Synthetic and structural investigations of some lithium thiolates and thiocarboxylates

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SYNTHETIC AND STRUCTURAL INVESTIGATIONS OF SOME LITHIUM THIOLATES AND THIOCARBOXYLATES

Wendy Rawstron Gill

A Thesis submitted for the degree of Ph.D to the
University of Durham.

November 1987

To David,
Christopher and Katrina

"In the space age the most important
space is between the ears".
Ann Armstrong
Guardian 30.1.74

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MEMORANDUM

The work carried out in this thesis was carried out by me in the Chemistry Department of the University of Durham between October 1984 and July 1987. I declare that the work has not been submitted previously for a degree at this or any other University. This thesis is my original work, except where acknowledged by reference. The copyright of this thesis rests with the author. No quotation from it should be published without her written consent and information derived from it should be acknowledged. Material from this thesis has been or will be included in the following publications:

(a) "The First Crystal Structure Characterization of an Alkali Metal Monothiocarboxylate, $[PhCOSLi.TMEDA]_2$ (TMEDA=tetramethylethylenediamine): a Chair-shaped Eight Membered $(COSLi)_2$ Ring System" D.R.Armstrong, A.J.Banister, W.Clegg and W.R.Gill, J. Chem. Soc., Chem. Commun., 1986, 1673.

(b) "X-Ray Crystal Structures of Some Lithium Aryl Thiolates: Monomeric $[0\text{-}MeC_6H_4SLi.(NC_5H_5)_3]$, Chain $[PhSLi.(NC_5H_5)_2]_\infty$ and the Unique Folded Ladder of $[PhCH_2SLi.NC_5H_5]_\infty$ with Li-S Rungs." A.J.Banister, W. Clegg and W.R.Gill, J. Chem. Soc., Chem. Commun., 1987, 850.

(c) "Preparation and Crystal Structure of a Novel Lithium Thiolate Cluster: $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$" A.J.Banister, W.Clegg and W.R.Gill, J. Chem. Soc., Chem. Commun., No. 1076 in publication.

(d) "Preparative, Structural and Theoretical Studies of Some Lithium Thiolates." D.R.Armstrong, A.J. Banister, W.Clegg and W.R.Gill, J. Chem. Soc., Dalton Trans., in preparation.

X ray crystal structures were carried out by Dr. W. Clegg, Newcastle University and *ab initio* calculations by Dr. D.R. Armstrong, Strathclyde University,

Synthetic and Structural Investigations of Some Lithium Thiolates and Thiocarboxylates.

W. R. Gill

Abstract

A series of closely related lithium aryl thiolates with pyridine as a donor ligand have been prepared. X-ray structure determination (Dr. W. Clegg) has shown that $[PhSLi.(NC_5H_5)]_\infty$ crystallises as an infinite chain polymer. Insertion of a methylene group between the phenyl ring and sulphur as in $[PhCH_2SLi.NC_5H_5]_\infty$ produced an infinitely folded ladder polymer with Li–S rungs, while introduction of an o-methyl group produces the monomeric complex $[o\text{-}MeC_6H_4SLi.(NC_5H_5)_3]$.

The unusual symmetrical complex $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$ has been prepared, in which a central sulphur atom is surrounded by a distorted cube of lithium atoms, each edge of which is bridged by a benzyl thiolate group such that the twelve S atoms form a cubo-octahedron: a further six Li atoms form a larger outer octahedron. When TMEDA is present in excess it appears that both PhSLi and $PhCH_2SLi$ form dimeric compounds with a central Li_2S_2 ring but structure determination of these complexes is incomplete.

$[PhCOSLi.TMEDA]_2$ has been prepared and crystallises as a centrosymmetric dimer containing a chair shaped central eight membered $(COSLi)_2$ ring with the Li atoms out of the $(COS)_2$ molecular plane. Lithiation of the related acids PhCOOH and PhCSSH has been carried out in the presence of TMEDA but crystal growth has so far been unsuccessful. Ab initio m.o. calculations on related model compounds are included.

A preliminary study has been carried out on the lithiation of the thio-oxime ($Ph_2C{=}NSH$). Results were encouraging but detailed investigation is needed.

The reaction of S_4N_4 with BI_3 produces, not the expected adduct, $S_4N_4.BI_3$, but an intractable polymer, empirical formula, S_3N_3BI. Other adducts of S_4N_4 and $(PhCN_2S_2)_2$ were prepared but were unsuitable for further reactions.

The reaction of lithium borohydride and sulphur in THF to produce sulphurated lithium borohydride has been modified to give a controllable reaction. Further reaction with TMEDA gives clear orange crystals of a complex the composition of which is still unknown.

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CHAPTER 1

GENERAL INTRODUCTION

1.1 HISTORICAL BACKGROUND

Sulphur and carbon were the only two non-metallic elements known in prehistoric times. Homer described the use of sulphur as a fumigant and its presence in volcanic materials was described by Pliny in A.D. $\sim$70. The association of sulphur with unpleasant smells and pollution was already appreciated in the 17th century when the effects of sulphur dioxide pollution in London were reported to Charles II by John Evelyn.[1]

The first organosulphur compound to be prepared was ethanethiol (Zeise 1834, Liebig 1834],[2] which has a particularly foul smell. However, the combination of unpleasant smell and low concentration has recently been made use of by the introduction of very small amounts of some lower alkyl thiols e.g. t-butyl thiol, into natural gas.[3]

Lithium, on the other hand, is a relatively 'young' element. In 1817 J. A. Arfredson, working in the laboratory of J. J. Berzelius, isolated it from the sheet silicate mineral, petalite, $LiAlSi_4O_{10}$, and chose the name lithium (Greek = stone). The element and its compounds did not achieve industrial importance for over a hundred years, and it is only in the past twenty years that so many lithium compounds have become available in bulk.

The chemistry of the alkali metals and their compounds has for very many years been considered to be a thoroughly researched and predictable area, dominated by the low ionization enthalpies for the outer electrons and the low polarizing power of the resulting M^+ ions. The current interest in the structure and bonding of organolithium compounds and the preparation of alkali-metal crown ether complexes has regenerated interest in this neglected area of chemistry.

To date, a wealth of exciting structures have been reported for lithium compounds of carbon, nitrogen and oxygen[4] backed up by many theoretical studies. The bonding implications have generated considerable controversy, see-sawing between, on the one hand, an almost completely covalent approach, and, on the other, an almost completely ionic explanation, and often coming to rest somewhere in between.

Complexes of sodium and potassium are likely to form equally interesting and varied structures but so far few have been published.

1.2 ORGANOLITHIUM COMPOUNDS - some general points

In the last twenty years there has been considerable interest generated in the structures and bonding of organolithium compounds, partly due to the vast improvement in the speed of X-ray analysis and partly due to mechanistic studies of their use in organic reactions.

It would be inappropriate, in this introduction, to review the present state of organolithium chemistry, since many excellent reviews and surveys have appeared in the literature.[5-9] However, some general observations, which encompass the whole field will be made in the hope that they will indicate the excitement and constant surprises that this chemistry produces, and the compulsion to seek new areas to examine.

Lithium structural chemistry dates only from 1963 when H. Dietrich reported the crystal structure of ethyl lithium,[10] to be followed a year later by the structural determination of methyl lithium by E. Weiss,[11] since which numerous structures have been reported.[4] Initially, interest centred on these alkyl and aryl lithiums, but recently many lithium - nitrogen compounds have been studied and, to a lesser extent, lithium - oxygen and lithium - phosphorus compounds.

Some general trends can be observed in all these organolithium complexes. They are usually associated molecules commonly forming dimers, tetramers and other oligomers. Complexes with additional donor ligands such as pentamethyldiethylenetriamine (PMDETA), tetramethylethylenediamine (TMEDA) and hexamethylphosphoramide (HMPA), and solvents such as diethyl ether and tetrahydrofuran (THF) are common. The presence of a strong chelating donor such as TMEDA usually results in smaller co-ordinated oligomers, with one molecule of TMEDA to each lithium atom (methyl lithium tetramer is a notable exception). Consistent with this it is also well known that organolithium - TMEDA complexes are more reactive in organic synthesis than the unco-ordinated species.[12-15]

Lithium often adopts a distorted tetrahedral environment in these complexes though this seems to be largely governed by steric effects and compounds are known where lithium is 3, 5 and 6 co-ordinate.

The nature of the bonding in these complexes has been the subject of much controversy, since a satisfactory explanation has to account for many conflicting features. Lithium is a highly electropositive element and is expected to form highly ionic bonds with less electropositive elements. However, many properties of e.g. the alkyl lithiums seem to be consistent only with covalent bonding. Theories involving only covalency have been countered by those involving purely ionic bonding culminating in the compromise of regarding methyl lithium, for example, as an electron deficient, multicentre, covalently bonded molecule with considerable ionic character. In general, the current view is that most organolithium complexes are substantially ionic with quite significant covalent contributions.

1.3 ORGANOLITHIUM COMPOUNDS - some structures

1.3.1 Lithium - Carbon Compounds

Many structures of lithium - carbon complexes have been described, both with and without donor ligands.[4,16] Methyl lithium itself has been the subject of much study. It exists, in the solid state and in solution, as a tetramer, $(LiMe)_4$, its structure being determined by Weiss from X-ray powder data.[11] The four lithium atoms are located at the corners of a tetrahedron with the methyl carbon atoms over the centres of the four tetrahedral faces such that they also form a tetrahedron. It forms a co-ordination complex with TMEDA, $[(LiMe)_4(TMEDA)_2]$ where TMEDA bridges the $(LiMe)_4$ units.[17,18] Many other tetrameric structures are known, especially where steric hindrance is low e.g. $(LiEt)_4$ and the substituted lithium acetylide, $(t\text{-}BuC{\equiv}CLi)_4(THF)_4$. Dimeric compounds with central Li_2C_2 rings are also common e.g. $(PhLi.TMEDA)_2$ and 2-lithio biphenyl, while cyclohexyl lithium is a hexameric complex, $[(C_6H_{11}Li)_6.2C_6H_6]$.

There are a variety of structures where lithium interacts with a delocalized hydrocarbon system and these illustrate admirably the fact that four outer orbitals do not limit the Li atom to four coordination. In the cyclopentadienyllithium complex, $(Me_3Si-C_5H_4.Li.TMEDA)$ each lithium is co-ordinated to seven other atoms (5 carbon and 2 nitrogen atoms) but gains only a fraction of the electron density available. For many of these structures lithium positions itself such that it can interact with as many other atoms as possible, steric constraints permitting, e.g. dilithionaphthalene, indenyllithium and dilithioanthracene show each lithium associated with the ring face.

1.3.2 Lithium - Nitrogen Compounds

In recent years, lithium - oxygen, lithium - phosphorus and, particularly, lithium - nitrogen complexes have been the subject of detailed studies.[4]

Stacked rings are a common feature of iminolithiums, while amidolithiums prefer the lateral association of ladder formation.[18,19] In iminolithium hexamers, $(R'R''=NLi)_6$ stacked cyclic trimers with three centre NLi_2

bonds are expected, (see Figure 1.1) unless this is prevented by the bulk of the substituent groups R' and R". In lithium amides $(R'R''NLi)_n$ the substituent groups R' and R" protrude above and below the rings, so that ring stacking is impossible and these complexes associate sideways to form ladders (see Figure 1.1)

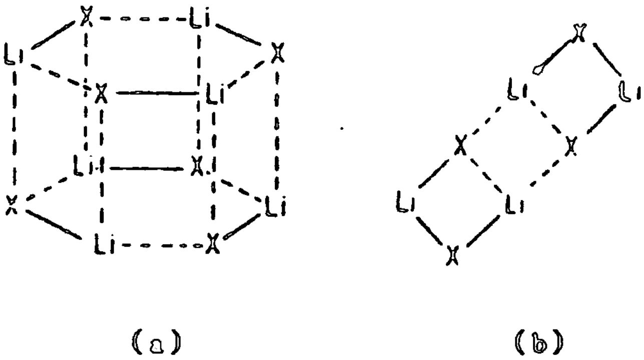

Figure 1.1 (a) Ring stacking in iminolithium hexamers and (b) Ladder formation in lithium amides.

The variety of structural types is further extended by introduction of donor ligands such as pyridine and HMPA, e.g. $(Bu^t{}_2C = NLi.HMPA)_2$ with a central N_2Li_2 ring, $(Ph_2C = NLi.NC_5H_5)_4$ with a pseudo cubane structure.[20,21] All of these structures reflect, once more, the tendency of lithium to attain the maximum possible co-ordination number that is compatible with steric constraints.

Monomeric structures occur only rarely, when bulky groups on either the ligand or donor molecule or both prevent association. e.g. $[LiN(SiMe_3)_2.12\text{-crown-}4]$,[22] $[Li(NHC_6H_2Bu^t{}_3\text{-}2,4,6).TMEDA]$.[23]

The compounds described above are only a fraction of those now published. No attempt has been made to cover all complexes, but it is hoped that the major structural types discussed give some indication of the interest that has been generated in this area of chemistry.

1.4 LITHIUM - SULPHUR COMPOUNDS

Prior to the study presented in the following chapters there had been no systematic study of lithium - sulphur compounds. A number of structures had been reported, generally as a consequence of other lithium investigations. These will be briefly described together with the implications arising out of their structures.

Seebach and co-workers studied the reactivity of the carbon - lithium bond and, in particular, the stabilization of the carbanionoid centre by adjacent heteroatoms. In 1966 they reported that thioanisole, $PhSCH_3$,[24] is metallated by n-butyl-lithium at the methyl group to give phenylthiomethyllithium, whereas anisole itself, in a similar reaction is lithiated on the phenyl ring to give o-methoxy phenyl lithium. Yields of the thio derivative were considerably improved by carrying out the reaction in the presence of DABCO (1,4 diaza,bicyclo[2.2.2]octane). It was subsequently reported by Petersen[25] that high yields of $MeSCH_2Li$ were obtained by reacting dimethyl sulphide with n-butyl-lithium and TMEDA. The structures of the TMEDA complexes of both methylthiomethyllithium and phenylthiomethyllithium were published by Seebach in 1984.[26] $(PhCH_2SLi.TMEDA)_2$ is dimeric with a chair-like central six-membered ring with Li.TMEDA bonding to the S atom of one $PhSCH_2$ unit and the C atom of the other (see Figure 1.2(a)), whereas in $(MeSCH_2Li.TMEDA)_2$, also a dimer, lithium is bonded to the methylene carbon atom of each $MeSCH_2$ unit to form a central four-membered C_2Li_2 ring (see Figure 1.2(b)).

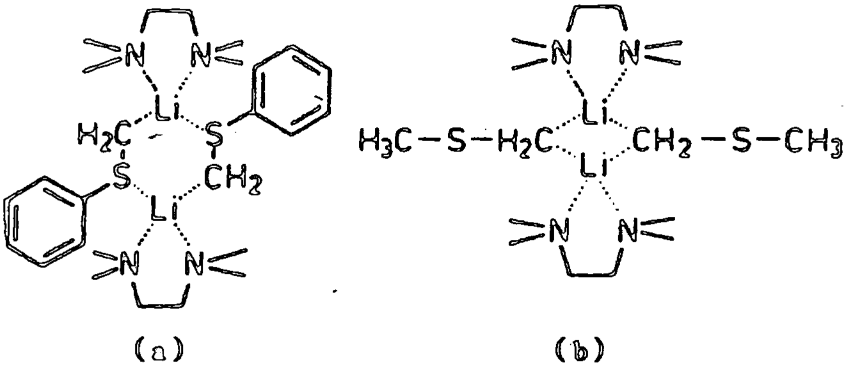

Figure 1.2 (a) $(PhCH_2SLi.TMEDA)_2$ (b) $(MeSCH_2Li.TMEDA)_2$

During the same studies, Seebach investigated the lithiation of some dithianes[27,28] and found that 2-phenyl-

1,3,dithiane and 2-methyl-1,3,dithiane produced compounds with different structures (see Figures 1.3(a) and (b)) The two structures are not directly comparable, however, since 2-lithio-2-phenyl-1,3,dithiane was prepared with n-butyl-lithium.TMEDA in hexane/THF (3:1) whereas 2-lithio-2-methyl-1,3,dithiane was prepared with n-butyl-lithium.TMEDA in hexane/cyclohexane (1:1) i.e. no extra co-ordinating ligand; this could be the reason for the difference in the two structures. Seebach proposed that in the latter complex lithium interacts equally strongly with the carbon of one ring and the sulphur of the other.

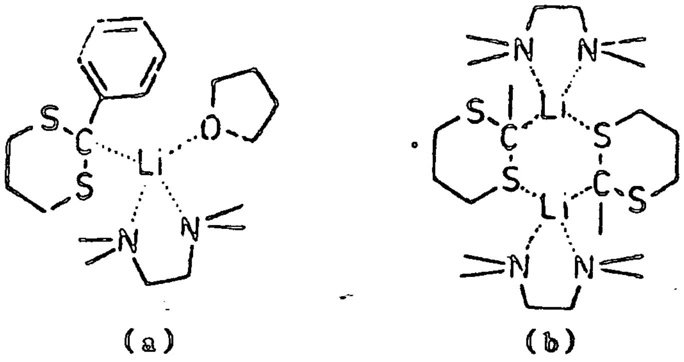

Figure 1.3 Structures of the dithianes.

The first X-ray crystal structure of an alkali metal alkyl thiolate was reported by P. P. Power and co-workers in 1985.[29] Using heavily hindered thiols, the two dimers, $[Li_2(THF)_4\{SCH(SiMe_3)_2\}_2]$ and $[Li_2(THF)_{3.5}\{SC(SiMe_3)_3\}_2]$, were prepared. Both have central Li_2S_2 rings with three co-ordinate sulphur and approximately tetrahedral lithium.

Although the number of structures investigated at this time was small, it was already apparent that many of the major effects discernible in lithium - carbon and lithium - nitrogen chemistry were likely to hold for lithium - sulphur compounds. There is a similar tendency to form associated molecules - all the reported structures are dimeric, even those with bulky thiol ligands, and all use donors such as TMEDA and THF to provide additional co-ordination at lithium. Attention had already been drawn to structural differences between lithium - sulphur and analogous lithium - oxygen compounds. A systematic study of lithium - sulphur complexes with a variety of donor ligands seemed likely to reveal new structures giving further insight into the bonding characteristics of this versatile element.

1.5 A BRIEF REVIEW OF THE THESIS

The following chapters are divided by the category of organic sulphur compound used as the major ligand. Chapter 3 describes the preparative techniques and structural analysis of a variety of lithium thiolates. Compounds were synthesized using co-ordinating ligands such as PMDETA, TMEDA, HMPA and pyridine. Solvents were restricted to hexane and toluene.

A preliminary study has been undertaken of the lithiated derivatives of the thio-oxime $Ph_2C=NSH$ and this is described in Chapter 4.

Chapter 5 deals with the preparation of lithium derivatives of a series of benzene carboxylic and thio-acids and the structural implications of lithium monothiobenzoate tetramethylethylenediamine dimer. Ab initio studies of a series of related acids are included.

Appendix 1 describes an early speculative study into the preparation of some sulphur-nitrogen boron adducts with a view to forming S-N-B rings or clusters and finally Appendix 2 draws together the synthetic details of reactions between lithium borohydride and sulphur, which are, as yet, only in the initial stages of investigation.

Throughout the thesis the synthetic restrictions are dominated by the air and moisture sensitivity of all the compounds and by the need to choose reaction conditions and donor ligands that would produce crystals suitable for X-ray structure determination.

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CHAPTER 2

GENERAL EXPERIMENTAL PROCEDURES

2.1 General Techniques

(a) Manipulation of air and moisture sensitive materials.

All complexes prepared were sensitive to moisture and oxygen and so were always handled under an atmosphere of dry nitrogen or *in vacuo*. For experiments carried out at the bench, nitrogen from the Departmental supply line was purified first by passage through a heated copper tower (to remove oxygen) and through a P_4O_{10} tower (to remove moisture). Other manipulations e.g. examination and sorting of crystals, were performed under an atmosphere of dry nitrogen in a Vacuum Atmospheres glove box (Type HE43-2) fitted with a recirculating pump and molecular sieve drying column (HE493 DRITRAIN). The pressure in the glove box was regulated with a Pedatrol HE-63-P regulating unit and the nitrogen was supplied from a high pressure cylinder (BOC white spot grade).

(b) Infra red spectra

Infra red spectra were recorded on Perkin-Elmer grating spectrophotometers (Type 477 or 577). Unless otherwise stated the spectra of solids were recorded as nujol mulls on KBr plates. Liquids were recorded as thin films.

(c) Nuclear magnetic resonance spectra.

Nuclear magnetic resonance spectra were recorded on a Bruker AC250 at room temperature (20 °C) using a multinuclear probe.

^{7}Li spectra were recorded at 97.2 MHz using phenyl lithium as a standard.

^{11}B spectra were recorded at 80.239 MHz using boron trifluoride etherate as a standard.

(d) Mass spectra.

Mass spectra were recorded on an A.E.I.(MS9) spectrometer at 120 - 180 °C and 70 eV with an accelerating potential of 8 KV. Samples were introduced by direct insertion into the ion source.

(e) X-ray oscillation and Weissenberg photographs

Crystals were examined and sorted in the glove box using an Olympus microscope, magnification 10-40. Suitable crystals were mounted in 0.3 or 0.5 mm Lindemann capillaries and sealed. X-ray photgraphs were recorded using a Nonius integrating Weissenberg goniometer with a Philips X-ray generator Type PW 1009/30, fitted with an X-ray tube with a Cu anode and Ni filter, at 42 KV and 16 milliamps. The image was recorded using Agfa-Gevaert Osray X-ray film.

(f) X-ray structure determination.

X-ray structure determinations were carried out at Newcastle University by Dr. W. Clegg, on a Siemens AED2 diffractometer with graphite monochromator using either CuKα or MoKα radiation (λ = 1.54184/0.71073 Å). ω/θ scan mode was used for data collection, with appropriately chosen scan width and time. Programs were SHELTXL and local software on a Data General Model 30 computer.

(g) Elemental analyses.

Elemental analyses were performed in this Department by Mr. R. Coult (S, N, Li, B, I) or by Mrs. M. Cocks (C, H, N). Carbon and hydrogen analyses were carried out using a Perkin-Elmer 240 Elemental Analyser or a Carlo Erba Elemental Analyser 1106.

Sulphur was determined by oxygen flask combustion followed by visual titration of sulphate ions. Nitrogen was determined by the micro-Kjeldhal method. Lithium and boron were determined by Atomic Absorption spectroscopy on a Perkin-Elmer 5000. Iodine was determined by oxygen flask combustion.

(h) Glassware

All Pyrex glassware used was either dried in the oven (ca. 100 °C) for at least 60 minutes, or gently flamed with a hand torch (ca. 500 °C) in a flow of nitrogen before use.

(i) Vacuum lines

A Pyrex vacuum manifold fitted with J. Young's Teflon stemmed valves was used, achieving a vacuum of about 10^{-2} torr; connection to reaction vessels was via tap adaptors and rubber tubing.

(j) Constant low temperature control.

Cooling as low as -20 °C was achieved by use of an alcohol-filled Haake bath circulator; the temperature could be adjusted to ±1 °C.

2.2 Preparative techniques for thiols.

Most thiols used had unpleasant smells and all manipulations with these compounds took place in a fumes hood. Hands were protected by disposable and rubber gloves. Preparations were carried out in Schlenk type glassware (see Figure 2.1) under an atmosphere of dry nitrogen and all liquid reactants were added from a dry syringe. Traces of thiol were removed from glassware by initial washing in a beaker of alkali metal hydroxide.

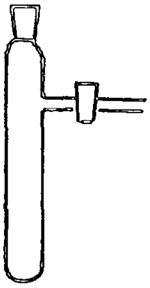

Figure 2.1 Diagram of type of Schlenk used.

2.3 Miscellaneous reagents.

(a) Thiophenol, PhSH; benzyl mercaptan, $PhCH_2SH$; o-thiocresol, o-$CH_3C_6H_4SH$; t-butyl mercaptan, t-BuSH; pentafluorothiophenol, C_6F_5SH; thiobenzoic acid, PhCOSH; supplied by Aldrich Chemical Co. and used without further purification.

(b) Benzoic acid, PhCOOH; suppled by BDH and dried in a vacuum desiccator.

(c) n-Butyl lithium; supplied by Aldrich Chemical Co. as a 1.6M solution in hexane. Standardised by Mr. B.

Hall according to the literature.[1]

(d) Phenyl lithium; supplied by Aldrich Chemical Co. as a 1.95M solution in 70/30 cyclohexane/ether. Standardised according to literature methods.[1]

(e) Tetramethylethylene diamine, TMEDA; supplied by Fluka and dried over molecular sieve type 4A.

(f) Pentamethylethylenediamine, PMDETA; supplied by Lancaster Synthesis Ltd., and dried over molecular sieve type 4A.

(g) Pyridine; supplied by Aldrich Chemical Co., distilled and stored in a flask fitted with a Rotaflo adaptor under nitrogen.

(h) Hexamethylphosphoramide, HMPA; supplied by Aldrich Chemical Co., distilled and stored, under nitrogen, in a flask fitted with a Rotaflo adaptor, over molecular sieve type 4A.

(i) Toluene; supplied by May and Baker Ltd., shaken with CaH_2, distilled and stored in a Winchester under nitrogen.

(j) Hexane; supplied by May and Baker Ltd., shaken with $CaCl_2$, distilled and stored in a Winchester under nitrogen.

(k) Dichloromethane, CH_2Cl_2; supplied by May and Baker, dried over P_2O_5, distilled and stored under nitrogen.

(l) Tetrasulphur tetranitride, S_4N_4; ex. Dr. Z. V. Hauptman, prepared according to literature methods.[2]

(m) 4-Phenyl-1,2,3,5 dithiazole, $(PhCN_2S_2)_2$, prepared by Mr. I. B. Gorrell according to literature methods.[3]

(n) 9-Borabicyclo(3,3,1)nonane; supplied by Aldrich Chemical Co. and used without further purification.

(o) Boron triodide, BI_3; prepared according to literature methods.[4] The solvent heptane was replaced by hexane. Purification was by vacuum sublimation at 45 - 55 °C onto a water cooled cold finger.

(p) Sulphur; supplied by BDH and dried in a vacuum desiccator for several days.

(q) Lithium borohydride; supplied by Aldrich Chemical Co. and used without further purification.

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CHAPTER 3

THE PREPARATION AND STRUCTURES OF SOME LITHIUM THIOLATES

3.1 INTRODUCTION

Organosulphur compounds have been known for over a hundred and fifty years, ethanethiol being first prepared in 1834 by Zeise[1] and Leibig.[2] They are often notorious because of their unpleasant smell and this is especially true of the lower alkyl thiols (also called mercaptans). As little as one part in fifty billion can be detected by smell. Some low molecular weight thiols are used in low concentrations to impart smell to natural gas and it has been known for whole buildings to be evacuated following the leakage of a small amount of thiol from a nearby laboratory! The use of oxidising solutions such as hypochlorite or alkaline peroxide can avoid this.[3]

Alkali metal thiolates have been known for very many years but rarely isolated - they are usually used 'in situ' and structural investigations are few. Sodium methyl thiolate is reported to separate out of solution, in alcohol and water, as long flat needles, $CH_3SNa.4.5H_2O$,[4] and in 1926 C.G.Moses and E.E.Reid prepared some sodium thiolates in dry ether.[5] They reported the products as white flaky solids from which ether could not be eliminated entirely, even after warming under vacuum. It is probable that complexes were formed with ether as a coordinating ligand to sodium.

Very considerable use has been made of alkali metal thiolates in the petroleum industry by using, particularly, NaOH to remove unwanted thiols from the distillates. An early patent for purifying naphthas by heating with sodium hydroxide solution was granted in 1866.[6] This use has declined in recent years as smaller quantities of sulphur compounds are produced by catalytic cracking.

Thiolates are strong donor ligands and have a high affinity for most metal ions, so it is not surprising that there has been an enormous increase in the chemistry of transition metal thiolates in recent years. This is, in part, a consequence of the fact that sulphur co-ordination occurs for some transition metal ions in metalloenzymes e.g. nitrogenase, ferredoxin, and also of the tremendous advances in structure determination by X-ray crystallography. There are several reviews of metal thiolate complexes[7-9] and reference will be made here only to those that seem to have some relationship to alkali metal thiolates. The complexes and clusters of transition metal thiolates have produced an enormous variety of structures, and careful design of the substituent thiolate group could lead to many others. The biochemical relationship has meant that a great deal of work has concentrated on the metals iron, molybdenum and copper.

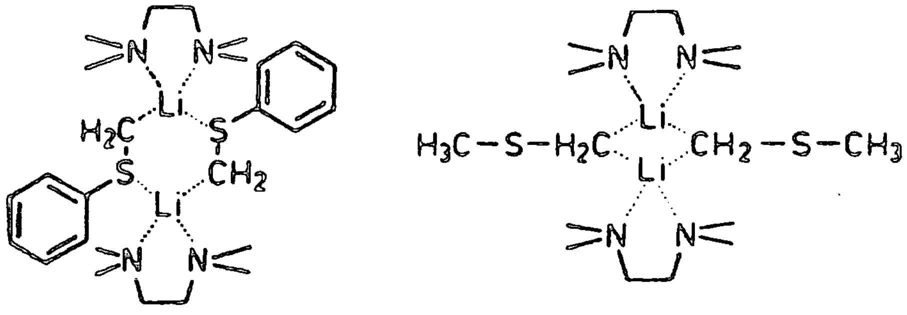
Sulphur often acts as a bridging ligand because the thiolate group is very polarizable and divalent sulphur has the ability to stabilize centres of high electron density. Many neutral transition metal thiolates are insoluble bridged polymers,[10] but it is reported that they become less intractible when prepared in the presence of excess thiol and triethylamine, possibly because of the donor properties of the latter. Mercury(II) thiolates are very well known (the name mercaptan derives from the attraction of thiols for Hg(II) ions) and a number of these are crystalline compounds with known structures.[11] The neutral molybdenum thiolate $Mo(S^tBu)_4$ is crystalline and diamagnetic and has proved a versatile starting material for a wide range of thiolato-molybdenum complexes.[12]

There is a great deal of information on anionic thiolate complexes such as $[M(SPh)_4]^{2-}$ M = Mn, Fe, Co, Ni, Zn, and $[M(SPh)_2dts^*]^{2-}$ M = Mn, Fe, Co, Ni.[13-15] Cluster compounds occur for anionic silver and copper compounds e.g. $[Ag_6(SPh)_8]^{2-}$, $[M_5(SPh)_7]^{2-}$ M = Ag, Cu, with the thiolato ligand often forming multinuclear complexes in which the metal ions are held in small clusters by

* dithiosquarate

bridging thiolate groups.[16-18] A recent paper[19] has reported the use of bulky ligands to reduce oligomerisation in Ag(I) compounds.

Prior to our own work only three lithium thiolate structures had been reported. As part of their investigations into the nature of the C-Li bond and the stabilization of the carbanionoid centre by adjacent heteroatoms, Seebach and co-workers investigated the lithiation of thioanisole and dimethyl sulphide, using TMEDA (tetramethylethylenediamine) as a co-ordinating ligand.[20]. The complex, $[PhSCH_2Li.TMEDA]_2$, prepared from thioanisole, is a centrosymmetric dimer containing a chair-like six membered ring in which each Li atom is linked to the terminal C atom of one thioanisole fragment and to the S atom of the other. A TMEDA molecule completes the tetrahedral co-ordination at Li.



3.1 3.2

Figures 3.1 and 3.2 Structures of $[PhSCH_2Li.TMEDA]_2$ and $[MeSCH_2Li.TMEDA]_2$

Dimethyl sulphide produces a dimeric structure with a central four-membered C_2Li_2 ring and no Li-S bonds. (see Figures 3.1 and 3.2)

The first structural determination of an alkali metal alkyl thiolate was reported in 1985.[21] The use of two bulky ligands produced the dimers: $\{Li_2(thf)_4[SCH(SiMe_3)_2]_2\}$ (1), $\{Li_2(thf)_{3.5}[SC(SiMe_3)_3]_2\}$ (2), having a central four membered ring comprising a rhombus of two Li atoms and two S atoms. Sulphur is three co-ordinate, the geometry being pyramidal in (1) and planar in (2), probably as a result of greater steric hindrance in (2). Lithium is, in both compounds, tetrahedral with THF as the co-ordinating ligand.

The following results constitute the first major investigation into the lithiation of a series of organic thiolates.

3.2 RESULTS AND DISCUSSION

The following abbreviations will be used:

TMEDA tetramethylethylenediamine $Me_2N(CH_2)_2NMe_2$

PMDETA pentamethyldiethylenetriamine - $Me_2N(CH_2)_2NMe(CH_2)_2NMe_2$

HMPA hexamethylphosphoramide $O{=}P(NMe_2)_3$

3.2.1 Preparation of $[PhSLi.(NC_5H_5)_2]_\infty$

The reaction of thiophenol with n-butyl-lithium in the presence of an equimolar amount of pyridine produces a product insoluble in hexane and slightly soluble in toluene. Recrystallisation (toluene-pyridine) gave transparent colourless needles on cooling. Filtration, washing and drying must be carried out with care in order to produce crystals of good quality. The use of too much hexane in washing and/or too prolonged vacuum drying produces a white coating on the surface of the crystals.

Elemental analyses of the crystals were consistent with the formula $[PhSLi.(NC_5H_5)_2]_n$. The absence of the SH stretching frequency in the infra red spectrum (ν = 2500 cm^{-1}) indicates that the product is not contaminated with starting material. ^7Li high field n.m.r. at 20 °C in $[^2H_8]$ toluene showed only a sharp singlet, indicating the presence of only one lithium environment in solution. Only one, therefore, was likely in the solid state structure. (Experimental details p.85)

3.2.2 Structure of $[PhSLi.(NC_5H_5)_2]_\infty$

The crystals were examined under a microscope. They were long thin needles, many of them aggregates and many of them with a fine white coating on the surface. A small number were clear and colourless and several of these were mounted in 0.3 mm glass capillaries under nitrogen. Two of them, shown by X-ray oscillation photographs to be single crystals, were submitted for full X-ray structure determination, and the results of this analysis are shown in Tables 3.1 to 3.4 and Figures 3.3 to 3.4. p. 31-36.

