous lithium). Comparison of these values with the Li–Li distances in complex (**2**) [Li(1)–Li(2) 3.092(8), Li(2)–Li(2b) 3.243(8) Å, see Figure 1] suggest that Li–Li interactions may be relatively unimportant. Similar conclusions were drawn for the compound $[Li_2(\mu_3\text{-}Bu^t{}_2P)(\mu_2\text{-}Bu^t{}_2P)(C_4H_8O)_2]^6$ [Li–Li distances of 3.065(13) and 3.025(19) Å]. This complex, together with

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† Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

$[(H_2\overline{C(CH_2)_3N}Li)_3\cdot(PMDETA)]_3$[7] (PMDETA = pentamethyldiethylenetriamine), show some structural similarities to complex (**2**), having a restricted four-rung ladder with planar central rings of Li_2P_2 and Li_2N_2 respectively.

A starting material related to benzyl thiol is the isomeric thioanisole. Lithiation of the latter in the presence of TMEDA produces a cyclic dimer $[PhSCH_2Li\cdot(TMEDA)]_2$ held together by Li–S bonds (Li–S = 2.555 Å).[4] Tetrahedral co-ordination at lithium is completed by one molecule of TMEDA. Steric constraints would make polymer formation unlikely in this molecule.

Removal of the interposed CH_2 group (between S and Ph), as in complex (**1**), is sufficient to prevent association of the $(LiS)_\infty$ chains and results in a fall in the co-ordination number at sulphur from four to three. A second pyridine molecule fills the fourth co-ordination site at lithium (see Figure 2).

Introduction of an *ortho*-methyl group into (**1**) is just sufficient to break up the infinite S–Li chains. Figure 3 shows the structure of monomeric lithium *o*-thiocresolate (**3**), where lithium completes its tetrahedral co-ordination with three pyridine molecules and S is two co-ordinate. Crystals of complex (**3**) precipitated from the filtrate as transparent, colourless platelets. Complex (**4**) crystallised as long white needles similar to complex (**1**), and may have an analogous structure, *i.e.* $[o\text{-}MeC_6H_4SLi\cdot(NC_5H_5)_2]_\infty$ where steric crowding by the *ortho*-methyl group has not prevented oligomerisation. To date, the crystals obtained of (**4**) have been unsuitable for *X*-ray structure determination.

Similar Li–S distances are found in complexes (**1**) and (**2**) [(**1**), 2.459(7), 2.513(6) Å; (**2**), 2.454(5)—2.508(2) Å]. This is in contrast to complex (**3**) where the lower co-ordination at sulphur is reflected in slightly stronger Li–S bonding [2.412(6) Å].

The pyridine-complexed lithium thiolates of PhSH, $o\text{-}MeC_6H_4SH$, and $PhCH_2SH$ illustrate clearly how major changes in structural type can be effected by simple but strategic steric control.

We thank the S.E.R.C. for research grants (to W. C. and W. R. G.).

Received, 29th January 1987; Com. 110

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