$[PhSLi.(NC_5H_5)_2]_\infty$ is a crystalline polymer containing an infinite chain of Li-S atoms. Sulphur is three co-ordinate, being attached to two lithium atoms of the chain and one phenyl group; adjacent phenyl groups are bent away from each other. Approximate tetrahedral co-ordination at lithium is completed by two pyridine molecules and the planes of these are perpendicular to each other. Alternate pairs of pyridine molecules are in the same plane, Li-S distances (see Table 3.1) are similar to those found in other Li-S compounds: E.g. 2.47 Å in Li_2S,[22,23], 2.555(3) Å in $[PhSCH_2Li.TMEDA]_2$.[20] and 2.41 Å (av) in $\{Li_2(THF)_4[SCH(SiMe_3)_2]_2\}$ and $\{Li_2(THF)_{3.5}[SC(SiMe_3)_3]_2\}$[21].

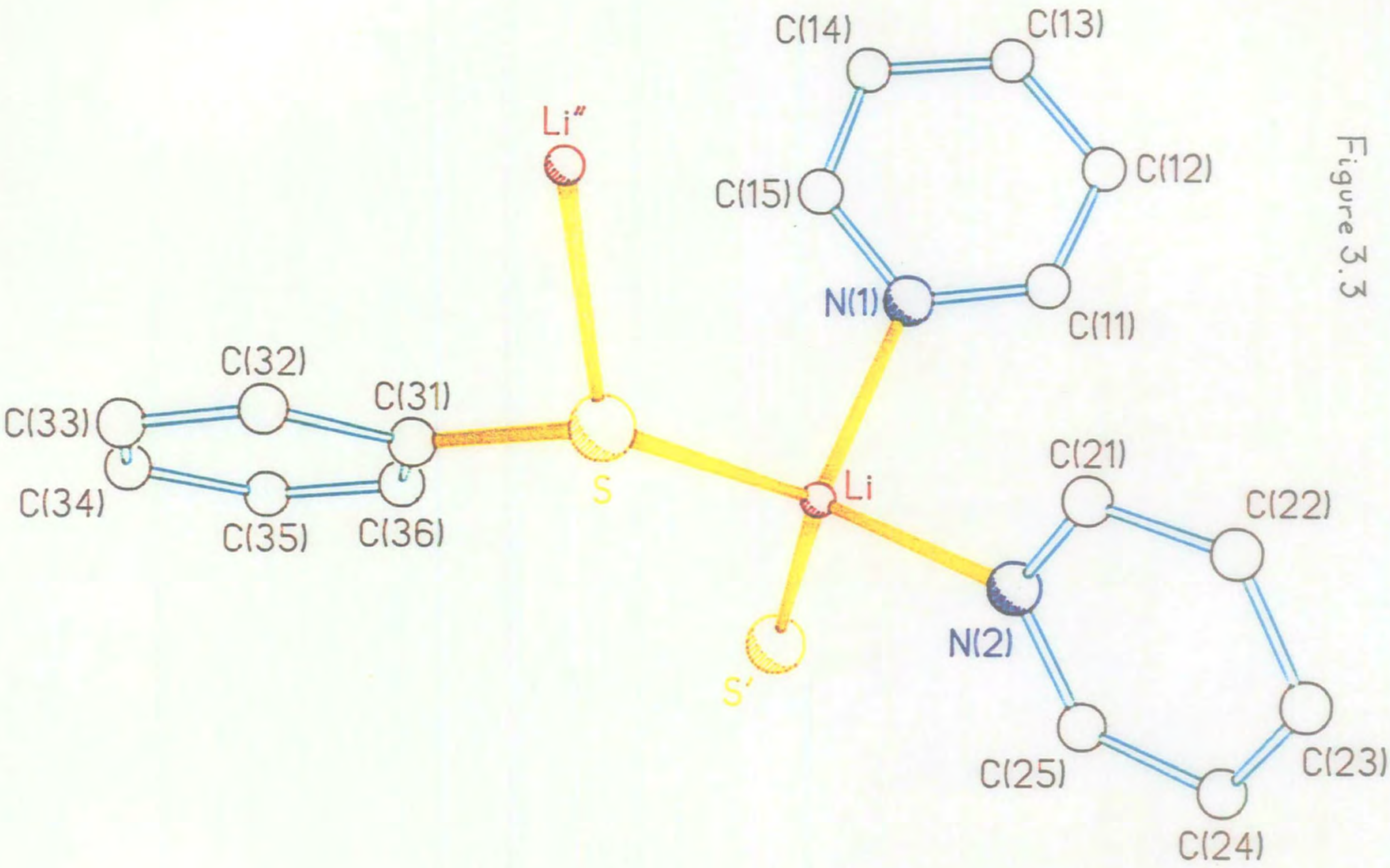
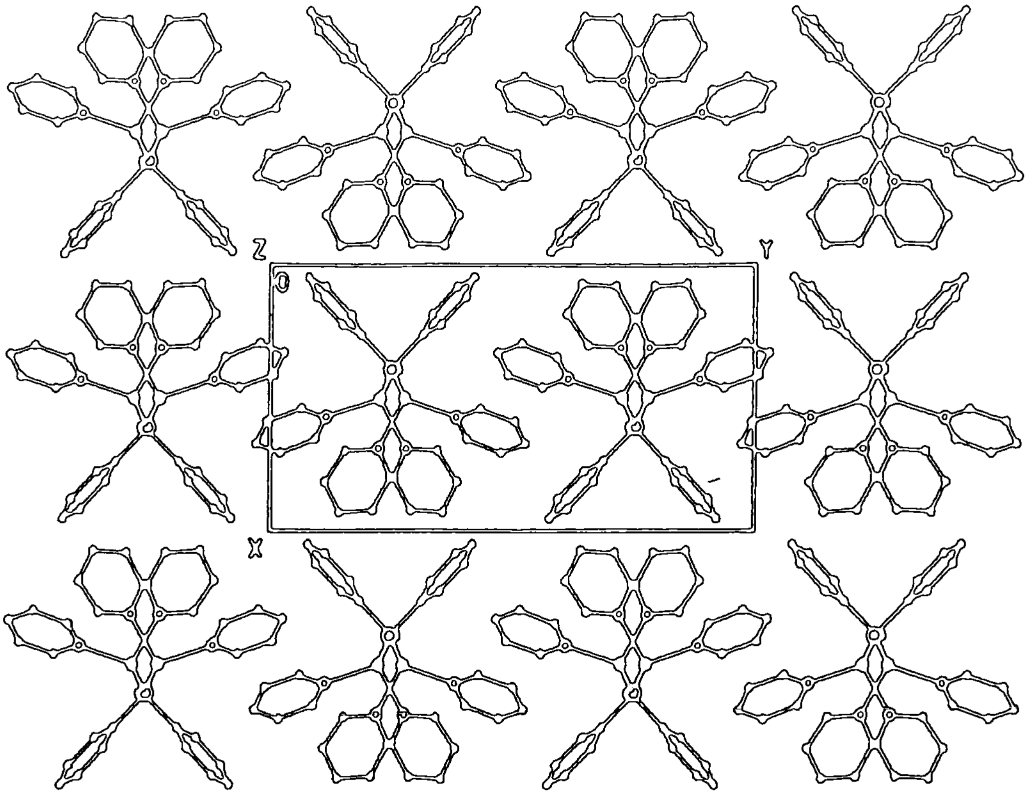

C(14)
C(13)
Li"
C(12)
C(15)
N(1)
C(11)
C(32)
C(31)
C(33)
S
Li
C(21)
C(34)
C(35)
C(36)
C(22)
N(2)
S'
C(25)
C(23)
C(24)

Figure 3.3

Figure 3.4 Two projections of the polymeric structure of $[PhSLi.(NC_5H_5)_2]_\infty$



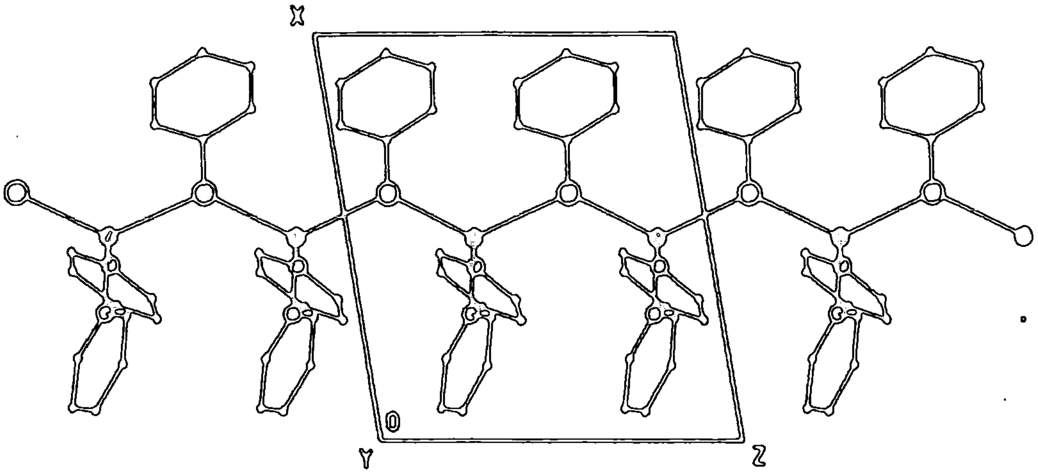


Table 3.1 Crystal data, bond lengths (Å) and bond angles (°) for $[PhSLi.(NC_5H_5)_2]_\infty$

Crystal data

$C_{16}H_{15}LiN_2S$ monomeric unit, M_r = 274.31, monoclinic, space group P2 /c,
a = 9.8032(7), b = 18.004(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>3σ(F) and 2θ≤115°
Symmetry transformations for primed (') atoms x,$\frac{3}{2}$-y, $\frac{1}{2}$+z; for double primed (") atoms x,$\frac{3}{2}$-y,-$\frac{1}{2}$+z. (see Figure 3.3)

Bond lengths (Å) and bond angles (°)

Li-N(1)	2.063(6)	Li-N(2)	2.085(6)
Li-S	2.513(6)	Li-S"	2.459(7)
N(1)-C(11)	1.316(5)	N(1)-C(45)	1.302(6)
C(11)-C(12)	1.348(6)	C(12)-C(13)	1.340(8)
C(13)-C(14)	1.371(8)	C(14)-C(15)	1.362(8)
N(2)-C(21)	1.318(5)	N(2)-C(25)	1.321(5)
C(21)-C(22)	1.385(6)	C(22)-C(23)	1.344(7)
C(23)-C(24)	1.375(7)	C(24)-C(25)	1.364(6)
S-C(31)	1.752(3)	C(31)-C(32)	1.398(4)
C(31)-C(36)	1.381(5)	C(32)-C(33)	1.369(5)
C(33)-C(34)	1.366(6)	C(34)-C(35)	1.373(6)
C(35)-C(36)	1.376(5)		

N(1)-Li-N(2)	100.2(3)	N(1)-Li-S	108.0(3)
N(2)-Li-S	106.0(3)	N(1)-Li-S"	104.4(2)
N(2)-Li-S"	110.9(3)	S-Li-S"	124.7(2)
Li-N(1)-C(11)	123.8(3)	Li-N(1)-C(15)	119.5(3)
C(11)-N(1)-C(15)	116.4(3)	N(1)-C(11)-C(12)	125.6(4)
C(11)-C(12)-C(13)	117.0(4)	C(12)-C(13)-C(14)	119.6(6)
C(13)-C(14)-C(15)	118.4(6)	N(1)-C(15)-C(14)	123.0(4)
Li-N(2)-C(21)	119.8(3)	Li-N(2)-C(25)	123.7(3)
C(21)-N(2)-C(25)	116.6(3)	N(2)-C(21)-C(22)	124.0(4)
C(21)-C(22)-C(23)	118.1(4)	C(22)-C(23)-C(24)	119.0(4)
C(23)-C(24)-C(25)	118.9(4)	N(2)-C(25)-C(24)	123.4(4)
Li-S-C(31)	113.6(2)	Li-S-Li'	129.8(2)
C(31)-S-Li'	100.7(2)	S-C(31)-C(32)	121.6(3)
S-C(31)-C(36)	122.4(2)	C(32)-C(33)-C(36)	116.1(3)
C(31)-C(32)-C(33)	121.8(3)	C(32)-C(33)-C(34)	121.1(4)
C(33)-C(34)-C(35)	118.2(4)	C(34)-C(35)-C(36)	121.0(4)
C(31)-C(36)-C(35)	121.8(3)		

Table 3.2 Atomic co-ordinates ($\times 10^4$) for $[PhSLi.(NC_5H_5)_2]_\infty$

Atom	x	y	z
Li	4984(6)	7761(3)	-1421(7)
N(1)	3115(3)	7206(2)	-1855(4)
C(11)	2007(4)	7458(2)	-2772(5)
C(12)	788(4)	7098(3)	-3137(5)
C(13)	716(6)	6416(4)	-2549(6)
C(14)	1857(7)	6119(4)	-1622(7)
C(15)	3028(5)	6539(3)	-1307(5)
N(2)	4285(3)	8857(2)	-1498(3)
C(21)	3462(4)	9076(2)	-552(4)
C(22)	2952(4)	9791(3)	-510(5)
C(23)	3295(4)	10291(2)	-1512(5)
C(24)	4139(4)	10074(2)	-2522(5)
C(25)	4607(4)	9359(2)	-2469(4)
S	6075(1)	7522(1)	1338(1)
C(31)	7385(3)	6849(2)	1550(4)
C(32)	8133(3)	6658(2)	3000(4)
C(33)	9174(3)	6141(2)	3169(5)
C(34)	9515(4)	5784(2)	1921(5)
C(35)	8780(5)	5952(2)	486(5)
C(36)	7741(4)	6476(2)	307(4)

Table 3.3 Anisotropic thermal parameters ($Å^2 \times 10^3$) for $[PhSLi.(NC_5H_5)_2]_\infty$. (The anisotropic temperature factor exponent takes the form $-2\pi^2(h^2a^{\circ 2}U_{11} + \ldots .2hka^\circ b^\circ U_{12})$

	U_{11}	U_{23}	U_{33}	U_{23}	U_{13}	U_{12}
Li	66(4)	59(4)	66(4)	3(3)	8(3)	0(3)
N(1)	64(2)	63(2)	67(2)	2(2)	8(2)	1(2)
C(11)	85(3)	76(3)	102(3)	-10(3)	-14(2)	12(3)
C(12)	64(3)	167(4)	108(4)	-37(3)	-5(3)	1(3)
C(13)	127(5)	270(8)	94(4)	2(5)	9(4)	-126(5)
C(14)	200(7)	187(6)	125(5)	53(5)	-30(5)	-131(6)
C(15)	112(4)	102(4)	91(3)	29(3)	-8(3)	-24(3)
N(2)	81(2)	55(2)	60(2)	0(2)	4(2)	2(2)
C(21)	96(3)	70(3)	76(3)	-2(2)	14(2)	-1(2)
C(22)	83(3)	82(3)	100(4)	-27(3)	4(3)	14(3)
C(23)	89(3)	54(3)	127(4)	-8(3)	-23(3)	8(2)
C(24)	101(3)	69(3)	114(4)	24(3)	6(3)	6(3)
C(25)	90(3)	70(3)	70(3)	9(2)	5(2)	3(3)
S	70(1)	72(1)	48(1)	2(1)	9(1)	13(1)
C(31)	47(2)	51(2)	51(2)	0(2)	9(2)	-7(2)
C(32)	66(2)	73(2)	51(2)	-3(2)	3(2)	7(2)
C(33)	73(3)	82(3)	69(3)	-2(2)	-9(2)	13(2)
C(34)	89(3)	80(3)	96(4)	-3(3)	-1(3)	26(3)
C(35)	112(4)	82(3)	80(3)	20(3)	20(3)	28(3)
C(36)	76(3)	67(2)	52(2)	-8(2)	8(2)	7(2)

Table 3.4 The atomic co-ordinates (x 10^4) and isotropic thermal parameters ($\mathring{A}^2$ x 10^3) for the hydrogen atoms.

	x	y	z	U
H(11)	2071	7941	-3218	110
H(12)	7	7321	-3792	139
H(13)	-131	6137	-2773	199
H(14)	1831	5627	-1208	214
H(15)	3825	6334	-650	126
H(21)	3201	8717	151	97
H(22)	2369	9927	215	107
H(23)	2956	10791	-1523	114
H(24)	4396	10420	-3253	115
H(25)	5201	9214	-3175	93
H(32)	7911	6896	3901	77
H(33)	9672	6029	4182	92
H(34)	10249	5424	2043	109
H(35)	8994	5701	-404	109
H(36)	7250	6585	-712	79

3.2.3 Preparation of (PhSLi.PMDETA)

The initial reaction of thiophenol and n-butyllithium in hexane gave a thick white precipitate highly insoluble and most likely polymeric. On addition of PMDETA this became a more finely divided cream solid which was soluble in warm toluene.

The crystals which formed on cooling were long, colourless needles. Many of them were aggregates and extremely fragile. Elemental analyses (giving the empirical formula PhSLi.PMDETA) and ^{7}Li high field n.m.r.(in [$^{2}H_{8}$]toluene) at 20 °C indicated only one lithium environment. However, monomeric lithium complexes are often restricted to those where the ligands contain bulky groups e.g. $[(Me_3Si)_2CHLi.PMDETA]$[24] and, in comparison (PhSLi.PMDETA) is not so sterically hindered. The initial crystals were either coated with a polycrystalline layer or were multi-twinned. It is possible that by further recrystallisation and careful drying crystals suitable for full X-ray determination will be obtained. (Experimental details p.82)

3.2.4 Preparation of $(PhSLi.TMEDA)_2$

Thiophenol reacts with n-butyl-lithium in hexane and a small excess of TMEDA to produce a white precipitate. Colourless needles were obtained on dissolving the precipitate in hexane and allowing to cool. As with the previous lithium thiophenolates it proved important not to leave the crystals under vacuum for more than a few seconds or a white opaque coating formed on the surface.

The crystals analysed to an empirical formula (PhSLi.TMEDA) and X-ray oscillation photographs indicated single crystals with a large unit cell. An X-ray structure determination was carried out at room temperature but the data could only be refined to 19%. Preliminary results appear in Table 3.5. As illustrated in Figure 3.4 the complex is a dimer with a central, essentially planar, Li_2S_2 ring. Sulphur is three co-ordinate with a distorted pyramidal arrangement while approximately tetrahedral co-ordination at lithium is completed by a TMEDA molecule. Low temperature X-ray data collection will be used to obtain more accurate results. The Li_2X_2 four membered central ring is commonly seen in dimeric lithium structures where X = C, X = O and X = N.[24] (Experimental details p.83)

Figure 3.5 Dimeric Structure of $[PhSLi.TMEDA]_2$

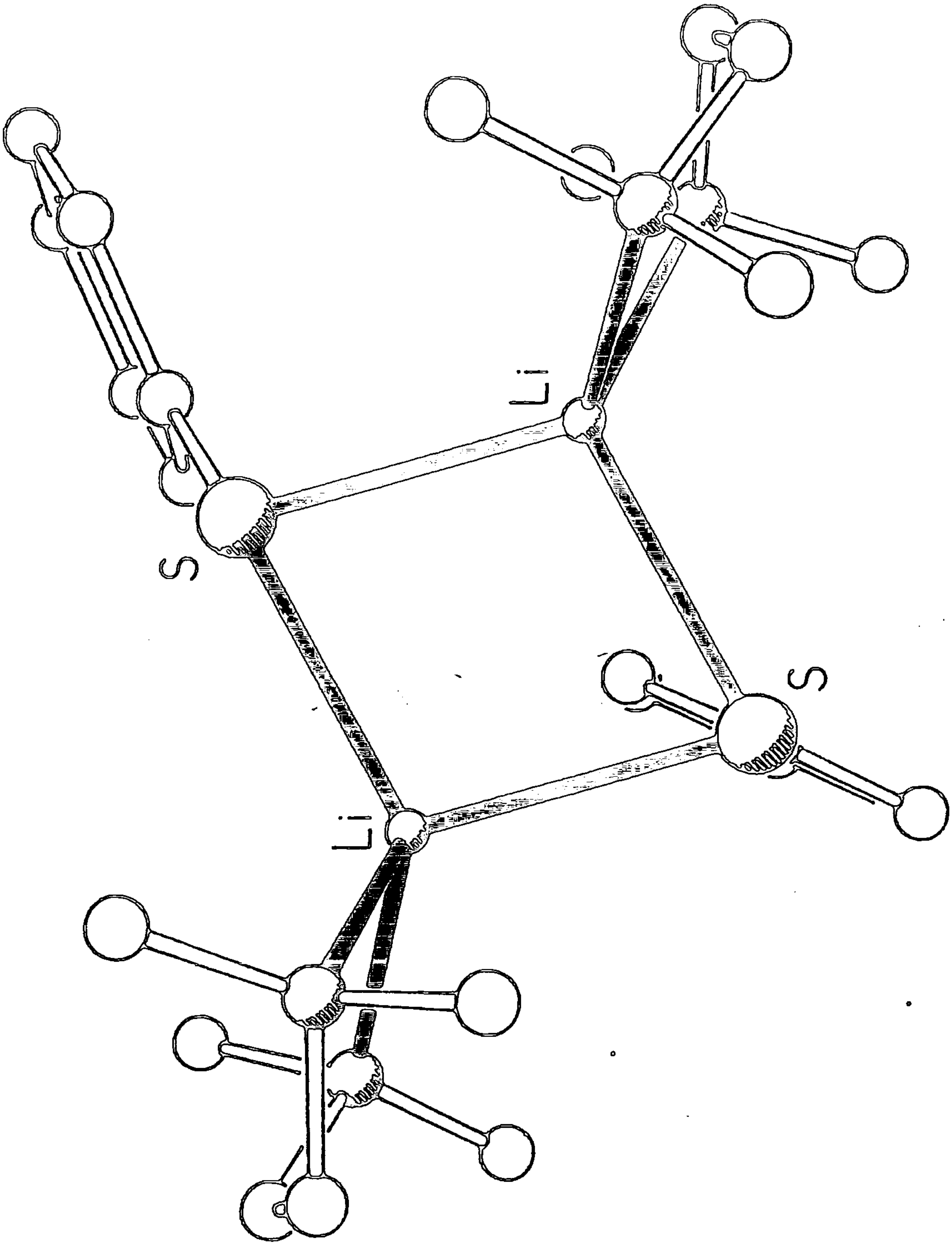


Table 3.5 Preliminary crystal data, bond lengths (Å) and bond angles (°) for $[PhSLi.TMEDA]_2$

$C_{24}H_{42}Li_2N_4S_2$, orthorhombic, space group Pbca,
a = 11.2856, b = 16.7250, c = 31.5621 Å
Current R = 0.19 for 2335 reflections

Bond lengths (Å) and Bond Angles (°)

Li(1)-N(41)	2.159	Li(2)-N(31)	2.152
Li(1)-N(42)	2.066	Li(2)-N(32)	2.134
Li(1)-S(1)	2.494	Li(2)-S(1)	2.450
Li(1)-S(2)	2.438	Li(2)-S(2)	2.477
S(1)-C(11)	1.766	S(2)-C(21)	1.775
N(41)-C(41)	1.434	N(42)-C(45)	1.420
N(41)-C(42)	1.431	N(42)-C(46)	1.443
N(41-C(43)	1.448	N(42)-C(44)	1.501
C(43)-C(44)	1.290		
C-C (in phenyl ring)	1.400		

esd's approximately 0.02 Å

S(1)-Li(1)-S(2)	103.8	S(1)-Li(2)-S(2)	104.0
Li(1)-S(1)-Li(3)	75.8	Li(1)-S(2)-Li(2)	76.3
N(41)-Li(1)-N(42)	90.1	N(31)-Li(2)-N(32)	87.2
Li(2)-S(1)-C(11)	98.6	Li(1)-S(2)-C(21)	128.5
Li(1)-S(1)-C(11)	98.1	Li(2)-S(2)-C(21)	102.8
N(41)-Li(1)-S(2)	129.1		

esd's approximately 1 °

3.2.5 Reactions of PhSH with n-Butyl-Lithium using Hexamethylphosphoramide (HMPA) as a Co-ordinating Ligand.

Two preliminary reactions have been carried out using HMPA as a co-ordinating ligand. It is uni-dentate, $O=P(NMe_2)_3$, co-ordinating through the oxygen atom and has been used successfully in the preparation of other crystalline lithium compounds e.g. $[(PhCH_2)_2NLi.O=P(NMe_2)_3]_2$.[25]

Both reactions produced a small number of white crystals on cooling overnight, but these were dispersed in a yellow oil. It proved impossible to collect them, either by filtration, or, by manual extraction, from the oil. It is possible that, as the system warmed up, the crystals dissolved in excess HMPA, (there was a three molar excess of HMPA w.r.t PhSLi) in which case, further investigation reducing the concentration of HMPA may yield better results. (Experimental details p.84)

3.2.6 Preparation of $[PhCH_2SLi.NC_5H_5]_\infty$

One of the initial criteria for this investigation was that the thiols used should have only one reactive sulphur site and differ from each other by a simple organic fragment. This should produce structures that could be readily solved by standard techniques such as elemental analysis, n.m.r. and X-ray crystallography. As described in Sections 3.2.1 to 3.2.6 the first reactions had involved the simplest aromatic thiol, thiophenol, PhSH, and n-butyl-lithium in the presence of a number of different chelating ligands. A logical extension of this was to examine similar reactions using benzyl mercaptan, $PhCH_2SH$, which differs from thiophenol only by the insertion of a methylene group between the sulphur and the phenyl group. Meaningful comparisons of several compounds are only possible if the same chelating ligand can be used with a series of related aryl derivatives, under similar reaction conditions.

The first reaction, therefore, was carried out using pyridine as a donor ligand, in the hope that a product would be obtained for comparison with $[PhSLi.(NC_5H_5)_2]_\infty$ (see Section 3.2.1).

Benzyl mercaptan was reacted with n-butyl-lithium and pyridine in toluene and, after recrystallization from toluene/pyridine, clear, colourless platelets were collected. The X-ray structure determination of the complex showed that the lithium benzylthiolate units are compactly arranged in an infinite wave-shaped ladder composed of alternate planar and buckled Li_2S_2 rhombs. (see Figures 3.6 and 3.7). Comparing this with the infinite chain obtained for the complex, $[PhSLi.(NC_5H_5)_2]_\infty$ (see Figures 3.3 and 3.4), the new structure could be

Figure 3.6 View 1 of the buckled infinite ladder of $[PhCH_2SLi.NC_5H_5]$

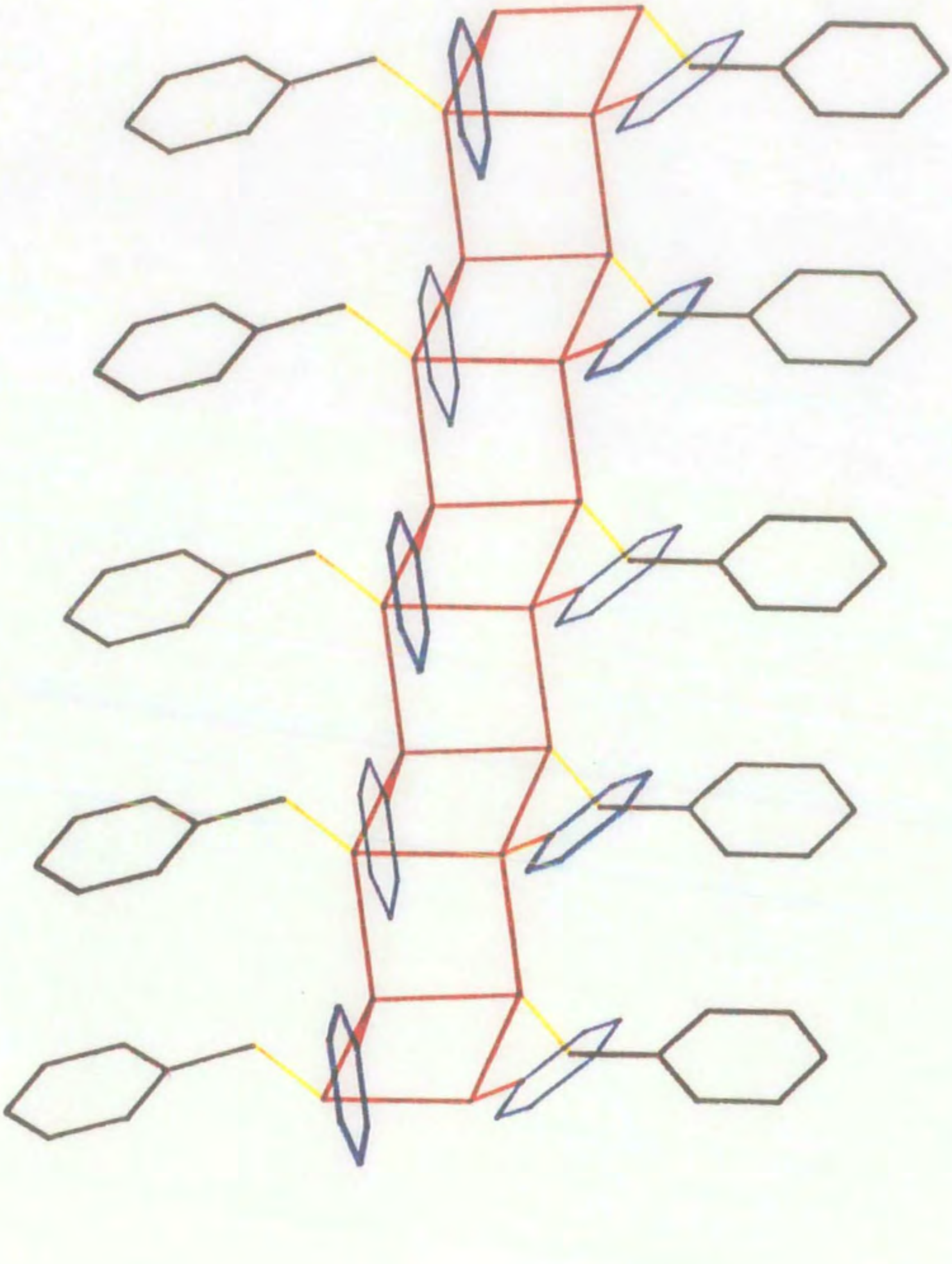
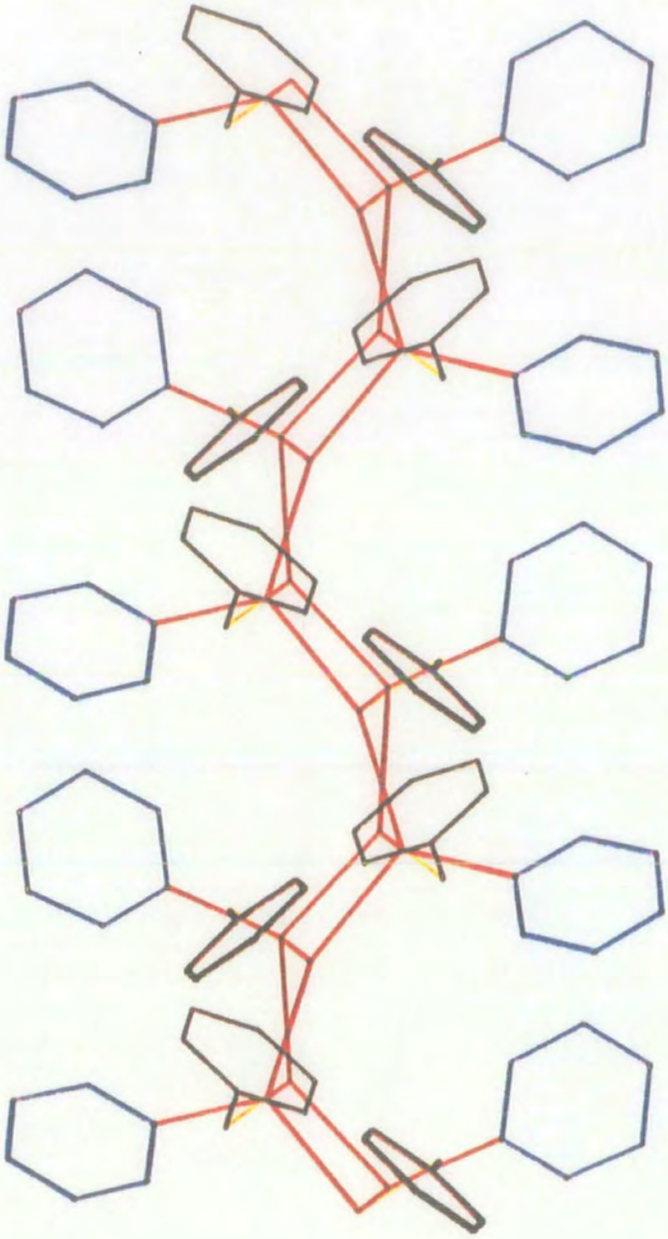


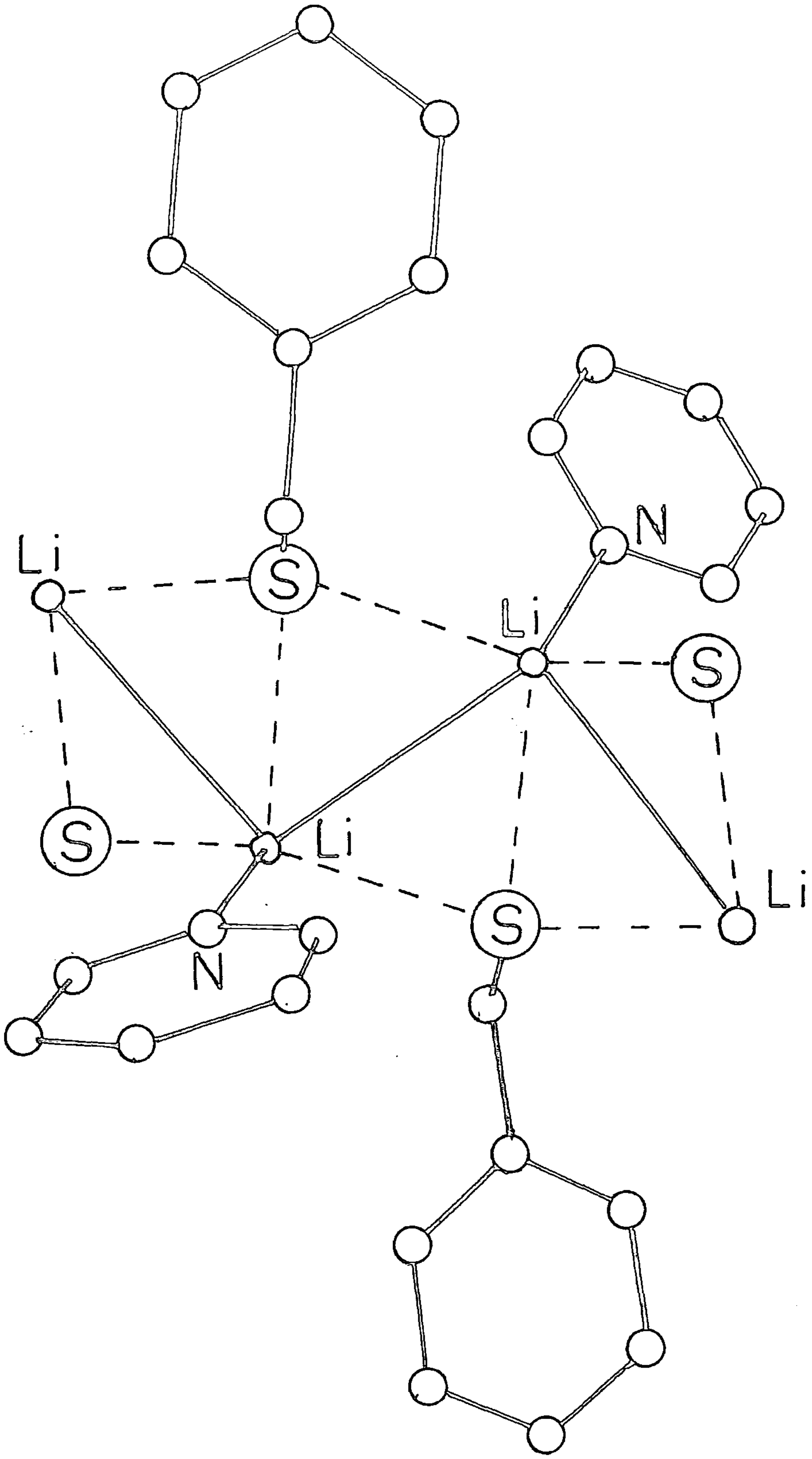
Figure 3.7 View 2 of the buckled infinite ladder of $[\mathrm{PhCH_2SLi.NC_5H_5}]$



regarded as two $(LiS)_\infty$ infinite chains clipped together, in which the possible benefit of a second co-ordinating pyridine at lithium is overridden by additional Li-S interaction. Li-S distances (Table 3.6) vary between 2.454(5) Å and 2.508(2) Å (Average 2.48 Å) and again these are similar to those already quoted (e.g. 2.47 Å in Li_2S). The average C-S distance of 1.825 Å is typical of the C-S single bond in paraffins and saturated heterocycles (e.g CH_3SH 1.819 + 0.005 Å).

An alternative way of looking at the complex is as a distorted zig-zag of lithium atoms bridged by benzylthiolate groups. However, the Li-Li distance in lithium metal is 3.04 Å and the covalent bond in gaseous lithium is even smaller, 2.67 Å.[28] Comparison of these values with the Li-Li distances in this complex, (Li(1)-Li(2) 3.092(8), Li(2)-Li(2b) 3.243(8) Å - see Figure 3.7) would suggest that any interactions between lithium atoms in the chain are minimal. Similarly, the complex could be considered as a zig-zag of sulphur atoms bridged by Li.pyridine units but again the S-S distances are always greater than the sum of the van der Waals radii (~3.7 Å). To our knowledge this is the only example in either lithium complexes or ArS^- complexes of an infinite ladder of this nature.

Figure 3.8 A view of $[PhCH_2SLi.NC_5H_5]$ showing the Li–Li zig-zag.



Compounds have been reported that bear some structural similarity to $[PhCH_2SLi.NC_5H_5]_\infty$. A lithium phosphorus compound, $[Li_2(\mu_3\text{-}t\text{-}Bu_2P)(\mu_2\text{-}t\text{-}Bu_2P)(C_4H_8O)]_2$ is a four rung ladder of Li-P rungs, but the overall Li_4P_4 framework is virtually planar.[27] The authors drew attention to the 'unusual distorted Z of four lithium atoms' but they considered that, with Li-Li distances of 3.065(13) Å and 3.025(19) Å, direct Li-Li bonding is 'relatively unimportant'. A similar four rung ladder is found in the compound $\{[H_2\overline{C(CH_2)_3N}Li]_3.PMDETA\}_2$ with four central amido-N-Li rungs.[28] The two terminal N-Li units are complexed by PMDETA and this prevents further association. In this compound the central Li_2N_2 unit and the nitrogen atoms of the outer rungs are in the same plane with the outer lithium atoms deviating by ± 0.71 Å.

Insertion of a methylene group between the phenyl ring and the S atom in benzyl mercaptan allows association of the two S-Li chains by removing the phenyl ring out of the way of the pyridine rings. It ought to be possible, by judicious choice of donor ligand to restrict the length of the ladder or fold it round into a cube.

Table 3.6 Crystal Data and Bond Lengths (Å) for $[PhCH_2SLi.NC_5H_5]_\infty$.

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 $2\theta \leq 130$ °.

Bond lengths (Å)

Li(1)-N(11)	2.045(5)	Li(1)-S(3)	2.508(2)
Li(1)-S(4)	2.473(4)	Li(1)-S(4b)	2.470(1)
Li(2)-N(21)	2.068(6)	Li(2)-S(3)	2.477(5)
Li(2)-S(4)	2.498(5)	Li(2)-S(3a)	2.454(5)
N(11)-C(12)	1.314(4)	N(11)-C(16)	1.329(4)
C(12)-C(13)	1.368(5)	C(13)-C(14)	1.366(5)
C(14)-C(15)	1.361(5)	C(15)-C(16)	1.365(5)
N(21)-C(22)	1.330(5)	N(21)-C(26)	1.333(4)
C(22)-C(23)	1.366(6)	C(23)-C(24)	1.350(7)
C(24)-C(25)	1.344(7)	C(25)-C(26)	1.371(5)
S(3)-C(31)	1.837(3)	C(31)-C(32)	1.486(4)
C(32)-C(33)	1.386(5)	C(32)-C(37)	1.382(4)
C(33)-C(34)	1.386(6)	C(34)-C(35)	1.354(5)
C(35)-C(36)	1.364(6)	C(36)-C(37)	1.376(4)
S(4)-C(41)	1.813(3)	C(41)-C(42)	1.504(4)
C(42)-C(43)	1.378(4)	C(42)-C(47)	1.379(5)
C(43)-C(44)	1.379(5)	C(44)-C(45)	1.373(6)
C(45)-C(46)	1.379(5)	C(46)-C(47)	1.378(5)

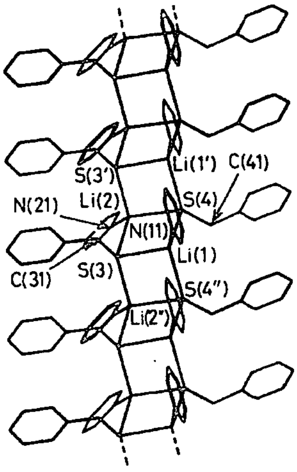


Table 3.7 Bond Angles (°) for $[PhCH_2SLi.NC_5H_5]_\infty$

N(11)-Li(1)-S(3)	108.8(1)	N(11)-Li(1)-S(4)	106.9(1)
S(3)-Li(1)-S(4)	103.0(1)	N(11)-Li(1)-S(4b)	115.4(2)
S(3)-Li(1)-S(4b)	94.5(1)	S(4)-Li(1)-S(4b)	125.4(2)
N(21)-Li(2)-S(3)	107.4(2)	N(21)-Li(2)-S(4)	122.5(2)
S(3)-Li(2)-S(4)	103.1(2)	N(21)-Li(2)-S(3a)	111.3(2)
S(3)-Li(2)-S(3a)	117.6(2)	S(4)-Li(2)-S(3a)	95.2(2)
Li(1)-N(11)-C(12)	124.7(2)	Li(1)-N(11)-C(16)	118.4(2)
C(12)-N(11)-C(16)	116.9(3)	N(11)-C(12)-C(13)	124.0(3)
C(12)-C(13)-C(14)	118.3(3)	C(13)-C(14)-C(15)	118.7(3)
C(14)-C(15)-C(16)	119.1(3)	N(11)-C(16)-C(15)	122.9(3)
Li(2)-N(21)-C(22)	120.1(3)	Li(2)-N(21)-C(26)	123.1(3)
C(22)-N(21)-C(26)	116.8(3)	N(21)-C(22)-C(23)	121.8(4)
C(22)-C(23)-C(24)	120.5(5)	C(23)-C(24)-C(25)	118.8(4)
C(24)-C(25)-C(26)	118.7(4)	N(21)-C(26)-C(25)	123.5(4)
Li(1)-S(3)-Li(2)	76.7(1)	Li(1)-S(3)-C(31)	106.0(1)
Li(2)-S(3)-C(31)	102.3(2)	Li(1)-S(3)-Li(2b)	81.6(1)
Li(2)-S(3)-Li(2b)	144.9(2)	C(31)-S(3)-Li(2b)	110.1(2)
S(3)-C(31)-C(32)	112.8(2)	C(31)-C(32)-C(33)	122.0(3)
C(31)-C(32)-C(37)	120.9(3)	C(33)-C(32)-C(37)	117.2(3)
C(32)-C933)-C(34)	120.8(3)	C(33)-C(34)-C(35)	120.3(4)
C(34)-C(35)-C(36)	120.3(4)	C(35)-C(36)-C(37)	119.5(3)
C(32)-C(37)-C(36)	121.9(3)	Li(1)-S(4)-Li(2)	76.9(1)
Li(1)-S(4)-C(41)	105.3(1)	Li(2)-S(4)-C(41)	123.7(2)
Li(1)-S(4)-Li(1a)	131.6(1)	Li(2)-S(4)-Li(2a)	81.5(1)
C(41)-S(4)-Li(1a)	122.6(1)	S(4)-C(41)-C(42)	113.2(2)
C(41)-C(42)-C(43)	120.7(3)	C(41)-C(42)-C(47)	121.1(3)
C(43)-C(42)-C(47)	118.2(3)	C(42)-C(43)-C(44)	121.0(3)
C(44)-C(45)-C(46)	119.2(4)	C(44)-C(45)-C(46)	119.2(4)
C(45)-C(46)-C(47)	120.2(4)	C(42)-C(47)-C(46)	121.1(3)

Table 3.8 Atomic co-ordinates ($x10^4$) for $[PhCh_2SLi.NC_5H_5]_\infty$

Atom	x	y	z
Li(1)	5000	511(3)	5000
Li(2)	6126(3)	-637(3)	7353(6)
N(11)	4896(2)	1576(1)	5950(3)
C(12)	4659(2)	2191(2)	5046(4)
C(13)	4604(2)	2903(2)	5699(5)
C(14)	4819(2)	2984(2)	7393(5)
C(15)	5076(2)	2355(2)	8354(5)
C(16)	5103(2)	1665(2)	7597(4)
N(21)	6615(2)	-1700(1)	7076(3)
C(22)	7179(2)	-1771(2)	6213(4)
C(23)	7532(2)	-2560(3)	6037(5)
C(24)	7311(3)	-3097(3)	6738(6)
C(25)	6736(3)	-3040(2)	7605(3)
C(26)	6403(2)	-2336(2)	7755(4)
S(3)	6490(1)	230(1)	5283(1)
C(31)	7062(2)	991(2)	6609(4)
C(32)	7964(2)	918(2)	6866(3)
C(33)	8406(2)	1400(2)	6084(4)
C(34)	9248(2)	1315(2)	6338(4)
C(35)	9650(2)	755(2)	7350(5)
C(36)	9234(2)	278(2)	8153(5)
C(37)	8399(2)	360(2)	7904(4)
S(4)	4620(1)	-422(1)	6924(1)
C(41)	3840(2)	-1024(2)	5619(4)
C(42)	3001(2)	-908(2)	5910(3)
C(43)	2538(2)	-276(2)	5273(4)
C(44)	1758(2)	-179(2)	5486(5)
C(45)	1426(2)	-714(2)	6342(4)
C(46)	1887(2)	-1344(2)	7001(4)
C(47)	2667(2)	-1436(2)	6788(4)

Table 3.9 Anisotropic thermal parameters ($Å^2$ x 10^3)

The anisotropic temperature factor exponent takes the form

$-2\pi^2(h^2a^{*2}U_{11} + \dots 2hka^{*}b^{*}U_{12})$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li(1)	61(3)	57(3)	47(3)	1(2)	21(2)	3(3)
Li(2)	62(3)	53(3)	43(3)	4(2)	17(2)	5(3)
N(11)	66(2)	59(2)	50(1)	-2(1)	20(1)	5(1)
C(12)	63(2)	68(2)	52(2)	3(2)	20(2)	0(2)
C(13)	89(3)	56(2)	79(3)	18(2)	29(2)	1(2)
C(14)	114(4)	58(2)	84(3)	-14(2)	42(3)	-3(2)
C(15)	99(3)	85(3)	51(2)	-13(2)	20(2)	4(2)
C(16)	89(3)	67(2)	56(2)	0(2)	24(2)	18(2)
N(21)	66(2)	54(2)	47(1)	-2(1)	18(1)	3(1)
C(22)	71(2)	70(2)	62(2)	-5(2)	26(2)	-1(2)
C(23)	80(3)	95(3)	106(3)	-26(3)	40(3)	12(3)
C(24)	84(3)	69(3)	128(4)	-18(3)	-9(3)	25(3)
C(25)	94(3)	58(2)	80(3)	15(2)	-7(2)	-6(1)
C(26)	68(2)	76(3)	52(2)	7(2)	15(2)	-4(2)
S(3)	46(1)	54(1)	38(1)	2(1)	10(1)	-6(1)
C(31)	59(2)	61(2)	53(2)	-9(2)	10(1)	0(2)
C(32)	57(2)	44(2)	39(2)	-4(1)	8(1)	-8(1)
C(33)	81(3)	65(2)	47(2)	6(2)	8(2)	-15(2)
C(34)	83(3)	106(3)	63(2)	-6(2)	30(2)	-43(2)
C(35)	58(2)	104(3)	90(3)	-24(2)	23(2)	-6(2)
C(36)	66(2)	75(2)	80(3)	-4(2)	-5(2)	8(2)
C(37)	59(2)	57(2)	62(2)	6(2)	5(2)	-8(2)
S(4)	47(1)	78(1)	39(1)	5(1)	9(1)	-14(1)
C(41)	55(2)	73(1)	59(2)	-14(2)	13(2)	-6(2)
C(42)	41(2)	57(2)	48(2)	-9(1)	4(1)	-3(1)
C(43)	60(2)	56(2)	69(2)	0(2)	11(2)	-10(2)
C(44)	61(2)	62(3)	93(3)	-5(2)	4(2)	5(2)
C(45)	48(2)	105(3)	73(2)	-10(2)	13(2)	-3(2)
C(46)	61(2)	100(3)	67(2)	18(2)	12(2)	-12(2)
C(47)	49(2)	75(2)	63(2)	11(2)	2(2)	0(2)

Table 3.10 H atoms: atomic co-ordinates ($x10^4$) and isotropic thermal parameters ($Å^2$ x 10^3)

	x	y	z	U
H(12)	4516	2138	3854	72
H(13)	4419	3333	4984	88
H(14)	4790	3474	7897	99
H(15)	5235	2397	9548	94
H(16)	5279	1224	8285	84
H(22)	7344	-1326	5699	79
H(23)	7940	-2492	5411	109
H(24)	7559	-3581	6619	119
H(25)	6563	-3484	8108	99
H(26)	5996	-2298	8382	79
H(31a)	6935	971	7677	70
H(31b)	6982	1476	6091	70
H(33)	8127	1796	5359	79
H(34)	9546	1655	5794	99
H(35)	10231	694	7504	100
H(36)	9522	-112	8887	94
H(37)	8110	20	8467	73
H(41a)	3995	-1549	5847	75
H(41b)	3814	-911	4472	75
H(43)	2762	102	4670	75
H(44)	1444	265	5034	89
H(45)	880	-650	6479	91
H(46)	1663	-1720	7610	92
H(47)	2983	-1876	7258	77

3.2.7 Preparation of [$Li_{14}(SCH_2Ph)_{12}S(TMEDA)_8$]

Benzyl mercaptan was reacted with n-butyl-lithium, this time using the bidentate ligand TMEDA to co-ordinate the lithium. It was thought that this ligand may restrict the ladder formation by bonding to two lithium atoms, although there are few examples of TMEDA bridging two separate lithium atoms,e,g [$(LiMe)_4(TMEDA)_2$].[29] In addition, organolithium compounds often show enhanced reactivity when used in TMEDA and, therefore, examination of these complexes could give insight into the mechanism of the reactions.[29-32]

Of particular interest was the reaction where the molar ratio of TMEDA to lithium was 1:2 (i.e. two NC_5H_5 units replaced by one TMEDA molecule). In this reaction benzyl mercaptan was dripped into a chilled solution of n-butyl-lithium TMEDA and hexane to give a clear deep orange solution. As it warmed to room temperature a deep orange precipitate formed, that turned to yellow-brown when attempting to dissolve it in toluene. On filtering, the act of turning the reaction vessel (fitted with filter stick and receiving Schlenk) upside down under nitrogen caused the colour to fade rapidly, leaving a white solid in a straw-coloured liquid. Small colourless rhombic crystals were obtained from the filtrate. Elemental analysis and infra-red spectra were the same for both precipitate and crystals. The latter, as expected, showed no SH stretching frequency at ν 2500 cm^{-1}, but it was difficult to suggest a logical structure from the elemental analysis.

Further experiments were carried out to investigate this colour change. These suggested that the order of addition of reactants is crucial. In the above reaction n-butyl-lithium is always present in excess, the final reaction mixture containing n-butyl-lithium to benzyl mercaptan in the molar ratio 11:10. It is suggested that a small amount of unstable dilithiated product, probably $PhCHSLi_2$, orange, is formed, which decomposes under the conditions of the reaction to form Li_2S. This dilithiated intermediate could be that reported by Seebach et al in 1974.[34] They reacted lithiated benzyl mercaptan, $PhCH_2SLi$, with n-butyl-lithium in the presence (2.5 h) or absence (4.0 h) of TMEDA at -5 °C in THF/pentane (1:1) and obtained an orange coloured suspension. They deduced, from its reaction with a number of different electrophiles, that this was the salt, $PhCHSLi_2$, (see Figure 3.9). They claimed that it has good stability, 70% decomposition occurring only after two weeks storage at 5 °C. There was no examination of decomposition products.

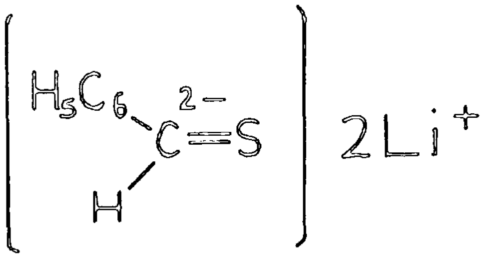


Figure 3.9 Suggested formula of $PhCHSLi_2$.

3.2.8 X-ray structure determination for $[Li_{14}(SCH_2Ph)_{12}S.(TMEDA)_6]$.

The crystals were clear, colourless, well facetted rhomboids that oscillation photographs showed clearly to be single crystals suitable for full structure determination.

This analysis showed that the complex is a unique type of Li-S cluster of molecular formula $[Li_{14}(SCH_2Ph)_{12}S.(TMEDA)_6]$. A single sulphur atom is at the centre of a distorted cube of lithium atoms; each of the twelve edges of the cube is bridged by an SCH_2Ph unit such that these twelve S atoms form a cubo-octahedron. Each pair of S atoms is bridged by a Li.TMEDA unit, and these six lithium atoms form a huge outer octahedron. Figure 3.10 shows the arrangement of the lithium atoms and of the sulphur atoms in the molecule; lines are drawn between atoms to indicate the shapes of the polyhedra, and do not imply direct bonding. Figure 3.11 shows the molecular structure of the complex and Figure 3.12 the

(cont. p.59)

Figure 3.10 The arrangement of the lithium and sulphur atoms in $[Li_{14}(SCH_2Ph)_{12}S.(TMEDA)_6]$; both are shown in projection along the S_6 (3) axis.

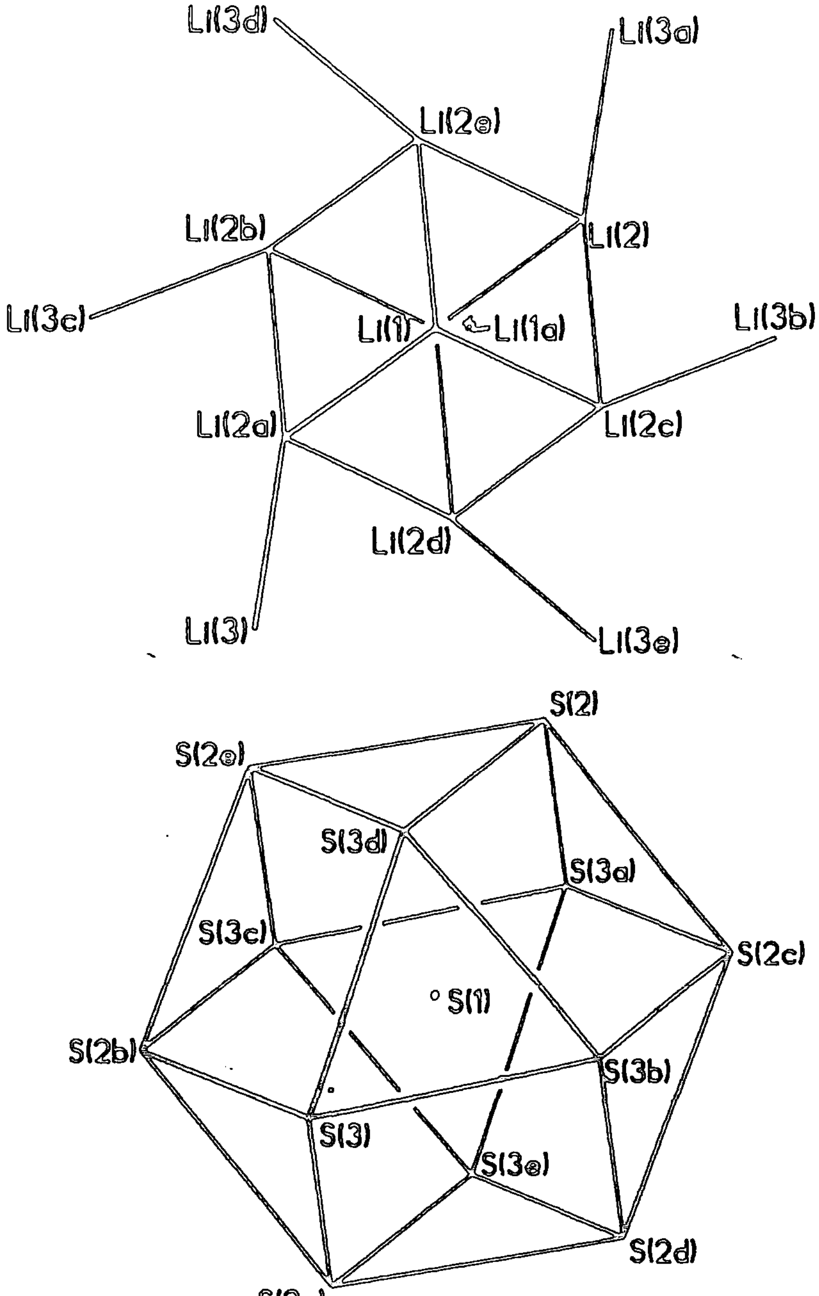


Figure 3.11 The molecular structure of $[Li_{14}(SCH_2Ph)_{12}S.(TMEDA)_6]$ seen along the S_6 axis: Li atoms filled, S large circles, N small circles, bonds to Li broad, H atoms omitted.

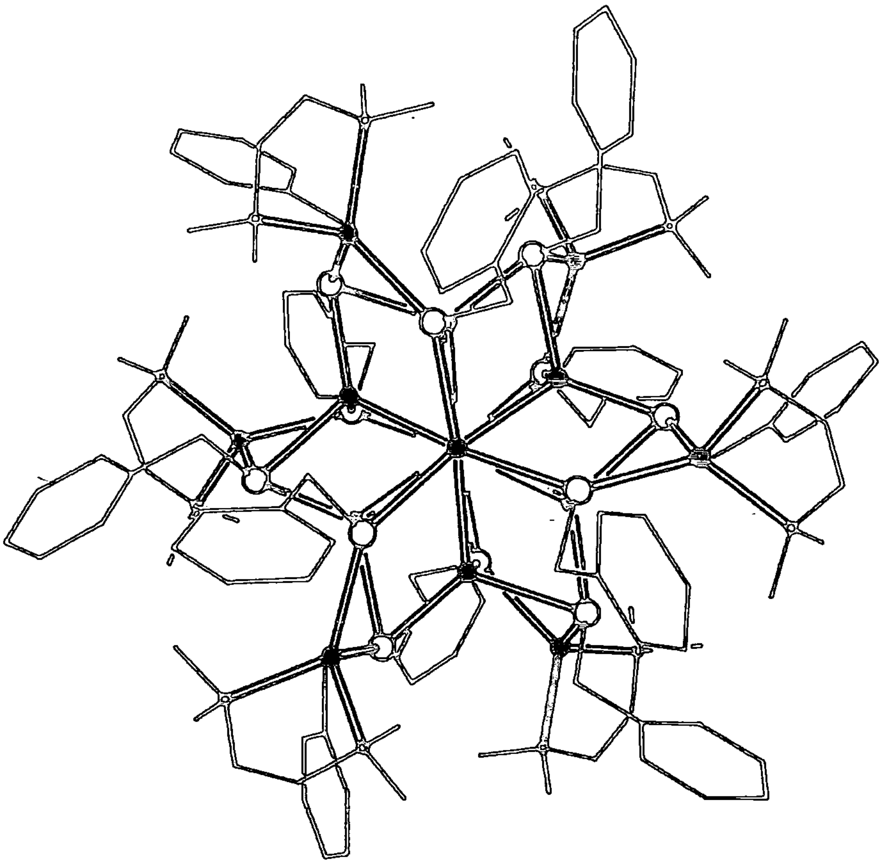
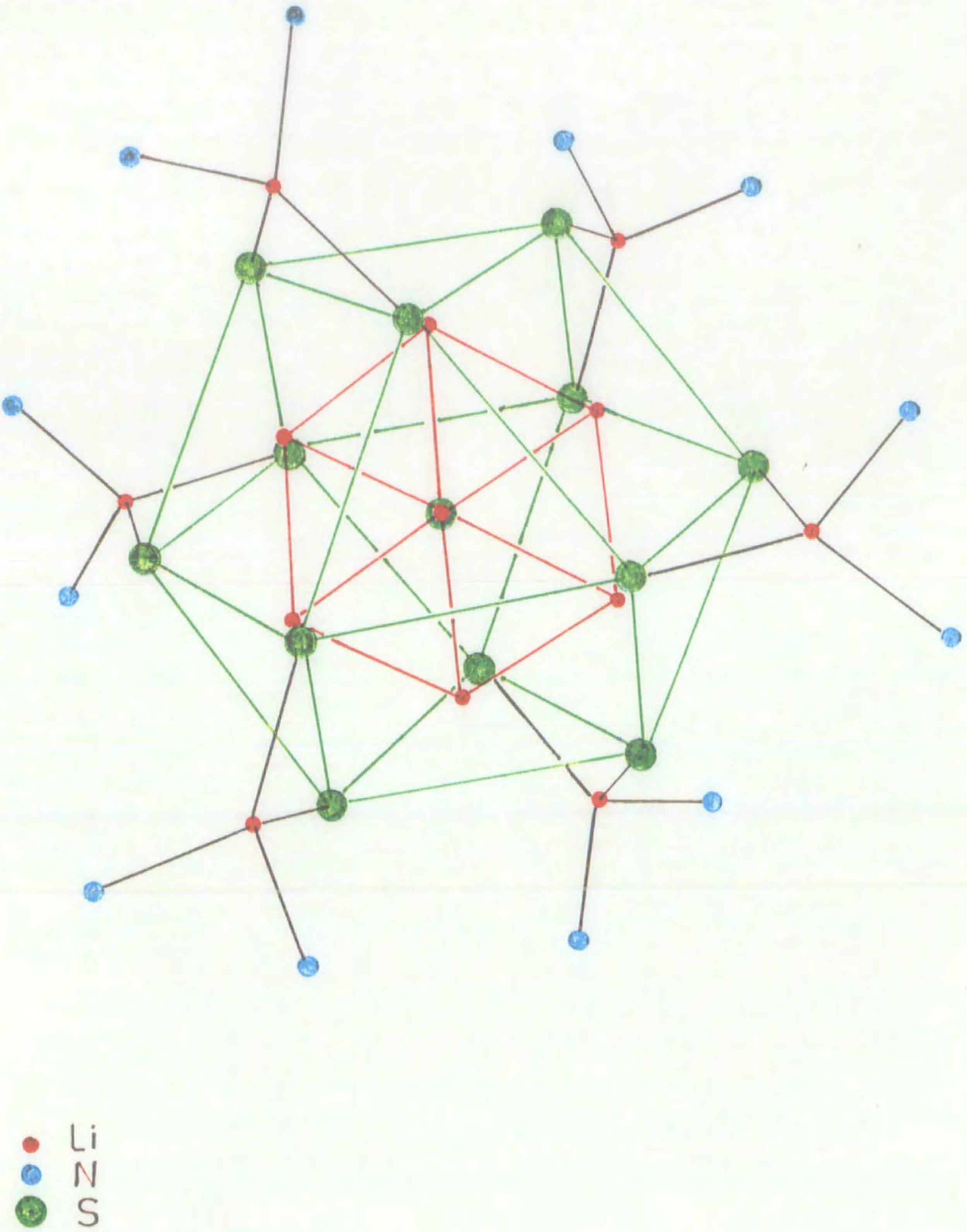


Figure 3.12 The arrangement of the cube lithium atoms in relation to the cubo-octahedron sulphur atoms in $[Li_{14}(SCH_2Ph)S.(TMEDA)_6]$



position of the cube lithium atoms in relation to the cubo-octahedron sulphur atoms.

Alternatively, the cluster can be described as a cubic close packed lattice of sulphur atoms with the 8 lithium atoms in the tetrahedral holes. This reproduces, essentially, the atomic arrangement found in the Li_2S lattice, where there is an approximatley cubic close packed array of S^{2-} ions with Li^+ ions occupying all the tetrahedral holes. This complex can, therefore be regarded as an Li_8S_{13} fragment of the Li_2S lattice, stabilized by twelve terminal benzyl groups and six TMEDA.Li ligands.

The Li-S bond lengths (see Table 3.11) between the central sulphur atom and the cubic lithium atoms are 2 x 2.50(2) and 6 x 2.55(2) Å (average 2.54 Å), while those from cubic lithium atoms to the thiolate sulphur atoms in the cubo-octahedron are 4 x 2.52(1), 4 x 2.46(1), 4 x 2.47(1) and 4 x 2.44(1) Å (average 2.47 Å). The overall average (2.49 Å) is close to the Li-S distance in Li_2S (2.47 Å). These values are also similar to those found in Li-S compounds described earlier (see Tables 3.1, 3.5 and 3.6, pages 33, 40, 48). All the lithium atoms have a slightly distorted tetrahedral environment, those in the cube being surrounded by four sulphur atoms, while the

(cont. p.64)

Table 3.11 Crystal data, bond lengths (A) and bond angles (°) for $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$.

Crystal data:

$C_{120}H_{180}N_{12}S_{13}Li_{14}$, M_r = 2304.8
rhombohedral, space group $R\bar{3}$
a = 26.853(2), c = 16.595(1) Å (hexagonal axes),
U = 10363 Å^3, Z = 3.

Bond lengths (Å) and bond angles (°)

S(1)-Li(1)	2.503(16)	S(1)-Li(2)	2.549(15)
S(2)-Li(2)	2.523(10)	S(2)-C(21)	1.839(9)
S(2)-Li(2e)	2.461(5)	S(2)-Li(3a)	2.448(11)
S(3)-Li(1)	2.466(5)	S(3)-Li(3)	2.408(12)
S(3)-C(31)	1.839(9)	S(3)-Li(2a)	2.444(10)
Li(3)-N(41)	2.155(11)	Li(3)-N(42)	2.155(18)
C(21)-C(22)	1.502(9)	C(31)-C(32)	1.446(13)
N(41)-C(41)	1.425(17)	N(41)-C(42)	1.410(13)
N(41)-C(43)	1.401(24)	N(42)-C(44)	1.458(12)
N(42)-C(45)	1.432(16)	N(42)-C(46)	1.455(11)
C(43)-C(44)	1.273(22)		

Li(1)-S(1)-Li(2)	108.2(2)	Li(1)-S(1)-Li(1a)	180.0
Li(2)-S(1)-Li(2b)	110.7(2)	Li(2)-S(2)-C(21)	101.4(3)
Li(2)-S(2)-Li(2e)	71.1(5)	C(21)-S(2)-Li(2e)	103.6(3)
Li(2)-S(2)-Li(3a)	76.1(3)	C(21)-S(2)-Li(3a)	115.0(5)
Li(2e)-S(2)-Li(3a)	133.3(4)	Li(1)-S(3)-Li(3)	134.4(4)
Li(1)-S(3)-C(31)	102.2(5)	Li(3)-S(3)-C(31)	123.1(5)
Li(1)-S(3)-Li(2a)	74.3(5)	Li(3)-S(3)-Li(2a)	78.4(4)
C(31)-S(3)-Li(2a)	119.6(3)	S(1)-Li(1)-S(3)	107.0(3)
S(3)-Li(1)-S(3b)	111.8(3)	S(1)-Li(2)-S(2)	107.8(4)
S(1)-Li(2)-S(2b)	109.8(4)	S(2)-Li(2)-S(2b)	112.5(50
S(1)-Li(2)-S(3a)	106.2(5)	S(2)-Li(2)-S(3a)	94.9(3)
S(2b)-Li(2)-S(3a)	124.1(5)	S(3)-Li(3)-N(41)	116.5(6)
S(3)-Li(3)-N(42)	122.2(5)	N(41)-Li(3)-N(42)	85.2(5)
S(3)-Li(3)-S(2a)	97.9(5)	N(41)-Li(3)-S(2a)	117.0(5)
N(42)-Li(3)-S(2a)	119.8(6)	S(2)-C(21)-C(22)	116.8(5)
C(21)-C(22)-C(23)	122.4(3)	C(21)-C(22)-C(27)	117.6(3)
S(3)-C(31)-C(32)	116.0(6)	C(31)-C(32)-C(33)	117.7(6)
C(31)-C(32)-C(37)	122.2(6)	Li(3)-N(41)-C(41)	113.2(6)
Li(3)-N(41)-C(42)	112.5(7)	C(41)-N(41)-C(42)	110.7(9)
Li(3)-N(41)-C(43)	101.7(8)	C(41)-N(41)-C(43)	108.2(12)
C(42)-N(41)-C(43)	110.0(12)	Li(3)-N(42)-C(44)	102.4(7)
Li(3)-N(42)-C(45)	112.6(8)	C(44)-N(42)-C(45)	110.0(9)
Li(3)-N(42)-C(46)	109.3(8)	C(44)-N(42)-C(46)	110.5(8)
C(45)-N(42)-C(46)	110.8(8)	N(41)-C(43)-C(44)	127.3(16)
N(42)-C(44)-C(43)	122.2(15)		

Table 3.12 Atomic co-ordinates ($\times 10^4$) for $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$.

atom	x	y	z
S(1)	0	0	0
S(2)	-1637(1)	-269(1)	-213(1)
S(3)	668(1)	-327(1)	1942(1)
Li(1)	0	0	1508(9)
Li(2)	-592(5)	446(4)	-479)6)
Li(3)	1635(4)	-72(5)	1582(6)
C(21)	-1807(3)	98(3)	584(4)
C(23)	-2875(3)	-613(2)	439(3)
C(24)	-3430	-883	758
C(25)	-3524	-742	1530
C(26)	-3064	-332	1984
C(27)	-2509	-62	1665
C(22)	-2414	-203	892
C(31)	209(4)	-941(4)	2595(5)
C(33)	460(4)	-1451(3)	3579(5)
C(34)	712	-1474	4302
C(35)	953	-1000	4818
C(36)	941	-503	4609
C(37)	689	-479	3886
C(32)	449	-953	3371
N(41)	2307(2)	514(3)	2380(4)
N(42)	1974(3)	-637(3)	1802(4)
C(41)	2096(5)	668(7)	3068(7)
C(42)	2730(7)	1009(6)	1979(8)
C(43)	2543(8)	179(6)	2642(12)
C(44)	2450(5)	-299(4)	2352(7)
C(45)	2175(6)	-773(5)	1081(7)
C(46)	1538(5)	-1157(4)	2196(8)

Table 3.13 Anisotropic thermal parameters ($Å^2 \times 10^3$) for $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$.

The anisotropic temperature factor exponent takes the form $-2\pi^2(h^2a^{\circ 2}U_{11} + \ldots + 2hka^{\circ}b^{\circ}U_{12})$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
S(1)	43(1)	43(1)	35(2)	0	0	21(1)
S(2)	55(1)	66(1)	54(1)	3(1)	-1(1)	29(1)
S(3)	57(1)	74(1)	43(1)	9(1)	0(1)	38(1)
Li(1)	72(7)	72(7)	46(9)	0	0	36(4)
Li(2)	65(6)	67(7)	53(6)	11(5)	1(5)	32(6)
Li(3)	62(7)	88(8)	62(6)	-3(6)	0(5)	45(6)
C(21)	64(5)	90(5)	77(5)	1(4)	1(4)	39(4)
C(23)	62(5)	108(6)	105(6)	13(5)	8(5)	32(5)
C(24)	61(6)	105(7)	194(11)	17(7)	3(7)	36(5)
C(25)	109(9)	120(9)	190(12)	40(9)	54(9)	72(8)
C(26)	134(9)	118(8)	130(8)	31(7)	46(8)	96(7)
C(27)	98(6)	109(6)	88(6)	19(5)	28(5)	69(5)
C(22)	70(5)	81(5)	90(6)	22(4)	2(4)	49(4)
C(31)	103(6)	122(7)	79(5)	13(5)	-19(5)	46(6)
C(33)	176(11)	183(11)	114(8)	57(8)	47(7)	133(10)
C(34)	201(16)	335(25)	214(17)	192(19)	91(14)	201(18)
C(35)	94(9)	400(33)	126(12)	102(17)	-9(8)	-1(14)
C(36)	262(22)	257(22)	105(11)	51(12)	-59(12)	-95(17)
C(37)	245(15)	111(9)	81(7)	3(6)	-5(8)	32(9)
C(32)	58(4)	96(5)	72(4)	29(4)	17(4)	40(4)
N(41)	70(4)	87(4)	81(4)	-7(3)	-10(3)	33(3)
N(42)	79(4)	86(5)	100(5)	0(4)	1(4)	48(4)
C(41)	103(8)	253(16)	137(9)	-94(10)	-1(7)	63(9)
C(42)	211(15)	130(10)	128(10)	-8(8)	-40(10)	-63(11)
C(43)	266(18)	176(12)	334(21)	-154(14)	-230(18)	169(14)
C(44)	119(8)	123(8)	163(9)	-8(7)	-48(7)	78(7)
C(45)	191(11)	170(10)	117(8)	29(7)	52(8)	129(10)
C(46)	121(8)	105(7)	185(11)	40(7)	55(8)	53(6)

Table 3.14 Atomic co-ordinates ($x10^4$) and isotropic thermal parameters ($Å^2$ x 10^3) for the H atoms for $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$

	x	y	z	U
H(21a)	-1718	469	381	93
H(21b)	-1561	147	1033	93
H(23)	-2810	-709	-93	117
H(24)	-3746	-1165	446	149
H(25)	-3906	-928	1750	155
H(26)	-3129	-236	2516	137
H(27)	-2192	220	1977	109
H(31a)	112	-1287	2304	130
H(31b)	-133	-922	2694	130
H(33)	295	-1777	3224	179
H(34)	720	-1817	4446	260
H(35)	1126	-1016	5315	351
H(36)	1107	-177	4964	405
H(37)	681	-137	3742	210
H(41a)	1932	898	2906	207
H(41b)	2406	882	3438	207
H(41c)	1806	325	3326	207
H(42a)	2872	910	1512	264
H(42b)	3042	1229	2343	264
H(42c)	2557	1232	1818	264
H(43a)	2446	114	3203	293
H(43b)	2950	430	2585	293
H(44a)	2795	-229	2082	156
H(44b)	2385	-541	2812	156
H(45a)	2465	-427	831	179
H(45b)	1856	-971	719	179
H(45c)	2332	-1016	1206	179
H(46a)	1232	-1365	1820	171
H(46b)	1391	-1063	2663	171
H(46c)	1669	-1391	2353	171

outer lithium atoms co-ordinate to two sulphur atoms in addition to the two nitrogen atoms in the TMEDA molecule. There appears to be no interaction between the central sulphur atom and those in the cubo-octahedron, since S-S distances (6 x 4.00(1) and 6 x 4.10(1) Å, see Table 3.15) exceed the sum of the Van der Waals radii (~3.7 Å). There are six 'short' S-S distances in the polyhedron (3.66(1) Å) and these are between sulphur atoms co-ordinated to the same lithium atom. Li-Li distances (2.903 - 4.225 Å) suggest that there is little interaction between the cube lithium atoms or between the cube lithium atoms and those in the outer octahedron (see Table 3.15).

The structure of this complex could be compared with some octanuclear copper and silver complexes.[34-40] It shows some similarity to those where a central atom, usually halogen, is surrounded by a $[Cu(I)_8S_{12}Cu(II)_6]$ structure . e.g. $[Cu(I)_8Cu(II)_6L_{12}Cl]^{5-}$
$L = \{^-SCC(Me)_2CH(NH_2)CO_2^-\}$, this crystallises as a highly hydrated ($\sim 18H_2O$) thallium(I) salt[34] and
$\{[Cu^+]_8[Cu^{2+}]_8[SC(CH_3)_2CH_2NH_2]_{12}Cl\}.\sim 3.5SO_4.\sim 19H_2O$.[34] In these complexes a central Cl^- ion is bound in the antifluorite manner by an approximately cubic array of eight copper atoms; sulphur atoms bridge each edge of the cube, the remaining six copper atoms each bond to two sulphur atoms and two nitrogen atoms in an approximately

Table 3.15 S-S bond distances (Å) and bond angles (°) and Li-Li bond distances (Å) in $Li_{14}(SCH_2Ph)_{12}S.(TMEDA)_6$]

S(1)-S(2)	4.096	S(1)-S(3)	3.993
S(2)-S(3a)	3.657	S(2)-S(2c)	4.141
S(2)-S(3d)	4.327	S(3)-S(3b)	4.088

S(2e)-S(2)-S(3a)	97.0	S(2)-S(3a)-S(3c)	92.2
S(3a)-S(3c)-S(2e)	88.0	S(3d)-S(3)-S(3b)	60.0
S(3c)-S(2e)-S(2)	82.6	S(2e)-S(2)-S(3d)	51.1
S(2)-S(3d)-S(2e)	61.8	S(3d)-S(2e)-S(2)	67.1

Li(1)-Li(2)	4.084	Li(1)-Li(2a)	2.974
Li(2)-Li(2b)	4.225	Li(2)-Li(2c)	2.903
Li(2)-Li(3a)	3.065		

planar cis S_2N_2 arrangement. Dance describes the high symmetry $(^-SR)_{12}M_8$ structures as belonging to a set of four structures in which an icosahedron or cubo-octahedron of doubly bridging thiolate ligands is associated with a cube or bitetrahedron of metal atoms: the array of carbon atoms is close to a cubo-octahedron when S_{12} is an octahedron and close to an icosahedron when S_{12} is a cubo-octahedron.

A Cu_8S_{12} structural unit also seems to be a common feature of copper(I) complexes with dithiolate ligands. Here there is no central atom, but a cube of copper atoms is surrounded by a distorted icosahedron of sulphur atoms. Sulphur is co-ordinated to two copper atoms and each copper atom is trigonally bound by three sulphur atoms of different ligands. Copper - copper interactions are postulated as holding the structure together, although Dance suggests[7] that there has also to be some S-S interactions along the icosahedron edges to confer self-sufficient rigidity and that Cu-Cu bonding alone is insufficient.

In our compound, $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$, with a core sulphur atom surrounded, in turn, by a Li_8 cube, a $(RS)_{12}$ cubo-octahedron and a large $(TMEDA.Li)_6$ octahedron, we have a beautifully symmetrical metal-sulphur composite cluster of a type completely unprecedented in alkali metal chemistry , indeed in metal-sulphur chemistry in general since none of the Cu(I) and Ag(I) clusters described above have a central S atom.

The method of preparation of this complex using thiolate ligands as the sole source of sulphur, yet, nevertheless, producing sulphur atoms not attached to carbon, hints at a metal degradation of such ligands that must be considered, and, possibly, exploited in other metal thiolate reactions.

3.2.9 Reaction of $PhCH_2SH$ with n-butyl lithium and Li_2S in TMEDA and toluene.

An attempt was made to prepare the same compound, $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$ directly i.e. by reacting the structural components in the correct molar quantities, i.e. 12 moles $PhCH_2SH$, 12 moles n-butyl lithium, 1 mole Li_2S and 6 moles of TMEDA. However, solid lithium sulphide is insoluble in the solvent mixture used and took no part in the reaction. It seems to be essential that sulphide ion is available in solution during the reaction for it to form a building block of the final cluster. (Experimental details p.90)

3.2.10 Dilithiation reactions of $PhCH_2SH$

Preliminary experiments were carried out to investigate the dilithiation of benzyl mercaptan using pyridine as a donor ligand. Problems arose due to the high solubility of the product in toluene and the tendency to form an oil in hexane. Attempts to filter the yellow precipitate resulted in decomposition.

Dilithiation of $PhCH_2SH$ using TMEDA as a donor ligand gave the complex $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$, on filtration.

(Experimental details p.89)

3.2.11 Preparation of $[PhCH_2SLi.TMEDA]_n$

As described above, the complex, $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$, is formed from the reaction of benzyl mercaptan with TMEDA and n-butyl lithium, the latter always being present in excess. In order to show that the cluster is only formed using specific reaction conditions and that if these are changed then the product will have a different structure, the reaction was carried out taking great care that the n-butyl lithium was never present in excess. The use of excess TMEDA was expected to cause the formation of a simpler structure. Elemental analysis gives the empirical formula, $[PhCH_2SLi.TMEDA]$. Examination of the product under a microscope showed colourless, translucent, chunky crystals, very poorly facetted. Nevertheless, X-ray oscillation photographs confirmed two single crystals and suggested a large unit cell with some thermal disorder. A full structure determination is not yet complete and will be reported later.

3.2.12 Preparation of [o-$MeC_6H_4SLi.(NC_5H_5)_3$]

o-Thiocresol is isomeric with benzyl mercaptan but has a methyl group on the phenyl ring. Again, this differs from thiophenol only by a small organic fragment, CH_2, to give a slightly more hindered molecule. The effect of this very small change in thiolate ligand on the structure of its lithium complexes was the next step to consider.

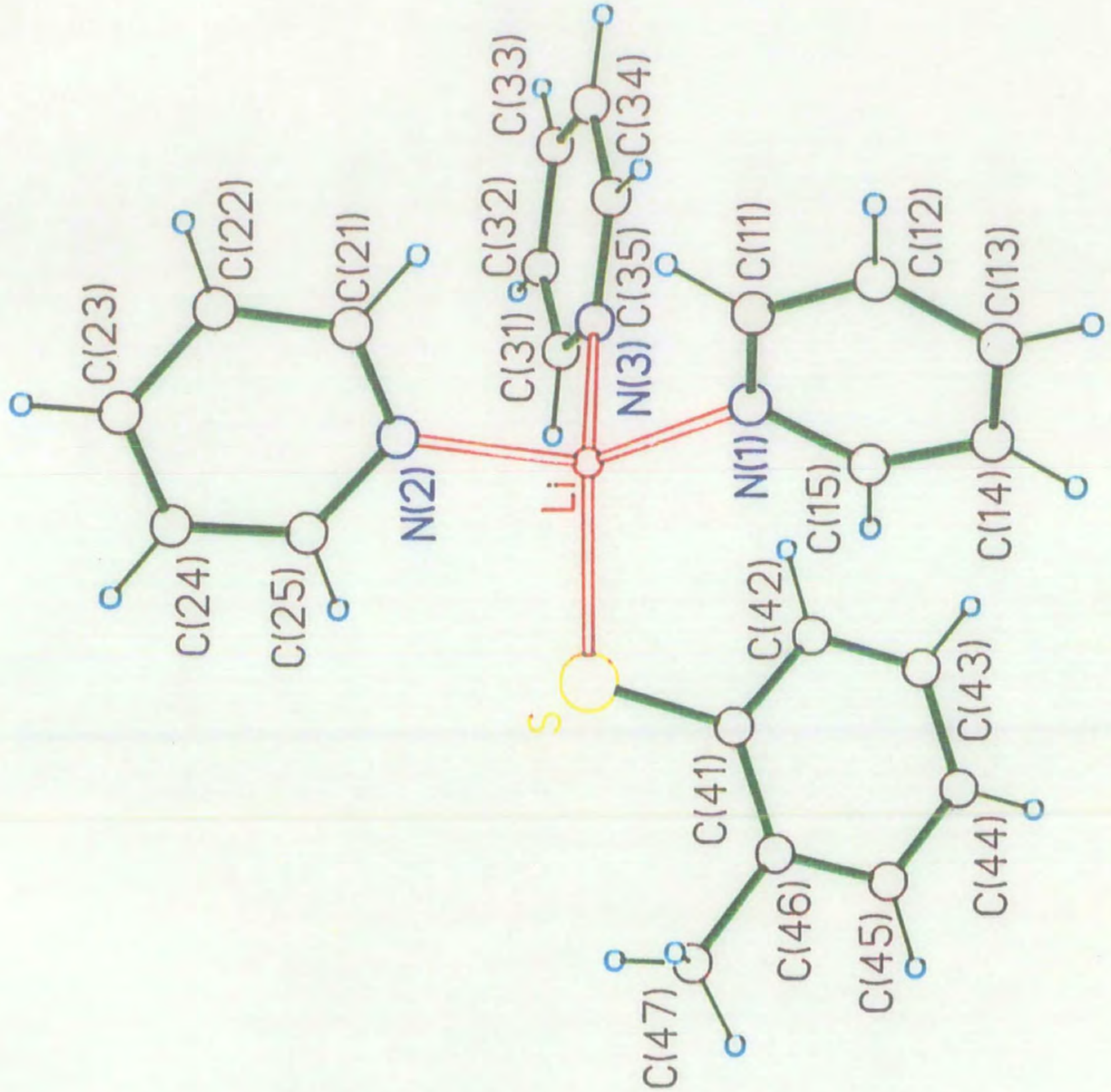
Reaction of o-thiocresol with n-butyl lithium in pyridine and toluene leads to the formation of two sets of crystals. White needle crystals formed most readily and were obtained from solution after leaving the reaction mixture in the freezer overnight. X-ray oscillation photographs of these showed them to be polycrystalline, and, to date, no crystals suitable for a complete structure determination have been prepared. A possible structure is discussed below (p.72).

After filtration, small, clear, colourless rectangular crystals were formed on cooling the filtrate. These were less sensitive than other complexes to formation of a white coating on washing with hexane and vacuum drying, and examination under the microscope showed a number of small, well-formed crystals. X-ray oscillation photographs were used to select suitable crystals for a full structure determination. This showed that the complex was monomeric with lithium co-ordinated to one thiocresol unit and three pyridine molecules in an approximately tetrahedral configuration. (see Figure 3.13) Sulphur is two co-ordinate and this is reflected in the slightly stronger Li-S bonding (2.412(6) Å). (For bond lengths and bond angles see Table 3.15) The three Li-N distances are equivalent, within experimental error, and the C-S bond length is similar to those found in other aromatic thiol compounds. The phenyl group is bent towards one pyridine molecule to accommodate the electron density of the lone pairs on sulphur.

Monomeric lithium complexes are normally associated with a large amount of steric bulk in the region of the lithium atom. e.g. $[(Me_3Si)_2CHLi.PMDETA]$ and 2-lithio-2-phenyl-1,3-dithiane.THF.TMEDA,[41,42] and this has also been reported as a property of transition-metal thiolates; i.e. monomeric structures are only achieved with heavily hindered thiols. In $[o\text{-}MeC_6H_4SLi.(NC_5H_5)_3]$ the introduction of only a methyl group into the ortho

(cont. p. 72)

Figure 3.13 Molecular structure of [o-MeC$_6$H$_4$SLi.(NC$_5$H$_5$)$_3$]



position of the phenyl ring has been sufficient to prevent the formation of the infinite chains found in $[PhSLi.(NC_5H_5)_2]_\infty$. Figure 3.14 and Figure 3.15 show two projections of the packing of the crystal in the unit cell. It seems likely, therefore, that steric effects alone are not responsible for the formation of monomeric species. Isolation of the two types of crystals took place under different reaction conditions. The white needles precipitated out of the initial reaction solution (toluene, hexane, pyridine) after 24 hours at −10 °C. Removal of approximately one third of the solvent to leave a higher percentage proportion of toluene and cooling to 5 °C was necessary to promote crystallisation of the monomeric $[o\text{-}MeC_6H_4SLi.(NC_5H_5)_3]$. These solubility effects could be an important factor in the preparation of monomeric complexes of lithium and of other metal thiolates. The white needles produced initially were similar in crystalline form to those of the complex, $[PhSLi.(NC_5H_5)_2]_\infty$ and may have an analagous structure, i.e. $[o\text{-}MeC_6H_4SLi.(NC_5H_5)_2]_\infty$. This would indicate that the underlying effects are only just sufficient for monomer formation and that a monomer/oligomer equilibrium is present. Further work is planned with this system in the hope that it will be possible to determine the

(cont. p. 79)

Figure 3.14 Packing of the molecules of [o-MeC$_6$H$_4$SLi.(NC$_5$H$_5$)$_3$] in the unit cell. Projection along the Y axis.

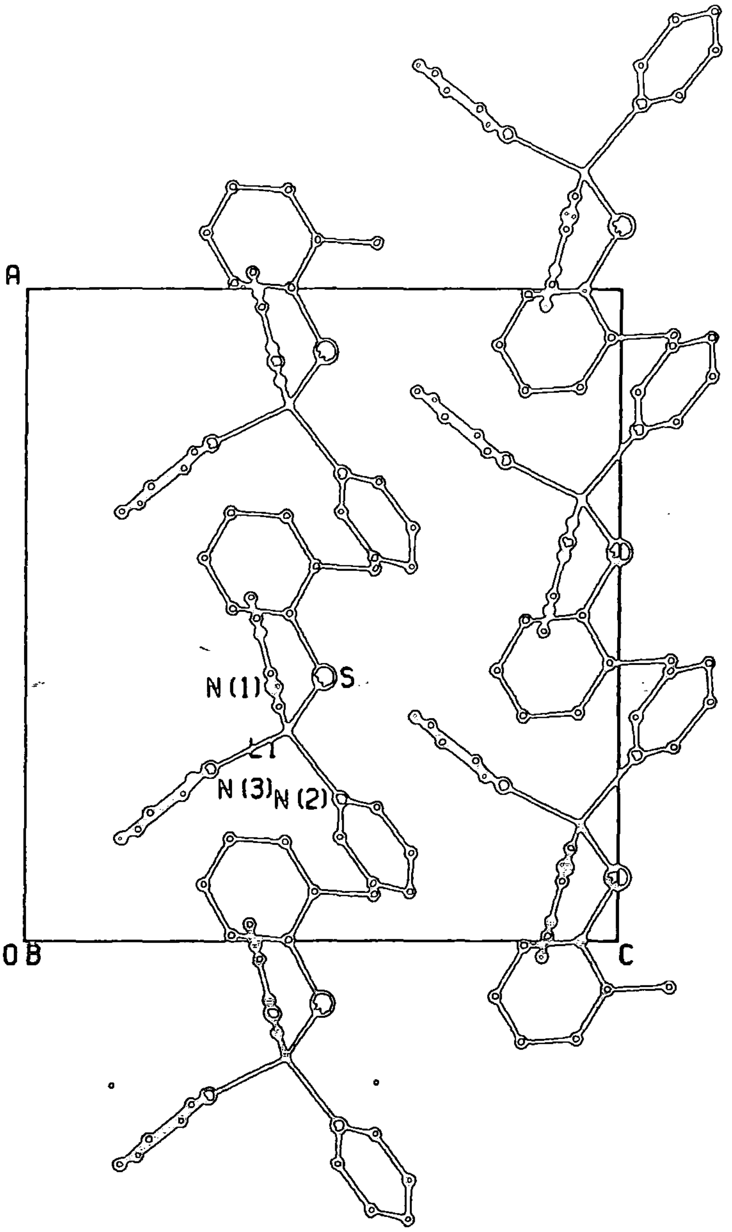


Figure 3.15 Packing of the molecules of [o-$MeC_6H_4SLi.(NC_5H_5)_3$] in the unit cell. Projection along the Z axis.

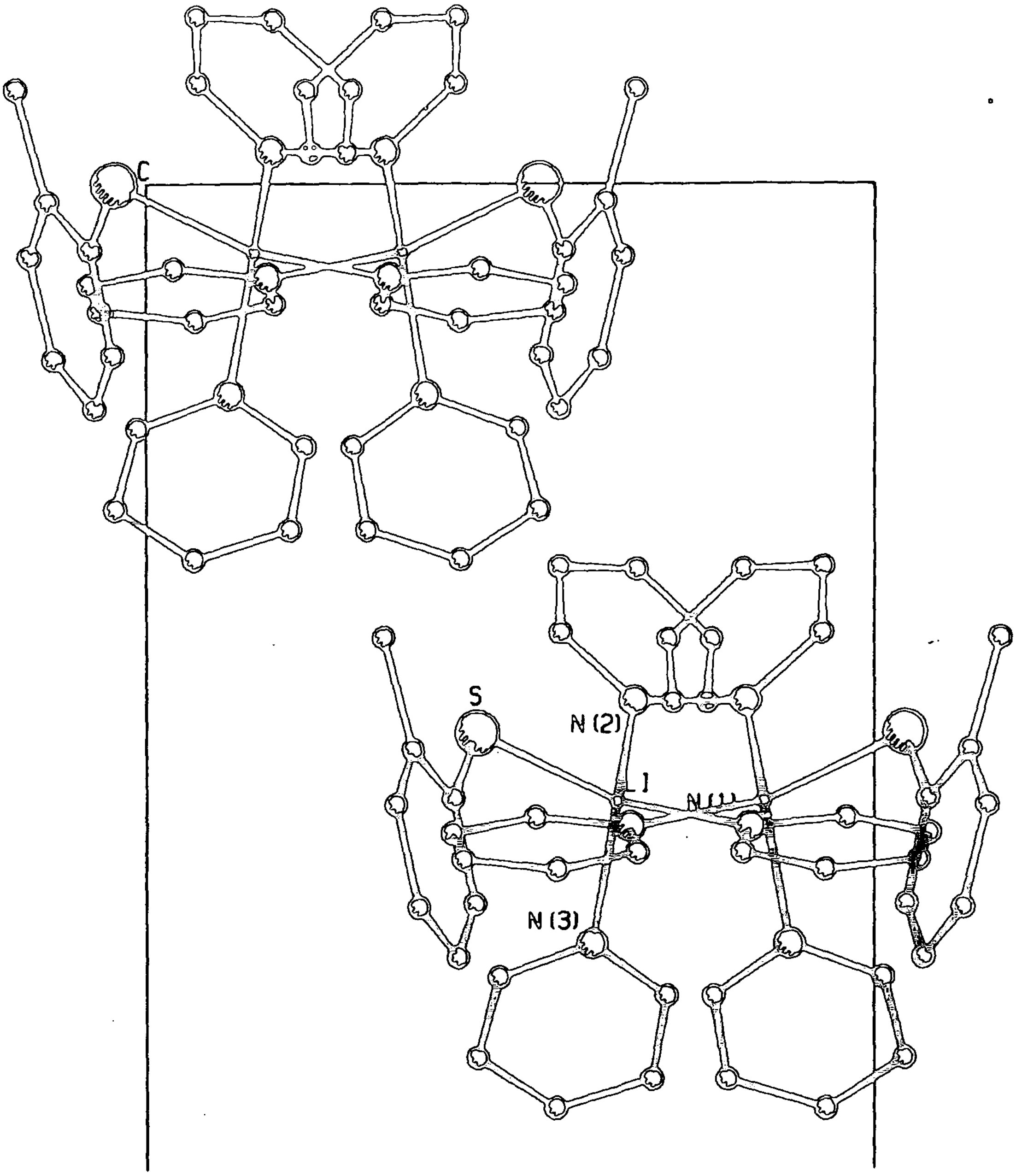


Table 3.15 Crystal data, bond lengths (Å) and bond angles (°) for [o-MeC$_6$H$_4$SLi.(NC$_5$H$_5$)$_3$]

Crystal data: C$_{22}$H$_{22}$LiN$_3$S, M$_r$=367.44, orthorhombic, space group Pna2$_1$, a=15.3020(9), b=9.6656(7), c=14.2885(5) A, Z=4, R=0.055 for 2461 reflections with F>3σ(F) and 2Θ≤115o

Bond lengths (Å) and bond angles (°)

Li-N(1)	2.081(7)	Li-N(2)	2.083(6)
Li-N(3)	2.081(7)	Li-S	2.412(6)
N(1)-C(11)	1.327(5)	N(1)-C(15)	1.319(5)
C(11)-C(12)	1.374(5)	C(12)-C(13)	1.336(5)
C(13)-C(14)	1.357(5)	C(14)-C(15)	1.354(5)
N(2)-C(21)	1.324(5)	N(2)-C(25)	1.334(5)
C(21)-C(22)	1.361(6)	C922)-C(23)	1.373(6)
C(23)-C(24)	1.368(6)	C(24)-C(25)	1.366(6)
N(3)-C(31)	1.321(5)	N(3)-C(35)	1.335(5)
C(31)-C(32)	1.354(6)	C(32)-C(33)	1.373(8)
C(33)-C(34)	1.342(7)	C(34)-C(35)	1.378(6)
S-C(41)	1.751(3)	C(41)-C(42)	1.406(5)
C(41)-C(46)	1.397(4)	C(42)-C(43)	1.385(5)
C(43)-C(44)	1.362(6)	C(44)-C(45)	1.370(7)
C(45)-C(46)	1.397(5)	C(46)-C(47)	1.516(6)

N(1)-Li-N(2)	112.6(3)	N(1)-Li-N(3)	101.7(3)
N(2)-Li-N(3)	104.5(3)	N(1)-Li-S	117.4(2)
N(2)-Li-S	104.8(3)	N(3)-Li-S	115.4(3)
Li-N(1)-C(11)	128.6(3)	Li-N(1)-C(15)	117.0(3)
C(11)-N(1)-C(15)	114.4(3)	N(1)-C(11)-C(12)	124.4(3)
C(11)-C(12)-C(13)	119.1(3)	C(12)-C(13)-C(14)	117.9(3)
C(13)-C(14)-C(15)	119.5(4)	N(1)-C(15)-C(14)	124.7(3)
Li-N(2)-C(21)	126.4(3)	Li-N(2)-C(25)	117.1(3)
C(21)-N(2)-C(25)	116.4(3)	N(2)-C(21)-C(22)	124.5(3)
C(21)-C(22)-C(23)	118.5(4)	C(22)-C(23)-C(24)	118.0(4)
C(23)-C(24)-C(25)	119.6(4)	N(2)-C(25)-C(24)	123.0(4)
Li-N(3)-C(31)	120.8(3)	Li-N(3)-C(35)	121.4(3)
C(31)-N(3)-C(35)	116.7(3)	N(3)-C(31)-C(32)	123.6(4)
C(31)-C(32)-C(33)	117.7(5)	C(32)-C(33)-C(34)	121.3(5)
C(33)-C(34)-C(35)	116.5(4)	N(3)-C(35)-C(34)	124.1(4)
Li-S-C(41)	114.0(2)	S-C(41)-C(42)	120.5(2)
S-C(41)-C(46)	122.3(3)	C(42)-C(41)-C(46)	117.2(3)
C(41)-C(42)-C(43)	121.5(3)	C(42)-C(43)-C(44)	120.0(4)
C(43)-C(44)-C(45)	120.3(4)	C(44)-C(45)-C(46)	120.7(4)
C(41)-C(46)-C(45)	120.3(4)	C(41)-C(46)-C(47)	120.6(3)
C(45)-C(46)-C(47)	119.1(3)		

Table 3.16 Atomic co-ordinates ($x10^4$) for [o-$MeC_6H_4SLi.(NC_5H_5)_3$]

Atom	x	y	z
Li	3211(3)	6488(6)	4377(4)
N(1)	3880(2)	8331(3)	4145(2)
C(11)	3590(2)	9619(4)	4231(3)
C(12)	4092(2)	10779(3)	4088(3)
C(13)	4930(2)	10629(3)	3847(3)
C(14)	5246(2)	9324(4)	3754(3)
C(15)	4711(2)	8232(4)	3912(3)
N(2)	2163(2)	6727(3)	5294(2)
C(21)	1581(2)	7740(4)	5285(3)
C(22)	869(2)	7803(4)	5855(3)
C(23)	743(3)	6761(5)	6494(3)
C(24)	1337(3)	5705(4)	6517(3)
C(25)	2032(3)	5720(4)	5917(3)
N(3)	2631(2)	6147(3)	3080(2)
C(31)	2487(2)	4876(4)	2776(3)
C(32)	1962(3)	4576(5)	2040(3)
C(33)	1571(3)	5660(6)	1581(3)
C(34)	1702(3)	6974(5)	1850(3)
C(35)	2246(2)	7170(5)	2607(3)
S	4034(1)	4570(1)	5000
C(41)	5012(2)	4241(3)	4404(2)
C(42)	5088(2)	4542(3)	3444(2)
C(43)	5857(2)	4302(4)	2959(3)
C(44)	6561(3)	3755(4)	3411(3)
C(45)	6510(2)	3430(4)	4343(4)
C(46)	5742(2)	3669(3)	4846(3)
C(47)	5702(3)	3255(4)	5869(3)

Table 3.17 Anisotropic thermal parameters ($Å^2$ x 10^3) for $[o\text{-}MeC_6H_4SLi.(NC_5H_5)_3]$

The anisotropic temperature factor exponent takes the form

$$-2\pi^2(h^2a^{\circ 2}U_{11} + \ldots + 2hka^{\circ}b^{\circ}U_{12})$$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li	45(3)	61(4)	75(4)	7(3)	-1(3)	6(3)
N(1)	51(2)	57(2)	80(2)	4(2)	3(2)	-2(2)
C(11)	51(2)	72(3)	95(3)	2(2)	18(2)	10(2)
C(12)	74(2)	51(2)	100(3)	0(2)	18(2)	-2(2)
C(13)	73(2)	54(2)	78(3)	0(2)	1(2)	-19(2)
C(14)	49(2)	75(3)	155(4)	8(3)	25(3)	0(2)
C(15)	57(2)	53(2)	147(4)	2(3)	13(3)	7(2)
N(2)	58(2)	62(2)	70(2)	4(1)	9(2)	3(2)
C(21)	65(2)	66(3)	97(3)	15(2)	16(3)	7(2)
C(22)	72(3)	77(3)	108(3)	16(3)	25(3)	22(2)
C(23)	76(3)	110(4)	88(3)	4(3)	35(3)	13(3)
C(24)	93(3)	88(3)	93(3)	30(3)	33(3)	21(3)
C(25)	82(3)	82(3)	81(3)	15(2)	21(3)	24(3)
N(3)	61(2)	63(2)	70(2)	8(2)	-1(2)	3(2)
C(31)	77(3)	72(3)	80(3)	-4(2)	-2(2)	10(2)
C(32)	118(4)	108(4)	94(4)	-26(3)	-7(3)	-1(3)
C(33)	113(4)	174(6)	66(3)	-6(3)	-14(3)	2(4)
C(34)	96(3)	122(4)	97(3)	43(3)	-8(3)	-1(3)
C(35)	65(3)	83(3)	102(3)	24(3)	-1(3)	2(2)
S	59(1)	62(1)	74(1)	14(1)	8(1)	11(1)
C(41)	47(2)	36(2)	76(2)	2(2)	-5(2)	0(2)
C(42)	63(2)	60(2)	64(2)	4(2)	1(2)	4(2)
C(43)	83(3)	67(3)	79(3)	-7(2)	18(2)	-15(2)
C(44)	68(3)	69(3)	107(4)	-20(3)	24(3)	-14(2)
C(45)	45(2)	61(3)	126(4)	-10(3)	-3(3)	-5(2)
C(46)	52(2)	48(2)	72(3)	-4(2)	-8(2)	-3(2)
C(47)	79(3)	87(3)	104(4)	17(3)	-25(3)	7(2)

Table 3.18 H atoms: atomic co-ordinates (x 10^4) and isotropic thermal parameters ($\mathring{A}^2$ x 10^3) for $[o\text{-}MeC_6H_4SLi.(NC_5H_5)_3]$

	x	y	z	U
H(11)	2990	9749	4406	87
H(12)	3844	11684	4159	90
H(13)	5298	11419	3743	82
H(14)	5844	9177	3577	112
H(15)	4955	7322	3850	103
H(21)	1666	8480	4847	91
H(22)	464	8559	5811	103
H(23)	251	6771	6911	109
H(24)	1267	4958	6953	110
H(25)	2445	4973	5946	98
H(31)	2770	4125	3093	91
H(32)	1865	3637	1847	128
H(33)	1196	5474	1057	142
H(34)	1432	7737	1532	126
H(35)	2354	8102	2809	100
H(42)	4595	4924	3118	75
H(43)	5895	4521	2305	92
H(44)	7095	3595	3075	98
H(45)	7007	3036	4653	92
H(47a)	5267	2546	5937	108
H(47b)	5538	4048	6233	108
H(47c)	6256	2912	6083	108

structure of the needles and hence assist in determining the relative importance of solubility and steric effects in the formation of the monomeric complex.

3.2.13 Reactions of pentafluorothiophenol with n-butyl-lithium.

Two preliminary reactions were carried out with pentafluorothiophenol, C_6F_5SH, to assess the effect of electron withdrawing groups in the phenyl ring on the structure of the complex. Lots of tiny white needle crystals were formed dispersed in a brown liquid. Although they were transferred to the glove box immediately after filtration and stored in a closed sample bottle the crystals turned brown overnight. Identical results were obtained from a second experiment. It is possible that the product is light sensitive, or that, despite taking great care to wash with hexane, they were still contaminated with the brown mother liquor. Further work is planned with this system.

3.2.14 Reaction of t-butyl-mercaptan with n-butyl-lithium

On examining the structure of the ladder polymer, $[PhCH_2SLi.NC_5H_5]_\infty$ it was felt that by careful choice of both thiol and chelating ligand it ought to be possible to generate other structural types, such as a Li-S cube. This may be formed if the thiol and ligand are much more symmetrical, e.g. t-butyl-mercaptan , $(Me)_3CSH$, and trimethylamine, Me_3N. As a preliminary step, following on from work already carried out, t-butyl-mercaptan was reacted with n-butyl-lithium using pyridine as a ligand. This would supply greater symmetry in the thiol part of the complex while it was hoped that the pyridine would give sufficient rigidity to enable an X-ray structure determination to be carried out. The use of pyridine also enables a direct comparison to be made with structures already obtained.

Small colourless rectangular crystals were obtained that were extremely sensitive to air and moisture. No conclusions could be drawn from the elemental analysis, the carbon and hydrogen results being especially troublesome. Single crystals were mounted in Lindemann capillaries and submitted for X-ray structure determination. The presence of the t-butyl group caused sufficient thermal disorder for a low temperature analysis to be necessary. This will be reported later.

3.3 Conclusions

The reactions of a relatively simple range of thiol compounds with n-butyl-lithium has provided a variety of structural types, some of which have not previously been found in the chemistry of lithium compounds.

In a series of three simple aryl thiolates using the same donor ligand, pyridine, the structure in the solid state is considerably modified by small changes in the group attached to the benzene ring. Thus, $[PhCH_2SLi.NC_5H_5]_\infty$ crystallises as an infinite buckled ladder composed of alternate planar and buckled Li_2S_2 rhombs. Removal of the interposed CH_2 group (between S and Ph) in $[PhSLi.(NC_5H_5)_2]_\infty$ is sufficient to prevent association of the $(LiS)_\infty$ chains and results in co-ordination at S falling from four to three, while a second pyridine molecule fills the fourth co-ordination site at lithium. Introduction of an ortho methyl group into the phenyl ring is just sufficient to prevent formation of the infinite S-Li chains and $[o\text{-}MeC_6H_4SLi.(NC_5H_5)_3]$ crystallises as a monomer.

In $[Li_{14}(PhCH_2S)_{12}S(TMEDA)_6$, the apparent production of sulphide ions 'in situ' during the reaction has allowed the formation of an unusual cluster compound in which a central sulphur atom is surrounded by a distorted cube of lithium atoms, each edge of which is bridged by a benzyl thiolate group such that the twelve sulphur atoms form a cubo-octahedron: a further six lithium atoms form a larger outer octahedron, each one sitting above an S-S edge and tetrahedral co-ordination being completed by a TMEDA molecule. Although this symmetrical complex shows some similarities to compounds of Ag(I) and Cu(I), there are no completely analogous structures in alkali metal or thiolate chemistry.

Crystals of four other complexes are awaiting X-ray analysis and will be reported in due course. $[PhSLi.TMEDA]_2$ is known to be a dimer with a central Li_2S_2 ring, not unlike the previously reported Li-S compounds (see Section 3.1). Further refinement is necessary here. $[PhCH_2SLi.TMEDA]_n$ could have a similar structure while elemental analysis of [PhSLi.PMDETA] suggests a simple monomeric molecule. To date no conclusions can be drawn from results obtained on the complex formed from t-butyl mercaptan and n-butyl-lithium.

3.4 EXPERIMENTAL SECTION

3.4.1 Reaction of PhSH with n-butyl-lithium in PMDETA and hexane.

PhSH (2.203 g, 2.05 cm^3, 20 mmol) was dispersed in hexane (30 cm^3) in a Schlenk (see Figure 2.1 p.19) containing a magnetic stirrer. The mixture was cooled to about -20 °C and this temperature maintained throughout the reaction. n-Butyl lithium (1.41 g, 13.33 cm^3, 1.65 M solution in hexane, 22 mmol) was added and there was immediate precipitation of a white gelatinous solid. PMDETA (4.51 g, 4.4 cm^3, 26 mmol) was added and the precipitate became cream-coloured and much finer. It was dissolved by addition of toluene (20 cm^3) and warming to 70 °C. Cooling slowly to room temperature (20 °C) deposited long feathery needles. These were filtered, washed with hexane and dried. A small amount (0.5 g) was recrystallised from hexane/toluene (50/50).

Yield 3.0 g 52 % (based on the formula [PhSLi.PMDETA]
Elemental analysis: S 11.37 %, N 14.96 %, Li 2.31 %, C 63.35 %, H 12.63 %. Calculated for [PhSLi.PMDETA] S 11.08 %, N 14.52 %, Li 2.40 %, C 62.25 %, H 9.75 %.
M.p 98-100 °C
Infra red spectrum: see Table 3.19

3.4.2 Reaction of PhSH with n-butyl-lithium in TMEDA and hexane.

n-Butyl-lithium (0.641 g, 6.7 cm^3, 1.49 M solution in hexane, 10 mmol) and TMEDA (1.74 g, 2.26 cm^3, 15 mmol) were added to chilled (-20 °C) hexane (10 cm^3) in a Schlenk containing a magnetic stirrer. This temperature was maintained during dropwise addition of PhSH (1.10 g, 1.0 cm^3, 10 mmol), when a white solid precipitated. The reaction mixture was allowed to warm up to room temperature and hexane (5 cm^3) added to break up the precipitate. Gentle warming dissolved the precipitate and on allowing to cool slowly, white needles settled out of solution. These were filtered carefully under vacuum and washed with hexane (3 x 2 cm^3) and dried under a stream of nitrogen.

Yield 1.2 g 52 % (based on PhSLi.TMEDA)

Elemental analysis: S 14.25 %, N 12.1 %, Li 2.81 %, C 60.6 %, H 7.70 %. (Calculated for PhSLi.TMEDA S 13.8 %, N 12.06 %, Li 2.98 %, C 62.0 %, H 9.1 %.

Infra red spectrum: see Table 3.20 p.

3.4.3 Reaction of PhSH with n-butyl-lithium and HMPA in hexane.

n-Butyl-lithium (1.41 g, 13.33 cm^3, 1.65 M solution in hexane, 22 mmol) was added to a chilled (ca. -20 °C) solution of PhSH (2.203 g, 2.05 cm^3, 20 mmol) in hexane (20 cm^3). There was immediate precipitation of a white flocculent solid, which dissolved after addition of HMPA (10.75 g, 60 mmol) and gentle warming. The reaction mixture separated into two layers, an oily lower layer and a colourless upper layer. Toluene (20 cm^3) was added and the mixture warmed gently, but this produced no change.

After leaving in the freezer overnight (-10 °C), white crystals had formed in the lower layer. These were filtered off but rapidly decomposed on the filter stick.

3.4.4 Reaction of PhSH with n-butyl-lithium and HMPA in toluene/hexane.

n-Butyl-lithium (1.41 g, 13.33 cm^3, 1.65 M solution in hexane, 22 mmol) was added to stirred, chilled (ca. -20 °C) hexane (20 cm^3). Maintaining this temperature, PhSH (2.203 g, 2.05 cm^3, 20 mmol) was added dropwise. A white solid precipitated that turned pale yellow on addition of HMPA (3.6 g, 20 mmol). The precipitate dissolved on addition of toluene (40 cm^3) and gentle warming. On cooling to room temperature two layers separated out. A small number of crystals formed in the lower layer overnight at -10 °C but decomposed on attempting to remove them from solution under nitrogen.

3.4.5 Preparation of $[PhSLi.(NC_5H_5)_2]_\infty$.

Thiophenol (1.10 g, 1.03 cm^3, 10 mmol) and pyridine (0.79 g, 0.8 cm^3, 10 mmol) were added to chilled (-20 °C) toluene (20 cm^3) in a Schlenk and stirred under nitrogen. n-Butyl-lithium was added slowly to the cold, pale yellow solution, stirring continuously. A creamy white precipitate formed which became quite dense after addition of all the n-butyl-lithium. The mixture was allowed to warm up to room temperature. The solid dissolved on addition of toluene (10 cm^3) and pyridine (4 cm^3) and heating to boiling point. Fine white needles came down on cooling and these were filtered, washed with three 5 cm^3 portions of hexane, filtered carefully under vacuum and dried under nitrogen. These reaction conditions were found to produce good yields of crystals, addition of reactants in any other order giving rise to dissolution problems.

Yield 2.49 g, 91 %, based on $[PhSLi.(NC_5H_5)_2]$

Elemental analysis: S 12.03 %, N 10.2 %, Li 2.56 %, C 69.4 %, H 5.1 %. Calculated for $[PhSLi.(NC_5H_5)]$ S 11.69 %, N 10.2 %, Li 2.53 %, C 70.1 %, H 5.5 %.

M.p. 114-116 °C

Infra red spectrum: see Table 3.21

3.4.6 Preparation of $[PhCH_2SLi.NC_5H_5]_\infty$.

$PhCH_2SH$ (1.24 g, 1.17 cm^3, 10 mmol) and pyridine (0.78 g, 0.8 cm^3, 10 mmol) were added to chilled (-20 °C) toluene (20 cm^3) in a Schlenk and stirred vigorously. n-Butyl-lithium (0.641 g, 6.5 cm^3 of 1.6 M solution in hexane, 10 mmol) was added dropwise to the clear, colourless solution, keeping the temperature as above. As each drop of n-butyl-lithium touched the solution a deep yellow colouration appeared that quickly dispersed. Addition of the final drops (0.5 cm^3) caused a pale yellow precipitate to appear, becoming denser on allowing the reaction mixture to warm up to room temperature (18 °C). The precipitate dissolved on addition of toluene (10 cm^3) and pyridine (6 cm^3) and heating to boiling point. Colourless crystals appeared on allowing to cool to room temperature. These were filtered, washed with three 5 cm^3 portions of hexane and dried under nitrogen.

Yield: 2.0 g, 95 %, based on $[PhCH_2SLi.(NC_5H_5)]$
Elemental analysis: S 17.19 %, N 6.5 %, Li 3.24 %, C 69.0 %, H 5.7 %. Calculated for $[PhCH_2SLi.NC_5H_5]$: S 15.32 %, N 6.69 %, Li 3.32 %, C 68.89 %, H 5.78 %.
M.p. 143-145 °C
Infra red spectrum: see Table 3.22
N.m.r. ^{7}Li in $[^2H_8]$ toluene, at 20 °C, δ = 0.9094 ppm

3.4.7 Preparation of $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$.

n-Butyl lithium (0.704 g, 8.06 cm^3 of 1.36 M solution in hexane, 11 mmol) was added to a chilled (-20 °C), stirred solution of TMEDA (0.58 g, 0.75 cm^3, 5 mmol) in toluene (10 cm^3). $PhCH_2SH$ (1.24 g, 1.17 cm$_3$, 10 mmol) was added dropwise to the pale yellow solution which slowly deepened to a clear deep orange. It was allowed to warm up to room temperature (20 °C) and, after about thirty minutes stirring, an orange precipitate had formed. Addition of toluene (25 cm^3) and warming caused no dissolution, but the precipitate turned dark yellow-brown and the solution brown. Filtration caused the colour to fade, leaving a white precipitate on the frit and a pale straw-coloured filtrate. The precipitate was washed with hexane, dried and stored in the glove box under nitrogen. Removal of a small amount of solvent from the filtrate under vacuum produced a white precipitate which redissolved on warming (*ca*. 70 °C). On allowing to cool overnight (18 °C) small colourless rhombic crystals appeared. These were filtered, washed with hexane and dried under nitrogen.

Yield: Powder 0.97 g, Crystals 0.48 g, total yield 76 %, based on $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_8]$

Elemental analysis: S 16.78 %, N 7.03 %, Li 4.16 %.

Calculated based on $[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_8]$, S 18.08 %, N 7.29 %, Li 4.22 %.

Infra red spectrum: see tables 3.23 and 3.24

N.m.r. ^7Li in $[^2H_8]$ toluene, at 20 °C, δ= 1.685; 0.9157 ppm

3.4.8 Dilithiation of $PhCH_2SH$ with n-butyl lithium in pyridine and toluene.

Toluene (10 cm^3) was put into a Schlenk with a magnetic stirrer, followed by $PhCH_2SH$ (0.62 g, 0.59 cm^3, 5 mmol) and pyridine (0.79 g, 0.80 cm^3, 10 mmol). The mixture was cooled to _ca_. -20 °C and this temperature maintained throughout. n-Butyl lithium (0.641 g, 8.06 cm^3 of 1.36 M solution in hexane, 10 mmol) was added dropwise. As each drop was added a yellow colouration appeared which disappeared on stirring. It became permanent after the addition of _ca_. 4 cm^3 n-butyl-lithium and further addition produced a yellow precipitate. This precipitate dissolved on allowing the reaction to warm up to room temperature. Addition of hexane (5 cm^3) reprecipitated the yellow solid which dissolved on warming. Cooling to -10 °C over several days produced only a red oil.

3.4.9 Dilithiation of $PhCH_2SH$ with n-butyl-lithium in pyridine and hexane.

Repeat of 3.4.8 using hexane (10cm^3) as initial solvent. Addition of n-butyl-lithium produced, initially, a dense white precipitate; further addition beyond equimolar (based on $PhCH_2SH$) caused a yellow colouration, but the original white precipitate blocked the stirrer. The final reaction mixture consisted of both white and yellow solid in a yellow liquid. A further 10 cm^3 of hexane failed to disperse this.

3.4.10 Reaction of $PhCH_2SH$ with n-butyl-lithium and lithium sulphide in TMEDA and toluene.

Li_2S (0.115 g, 2.5 mmol) was weighed into a Schlenk under nitrogen. To this was added TMEDA (1.743 g, 2.26 cm^3, 15 mmol), $PhCH_2SH$ (3.726g, 3.52 cm^3, 30 mmol) and toluene (10 cm^3). Stirring at room temperature failed to dissolve the Li_2S. The mixture was now maintained at *ca.* -20 °C and n-butyl-lithium (1.92 g, 17.74 cm^3 of 1.69 M solution in hexane, 30 mmol) was added slowly. A red colouration appeared and disappeared during addition, becoming permanent with the last drops. The reaction mixture was allowed to warm up to room temperature and stirring continued for 12 hours. A white precipitate was formed in a straw-coloured liquid. The precipitate was filtered off and washed with hexane. Concentration of the filtrate gave no further product.

Yield: 6.37 g 93% based on $[Li_{14}(SCH_2Ph)_{12}S.(TMEDA)_6]$
Elemental analysis: S 15.58 %, N 6.82 %, Li 4.31 %. see p 88
Infra red spectrum: see Table 3.25

3.4.11 Reaction of $PhCH_2SH$ with n-butyl-lithium in TMEDA

TMEDA (4.62 g, 6.0 cm^3, 40 mmol) was put into a Schlenk with a magnetic stirrer and cooled to _ca_. -20 °C. This temperature was maintained during addition of $PhCH_2SH$ (1.24 g, 1.17 cm^3, 10 mmol) and the subsequent dropwise addition of n-butyl-lithium (0.641 g, 5.9 cm^3 of 1.69 M solution in hexane, 10mmol). A white precipitate was formed which dissolved on gentle warming. A small amount (_ca_. 2 cm^3) of solvent was removed under vacuum and colourless crystals precipitated out. These were filtered off, washed with hexane and collected under nitrogen. Further crystals precipitated from the filtrate but decomposed on the filter.

Yield: 0.48 g, 19.5 % (based on ($PhCH_2SLi$.TMEDA)

Elemental analysis: S 12.46 %, N 10.48 %, Li 2.66 %.

Calculated for [$PhCH_2SLi$.TMEDA] S 13.01 %, N 11.40 %, Li 2.82 %

Infra red spectrum: see Table 3.26

3.4.12 Reaction of $PhCH_2SH$ with n-butyl-lithium in TMEDA and hexane.

Hexane (10 cm^3) was put into a Schlenk containing a magnetic stirrer and the temperature maintained at _ca_. -20 °C. n-Butyl-lithium (0.641g, 6.7 cm^3. of 1.49 M solution in hexane, 10 mmol.) and TMEDA (1.74 g, 2.26 cm^3, 15 mmol.) were added, followed by $PhCH_2SH$ (1.24 g, 1.17 cm^3, 10 mmol) dropwise. A transient orange-pink colour appeared during addition but the final reaction mixture was colourless. On leaving to warm up to room temperature a white precipitate developed and most of this dissolved on gentle warming. Filtration was difficult due to the fine particle size of the precipitate. Attempts to recrystallize the product from hexane were unsuccessful.

Yield. 1.11g 47 % based on $[PhCH_2SLi.TMEDA]$

3.4.13 Preparation of $[o\text{-}MeC_6H_4SLi.(NC_5H_5)_3]$

$o\text{-}MeC_6H_4SH$ (0.62 g, 0.60 cm^3, 5 mmol) and pyridine (0.40 g, 0.40 cm^3, 5 mmol) were added to chilled (ca.-20 °C) toluene (10 cm^3) in a Schlenk and stirred vigorously. This temperature was maintained throughout dropwise addition of n-butyl-lithium (0.32 g, 3.02 cm^3 of 1.65 M solution in hexane, 5 mmol) when the solution became pale yellow. On allowing the reaction mixture to warm up to room temperature (20 °C) a white solid precipitated out. Addition of toluene (10 cm^3) and pyridine (1.5 cm^3) and warming failed to dissolve the solid but on cooling to room temperature the reaction mixture became completely clear. One third of the solvent was removed under vacuum and the clear solution kept at −10 °C for 24 hours. White needle crystals appeared dispersed in a pale straw-coloured liquid. These were washed with hexane and dried under nitrogen.(A). The filtrate was cooled to 5 °C over several hours and small, colourless platelets crystallised out. These were filtered, washed with three 5 cm^3 portions of hexane and dried under nitrogen. (B).

Yield: (A) 0.71 g, (B) 0.55 g, 30 %

Elemental analysis: (A) S 9.91 %, N 6.86 %, Li 2.06 %.

(B) S 9.69 %, N 6.91 %, Li 2.05 %

Calculated for $[o\text{-}MeC_6H_4SLi.(NC_5H_5)_3]$ S 11.12 %, N 9.72 %, Li 2.41 %.

Infra red spectra: (A) and (B) see Table 3.27.

3.4.14 Reaction of C_6F_5SH with n-butyl-lithium in pyridine and toluene.

n-Butyl-lithium (0.641 g, 6.04 cm^3, 1.655 M solution in hexane) was added dropwise to a chilled (−20 °C) mixture of pyridine (0.79 g, 0.80 cm^3, 10 mmol) and C_6H_5SH (2.00 g, 1.3 cm^3, 10 mmol) in toluene (10 cm^3). A white solid precipitated which was sufficiently dense to stop the stirrer. Leaving to warm up to room temperature revealed a white solid in a clear brown liquid. Addition of toluene (10 cm^3) and pyridine (1 cm^3) and warming (*ca*. 60 °C) dissolved the solid to form a red-brown solution, from which white needles crystallised on cooling. These were filtered under vacuum, washed with hexane and dried.

Yield: 0.4 g. 11 % based on $[C_6F_5SLi.(NC_5H_5)_2]$

3.4.15 Reaction of C_6F_5SH with n-butyl-lithium in toluene and pyridine.

Reaction 3.4.14 was repeated. Whitish crystals precipitated out of the brown solution so rapidly that the whole reaction mixture appeared to solidify. Toluene (15 cm^3) was added and on warming a clear solution was obtained again. Small white needles crystallised on cooling to 3 °C and were filtered under vacuum, washed with toluene (2 x 5 cm^3) and hexane (2 x 5 cm^3), and dried and stored immediately under nitrogen. More crystals were collected from the filtrate.

Yield 1.3 g 36 % based on $[C_6F_5SLi.(NC_5H_5)_2]$
Elemental analysis: S 11.55 %, N 6.37 %, Li 1.75 %.
Calculated for $[C_6F_5SLi.(NC_5H_5)_2]$ S 8.8 %, N 7.69 %, Li 1.91 %.
Infra red spectrum: see Table 3.28

3.4.16 Reaction of t-BuSH with n-butyl-lithium in pyridine and toluene.

Pyridine (0.4 g, 0.4 cm^3, 5 mmol) was added to a chilled (ca.-20 °C) mixture of t-butyl mercaptan (0.45 g, 0.56 cm^3, 5 mmol) in toluene (10 cm^3). This temperature was maintained during dropwise addition of n-butyl-lithium (0.32 g, 2.92 cm^3 of 1.715 M solution in hexane, 5 mmol.). A white precipitate gradually formed as the mixture warmed up to room temperature. This dissolved on addition of excess pyridine (0.79 g, 0.80 cm^3, 10 mmol.) and warming. A small amount (ca. 2.0 cm^3) solvent was removed under vacuum and the solution cooled to 0 °C over 2 hours, when small transparent colourless crystals were formed. These were filtered, washed with hexane (3 x 2 cm^3) and dried briefly under vacuum. More crystals were obtained from the filtrate.

Yield 0.84 g 66 % based on [t-BuSLi.$(NC_5H_5)_2$]
M.p. 178-180 °C
Elemental analysis: S 12.25 %, N 8.37 %, Li 3.16 %, { theory,
C 57.4 %, H 6.9 %.

3.4.17 Crystal Structure Determination

All crystals were examined under the microscope in the glove box. Suitable crystals were mounted in 0.3 mm or 0.5 mm Lindemann glass capillaries. Oscillation and full Weissenberg X-ray diffraction photographs were taken to identify good crystals suitable for the full X-ray structure determinations carried out by Dr. W. Clegg at the University of Newcastle upon Tyne.

Complete structure determinations have been carried out on four complexes and a partial determination on one, the results of which appear below.

(a) $[\mathrm{PhSLi.(NC_5H_5)_2}]_\infty$

Monoclinic, $P2_1/c$, a = 9.8032(7), b = 18.0044(12), c = 8.8064(4) Å, β = 100.172(5) °, U = 1529.9 Å^3, Z = 4 formulae/cell, D = 1.191 gcm^{-3}, F(000) = 576 (Cu-Kα)λ= 1.54184 Å, μ= 1.73 mm^{-1}.

Data collection and processing: Crystal 0.56 x 0.15 x 0.12 mm, Siemens AED diffractometer, T = 293 K, cell parameters from 2θ values of 32 reflections ($20<2\theta<40$) h-9 $\rightarrow$ 2, k-0 $\rightarrow$ 19, 1-10 $\rightarrow$ 10, 3 standard reflections, no significant intensity variation. No absorption corrections. 2786 reflections, 2079 unique, 1477 with $F>3\sigma(F)$.

Structure determination: Direct methods, blocked cascade refinement on F, $w^{-1} = \sigma^2(F)$. Aromatic H on external bisectors of ring angles, C-H 0.96 Å, U(H) = $1.2U_{150}$(C), R = 0.0592, R' = 0.0413 max.(shift/e.s.d.) = 0.020, mean = 0.005, slope of normal probability plot=1.71, max. peak in difference synthesis 0.21 eÅ^{-3}, largest hole -0.20 eÅ^{-3}

(b) $[\mathrm{PhCH_2SLi.NC_5H_5}]_{\infty}$

Monoclinic, Cc, a = 16.8293(8), b = 17.4783(10), c = 8.2787(4) Å, β = 104.494(6) °. U = 2357.6 Å^3 Z = 8 formulae/cell, D = 1.179 gcm^{-3}, F(000) = 880, (Cu-K$_\alpha$)λ=1.54184 Å, μ= 2.08 mm^{-1}

Data collection and processing: Crystal 0.15 x 0.15 x 0.30 mm, Siemens AED diffractometer, T = 293 K, cell parameters from 2 values of 32 relections ($30<2\theta<40$) h-19→19, k 0→20, l-9→9, 3 standard reflections, no significant intensity variations. Empirical absorbtion corrections, 3856 reflections, 3856 unique, 3182 with $F>4\sigma(F)$.

Structure determination: Direct methods, blocked cascade refinement on F, $w^{-1} = \sigma^2(F) + 0.00006F^2$ Anisotropic thermal parameters for non-H atoms, aromatic H on external bisectors of ring angles, C-H 0.96 Å, aliphatic H-C-H 109.5 °, U(H) = 1.2U150(C), R = 0.0371 R' = 0.0365, max.(shift/e.s.d.) = 0.112, mean 0.018, slope of normal probability plot = 1.39, max. peak in difference synthesis 0.26 eA^{-3}, largest hole -0.24 eA^{-3}.

(c) $[Li_{14}(SCH_2Ph)_{12}S.(TMEDA)_6]$

Rhombohedral, $R\bar{3}$, a = 26.853(2), c = 16.595(1) A, U = 10363 Å^3, Z = 3 formulae/cell, D = 1.108 gcm^{-3}, F(000) = 3702, (Mo-Kα)λ= 0.71073 A, μ= 0.24 mm^{-1}.

Data collection and processing: Crystal 0.27 x 0.27 x 0.38 mm, Siemens AED diffractometer, T = 293 K, cell parameters from 2 values of 30 reflections (20<2θ<25), h-28→0, k 0→28, l-17→3, 3 standard reflections, no significant intensity variation. No absorption corrections. 3804 reflections, 3006 unique, 1751 with F>4σ(F).

Structure determination: direct methods, blocked cascade refinement on F, anisotropic thermal parameters for all non-H, phenyl rings as rigid hexagons, C-C = 1.395 Å, aromatic H on external bisectors of ring angles, C-H = 0.96 Å, aromatic H-C-C 120 °, aliphatic H-C-H 109.5 °, U(H) = 1.2U_{oq}(C), R = 0·083, R' = 0·057 max.(shift/e.s.d.) = 0.092, mean = 0.020, max. peak in difference synthesis 0.50 eÅ^{-3}, largest hole 0.34 eÅ^{-3}.

(d) $[o\text{-}MeC_6H_4SLi.(NC_5H_5)_3]$

Orthorhombic, $Pna2_1$, a = 15.3020(9), b = 9.6656(7), c = 14.2885(5) Å, U = 2113.3 Å3, Z = 4 formulae/cell, D = 1.155 gcm^{-3}, F(000) = 776, (Cu-Kα)λ= 1.54184 Å, μ= 1.38 mm^{-1}.

Data collection and processing: Crystal 0.17 x 0.29 x 0.35 mm, Siemens AED diffractometer, T = 293 K, cell parameters from 2 values of 32 reflections ($20<2\theta<40^\circ$) h $0\rightarrow16$, k$-10\rightarrow10$, l$-15\rightarrow15$, 3 standard reflections: no significant intensity variation, no absorption corrections. 5555 reflections, 2886 unique, 2461 with $F>3\sigma(F)$.

Structure determination: direct methods, blocked cascade refinement on F, $w^{-1} = \sigma^2(F) + 0.0001F^2$, anisotropic thermal parameters for all non-H, aromatic H on external bisectors of ring angles, C–H = 0.96 Å, H–C–H = 109.5 °, rigid group CH_3, $U(H) = 1.2U_{iso}(C)$ R = 0.0546, R' = 0.0417, max.(shift/e.s.d) = 0.023. mean = 0.006, slope of normal probability plot = 1.26, max. peak in difference synthesis 0.30 $e\text{Å}^{-3}$, largest hole −0.31 $e\text{Å}^{-3}$.

For all structure determinations: Scattering factors from 'International Tables for X-ray Crystallography', Vol 1V. Programs: SHELXTL (G. M. Sheldrick, Gottingen, 1985, Revision 5) and local software.

Table 3.19 Infra red spectrum of $[PhSLi.PMDETA]_n$ (nujol mull) in wave no. cm^{-1}.

$(PhSLi.PMDETA)_n$	Assignments	
	PMDETA	PhSH
3050 m.		3060 m.
2780 w.	2760 s.	
2720 vw.		
1570 s.		1583 s.
1300 w.sh.		1302 w.
1292 s.	1282 m.	
1250 m.	1265 m.	
1215 w.		
1168 s.		1182 w.
1152 m.	1153 m.	
1111 s.	1100 m.	
1083 s.		1095 s.
1060 m.	1062 v.s.	
1036 s.		
1022 s.		1028 s.
997 w.		1002 w.
985 m.		
937 s.	936 m.	
900 m.		900 m.
886 w.	890 w.	
843 w.	835 m.	838 w.
792 s.	788 m.	
778 m.		
752 s.		
742 s.		737 v.s.
700 v.s.		701 s.
595 w.		
572 m.		
480 m.sh.		
450 m.		466 s.
395 w.		

Table 3.20 Infra red spectrum of $(PhSLi.TMEDA)_2$ (nujol mull) - in wave no. cm^{-1}.

	Assignments	
$(PhSLi.TMEDA)_2$	TMEDA	PhSLi
3060 m.		3060 m.
2790 m.	2760 s.	
2720 w.		
1950-1920 w.		1940-1920 w.
1865-1845 w.		1860-1840
1578 s.		1583 s,
1557 w.sh.		
1408 w.		
1359 m.	1360 w.	
1288 s.	1280 m.sh.	
1260 m.	1262 s.	
1253 m.		
1224 w.		
1186 m.		1182 w.
1172 w.		
1164 s.	1154 s.	
1132 s.	1138 s.	1120 m.
1100 w.	1096 m.	1095 s.
1088 v.s.		
1070 s.	1062 v.s.	1072 m.
1038 v.s.		
1027 s.		1028 s.
1000 m.		1002 w.
953 v.s.	962 m.	
892 m.	872 m.	900 m.
795 v.s.		
777 m.	763 m.	
748 v.s.		737 v.s.
700 v.s.		701 s.
615 w.		
585 m.		
485 m.	490 w.	
464 m.		466s.
435 m.		

Table 3.21 Infra red spectrum of $[PhSLi.(NC_5H_5)_2]_\infty$ (nujol mull) - in wave no. cm^{-1}.

	Assignments	
$[PhSLi.(NC_5H_5)_2]_\infty$	NC_5H_5	PhSH
3080 v.w.	3075 m.	
3020 w.	3020 m.	3020 w.sh.
2720 v.w.		
1924 w.	1925-1910 w.	
1592 s.	1598 m.	
1572 s.	1580 s.	
1442 s.	1438 v.s.	1443 s.
1310-1298 w.		1302 w.
1260 w.		
1218 s.	1217 m.	
1188 w.		1182 w.
1173 v.w.		
1147 s.	1145 m.	
1128 m.		1120 m.
1088 s.		1095 s.
1070 s.	1069 m.	1072 m.
1066 w.sh.		
1035 s.	1031 s.	1028 s.
1004 s.		1002 w.
995 m.	982 s.	
963 w.		
898 w.		900 m.
884 w.		
842 w.		838 w.
753 s.	748 s.	
740 s.		737 v.s.
706 v.s.	705 v.s.	701 s.
627 s.		
480 s.		
420 s.		

Table 3.22 Infra red spectrum of $[PhCH_2SLi.NC_5H_5]_\infty$ (nujol mull) - in wave no. cm^{-1}.

	Assignments	
$[PHCH_2SLi.NC_5H_5]_\infty$	$PhCH_2SH$	NC_5H_5
3080 w.	3080 m.	3075 m.
3060 w.	3060 m.	3050 w.
2720 w.		
1595 s.	1602 m.	1598 m.
1572 w.		1580 s.
1230 m.	1253 s.	
1216 s.		
1205 m.	1202 w.	
1185 v.w.	1182-1155 w.	
1173 w.		
1153 m.		1145 m.
1072 s.	1076 s.	1069 m.
1038 s.	1031 s.	
1030 m.sh.		1031 s.
1009 s.		
982 w.	975 m.	982 s.
968 w.		
950 v.w.		
910 m.	908 m.	
892 v.w.		
870 w.		
817 w.		
805 m.		
772 s.		
760 s.	760 s.	
700 v.s.	700 v.s.	705 v.s.
626 s.		
568 s.		
467 m.	470 s.	
420 m.		

Table 3.23 Infra red spectrum of product A (powder) from reaction of $PhCH_2SH$ and n-Bu Li in the presence of TMEDA. (nujol mull) - in wave no. cm^{-1}.

	Assignments	
Product A	TMEDA	$PhCH_2SH$
3075 w.		3080 m.
3050 m.		3060 m.
3020 m.		3030 s.
2780 m.	2730 s.	
1598 s.		1602 m.
1489 s.		1496 s.
1355 m.	1360 w.	
1320 w.	1330 w.	1320 w.
1292 m.		
1254 m.	1262 s.	1253 s.
1226 s.		
1200 w.		1202 w.
1180 w.		1182-1155 w.
1160 s.	1162 s.	
1132 m.		
1102 w.		
1068 s.		1076 s.
1039 s.	1033 v.s.	
1028 s.		1031 s.
1022 m.		
950 s.		
920 m.	933 m.	
852 m.	872 m	
806 w.	830 s.	
792 m.		
765 w.		760 s.
742 m.		
717 s.		
707 v.s.		700 v.s.
698 s.		679 s.sh.
586 w.		
560 m.		558 s.
462 m.		470 s.

Table 3.24 Infra red spectrum of

$[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$ (nujol mull) - in wave no. cm^{-1}

	Assignments	
$[Li_{14}(SCH_2Ph)_{12}S(TMEDA)_6]$	TMEDA	$PhCH_2SH$
3055 m.		3060 m.
3020 m.		3030 s.
2785 m.		
2720 w.		
1597 s.		1602 m.
1490 s.		
1423 w.		1428 w.
1356 m.	1358 w.	
1322 w.		1320 w.
1292 s.	1280 m.sh.	
1255 m.	1262 s.	1253 s.
1228 s.		
1200 w.		1202 w.
1180 m.		1182-1155 w.
1160 s.	1154 s.	
1132 m.	1138 s.	
1102 w.	1096 m.	
1070 s.	1062 v.s.	1076 s.
1042 s.		
1030 s.		1031 s.
1024 m.		
952 s.	962 m.	
920 m.		
852 m.		
808 w.		
795 m.		
775 m.		
765 m.	763 m.	760 s.
742 m.		
732 w.		
718 s.		
708 v.s.		700 v.s.
698 s.		679 s.sh.
587 m.		
561 m.		558 s.
465 s.		470 s.

Table 3.25 Infra red spectrum of product of reaction of $PhCH_2SH$ with n-Bu Li and Li_2S in TMEDA and toluene (nujol mull) - in wave no. cm^{-1}.

	Assignments	
Product	TMEDA	$PhCH_2SH$
3050 m.		3060 m.
3020 m.		3030 s.
2780 m.	2800 w.sh.	
2720 w.		
1938 w.		1945 w.
1868 w.		1870 w.
1795 w.		1805 w.
1597 s.		1602 m.
1580 w.		
1493 s.		1495 s.
1338 m.		1332 w.
1318 w.		1320 w.
1289 v.w.		
1278 m.	1280 m.sh.	
1255 m.	1262 s.	1253 s.
1230 s.		
1204 m.		1202 w.
1180 w.		1182-1155 w.
1160 s.	1154 s.	
1144 w.	1138 s.	
1133 w.		
1094 m.	1096 m.	
1071 m.		1076 s.
1064 m.	1062 v.s.	
1034 s.		1031 s.
1018 v.s.		
958 s.	962 m.	
868 m.	872 m.	
823 m.	830 s.	
812 w,		
800 w.		
790 w.		
767 s.	763 m.	760 s.
700 v.s.		700 v.s.
688 s.		679 s.sh.
566 s.		558 s.
520 m.		
472 m.		470 s.
420 m.		

Table 3.26 Infra red spectrum of [PhCH$_2$SLi.TMEDA]$_n$ (nujol mull) - in wave no. - cm^{-1}.

	Assignments	
[PhCH$_2$SLi.TMEDA]$_n$	TMEDA	PhCH$_2$SH
3080 w.sh.		3080 m.
3060 w.sh.		3060 m.
3020 w.sh		3030 s.
2775 w.	2760 s.	
2715 w.		
1596 m.		1602 m.
1492 m.		1496 s.
1348 w.	1358 w.	
1278 w.	1280 m.sh.	
1255 w.	1262 s.	1253 w.
1230 m.		
1203 w.		1202 w.
1160 m.	1154 s.	
1132 w.	1138 s.	
1066 m.	1062 v.s.	1076 s.
1032 m.		1031 s.
1018 m.		
948 w.		
868 m.	872 m.	
825 w.		
770 m.	763 m.	760 s.
720 w.		
708 m.sh.		
700 s.		700 v.s.
662 m.		679 s.sh.
591 m.		
565 m.		558 s.
492 m.	490 w.	
470 m.		470 s.

Table 3.27 Infra red spectrum of products of reaction of o-MeC_6H_4SH with n-Bu Li in pyridine and toluene (nujol mull) - in wave no. cm^{-1}.

		Assignments	
Product A	Product B	NC_5H_5	o-MeC_6H_4SH
3040 w.	3040 m.	3050 m.	3060 m.
2720 w.	2720 w.		
1595 v.s.	1594 s.	1598 m.	1590 m.
1572 s.	1572 s.	1580 s.	
1484 s.	1482 s.	1482 m.	
1442 v.s.		1438 v.s.	
1315-1295 w.	1320 w.		
1280 m.	1282 m.		1280 w.
1258 m.	1258 m.		
1235 w.	1237 w.		
1226 m.	1227 m.		
1217 s.	1218 s.	1217 m.	1208 s.
1190 m.	1191 m.		
1156 s.	1158 s.	1145 m.	1157 w.
1126 m.	1128 m.		
1075 m.	1078 m.sh		
1069 s.	1069 s.	1069 m.	1073 s.
1038 v.s.	1036 v.s.	1031 s.	
1004 s.	1005 s.		
980 w.	979 w.	982 s.	
952 w.	953 w.		
	936 w.		
892 w.	892 m.		
803 m.	802 s.		797 m.
760 v.s.	760 v.s.		746 v.s.
757 w.sh.	757 w.sh.		
736 m.	737 m.		
708 v.s.	707 v.s.	705 v.s.	
678 s.	678 s.		676 m.
658 w.	656 m.		
622 s.	622 s.		
	588 w.		
	555 w.		
535 w.	535 m.		
518 m.	519 m.		
502 w.	502 w.		
	455 m.		
	447 m.		
425 m.	425 s.		438 m.

Table 3.28 Infra red spectrum of product of reaction of C_6F_5SH with n-Bu Li in pyridine and toluene (nujol mull) - in wave no. cm^{-1}

	Assignments	
Product	NC_5H_5	C_6F_5SH
3085 w.	3075 m.	
3060 w.	3050 w.	
2720 w.		
2460 w.		2430 w.
1620 m.	1630 w.	
1596 s.	1598 m.	
1574 m.	1580 s.	
1502 v.s.		1494 s.
1444 m.	1438 v.s.	
1348 w.		
1327 w.		1332 m.
1270 m.		1275 w.
1245 w.		
1220 s.	1217 m.	
1172 w.		
1153 s.	1145 m.	1150 m.
1125 m.		
1090 m.		1092 v.s.
1080 s.		
1038 s.	1031 s.	
1007 m.		
998 w.		
969 v.s.		
920 w.sh.		925 s.
867 v.s.		870 v.s.
758 s.	748 s.	
712 v.s.	705 v.s.	
706 v.s.		
685 w.		
655 m.		
623 s.		
582 w.		
576 w.sh.		
560 v.w.		
540 w.		
520 w.		
485 m.		
435 m.		
426 m.		

Table 3.29 Infra red spectrum of product of reaction of t-BuSH with n-BuLi in pyridine and toluene (nujol mull) - in wave no. cm^{-1}.

	Assignments
Product	Pyridine
3075 w.	3075 m.
3038 m.	3050 w.
2715 w.	
2680 w.	
1926 w.	1925-1910 w.
1880-1860 w.	1875-1860 w
1700-1680 v.w.	
1645 w.	
1620 w.	1630 w.
1595 v.s.	
1570 s.	1580 s.
1485 s.	1482 m.
1350 s.	
1230 w.	
1216 s.	1217 m.
1205 w.	
1160 v.s.	
1150 v.s.	1145 m.
1082 s.	
1034 v.s.	1031 s.
1000 v.s.	
984 s.	982 s.
950 w.	
935 w.	
920 w.	
884 w.	
830 m.	
802 m.	
760 m.sh.	
752 v.s.	748 s.
744 m.	
702 v.s.	705 v.s.
670 w.	
653 w.	
618 s.	
600 m.	602 s.
452 m.	
420 m.	
390 m.	409 s.

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CHAPTER 4

SOME PRELIMINARY REACTIONS OF DIPHENYLKETIMINE WITH SULPHUR.

4.1 Introduction

Extensive investigations have been carried out in recent years into the structure and bonding characteristics of lithium derivatives of ketimines, RR'C=NH.[1-7] Whereas amidolithium oligomers $(LiNRR')_n$ have electron precise $(LiN)_n$ ring structures, it has been found that the imidolithiums provide examples of electron deficient bridging between the N atoms. The compounds, $[RR'C{=}NLi]_6$, R = R' = ^{t}Bu, NMe_2;
R = Ph, R' = ^{t}Bu; R = Ph, R' = NMe_2; have hexameric structures containing slightly folded Li_6 rings held together by triply bridging N=CRR' ligands (see Figure 4.1). These ligands bridge the six smaller of the eight triangular faces of the Li_6 core. Alternatively, the hexamers can be regarded as pairs of puckered Li_3N_3 six membered rings, the metal atoms of one almost eclipsing the N atoms of the other. The hexameric structure can only occasionally be broken down by addition of a co-ordinating ligand. E.g. $[^tBu_2C{=}NLi(HMPA)]_2$ is a dimer containing a central Li_2N_2 ring.

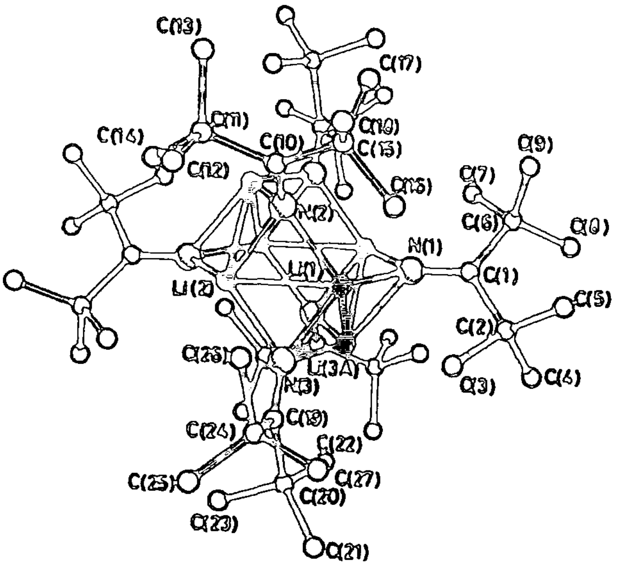


Figure 4.1 Molecular structure of $[\{Li(N{=}CBu^t{}_2)\}_6]$

Addition of other common donors such as tetrahydrofuran, pyridine, triethylamine. TMEDA, however, failed to reduce the oligomerisation of the hexamers and evidence suggests that the hexameric structure of the solid is largely retained in solution.[7]

The diaryl derivatives of the imidolithiums, e.g. $(Ph_2C{=}NLi)_n$ are polymeric powders that can be converted into oligomers by reacting with donor ligands. e.g. $[Ph_2C{=}NLi.NC_5H_5]_4$ has a Li_4N_4 cubic arrangement.[3] (see Figure 4.2).

Although ketimines, RR'C=NH, are relatively stable compounds some of which are available commercially, and

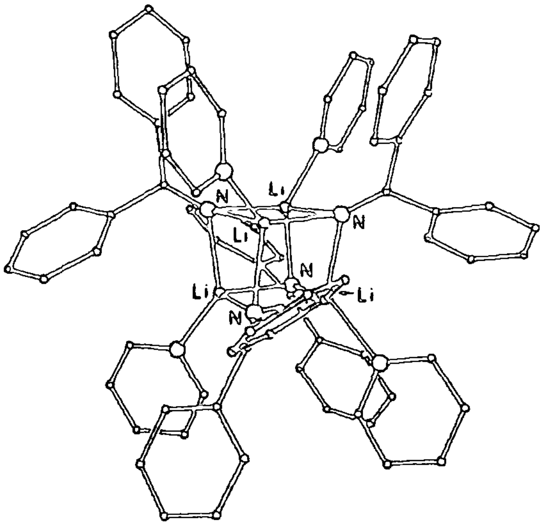
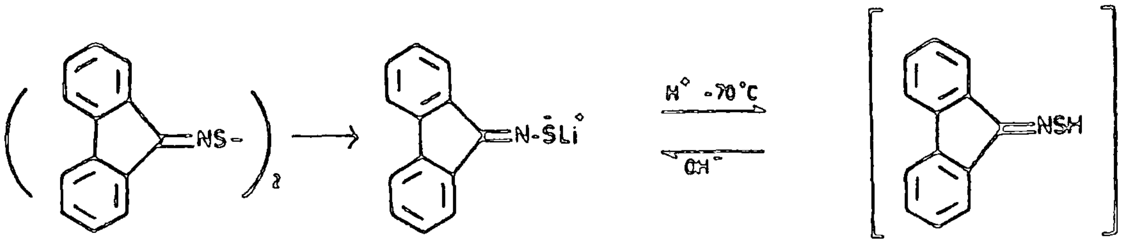


Figure 4.2 Molecular structure of $(Ph_2C=NLi.NC_5H_5)_4$

the related ketoximes, RR'C=NOH, are well known, only a little information is available on the analogous sulphur derivatives, the thio-oximes, RR'C=NSH.[8]

In 1974 simultaneous publications described the preparation of some thio-oxime compounds.[9,10] Barton et al treated a disulphide with lithium-ethylamine or lithium-ammonia at -50 °C, followed by addition of methyl iodide to produce the methyl derivative of the thio-oxime. In reaction scheme 4.1 the fluorenone derivative is converted to an air sensitive red lithium salt and they propose that the parent oxime can be formed from this by addition of acetic acid at -70 °C.

Brown and co-workers prepared the



Reaction scheme 4.1

2,4,dinitrofluorobenzene derivative of the benzophenonethio-oximate ion by reacting n-butyl-lithium with bis(diphenylmethylenamino)disulphide, $(Ph_2C{=}N-)_2S_2$ Both these routes gave several byproducts all involving disulphide cleavage.

In 1980 a new method of preparation of the thio-oxime, $Ph_2C{=}NSH$, was reported using diphenylketimine as a precursor[11]. It was proposed that lithiation of this with n-butyl-lithium and reaction of the product, $(Ph_2C{=}NLi)$, with elemental sulphur gave $Ph_2C{=}NSLi$ 'in situ'. Walton did not isolate this product but converted it to the trimethyl silyl derivative, $Ph_2C{=}NSSiMe_3$, a yellow oil which was stable at -25 °C but decomposed at room temperature.

In view of the interesting structures already examined for lithioketimines and their close relationship preparatively with the thio-oxime derivatives, as shown above, it was decided to try to prepare and isolate some lithium thio-oximates in order to examine their structure and stability.

4.2 RESULTS AND DISCUSSION

4.2.1 Preparation of $Ph_2C=NSLi$ in diethyl ether.

The preparation of $Ph_2C=NSLi$ has already been described in the literature, but the compound, an orange solid, was never isolated. Adding a suspension of one molar equivalent of elemental sulphur to lithiodiphenylketimine, $(Ph_2C=NLi)_n$, prepared 'in situ' in diethyl ether, produced an orange solution. The bright orange solid collected on removal of the diethyl ether under vacuum was obtained in 121 % yield (based on $Ph_2C=NLi$) which could be an indication of co-ordinated diethyl ether. The infra red spectrum shows ν_{max} = 1600 cm^{-1}, which can be assigned to C=N stretching mode. Elemental analysis gave a Li:N:S ratio of 1:1:1 as expected. Similarly, the Li:N:S:C ratio is 1:1:1:17 which would be consistent with one molecule of co-ordinated diethyl ether. Further investigation of this system will be concentrated on crystal growth and n.m.r. measurements.

4.2.2 Reaction of $Ph_2C=NSLi$ with PMDETA

The above preparation was repeated, but this time, PMDETA was added to the solution of $(Ph_2C=NSLi)_n$ in diethyl ether, producing an orange precipitate. Microscopic examination of this orange solid showed it to consist of a mixture of yellow microcrystals and tiny clear orange needles, all of which were too small to be examined by X-ray techniques.

4.2.3 Reaction of $Ph_2C=NLi$ with eight moles of sulphur.

The lithiation of diphenylketimine in diethyl ether produces a bright red solution. Addition of solid sulphur initially causes this to change to deep orange. Continuing the addition beyond one molar quantity (based on diphenylketimine) gradually causes precipitation of a canary yellow solid. Elemental analysis was inconclusive but did give a Li:N:S ratio of 1:1:7. The infra red spectrum showed no ν_{max} between 1500 and 1600 cm^{-1} indicating the disappearance of the carbon-nitrogen double bond. No further clarification was achieved with mass spectrometry; it appeared that the molecule fragmented completely under the test conditions of both electron ionisation and chemical ionisation. The molecular ion was a peak of low intensity at molecular mass 256, probably S_8, while the base peak, at molecular mass 180, can be assigned to $Ph_2C=N$.

Attempts to recrystallise the product showed that it was almost insoluble in solvents with which it did not react. The product was recovered unchanged from toluene, pentane and hexane; in tetrahydrofuran it formed a red oil and in dichloromethane complete decomposition occurred to leave a deposit of sulphur.

4.2.4 Sublimation of $Ph_2CNLi/8S$

An attempt was made to obtain crystals of $Ph_2CNLi/8S$ by sublimation on to a water cooled cold finger. A pale yellow powder solidified onto the finger leaving a yellow brown residue. An infra red spectrum of the sublimate gave no peaks at all, suggesting that the yellow solid was sulphur; this was confirmed by elemental analysis. It was impossible to mull the residue so no infra red spectrum was recorded. This, together with its failure to melt below 300 °C pointed to the possibility of a polymeric material.

4.2.5 Reaction of $Ph_2CNLi/8S$ with TMEDA in hexane.

A crystalline product was essential to determine the structure of this curious compound and from experiments already discussed it was concluded that the initial product was amorphous. A possible solution was to add a donor ligand that would provide additional co-ordination at lithium hopefully without disturbing the arrangement of the carbon, nitrogen and sulphur atoms. The product of the reaction of n-butyl-lithium with diphenylketimine is itself an insoluble polymer, $(Ph_2C=NLi)_n$, which gives a crystalline tetramer, $[Ph_2C=NLi.NC_5H_5]_4$ on reaction with pyridine.[3]

Consequently, the yellow powder, $Ph_2CNLi/8S$, was treated with TMEDA in hexane and this reaction produced two products. The second, obtained after removal of hexane from the filtrate was found, by infra red spectrum and elemental analysis to be sulphur. The yellow precipitate appeared non-crystalline and little could be deduced from either the infra red spectrum or elemental analysis.

4.2.6 Extraction of $Ph_2CNLi/8S$ with a mixture of hexane and toluene.

Microscopic examination of $Ph_2CNLi/8S$ in air on a watch glass showed rapid decomposition to leave a sticky orange solid interspersed with yellow dots of sulphur. Since sulphur has also been a product of two reactions described above, it was concluded that the yellow powder, $Ph_2CNLi/8S$ was probably contaminated with unreacted sulphur. Elemental sulphur is only sparingly soluble in inert solvents such as toluene and hexane so a large excess was used for 36 hours at room temperature and a further six hours at 70 °C. Undissolved solid was removed and the infra red spectrum of this was identical with the starting material. Small white needles were obtained from the filtrate and these were shown by the infra red spectrum and elemental analysis to be pure sulphur. Elemental analysis of the insoluble material now showed a Li:N:S ratio of 2.5:1:5.

Although much of the evidence described above is inconclusive and, as yet, there is no proof as to the structure of the compound (Ph_2CNLiS_x) the infra red evidence indicates that sulphur has reacted across the carbon - nitrogen double bond to form a CNS ring within the molecule. It is also known that organolithium compounds react with elemental sulphur apparently by insertion of polysulphur into the carbon-lithium bond;[12] e.g. s-butyl lithium, on reaction with S_8 in benzene gives $Bu^sS_4Bu^s$ with Bu^sS_nLi as a proposed intermediate.

4.3 Conclusions

The reactions of sulphur with lithiated diphenylketimine described in this chapter have produced several new compounds the structures of which have remained elusive because it has proved difficult to prepare crystalline products suitable for X-ray structure determination. Analysis of the orange compound isolated from the reaction of $Ph_2C{=}NLi$ with one molar equivalent of sulphur in diethyl ether points to a formula $[Ph_2C{=}NSLi.Et_2O]_n$. Addition of PMDETA to a solution of $[Ph_2C{=}NSLi]$ in ether gave a mixture of crystalline products, but this preparation is somewhat cluttered with the possibility of either PMDETA or diethyl ether or both acting as extra co-ordinating ligands to the lithium.

The use of a large molar excess of sulphur (i.e. eight equivalents based on $Ph_2C{=}NLi$) has given a product the formula of which is still unknown, although infra red evidence hints at the presence of a CNS ring.

Although the results described in this chapter are largely inconclusive they do give rise to interesting possibilities for future study. Use of an inert solvent such as toluene or hexane instead of diethyl ether could give cleaner reactions with only one donor ligand present. Reaction of sulphur with other ketimines e.g. $(^tBu_2C{=}NLi)_6$ and $[(Me_2N)_2C{=}NLi]_6$ in the presence of a donor compound may well produce crystalline complexes.

A series of reactions using 1–8 molar equivalents, and particularly 5, of sulphur would, perhaps, help to unravel the structure of (Ph_2CNS_xLi).

4.4 EXPERIMENTAL SECTION

The following abbreviations will be used:

TMEDA tetramethylethylenediamine

PMDETA pentamethyldiethylenetriamine

HMPA hexamethylphosphoramide

4.4.1 Reaction of $Ph_2C=NH$ with n-butyl lithium and one molar equivalent of sulphur in diethyl ether.

Diphenylketimine, $Ph_2C=NH$, (3.62 g, 20 mmol) was dissolved in diethyl ether (40 cm^3) in a 250 cm^3 two-necked flask under nitrogen, and the solution cooled to -10 °C. n-Butyl lithium (1.29 g, 13 cm^3, 1.55 M solution in hexane, 20 mmol) was added and the pale yellow solution became bright red. A suspension of sulphur (0.66 g, 20 mmol) in diethyl ether (20 cm^3) was run in slowly and the solution turned orange as all the sulphur dissolved. Stirring was continued for 16 hrs at room temperature and the diethyl ether removed under vacuum to leave a bright orange solid.

Yield: 5.29 g 90 %, based on $[Ph_2C=NSLi]Et_2O$

Elemental analysis: S 13.02 %, N 5.26 %, Li 2.32 %, C 72.69 %, H 4.90 %.

Calculated for $[Ph_2C=NSLi]Et_2O$: S 10.9 %, N 4.8 %, Li 2.4 %, C 69.6 %, H 6.9 %.

Infra red spectrum: see Table 4.1

4.4.2 Preparation of $Ph_2C=NSLi$ in diethyl ether and addition of PMDETA.

A suspension of sulphur (0.45 g, 14 mmol) in diethyl ether (10 cm^3) was added to a stirred solution of $Ph_2C=NLi$, prepared by addition of n-butyl-lithium (0.90 g, 8.8 cm^3 of 1.6 M solution in hexane, 14 mmol) to $Ph_2C=NH$ (1.81 g, 10 mmol) in diethyl ether (25 cm^3) at −10 °C. The sulphur gradually dissolved to give a deep orange, but slightly cloudy solution. Stirring was continued at room temperature for 4 hours. Addition of toluene (6 cm^3) and warming gave a clear orange solution. Cooling over several hours at −5 °C caused no precipitation. PMDETA (2 cm^3) was added to the cold solution which turned very dark red. An orange solid precipitated out as it warmed up to room temperature. This was filtered, washed with diethyl ether (2 x 5 cm^3) and dried. Microscopic examination showed a mixture of yellow microcrystals and clear orange needles.

M.p. 132-135 °C

Infra red spectrum: see Table 4.2

4.4.3 Reaction of diphenylketimine with n-butyl-lithium and an eight molar excess of sulphur.

Diethyl ether (40 cm^3) was added to n-butyl-lithium (2.56 g, 24.24 cm^3 of 1.65 M solution in hexane, 40 mmol) in a two-necked 250 cm^3 flask at room temperature under a stream of nitrogen. This was followed by diphenylketimine (7.24 g 40 mmol) and the solution turned bright red. Solid sulphur (10.26 g, 320 mmol) was added slowly via a banana joint, stirring constantly. A canary yellow precipitate appeared dispersed in an orange liquid. Stirring was continued at room temperature for 48 hours and at reflux temperature for 2 hours, before filtering and vacuum drying.

Yield: 18.27 g 103 % based on [$Ph_2C=NS_8Li$]

Elemental analysis: S 49.17 %, N 3.06 %, Li 1.50 %, C 39.23 %, H 2.56 %.

Calculated for [$Ph_2C=NS_8Li$]: S 57.8 %, N 3.2 %, Li 1.6 %, C 35.2 %, H 2.3 %.

Infra red spectrum: see Table 4.3.

4.4.4 Reactions to test the solubility of $Ph_2CNLi/8S$.

(a) Toluene - $Ph_2CNLi/8S$ (0.5 g) was put into a Schlenk under nitrogen with a magnetic stirrer. Toluene (10 cm^3) was dripped in and the mixture stirred vigorously. Very little solid appeared to dissolve, even on heating to B.p.

(b) Pentane - repeat of (a) above. Similar results.

(c) Hexane - repeat of (a) above. Similar results.

(d) Dichloromethane - repeat of (a) above. Effervescence occurred on addition of dichloromethane and the yellow solid dissolved. Removal of the solvent under vacuum left a very pale yellow solid.

Infra red spectrum: ν_{max} = none.

(e) Tetrahydrofuran - repeat of (a) above. Addition of THF produced a deep red oil.

4.4.5 Sublimation of $Ph_2CNLi/8S$.

$Ph_2CNLi/8S$ (1.0 g) was put into the bottom of a sublimer fitted with a water cooled cold finger. It was heated slowly, in an oil bath, under vacuum to 90 °C. A pale yellow solid sublimed onto the cold finger leaving a yellow-brown residue in the sublimer.

Infra red spectra: Yellow solid: ν_{max} = none.

Yellow-brown residue: failed to mull.

4.4.6 Decomposition of $Ph_2CNLi/8S$.

A small amount of the yellow powder, $Ph_2CNLi/8S$, was placed on a watch glass and examined under the microscope.

The colour immediately began to turn orange and after 30 seconds a sticky orange mass had formed with small yellow specks dispersed in it.

4.4.7 Reaction of $Ph_2CNLi/8S$ with TMEDA in hexane.

Hexane (25 cm^3) was added to $Ph_2CNLi/8S$ (0.5 g) in a two necked flask under nitrogen and stirred rapidly. TMEDA (1.54 g, 2.0 cm^3, 13 mmol) was dripped in slowly and the suspension darkened in colour. As the final 0.5 cm^3 was added the solid dissolved to leave an orange-yellow solution. A yellow solid precipitated out during stirring at room temperature for 24 hours. This was filtered, washed with hexane (3 x 2 cm^3) and dried under vacuum. (A). Hexane was removed from the filtrate under vacuum to leave a pale yellow solid. (B).

Yield: (A) 0.2 g.

(B) 0.15g

Elemental analysis: (A) S 55.13 %, N 5.84 %, Li 2.84 % C 21.82 %, H 4.98 %.

(B) S 99.5 %, N 0 %.

Calculated for $[Ph_2C{=}NS_8Li]$: S 57.8 %. N 3.2 %. Li 1.6 %, C 35.2 %, H 2.3 %.

Infra red spectra: (A) see Table 4.4.

(B) ν_{max} = none.

4.4.8 Extraction of $Ph_2CNLi/8S$ with hexane/toluene.

Hexane (20 cm^3) and toluene (20 cm^3) were added to $Ph_2CNLi/8S$ (1.0 g) in a Schlenk under nitrogen and stirred vigorously. The mixture was heated to 70 °C and a further 10 cm^3 toluene added. Stirring was continued at this temperature for 6 hours and at room temperature for 36 hours. The undissolved solid was filtered off, washed with hexane (3 x 5 cm^3) and dried under vacuum. (A). Approximately 60 % of the solvent was removed from the pale yellow filtrate and small white needles appeared. (B). These were filtered, washed with hexane (3 x 2 cm^3) and dried under vacuum.

Yield: (A) 0.30 g

(B) 0.165 g

Elemental analysis: (A) S 34.83 %, N 3.13 %, Li 3.80 %, C 46.88 %, H 4.66 %.

(B) S 99.29 %, N 0 %.

Calculated for $[Ph_2C{=}NS_4Li]$: S 40.7 %, N 4.4 %, Li 2.2 %, C 49.5 %, H 3.2 %.

Infra red spectra: (A) - identical with $Ph_2CNLi/8S$.

(B) ν_{max} = none.

Table 4.1 Infra red spectrum of [$Ph_2C=NSLi$] (nujol mull) in wave no. cm^{-1}.

[$Ph_2C=NSLi$]	[$Ph_2C=NLi$]
	1614 v.s.
1595 s.	1596 s.sh.
1566 m.	1573 s.
1540-1530 m.sh.	
	1480 s.
	1446 s.
	1382 s.
	1365 m.
1312 m.	1312 m.
1290 m.	
1270 w.sh.	1268 w.
1218 m.	1220 s.
	1196 w.
1180 m.	1180 m.
1156 m.	1160 w.
1120 w.	
	1096 w.
1072 m.	1072 s.
1028 m.	1032 s.
1000 m.	1002 m.
	974 m.
954 s.	
930 w.	932 m.
898 m.	894 s.
845 m.	850 s.
773 s.	765 v.s.
748 s.	740 m.
725 w.	
698 v.s.	700 v.s.
670 m.	675 v.s.
630 s.	632 m.
564 m.	
470 w.	

Table 4.2 Infra red spectrum of [Ph_2C=NSLi]PMDETA (nujol mull) in wave no. cm^{-1}.

	Assignments	
[Ph_2C=NSLi]PMDETA	Ph_2C=NLi	PMDETA
1300 m.	1312 m.	
1290 m.		1282 m.
1250 w.	1268 w.	1265 m.
1220 w.	1220 s.	
1168 m.	1180 m.	
1153 m.		1153 m.
1112 m.		
1050 m.	1060 w.	1062 v.s.
1035 m.	1032 s.	
1020 m.		
1000 w.	1002 m.	
980 m.	974 m.	
935 m.	932 m.	936 m.
900 w.	912 w.sh.	
850 w.	850 w.	
790 m.		788 m.
780 s.		
758 m.	765 v.s.	
722 w.		
700 s.	700 v.s.	
665 w.		
628 m.	632 m.	
580 w.		
568 w.		
528 s.		
440 m		

Table 4.3 Infra red spectrum of $Ph_2C=NLi/8S$ (nujol mull) in wave no. cm^{-1}.

$Ph_2C=NLi/8S$	$Ph_2C=NLi$
	1614 v.s.
	1596 s.sh.
	1573 s.
	1480 s.
	1446 s.
	1382 s.
	1365 m.
1318 w.sh.	1312 m.
1290 m.	
	1268 w.
	1220 s.
	1196 w.
	1180 m.
1164 w.	1160 w.
1150 m.	
	1096 m.
1066 m.	1072 s.
1040 s.	1032 s.
996 m.	1002 m.
	974 m.
952 s.	
	932 m.
910 m.	912 w.sh.
890 s.	894 s.
784 m.	
773 s.	765 v.s.
743 s.	740 m.
717 w.	
706 m.	
695 s.	700 v.s.
672 m.	675 v.s.
626 m.	632 m.
608 w.sh.	
560 m.	
514 s.	
462 m.	
434 m.	

Table 4.4 Infra red spectrum of [Ph_2C=NLi/8S.TMEDA] (nujol mull) in wave no. cm^{-1}.

	Assignments	
Product	Ph_2C=NLi	TMEDA
1282 s.		1280 m.sh.
1245 w.		
1172 m.sh.	1180 m.	
1151 s.		1154 s.
1128 s.		1138 s.
1092 w.	1096 m.	1096 m.
1068 m.	1072 s.	1062 v.s.
1031 m.sh.	1032 s.	
1017 s.		
946 s.		
888 w.sh.	894 s.	
790 s.		
773 m.	765 v.s.	
722 m.		
695 m.	700 v.s.	
582 m.		
508 s.		
458 s.		
435 s.		

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CHAPTER 5

PREPARATIVE, STRUCTURAL AND THEORETICAL STUDIES OF LITHIUM DERIVATIVES OF CARBOXYLIC ACIDS AND THIOCARBOXYLIC ACIDS.

5.1 INTRODUCTION

Lithium carboxylate structures have been reported in the literature but most of them are lithium complexes of dicarboxylate anions.[1] Most commonly Li is tetrahedrally co-ordinated to four oxygen atoms as in lithium succinate, $Li_2(CO_2CH_2CH_2CO_2)$, but five co-ordination is not unusual e.g. lithium hydrogen oxalate monohydrate, $LiH(C_2O_4).H_2O$, while lithium dihydrogen citrate, $LiH_2(C_6O_7H_5)$ is six co-ordinate with octahedral geometry.

The hydrates of lithium acetate and lithium formate have also been structurally investigated.[2-4] Lithium acetate crystallises as the dihydrate, $(CH_3COOLi.2H_2O)$, in which Li is in a tetrahedral environment, bonding to two oxygen atoms of two different acetate ions and two oxygen atoms of water molecules. Hydrogen bonds between water molecules hold the lattice together. Lithium formate monohydate has been investigated by two different groups[3,4] both showing lithium tetrahedrally co-ordinated to three formate oxygen atoms and one water oxygen. As with the acetate hydrogen bonds hold the molecules together.

Schleyer et al[5] have carried out m.o. calculations on lithium and magnesium derivatives of acetic acid 'dianions'. Using mainly a 3-21G basis set they predicted a highly ionic structure in which one lithium bridges the oxygen atoms of an $(O—C—O)^-$ unit and the second lithium bridges the (C—C—O) unit (see Figure 5.1)

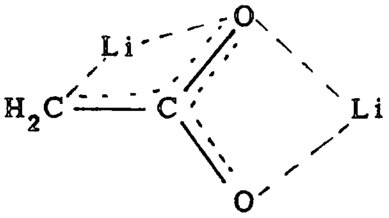


Figure 5.1. Proposed structure of dilithiated acetic acid.

Dilithiated carboxylic acids are widely used in synthetic reactions but no X-ray structures have been reported.

In view of this background it was decided to examine the lithium derivatives of a series of aromatic acids including thio acids, in the presence of donor ligands such as tetramethylethylenediamine (TMEDA) to provide extra co-ordination at lithium. It seemed of especial interest to examine the nature of a lithium salt where the anion contains one oxygen atom and a similarly placed but more polarizable atom such as sulphur. With this in mind monothiobenzoic acid, PhCOSH, was chosen as a readily available starting material and to complete the series lithium derivatives of benzoic acid, PhCOOH, and dithiobenzoic acid, PhCSSH, would be prepared.

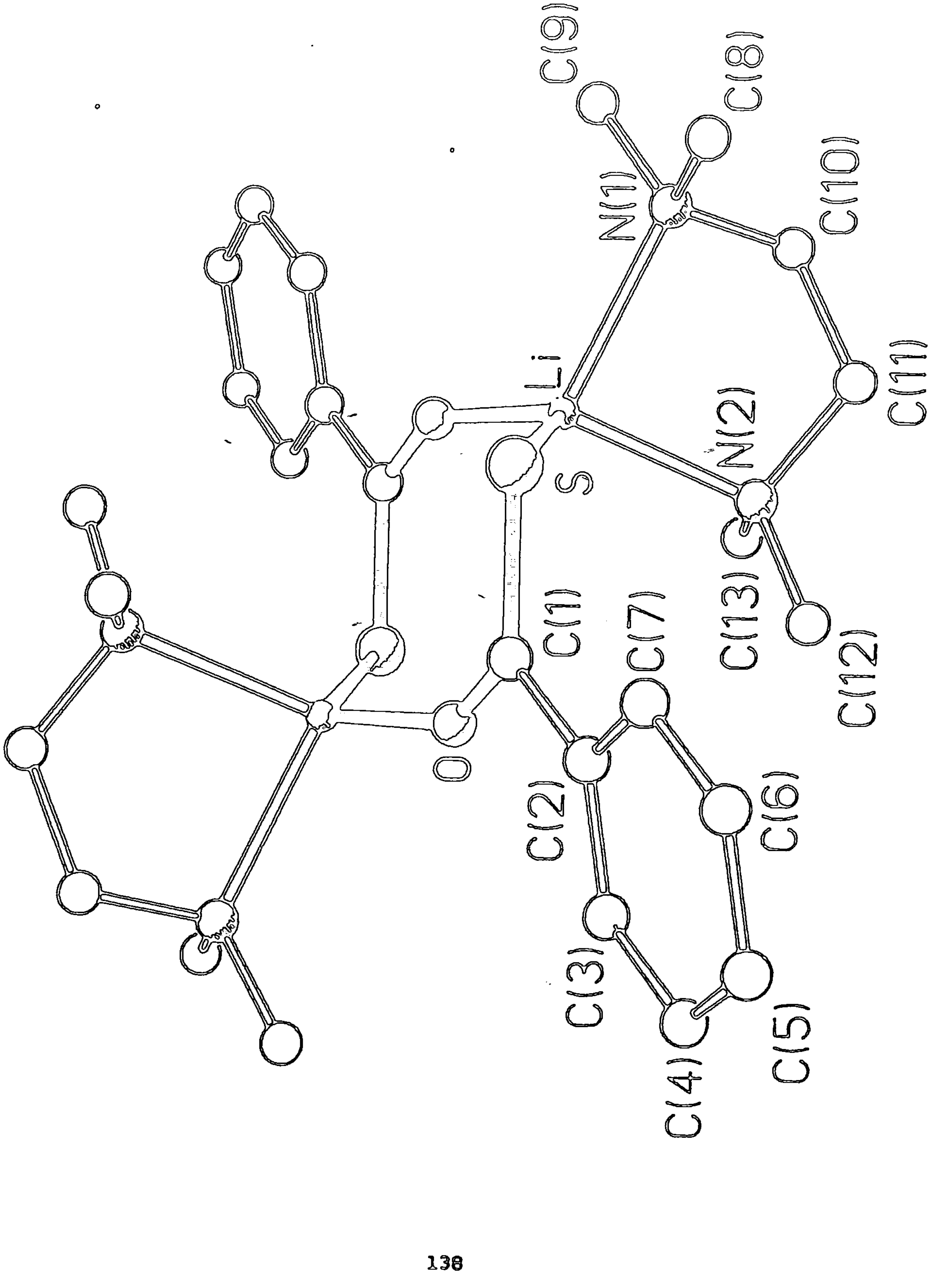
5.2 RESULTS AND DISCUSSION

5.2.1 Preparation of $[PhCOSLi.TMEDA]_2$

Pale yellow transparent crystals of the title compound were prepared by addition of thiobenzoic acid to a chilled solution of n-butyl lithium and TMEDA in toluene. The compound was sensitive to air and moisture and had to be handled under dry nitrogen. Microscopic examination of the crystals revealed that only a few were well facetted and a number of these were mounted in Lindeman glass capillaries for preliminary X-ray oscillation photographs. Most of these appeared to be twinned but two single crystals were sent to Newcastle for full X-ray structure determination.

As illustrated in Figure 5.2 $[PhCOSLi.TMEDA]_2$ crystallises as a centrosymmetric dimer with coplanar thiobenzoate anions. Each lithium completes its

Figure 5.2 Molecular Structure of [PhCOSLi.TMEDA]$_2$



appproximately tetrahedral environment by bonding to the N atoms of a TMEDA molecule; the Li-N distances, N-Li-N angles and C-N-Li angles (see Table 5.1) are typical of other Lithium-TMEDA complexes.[6] Clearly, lithium prefers to achieve such four co-ordination through dimerisation, bonding to the O and S atoms of two different anions, rather than remaining a monomeric complex, in which it would bridge O and S atoms in the same anion. Ab initio m.o. calculations at 6-31G level basis set (see Section 5.2.5) were carried out for uncomplexed HCOSLi and $(HCOSLi)_2$ (in the monomer with Li bridging O and S atoms and in the dimer with all atoms optimising planar) and show that there is an appreciable exothermic dimerisation energy of 52.4 kcal mol^{-1} (1kcal = 4.18 kJ).

In the anion of this complex both the C-O and C-S distances, 1.246(2) and 1.704(2) Å respectively, point to considerable multiple bond character (cf. 1.233 ∓ 0.001 Å for the shorter C-O bond in carboxylic acids and esters, 1.160 ∓ 0.001 Å for the C-O bond in CO_2, 1.71 ∓ 0.01 Å for the C-S bond in thioureas, 1.555 ∓ 0.001 Å for the C-S bond in CS_2, COS, CSTe),[7] implying that the PhCOS units are predominantly ionic, and held together by (TMEDA.Li) cations. In the ab initio structure of $(HCOSLi)_2$, the C-O and C-S distances are in close agreement with the above,

(cont. on p. 144)

Table 5.1 Bond lengths (Å) and bond angles (°) for $[PhCOSLi.TMEDA]_2$.

Bond lengths (Å)

Li-S	2.478(4)	Li-N(1)	1.194(5)
Li-N(2)	2.135(4)	Li-O'	1.881(4)
S-C(1)	1.704(2)	O-C(1)	1.246(2)
N(1)-C(8)	1.463(3)	N(1)-C(9)	1.465(4)
N(1)-C(10)	1.473(3)	N(2)-C(11)	1.475(4)
N(2)-C(12)	1.462(4)	N(2)-C(13)	1.461(3)
C(1)-C(2)	1.501(3)	C(2)-C(3)	1.390(3)
C(2)-C(7)	1.384(2)	C(3)-C(4)	1.383(4)
C(4)-C(5)	1.369(3)	C(5)-C(6)	1.372(3)
C(6)-C(7)	1.382(4)	C(10)-C(11)	1.495(4)

Bond Angles (°)

S-Li-N(1)	106.7(1)	S-Li-N(2)	109.4(2)
N(1)-Li-N(2)	86.1(2)	S-Li-O'	124.2(2)
N(1)-Li-O'	108.4(2)	N(2)-Li-O'	114.8(1)
Li-S-C(1)	98.4(1)	C(1)-O-Li'	147.1(2)
Li-N(1)-C(8)	112.1(2)	Li-N(1)-C(9)	115.3(2)
C(8)-N(1)-C(9)	108.7(2)	Li-N(1)-C(10)	100.7(2)
C(8)-N(1)-C(10)	111.6(2)	C(9)-N(1)-C(10)	108.3(2)
Li-N(2)-C(11)	102.7(2)	Li-N(2)-C(12)	116.2(2)
C(11)-N(2)-C(12)	108.7(2)	Li-N(2)-C(13)	108.9(2)
C(11)-N(2)-C(13)	111.0(2)	C(12)-N(2)-C(13)	109.1(2)
S-C(1)-O	124.5(2)	S-C(1)-C(2)	119.1(1)
O-C(1)-C(2)	116.4(2)	C(1)-C(2)-C(3)	119.4(2)
C(1)-C(2)-C(7)	122.5(2)	C(3)-C(2)-C(7)	118.1(2)
C(2)-C(3)-C(4)	120.8(2)	C(3)-C(4)-C(5)	120.2(2)
C(4)-C(5)-C(6)	119.8(2)	C(5)-C(6)-C(7)	120.3(2)
C(2)-C(7)-C(6)	120.8(2)	N(1)-C(10)-C(11)	112.7(3)
N(2)-C(11)-C(10)	112.6(2)		

Table 5.2 Atomic co-ordinates for $[\mathrm{PhCOSLi.TMEDA}]_2$

Atom	x	y	z
Li	5644(4)	-711(4)	6338(3)
S	5679(1)	1981(1)	7539(1)
O	3608(2)	1231(2)	5303(1)
N(1)	6900(2)	-1364(2)	7828(2)
N(2)	3443(2)	-2527(2)	6471(2)
C(1)	3973(2)	1839(2)	6566(2)
C(2)	2782(2)	2442(2)	7250(2)
C(3)	1260(2)	2085(3)	6498(2)
C(4)	127(3)	2602(3)	7103(2)
C(5)	506(3)	3502(3)	8454(2)
C(6)	2013(3)	3890(3)	9206(2)
C(7)	3139(2)	3352(2)	8614(2)
C(8)	7337(3)	-180(3)	9192(2)
C(9)	5618(3)	-1646(4)	7482(3)
C(10)	5618(3)	-2911(3)	7758(3)
C(11)	3955(3)	-2878(3)	7683(3)
C(12)	2047(3)	-2064(3)	6670(3)
C(13)	2959(3)	-3936(3)	5249(3)

Table 5.3 Anisotropic thermal parameters ($Å^2 \times 10^3$) for $[PhCOSLi.TMEDA]_2$.

The anisotropic temperature factor exponent takes the form $-2\pi^2(h^2a^{*2}U_{11} + ... + 2hka^*b^*U_{12})$

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Li	55(2)	59(2)	44(2)	11(1)	14(1)	30(2)
S	60(1)	72(1)	79(1)	1(1)	4(1)	42(1)
O	74(1)	92(1)	45(1)	4(1)	19(1)	36(1)
N(1)	59(1)	77(1)	54(1)	23(1)	12(1)	37(1)
N(2)	54(1)	61(1)	60(1)	18(1)	10(1)	26(1)
C(1)	53(1)	46(1)	48(1)	8(1)	16(1)	19(1)
C(2)	45(1)	43(1)	39(1)	14(1)	9(1)	19(1)
C(3)	54(1)	72(1)	46(1)	13(1)	7(1)	22(1)
C(4)	49(1)	100(2)	77(1)	28(1)	11(1)	37(1)
C(5)	65(1)	90(2)	79(1)	22(1)	28(1)	47(1)
C(6)	78(1)	78(1)	51(1)	9(1)	21(1)	43(1)
C(7)	57(1)	61(1)	40(1)	13(1)	9(1)	31(1)
C(8)	96(2)	109(2)	56(1)	16(1)	1(1)	46(2)
C(9)	81(2)	124(2)	97(2)	45(2)	25(1)	67(2)
C(10)	82(2)	90(2)	88(2)	46(1)	11(1)	44(1)
C(11)	73(2)	92(2)	85(2)	46(1)	19(1)	30(1)
C(12)	58(1)	86(2)	104(2)	29(1)	20(1)	32(1)
C(13)	87(2)	71(2)	88(2)	3(1)	11(1)	24(1)

Table 5.4 H atoms: atomic co-ordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$).

	x	y	z	U
H(3)	992	1472	5547	72
H(4)	-928	2328	6576	89
H(5)	-281	3863	8872	88
H(6)	2287	4538	10149	81
H(7)	4182	3612	9155	62
H(8a)	6412	91	9379	107
H(8b)	8244	763	9199	107
H(8c)	7643	-581	9875	107
H(9a)	9189	-622	7552	109
H(9b)	8128	-2370	6569	109
H(9c)	8752	-2081	8100	109
H(10a)	5614	-3732	6964	97
H(10b)	5873	-3161	8556	97
H(11a)	3956	-2063	8480	96
H(11b)	3181	-3909	7655	96
H(12a)	1722	-1845	5873	98
H(12b)	2331	-1123	7454	98
H(12c)	1155	-2940	6779	98
H(13a)	3857	-4271	5135	107
H(13b)	2679	-3655	4475	107
H(13c)	2026	-4800	5328	107

being 1.270 and 1.725 A repectively and the bond indices for these bonds are 1.559 and 1.572 respectively. The charges on O (-0.780 e), S (-0.166 e) and Li (+0.697 e) also support a largely ionic formulation.

However, the crystal structure of $[PhCOSLi.TMEDA]_2$ shows that there is a remarkable difference between C-S-Li (98.1(1) °) and C-O-Li (147.1(2) °), suggesting that there is significantly more covalent character in the Li-S bond compared with Li-O. Once more this is supported by the *ab initio* calculations on $(HCOSLi)_2$ which give Li-S and Li-O bond indices of 0.487 and 0.360 respectively.

The particularly interesting structural feature found for this complex is the placement of the Li atoms above and below the $(COS)_2$ ring plane. It is unfortunate that there are no $(RCOOLi.D)_n$ (D = ligand) structures available for direct comparison. Lithium amides $(R_2NLi)_n$, however, also often adopt an $(NLi)_n$ ring structure (cf. organolithiums and alkoxy lithiums which commonly prefer clustered arrangements),[1,8] but these are perfectly planar e.g. when n = 4, by calculation with R = H[9] and by X-ray diffraction with R = $Me_2C(CH_2)_3CMe_2N$.[10] In addition the *ab initio* calculations on $(HCOSLi)_2$ show that this is also completely planar and if the starting model used is based on a chair shaped structure it becomes planar during optimisation. However, comparison of the angles in

$[PhCOSLi.TMEDA]_2$ with the calculated model $(HCOSLi)_2$ shows significant differences. In the optimised structure, although the preferred angle at S (70.2 °) is already low, with S well away from the TMEDA, the angles at O (185 ° i.e. re-entrant O) and at Li (162.7 °) are very much larger (cf. 147.1 ° and 124.2 ° respectively in $[PhCOSLi.TMEDA]_2$). It is clear that the Li atoms in $(HCOSLi)_2$ could not possibly accommodate a bidentate donor each and achieve approximately tetrahedral configuration and also remain planar with the $(COS)_2$ unit. There needs to be considerable reduction in the angles at O and Li and this is accomplished in $[PhCOSLi.TMEDA]_2$ by the Li atoms displacing themselves out of the ring plane.

^7Li high field n.m.r. spectra at 20 and −95 °C in $[^2H_8]$ toluene solutions show only a sharp singlet, indicating the presence of only one lithium species in solution. In view of the structure in the solid, it seems likely that the dimer only is present in solution and that there is no detectable equilibrium between chair and boat conformations of the dimeric ring at the lowest temperature used.

Thiobenzoic acid has been frequently used as a ligand in transition metal chemistry but there is no structure comparable with that described above. The thiobenzoate anion similarly acts as a bidentate donor in the complex $[Ni(PhCOS)_2]_2.EtOH$.[11,12] In this complex the thiobenzoate groups bridge the two Ni atoms, one of which is surrounded by the four S atoms and the other by the four O atoms of the acid residues. Both Ni atoms complete six co-ordination by further weak interactions. The C-S bond length (av. 1.709(10) Å) and the C-O bond length (av. 1.247(12) Å) are similar to those found in $[PhCOSLi.TMEDA]_2$ above.

In zinc monothiobenzoate, $Zn(PhCOS)_2.2H_2O$, the monothiobenzoate groups bond as unidentate ligands through sulphur. Zinc is in a distorted tetrahedral configuration bonded to the two S atoms of the two equatorial ligands and the two O atoms from the two water molecules.[13]

Unidentate bonding is also present in the complex $Sb(PhCOS)_3$ with the thiobenzoate ligand co-ordinated through S. There is some secondary bonding between Sb and the O atoms of the ligand. This unsymmetrical co-ordination is reflected in the C-S and C-O bond lengths (1.77(2) and 1.23(2) Å respectively).[14]

In each of the above examples the phenyl ring is tilted with respect to the COS plane and, therefore, conjugation between the COS group and the phenyl ring is unlikely.

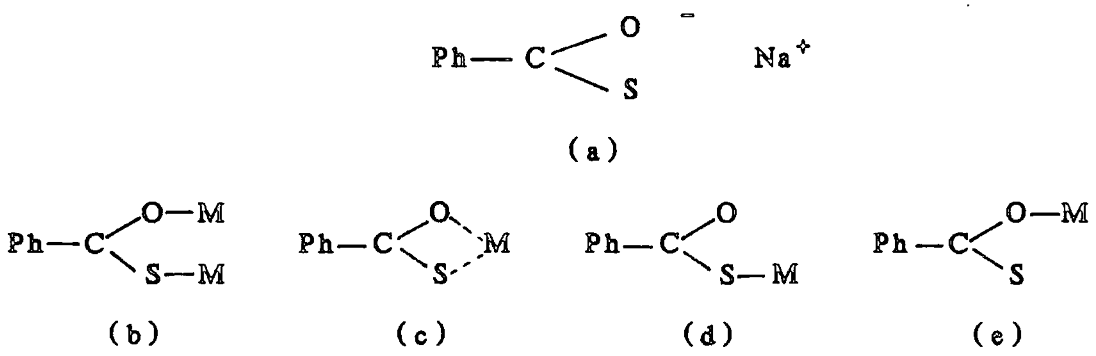
$[PhCOSLi.TMEDA]_2$ can also be compared to complexes such as $\{Me_2M[MeC(NMe)_2]\}_2$, where M = Al or Ga. These complexes form similar puckered eight membered rings where the central portion is coplanar and the metal atoms are above and below the ring plane. In this case, however, the ring angles are not so divergent, with all of them in the range 111-123 °.[15] Dimethylaluminium N-phenylbenzimidate, $[Me_2AlOCPhNPh]_2$, also crystallizes as a centrosymmetric eight membered ring with Al atoms bridged by OCN groups.[16]

5.2.2 Infra red data on $[PhCOSLi.TMEDA]_2$

In 1959 Nyquist and Potts[17] investigated the characteristic I.R frequencies of thiol acids and esters. Their published spectrum for thiobenzoic acid, in which they assign ν(C-S) at 949 cm^{-1}, ν (S-H) bend at 835 cm^{-1}, ν(S-H) stretch at 2585 cm^{-1} and ν(C=O) at 1690 cm^{-1}, is in close agreement with that measured in this investigation (see Table 5.18)

The infra red characteristics of some metal monothiobenzoates and their relationship to structure was reported by V. V. Savant et al in 1970.[18] Their results were based on a comparison of ν(C-O) and ν(C-S) of the complexes with those of the sodium salt. Sodium monothiobenzoate gives ν(C-O) and ν(C-S) at 1500 and 960 cm^{-1} respectively; this decrease in ν(C-O) and slight increase in ν(C-S) compared to monothiobenzoic acid was taken as an indication of an ionic structure - see Figure

5.3(a). Savant et al used the comparison of the ν(C-O) and ν(C-S) in the complexes with those in the sodium salt to distinguish the type of bonding between the monthiobenzoate anion and the metal centre. Bonding of the type shown in Figure 5.3(b) is expected to cause both ν(C-O) and ν(C-S) to decrease and this was not found in any of the complexes studied. If the bonding is that represented in Figure 5.3(c) then both absorptions should remain unchanged e.g. Ni(II) complex. When the metal co-ordinates only to sulphur as in Figure 5.3(d) then ν(C-O) should increase and ν(C-S) decrease whereas if the stronger bond is between the metal and the oxygen then ν(C-O) decreases and ν(C-S) increases.



(a) (b) (c) (d) (e)

Figure 5.3 Possible bonding modes for the monothiobenzoate anion.

Examination of the infra red spectrum of $[PhCOSLi.TMEDA]_2$ (see Table 5.18) and comparison with the above figures is not conclusive. However, the strong absorption at 1522 cm^{-1} can be assigned to ν(C–O) while ν(C–S) is probably the split band at 954 and 939 cm^{-1}. Following the above reasoning this would be an indication of an increased bond strength between lithium and sulphur as has already been proposed from other data.

5.2.3 Reactions of benzoic acid with n-butyl lithium and TMEDA.

A crystal structure of a polycrystalline film of lithium benzoate has been reported in a brief publication by M. M. Stasova.[19] There are no structures reported where the addition of other donor ligands enables lithium to achieve a higher co-ordination number without formation of a polycrystalline lattice. In order to compare the structure of $[PhCOSLi.TMEDA]_2$ with the analogous complexes where first sulphur is replaced by oxygen, as in benzoic acid, and then oxygen is replaced by sulphur, as in dithiobenzoic acid, attempts were made to prepare the complexes, $[PhCOOLi.TMEDA]_n$ and $[PhCSSLi.TMEDA]_n$.

Benzoic acid was reacted with n-butyl lithium in the presence of TMEDA. A white insoluble powder was produced in both hexane and toluene. Elemental analysis data show no nitrogen, and lithium analysis is consistent with a formula $[PhCOOLi]_n$ i.e. TMEDA has not co-ordinated to lithium. Further experiments are planned using only TMEDA as a solvent.

5.2.4 Reactions of phenyl lithium with carbon disulphide and TMEDA.

Dithioacids are reported to be highly coloured and unstable. One method of preparation is by reacting an alkyl or aryl lithium with carbon disulphide and treating with acid solution to liberate the free acid. In this investigation isolation of the lithio derivative of the dithio acid made liberation of the free acid unnecessary.

Addition of carbon disulphide to a chilled solution of phenyl lithium in toluene (or hexane) and TMEDA immediately produced a deep red colouration. Carrying out the reaction in hexane and cooling allowed red crystals to form but on filtration these became powdery. The product is very soluble in toluene and only precipitated out of this reaction on addition of hexane. Elemental analysis is consistent with a formulation $[PhCSSLi.TMEDA]_n$. Experimentation with mixed solvents is envisaged in order to isolate crystals. A further possible complication of this reaction is the fact that the phenyl lithium is obtained as a solution in cyclohexane/ether so that two potential donor ligands i.e. diethyl ether and TMEDA are present in solution.

5.2.5 *Ab initio* calculations on HCXYLi and $[HCXYLi]_2$ where X and Y are chalcogens(see Tables 5.5 - 5.13)

Ab initio molecular orbital calculations were carried out at Strathclyde University by Dr. D. Armstrong using a 6-31G basis set, on HCXYLi and $[HCXYLi]_2$, where X = Y = O; X = Y = S; X = S, Y =O; and the monomer has a four membered ring with Li bridging X and Y (see Figure 5.4)

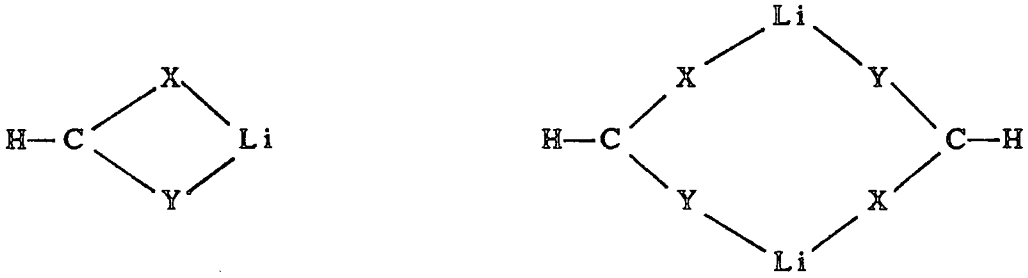


Figure 5.4 Arrangement of atoms in the monomer and dimer

For all three systems the dimer optimises planar and is more stable than the monomer, the dimerisation energies being in the order $[HCOOLi]_2 > [HCOSLi]_2 > [HCSSLi]_2$ (see Table 5.5). The bond angle at S is always smaller than that at O (see Table 5.7) but in the mixed anion the angle at S is 47 ° less than that in the dithio anion (70.2 and 117.0 ° respectively) while the angle at O is 44 ° greater than that in the formate (185.0 and 141.8 ° respectively). This is accompanied by a wide divergence in the angle at lithium i.e. 131.3, 162.7, 172.2 ° for $[HCOOLi]_2$, $[HCOSLi]_2$ and $[HCSSLi]_2$.

In planar $[HCOSLi]_2$ the large angles at O (185 ° i.e. re-entrant O) and at Li (162.7 °) are very much greater than those found in $[PhCOSLi.TMEDA]_2$ (147.1 and 124.2 ° respectively) and clearly Li is unable to accommodate the bidentate donor, TMEDA, in an approximately tetrahedral configuration and remain planar with the $(COS)_2$ unit. In this case reduction in the angles at O and Li is accomplished by the lithium atoms being displaced above and below the $(COS)_2$ ring plane.

Using similar reasoning it might be expected that the compound $(PhCOOLi.TMEDA)_n$ would be a dimer but with a much less buckled eight membered ring i.e. the $(COOLi)_2$ ring much closer to planar. In contrast $[PhCSSLi.TMEDA]_n$ should be dimeric with the lithium atoms again displaced out of the $(CSS)_2$ ring plane.

These ab initio calculations, and, in particular, the bond indices (which can be considered as a measure of covalent character[20]), confirm the earlier suggestion that, although these molecules must largely be considered to be ionic, there is greater covalent character in the Li-S bond than in the Li-O bond. In $(HCOSLi)_2$ the Li-S bond has a bond index of 0.487 which is substantially greater than that of the Li-O bond (0.360) and this increases still further in $(HCSSLi)_2$ to 0.645.

An overall largely ionic structure for these three systems is supported by the charge distribution figures (see Table 5.13). In summary, these calculations show an increase in covalency in the Li-X bond on going from two bonds where X = O to two bonds where X = S.

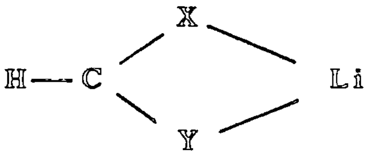
The geometry of the monothio derivative does, however, differ from the other two considerably (see Figure 5.5). $[HCOOLi]_2$ and $[HCSSLi]_2$ have symmetrical eight membered rings with $[HCOOLi]_2$ having internal angles closest to those of a regular octagon (135 °). The re-entrant angle at O in $[HCOSLi]_2$ gives this molecule a shape similar to that of two pentagons joined along the O-O axis. It also generates an Li-Li distance of 2.611 Å i.e. less than that found in lithium metal (3.04 Å) or gaseous lithium (2.67 Å).[21]

Table 5.5 Total energy (a.u.) and dimerisation energy (kcalmol^{-1}) for HCXYLi and [HCXYLi]$_2$.

Total Energy on Optimisation (a.u.)

Dimer	[HCOOLi]$_2$	[HCOSLi]$_2$	[HCSSLi]$_2$
	-391.33535	-1036.58845	-1681.82637
Monomer	HCOOLi	HCOSLi	HCSSLi
	-195.60826	-518.25250	-840.89320
Dimerisation Energy	74.559	52.359	25.079

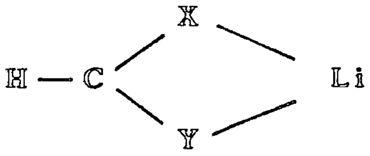
Table 5.6 Bond lengths (A) for the monomer HCXYLi



	HCOOLi (X=Y=O)	HCOSLi (X=S,Y=O)	HCOSLi(d) (X=S,Y=O)	HCSSLi (X=Y=S)
C-H	1.085	1.085	1.086	1.082
C-Y	1.271	1.255	1.264	
C-X		1.762	1.704	1.727
Li-Y	1.906	1.853	1.842	
Li-X		2.483	2.461	2.436
C-Li	2.191	2.393	2.374	2.665
X-Y	2.203	2.644	2.609	3.083

d = optimised with d orbitals on S

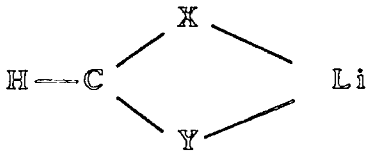
Table 5.7 Bond angles (°) for the monomer HCXYLi.



	HCOOLi (X=Y=O)	HCOSLi (X=S,Y=O)	HCOSLi(d) (X=S,Y=O)	HCSSLi (X=Y=S)
XYC	120.0	121.5	119.8	126.1
CYLi	84.7	98.8	97.9	
CXLi		66.1	63.3	77.7
YLiX	70.6	73.5	81.9	78.5
HCY	120.0	118.8	117.9	117.0
HCX	120.0	119.7	127.3	117.0

d = optimised with d orbitals on S

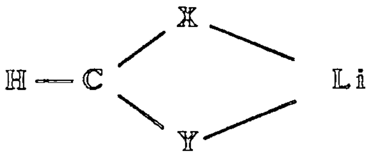
Table 5.8 Bond indices for the monomer HCXYLi



	HCOOLi (X=Y=O)	HCOSLi (X=S,Y=O)	HCOSLi(d) (X=S,Y=O)	HCSSLi (X=Y=S)
C-H	0.878	0.899	0.894	0.916
C-Y	1.644	1.742	1.699	
C-X		1.422	1.483	1.548
Li-Y	0.352	0.339	0.348	
Li-X		0.573	0.558	0.577
C-Li	0.120	0.115	0.111	0.107
X-Y	0.237	0.221	0.232	0.255

d = optimised with d orbitals on S.

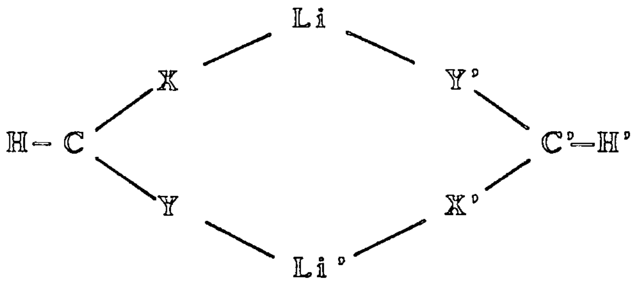
Table 5.9 Charge distribution for the monomer HCXYLi



	HCOOLi (X=Y=O)	HCOSLi (X=S, Y=O)	HCOSLi(d) (X=S, Y=O)	HCSSLi (X=Y=S)
H	+0.138	+0.178	+0.166	+0.235
C	+0.626	+0.044	+0.236	+0.608
Y	-0.744	-0.670	-0.705	
X		-0.256	-0.401	-0.111
Li	+0.725	+0.705	+0.705	+0.593

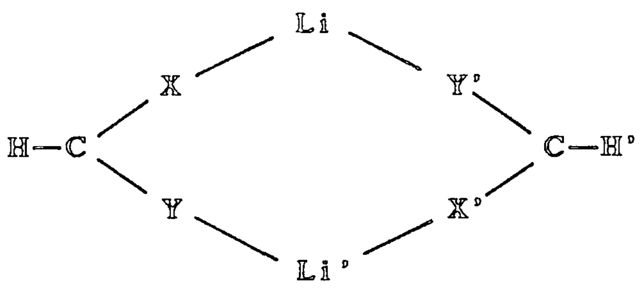
d = optimised with d orbitals on S

Table 5.10 Bond lengths (Å) for the dimer $(HCXYLi)_2$



	$(HCOOLi)_2$ (X=Y=O)	$(HCOSLi)_2$ (X=S,Y=O)	$(HCSSLi)_2$ (X=Y=S)
C–H	1.088	1.085	1.082
C–Y	1.262	1.270	
C–X		1.725	1.714
Li–Y'	1.781	1.791	
Li–X		2.576	2.380
X–Y	2.239	2.631	3.134
X–Y'	3.338	4.319	4.749
Li–Y	3.312	2.038	
Li–X'		4.288	4.06
Li–Li'	3.482	2.611	
X–X'		6.575	5.690
Y–Y'		2.812	

Table 5.11 Bond angles (°) in the dimer $(HCXYLi)_2$

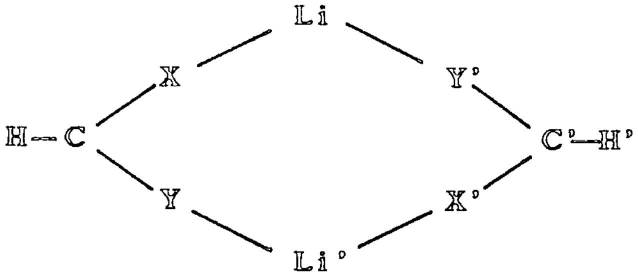


	$(HCOOLi)_2$ (X=Y=O)	$(HCOSLi)_2$ (X=S,Y=O)	$(HCSSLi)_2$ (X=Y=S)
YCX	125.1	122.1	132.1
CXLi		70.2	117.9
CYLi'	141.8	185.0	
XLiY'	131.3	162.7	172.2

Table 5.12 Charge distribution for the dimer $(HCXYLi)_2$

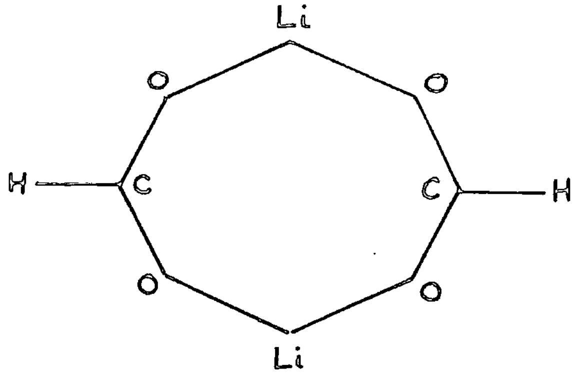
	$(HCOOLi)_2$ (X=Y=O)	$(HCOSLi)_2$ (X=S,Y=O)	$(HCSSLi)_2$ (X=Y=S)
H	+0.129	+0.186	+0.242
C	+0.685	+0.064	+0.559
Y	−0.767	−0.780	
X		−0.166	−0.104
Li	+0.719	+0.697	+0.524

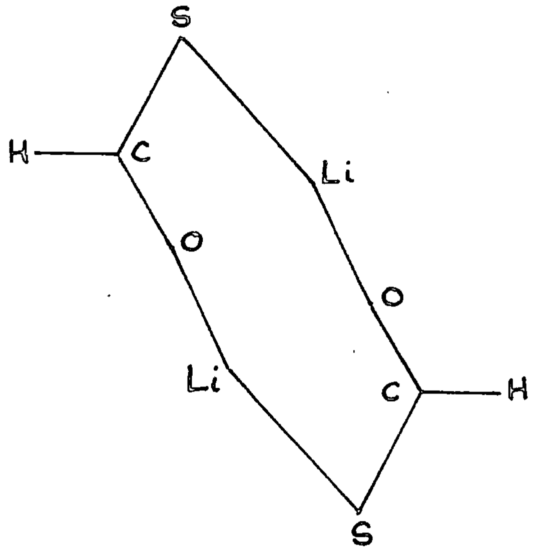
Table 5.13 Bond indices for the dimer $(HCXYLi)_2$

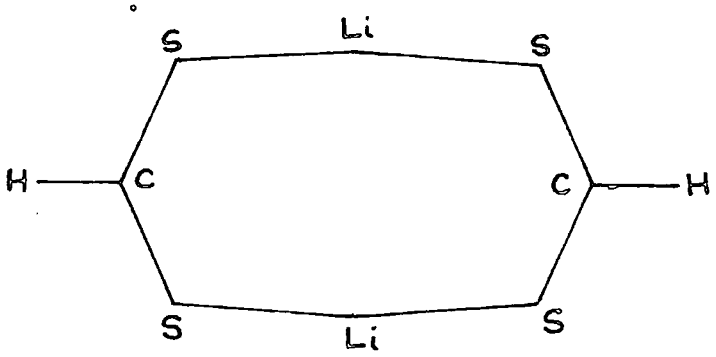


	$(HCOOLi)_2$ (X=Y=O)	$(HCOSLi)_2$ (X=S,Y=O)	$(HCSSLi)_2$ (X=Y=S)
C-H	0.883	0.895	0.919
C-Y	1.620	1.559	
C-X		1.572	1.560
Li-Y'	0.418	0.360	
Li-X		0.487	0.645
X-Y	0.210	0.214	0.229
Li-Y		0.188	
Li-Li'		0.075	

Figure 5.5 Geometry of the molecules $(HCXYLi)_2$







5.2.6 *Ab initio* calculations on HCOSLi and $HCOSLi.H_2O$

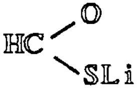
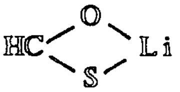
Ab initio calculations, again using a 6-31G basis set, were carried out to investigate the behaviour of the monomer HCOSLi both with and without a donor. Water being used in this model system. Results appear in Tables 5.14-5.17.

For the monomer, if the starting model places the lithium atom on the oxygen then this moves to a bridged structure on optimisation (see Figure 5.6)

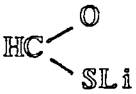
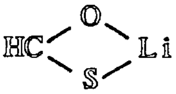
Figure 5.6 The starting and optimised structures of HCOSLi.

Placing the lithium atom on the S atom in the starting model does not result in a bridged structure on optimisation, but this conformation is less stable than the bridged structure by 26.82 $kcalmol^{-1}$

(cont. on p.168)

Table 5.14 Bond lengths (Å) and bond angles (°) for the model compounds  and .

Bond lengths (Å)

		
C–H	1.092	1.085
C–O	1.207	1.255
C–S	1.807	1.762
S–Li	2.235	2.483
O–Li		1.853

Bond angles (°)

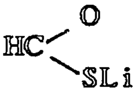
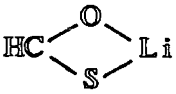
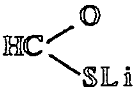
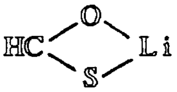
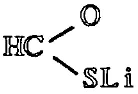
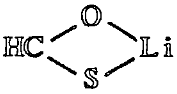
		
HCO	120.4	118.8
OCS	124.8	121.5
OLiS		73.5

Table 5.15 Bond indices and charge distribution for the monomers  and .

Bond indices

		
C–H	0.895	0.899
C–O	2.12	1.742
C–S	1.203	1.422
O–Li		0.339
S–Li	0.940	0.573

Charge Distribution

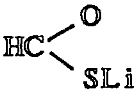
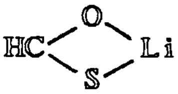
		
H	+0.119	+0.178
C	+0.076	+0.044
O	−0.459	−0.670
S	−0.344	−0.256
Li	+0.607	+0.705

Table 5.16 Bond lengths (Å) and bond angles (°) for HCOSLi.H_2O.

Bond lengths(Å)

	Planar	Perpendicular
C-H	1.086	1.086
C-O	1.253	1.253
C-S	1.759	1.758
O-Li	1.877	1.881
S-Li	2.554	2.564
Li-O'	1.861	1.873

Bond angles(°)

	Planar	Perpendicular
HCO	118.6	118.5
OCS	122.4	122.4
COLi	100.2	100.6
CSLi	65.7	66.0
SLiO	71.7	71.2

Table 5.17 Bond indices and charge distribution for $HCOSLi.H_2O$

Bond Indices

	Planar	Perpendicular
C–H	0.899	0.899
C–O	1.752	1.751
C–S	1.426	1.430
O–Li	0.333	0.330
S–Li	0.520	0.512
Li–O'	0.359	0.356

Charge Distribution

	Planar	Perpendicular
H	+0.165	+0.164
C	+0.047	+0.045
O	−0.660	−0.661
S	−0.292	−0.292
Li	+0.634	+0.638
O'	−0.711	−0.716

Two possible comformations were examined with water as a donor ligand on Li: the first of these is considered as a planar molecule, while the second has the H atoms of the water molecule perpendicular to the plane of the COSLi ring. Bond lengths, bond angles, bond indices and charge distribution are almost the same for both molecules (see Tables 5.16 and 5.17) but the planar molecule is slightly more stable i.e. by 0.9 kcalmol^{-1}.

5.3 CONCLUSIONS

Lithium derivatives of benzoic acid, monothiobenzoic acid and dithiobenzoic acid, using TMEDA as a second co-ordinating ligand, have been prepared. To date only the reaction with monothiobenzoic acid has produced crystals suitable for X-ray structure determination. $[PhCOSLi.TMEDA]_2$ forms clear, yellow crystals and is a centrosymmetric dimer containing a chair shaped eight membered $(COSLi)_2$ ring with the Li atoms displaced above and below the $(COS)_2$ plane. The lithium derivative of benzoic acid has been obtained as an insoluble white powder ; alteration of reaction conditions and/or solvents and more sophisticated crystal growth techniques may be needed to produce good crystals. There are also solubility problems with $[PhCSSLi.TMEDA]_n$ but it may be possible to solve these by a different hexane/toluene mixture.

Ab initio m.o. calculations on a series of model compounds where Ph is replaced by H and there is no donor ligand, optimise to planar structures. In $(HCOSLi)_2$ the large angle at Li indicates that in order for Li to accommodate a bidentate donor ligand it must move out of the ring plane. The calculated geometry of $(HCOOLi)_2$ suggests that, in this case Li could achieve tetrahedral co-ordination with a much smaller distortion in ring planarity.

The priority for future work is to prepare crystals of the lithium derivatives of benzoic and dithiobenzoic acids, after which it would be interesting to extend the work to other monothioacids to establish whether dimeric complexes containing an eight membered ring is the normal product.

5.4 EXPERIMENTAL

5.4.1 Preparation of $[PhCOSLi.TMEDA]_2$

TMEDA (1.16 g, 1.50 cm^3, 10 mmol) was added to a chilled (-20 °C) solution of n-butyl lithium (0.6406 g, 6.7 cm^3 of 1.49M solution in hexane, 10 mmol) in toluene (10 cm^3). PhCOSH (1.38 g, 1.18 cm^3, 10 mmol) was added dropwise to the pale yellow solution at −20 °C causing precipitation of a cream solid. Stirring was continued as the mixture warmed up to room temperature (20 °C), most of the solid dissolving to leave a cloudy liquid which did not clear on warming to 50 °C. The stirrer was stopped and the mixture left overnight. The pale yellow solid was filtered off, washed with hexane (3 x 5 cm^3) and dried under vacuum. Removal of a small amount of solvent (2 cm^3) from the yellow filtrate resulted in the precipitaton of pale yellow crystals. These were filtered off, washed with hexane (3 x 5 cm^3) and dried under vacuum. They were stored under nitrogen.

Yield: Insoluble solid 0.13 g, yellow crystals 0.89 g

% yield (crystals) 34%, based on $[PhCOSLi.TMEDA]_2$

Elemental analysis: S 12.84 %, N 10.62 %, Li 2.66 %,

C 60.0 %, H 9.3 %.

Calculated for $[PhCOSLi.TMEDA]_2$: S 12.32 %, N 10.76 %, Li 2.67 %, C 59.98 %, H 8.13 %

M.p. 122 °C

Infra red spectrum - see Table 5.18

Crystal data:

$[PhCOSLi.TMEDA]_2$, $C_{28}H_{42}N_4O_2S_2Li_2$, M_r = 520.64,

Triclinic, $P\bar{1}$, a = 8.876(2), b = 9.411(2), c = 10.428(2) Å

α = 106.34(1), β = 94.10(1), γ = 110.83(1) °,

$U = 767.57$ Å^3, $Z = 1$ dimer, $D_c = 1.126$ g cm^{-3}, $F(000) = 280$, λ(Mo-Kα) = 0.71073 Å, $\mu = 0.191$ mm^{-1}.

Data collection and processing: Crystal 0.38 x 0.69 x 0.73 mm, Siemens AED diffractometer, $T = 293$ K, cell parameters from 2 values of 32 reflections ($20 < 2\theta < 23°$), ω/θ scan, scan width 1.19 ° + α-doublet splitting, scan time 14-56 s, $h -10 \rightarrow 2$, $k -11 \rightarrow 11$, $l -12 \rightarrow 12$, $2\theta_{max}$ 50 °. 3 Standard reflections, no significant changes. No absorptiom or extinction corrections. 3597 reflections, 2693 unique ($R_{int} = 0.016$), 2226 with $F > 4\sigma(F)$.

Structure determination: Direct methods, blocked-cascade refinement on F, $w^{-1} = \sigma^2(F) + 0.00019F^2$. Anisotropic thermal parameters for non-H atoms, aromatic H on external bisectors of ring angles, aliphatic H-C-H 109.5 °, C-H 0.96 Å, $U(H) = 1.2U_{eq}(C)$. 175 parameters, $R = 0.043$, $R_w = 0.061$, max. (shift/e.s.d) = 0.002, mean = 0.001, slope of normal probability plot = 2.11, max. peak in difference synthesis 0.02 eÅ^{-3}, largest hole -0.17 eÅ^{-3}. Scattering factors from 'International Tables for X-ray Crystallography', Vol.IV, pp. 99, 149. Programs: SHELXTL (G. M. Sheldrick, Gottingen, 1985, Revision 5. N.m.r.: ^{7}Li in [$^2H_8$] toluene at -95 °C, $\delta = -0.9058$

5.4.2 Reaction of benzoic acid with n-butyl lithium and TMEDA in toluene.

n-Butyl lithium (0.320 g, 3.11 cm^3 1.61 M solution in hexane, 5 mmol) was added to a chilled (-20 °C) solution of benzoic acid (0.611 g, 5 mmol) in toluene (10 cm^3) and TMEDA (0.581 g, 0.75 cm^3, 5 mmol). A white precipitate was formed which became more dense on allowing to warm up to room temperature (20 °C). Addition of excess toluene (30 cm^3) and TMEDA(6 cm^3) and prolonged warming at 50 °C failed to dissolve the precipitate. It was filtered, washed with hexane (3 x 5 cm^3) and dried under vacuum. No solid was recovered on removal of solvent from the filtrate.

Yield: 0.38 g 60 % based on PhCOOLi

Elemental analysis: N 0 %, Li 5.75 %, C 64.7 %, H 3.6 %.

Calculated for PHCOOLi: Li 5.42 %, C 65.66 %, H 3.94 %.

Infra red spectrum: see Table 5.19

5.4.3 Reaction of benzoic acid with n-butyl lithium and TMEDA in toluene.

n-Butyl lithium (0.320 g, 2.92 cm^3 1.715 M solution in hexane, 5 mmol) was added to a chilled (-20 °C) solution of benzoic acid (0.61 g, 5mmol) in toluene (5 cm^3) and TMEDA (1.162 g, 1.5 cm^3, 10 mmol). A white precipitate was produced and the reaction mixture allowed to warm up to room temperature (19 °C). Addition of toluene (25 cm^3) and TMEDA (6 cm^3) and heating at 50 °C over 2 hours failed to dissolve the precipitate. The mixture was filtered hot and the fine white solid washed with hexane (3 x 5 cm^3) and dried under vacuum. Two thirds of the solvent was removed from the clear filtrate which was then left at -10 °C for several days. No solid precipitated out and no residue was obtained on removal of the remaining solvent.

Yield: 0.51 g, 79.70 % based on PhCOOLi.

Infra red spectrum: identical with 5.4.2.

5.4.4 Reaction of phenyl lithium with carbon disulphide in TMEDA and hexane.

Carbon disulphide (0.38 g, 0.30 cm^3,5 mmol) was added dropwise to a chilled (-20 °C) solution of phenyl lithium (0.42 g, 2.6 cm^3 1.95 M solution in 70/30 cyclohexane/ether, 5 mmol) in hexane (10 cm^3) and TMEDA (0.581 g, 0.75 cm^3, 5 mmol). The mixture turned from pale brown to deep red. After all the CS_2 had been added the mixture was allowed to warm up to room temperature (20 °C) when a red oil appeared at the bottom of the Schlenk. Heating with excess toluene (10 cm^3) did not dissolve this. The oil was filtered off leaving a deep red solution which was left at −10 °C overnight. Red crystals precipitated out but became powdery on filtration.

Yield: 0.31 g, 22.5 % based on $[PhCSSLi.TMEDA]_n$

Elemental analysis: S 24.97 %, Li 2.38 %, N 8.80 %.

Calculated for $[PhCSSLi.TMEDA]_n$: S 23.19 %, Li 2.5 %, N 10.13 %.

Infra red spectrum: see Table 5.20

5.4.5 Reaction of phenyl lithium with carbon disulphide in TMEDA and toluene.

Carbon disulphide (0.38 g, 0.30 cm^3, 5 mmol) was added dropwise to a chilled (−20 °C) solution of phenyl lithium (0.42 g, 2.6 cm^3 1.95 M solution in 70/30 cyclohexane/ether, 5 mmol) in toluene (10 cm^3) and TMEDA (1.54 g, 2.0 cm^3, 13.25 mmol). The colour became deep red with the first drop of CS_2 and deepened as addition continued. This solution was stirred at room temperature (20 °C) overnight. It was then left at −7 °C for 24 hr. and −15 °C for a further 24 hr. in a Haake bath but no precipitation occurred. Addition of hexane (2 cm^3) caused a red solid to precipitate, which was filtered, washed and dried.

Yield 0.44 g, 31.9 % based on $[PhCSSLi.TMEDA]_n$

Infra red spectrum: identical with 5.4.3

Table 5.18 Infra red spectrum of $[PhCOSLi.TMEDA]_2$ in wave no. cm^{-1} (nujol mull)

$[PhCOSLi.TMEDA]_2$	PhCOSH	TMEDA
3080 w.	3070 m.	
3060 w.		
2795 m.		
2780 m.sh		2760 s.
2720 w.		
1586 s.	1665 v.s.	
1520 v.s.	1598 m.	
1357 m.		1358 w.
1304 m.		
1292 s.	1290 w.	
1252 m.		1262 s.
1205 v.s.	1218 v.s.	
1187 w.	1182 s.	
1168 s.		1154 s.
1133 s.		1138 s.
1102 w.	1102 w.	
1075 s.	1078 m.	1062 v.s.
1040 s.		
1031 m.	1030 m.	
1023 s.		
1004 w.	1005 m.	
955 v.s.	957 s.	
938 s.		
790 v.s.	778 s.	
725 w.sh.	718 m.	
705 v.s.	692 v.s.	
664 s.	650 s.	
620 m.	618 m.	
588 m.		
560 m.		
490 s.	494 m.	
463 w.		
440 m.		

Table 5.19 Infra red spectrum of [PhCOOLi] in wave numbers cm^{-1} (nujol mull).

[PhCOOLi]	PhCOOH
3678 w.	
3078 w.	
3060 m.	
2730 v.w.	
1970 w.br.	1988 w.
1920 w.	1914 w.
1825 w.	
1627 m.	1670-1690 s.
1608 v.s.	1600 m.
1565 v.s.	1580 m.
1524 w.	
1492 m.	1494 m.
1434 v.s.	1420 s.
1412 m.sh.	
1318 m.	1325 s.
1308 m.	
1285 w.	1280-1290 s.
1182 w.	1180 s.
1151-1122 w.	1130s.
1112 w.	1102 m.
1077 s.	1076 s.
1030 s.	1030 v.s.
1006 m.	1004 s.
980 w.	995 m.
944 m.	940-920 s.
925 w.	
890 w.	
850 s.	
832 m.	812 s
725 v.s.	710 v.s.
696 s.	
684 s.	684 s.
617 w.	668 s.
546 m.	554 v.s.
490-498 s.	
445 m.sh.	
432 m.	432 m.
380 m.	

Table 5.20 Infra red spectrum of $[PhCSSLi.TMEDA]_2$ in wave numbers cm^{-1} (nujol mull)

$[PhCSSLi.TMEDA]_n$	TMEDA
3080 w.	
3060 w.	
2795 w.	
2720 w.	
1585 m.	
1408 m.	1450 s.
1355 s.	1358 w.
1300 m.	1280 m.sh.
1290 v.s.	1262 s.
1250 s.	
1210 v.s.	
1183 m.	
1172 v.s.	
1160 s.	1154 s.
1130 s.	
1098 m.	1096 m.
1084 v.s.	
1064 s.	1062 v.s.
1038 v.s.	
1027 s.	
1000 m.	
992 m.	
948 s.	962 m.
913 s.	
850 m.	872 m.
792 s.	
772 v.s.	763 m.
740-722 w.	
698 v.s.	
658 s.	
622 m.	
590 s.	
500 s.	490 w.
447 w.	
435 w.	

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APPENDIX 1

SOME REACTIONS OF SN COMPOUNDS WITH BORON DERIVATIVES.

A1.1 INTRODUCTION

Many boron-nitrogen heterocycles have been synthesized, but only the borazines, (-BR-NR'-)$_3$, have been studied in depth. More recently other six membered and some four and five membered ring compounds have been reported.[1,2]

Four, five and six membered boron-sulphur rings are well-known but not so well characterized as the boron-nitrogen rings.[1,3]

During the last fifteen years the synthesis of heterocycles containing boron, sulphur and nitrogen only have been reported in the literature. The five membered

(a) (b)

Figure A1.1

ring systems 1,2,dithia-4-aza-3,5,diborolidines (Figure A1.1(a), prepared from trithiadiborolanes and primary amines or substituted sulphinyl amines,[4-7] and 1,thia-3,5,-diaza-2,4,diborolidines (Figure A1.1(b)), prepared by reacting RS-BR-NR-NR-BR-SR with hydrogen sulphide,[7,8] have been investigated by H.Nöth et al and A. Mellor et al.

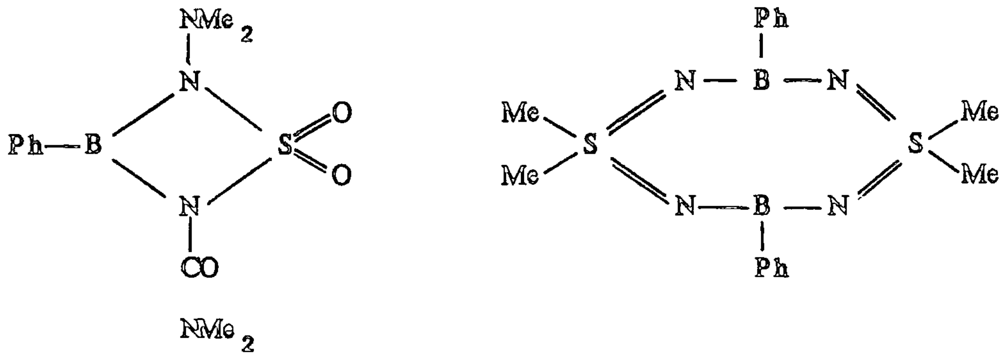
A number of six membered ring compounds have also been prepared. The reaction of 3,5,dimethyl-1,2,4,3,5,trithiadiborolane with a primary amine produces the compound shown in Figure A1.2(a), while Figure 1.2(b) shows compounds that can be prepared from 3,5,dibromo-1,2,4,trithia-3,5,diborolane azomethines.

(a) (b)

Figure A1.2

Figures A1.3 (a) and (b) show two other novel boron-sulphur-nitrogen heterocycles.[9,10]

Clearly, therfore, there are no shortage of ring systems containing boron, sulphur and nitrogen. Our own interest, however, was to make use of the complementary nature of sulphur-nitrogen compounds and boron



(a) (b)

Figure A1.3

derivatives. In tri-coordinated boron the octet is imcomplete and there is an unoccupied low-lying orbital, so that BX_3 compounds behave as acceptors towards those compounds with an electron excess. It was hoped that small reactive sulphur-nitrogen-boron species could be produced that could be used to build rings and cages of high stability.

A1.2 A brief overview of tetrasulphur tetranitride adducts.

Tetrasulphur tetranitride, S_4N_4, is the most readily prepared sulphur nitride and is used as a starting material for many other S-N compounds. It is obtained as orange-yellow, air stable crystals by passing NH_3 gas into a warm solution of S_2Cl_2 (or SCl_2) in CCl_4 or benzene. It is an eight-membered ring of alternating S and N atoms in a cage-like construction (see Figure A1.4), the four nitrogen atoms are in the same plane. All the S-N

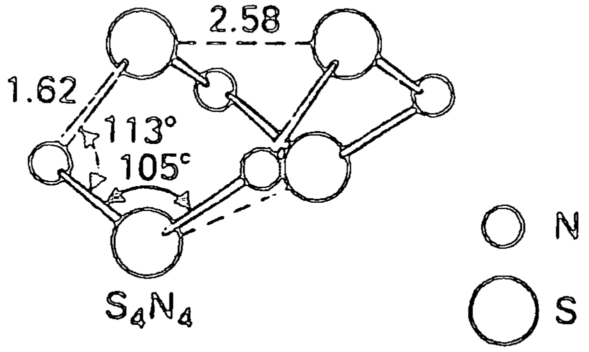


Figure A1.4

distances are similar (1.62 Å) and are short compared to the sum of the covalent radii (1.78 Å) and this has been attributed to a degree of delocalistion round the ring. There seems to be weak but structurally significant bonding between the pairs of sulphur atoms (2.58 Å).[11]

S_4N_4 has an excess of electrons and undergoes reactions where it behaves as an electron donor or Lewis base. It forms adducts with Lewis acids, many of which are already reported and discussed in the literature.[12,13] It was anticipated that an adduct between S_4N_4 and a trigonal boron species could be the basis for the subsequent formation of a boron-nitrogen-sulphur ring compound.

An examination of the literature showed that many of the S_4N_4 adducts already reported have a 1:1 stoichiometry but their structures were proposed on the basis of elemental analysis and spectral evidence. The first X-ray crystal structure was reported in 1960 by D.Neubauer and J. Weiss for the 1:1 adduct $S_4N_4.SbCl_5$.[14] It was found that co-ordination of the lone pair of electrons on one nitrogen to an acceptor site is sufficient to cause the cage structure of S_4N_4 to open in favour of a boat type arrangemnt with the ligand connected to one of the upper nitrogen atoms. The four sulphur atoms are now coplanar instead of the four nitrogen atoms, but the transannular S-S distances are 3.80 Å i.e. non-bonding. The structures of other adducts are similar e.g. $S_4N_4.BF_3$,[15] $S_4N_4.SO_3$,[16] $S_4N_4.FSO_2NCO$,[17] $S_4N_4.FeCl_3$,[18] $S_4N_4.AsF_5$,[19] $S_4N_4H^+BF_4^-$.[20] Many other adducts have been prepared with proposed structures similar to above.[21,22,23]

The crystal structure of $S_4N_4.CuCl$ is the only conclusive evidence for S_4N_4 behaving as a bidentate ligand,[24] although this is also proposed for the compounds $S_4N_4.2TiCl_4$ and $S_4N_4VCl_4$.[21]

The reaction of S_4N_4 with the boron halides has been investigated by K.J.Wynne and W.L.Jolly.[23] This work and subsequent reports concentrated on $S_4N_4.BF_3$ and

$S_4N_4.BCl_3$. They also described the preparation of $S_4N_4.BBr_3$ but investigated the reaction no further. This work was never extended to BI_3.

The action of the boron halides as Lewis acids is well documented and it is now recognised that the order of reactivity is $BF_3 < BCl_3 < BBr_3 \sim BI_3$. Although boron tri-iodide is considered to be the strongest Lewis acid, it has been much less thoroughly investigated than the other boron trihalides. In view of the earlier work it seemed likely that the reaction of S_4N_4 with BI_3 would give the adduct $S_4N_4.BI_3$ and that this could on pyrolysis lose iodine to form an S-N-B heterocycle. This, therefore, formed the starting point of this investigation.

A1.3 RESULTS AND DISCUSSION

A1.3.1 Reactions of S_4N_4 and BI_3

(For experimental details see p.194)

Several preparations were carried out with tetrasulphur tetranitride, S_4N_4, and boron tri-iodide, BI_3. The final product, a maroon amorphous solid, proved difficult to positively identify. Unlike the reaction of S_4N_4 with BF_3 and BCl_3 it does not form a simple 1:1 adduct with BI_3. Elemental analysis indicates that the product is not $S_4N_4.BI_3$ and this is supported by the fact that iodine is liberated during the reaction. The product was insoluble in common solvents and all attempts at recrystallisation failed. Elemental analysis was not conclusive but indicated the possible empirical formula, $S_3N_3.BI$. A reaction scheme for this is shown below:

$$4S_4N_4 + 4BI_3 \longrightarrow 4S_3N_3BI + 4I_2 + S_4N_4$$

This argument is strengthened by the fact that both iodine and small amounts of S_4N_4 can be recovered at the end.

Attempts to explain the structure using simple valence bond models are unsatisfactory. It is, however, possible to propose a Wade cage structure in the following way: the boron atom contributes one electron, each sulphur atom four and each nitrogen three, giving a total of twenty two skeletal bonding electrons. These eleven pairs could give rise to a ten vertex polyhedron in which seven vertices would be occupied by the three sulphur atoms, three nitrogen atoms and the boron atoms. This leaves the spare electron on boron which could form the basis of sulphur-sulphur interaction between two cages. A possible structure appears in Figure A1.6.

A second strong possibility is that the product is polymeric and this is supported by the insolubility and poor infra red spectrum. It would also explain the lack of a definite melting point. (S_4N_4 adducts are usually crystalline products with well defined melting points.)

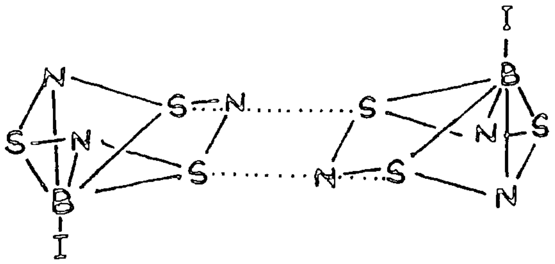


Figure A1.6 Hypothetical Cage Structure of S_3N_3BI

The preparation could also be complicated by secondary reactions taking place between the unreacted S_4N_4 and the iodine liberated. Monteil and Vincent report that S_4N_4 reacts with iodine to give a product analysing to $(SN)_3I$, but this reaction is slow at room temperature and hence unlikely at 0 °C.

Extensive attempts were made to solve the structure using mass spectroscopy, but neither electron ionisation or chemical ionisation proved helpful. There was no obvious molecular ion, the only fragments to be positively assigned were I, I_2 and S_x and many expected SN species were absent. The majority of peaks could not be identified even with the help of computer searching.

It is, however, not unusual for BI_3 to show unpredictable Lewis acid behaviour. E.g. BF_3 and BCl_3 form simple adducts with HMPA while BI_3 forms the compound

$(Me_2N)_3POBI_3(Me_2N)_2PIOI$[26] caused by breaking the P-N bond and although BI_3 forms 1:1 adducts with trimethylamine and dimethylthioformamide with pyridine it forms a complex $(BI_3-2C_5H_5N)$ thought to be

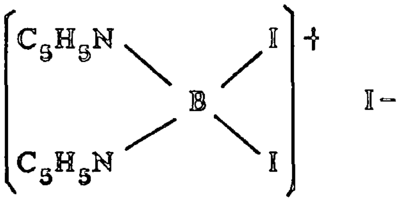


Figure A1.7

All the reactions were complicated by the light sensitivity of the product and by the large amounts of iodine liberated.

A1.3.2 Reactions of 4-phenyl-1,2,3,5,dithiadiazole dimer and boron tri-iodide.

The major product of this reaction is the same whatever the molar ratio of the reactants; when the ratio of $(PhCN_2S_2)_2:BI_3$ is 1:2 this dark red powder is produced in 80 % yield. Elemental analysis indicates that the empirical formula is $PhCN_2S_2.BI_3$ and it is most probable that this is an adduct between one nitrogen atom of the dithiadiazolium ring and the boron atom of BI_3.(see Figure A1.8)

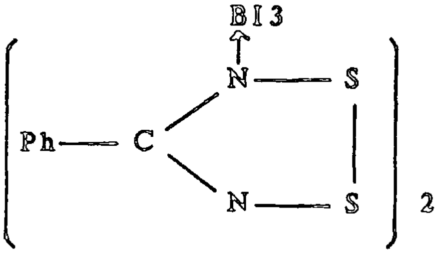


Figure A1.8 Proposed structure of the adduct $[PhCN_2S_2.BI_3]_2$

Heating this compound in a sealed capillary under nitrogen gave a m.p. of 130 °C, continued heating showed no evolution of iodine below 175 °C. This is unexpected considering the reactivity of the B-I bond.

Alteration of the molar ratio of the reactants gave a second product, orange microcrystals, in very low yield. To date only sufficient material for an infra red spectrum has been obtained.

A1.3.3 Reactions of S_4N_4 with 9-borabicyclo(3,3,1)nonane (9BBN).

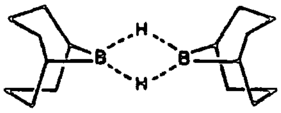


Figure A1.9 Structure of 9-BBN

9-BBN is a highly selective hydroborating agent. In reactions involving the hydroboration of olefins it gives a very high yield of the least hindered product.[28] 9-BBN forms stable complexes with tertiary amines such as triethylamine, pyridine and γ-picoline, but complexes are less stable with amines that are more sterically demanding.[29]

The infra red spectrum of this molecule shows a strong absorption at 1560 cm^{-1} either as a mineral oil mull or in solution. This indicates the presence of a boron-hydrogen-boron bridge confirming that 9-BBN is normally a dimer (see Figure A1.9). In the spectra of the complexes the B-H-B bridging frequency disappears to be replaced by a terminal BH frequency so that in these compounds it is the monomer that is complexing the amine.

The $S_4N_4.BI_3$ work suffered from two main disadvantages: (1) polymeric products and (2) high light and air sensitivity of the product. 9-BBN was considered as an acceptor because it had much better air stability than most boron compounds, making it easier to handle, and the steric hindrance of the ring reduces the reaction possibilities and makes polymer formation unlikely.

Elemental analysis of the product from the reaction of 9-BBN with S_4N_4 gave an empirical formula $S_4N_4.(9BBN)_2$. The infra red spectrum shows that the B-H-B bridging frequency has disappeared (this frequency is strong in the pure compound) indicating that 9-BBN dimer has broken down so the product could have one 9-BBN monomeric unit attached to each of two nitrogen atoms of the S_4N_4 ring. However, this would leave terminal BH groups on the molecule and these are not picked up in the infra red spectrum.

A1.3.4 Reactions of $(PhCN_2S_2)_2$ with 9-BBN.

Elemental analysis of the product corresponds to an empirical formula ($PhCN_2S_2$-9BBN). The infra red spectrum shows that the B-H-B bridge frequency is still strong, indicating the presence of 9-BBN dimer. This could be the way it is bound in the complex or the product could be contaminated with unreacted 9-BBN dimer.

The complexes formed from 9-BBN were very soluble in both THF and dichloromethane and analogy with the reactions of 9-BBN and pyridine[29] show that choice of solvent mix is extremely important to produce a crystalline product. Experimentation with other solvents is needed to achieve good crystals.

A1.4 CONCLUSIONS

Despite the problems already encountered with the S_4N_4/BI_3 reaction products i.e. high insolubility, extreme air and light sensitivity, there are advantages in the use of iodine derivatives. The B-I bond is the most reactive of all boron-halogen bonds and hence there is a greater possibility that thermolysis of compounds such as $S_4N_4.BI_n$ will cause loss of iodine and formation of S-N-B products. Pyrolysis experiments carried out so far have indicated that there may be crystalline derivatives. However, in view of the serious difficulties of the system, it seemed unprofitable to follow up this work.

Elemental analysis of the product from the reaction of 4-phenyl-1,2,3,5,dithiadiazole dimer and BI_3 gave the empirical formula ($PhCN_2S_2.BI_3$). Again problems of crystallinity were encountered and without an X-ray determination structural predictions are inconclusive.

Similar problems were met with the reactions of 9-BBN and it is difficult from the results obtained to predict the structure of such complicated systems.

In assessing this work and the problems it is clear that the use of starting materials with a complex molecular structure make it much more difficult to characterise unknown adducts without a definitive X-ray crystal structure.

A possibility for future work would be to use small reactive species such as S_2N^+ and the unknown $SNSO^+$ with suitable boron compounds e.g. (1) dico-ordinated boron molecules or (2) boron containing anions. E.g. thermolysis of the compound $SNSOBF_4$ may produce interesting rearrangements that could be monitored by ^{11}B n.m.r.

A1.5 EXPERIMENTAL

A1.5.1 Reaction of S_4N_4 and BI_3

Dichloromethane (30 cm^3) was added to S_4N_4 (0.3 g, 1.6 mmole) in a 100 cm^3 two-necked flask under a stream of nitrogen. The mixture was stirred at room temperature (20 °C until the S_4N_4 dissolved to give an orange solution, which was cooled to 0 °C in a Haake bath. A solution of boron tri-iodide (0.63 g, 1.6 mmole) in dichloromethane (8 cm^3) was added dropwise over 5 minutes keeping the temperature at 0 °C. A maroon precipitate formed and was filtered immediatly at 0 °C, dried under vacuum and stored in the absence of light under nitrogen. It is extremely important to protect the product from light so all the apparatus used was covered with aluminium foil. A lustrous grey solid was recovered by evaporation of the filtrate. Vacuum sublimation removed this grey solid to leave a small amount of orange crystals.

Elemental analysis - see Tables A1.1 and A1.2

Table A1.1

Elemental Analysis of Samples from Five Preparations

% Composition by weight

	S	N	B	I
1.	35.1	13.5		36.0
2.	34.8	14.6	3.5	40.9
3.	36.7	13.9		42.8
4.	31.3	12.4	3.6	54.8
5.	33.4	15.2		45.0

Table A1.2

Calculated % Composition

	S	N	B	I
$S_4N_4BI_3$	22.2	9.7	1.9	66.2
S_4N_4BI	39.8	17.4	3.4	39.5
$(S_4N_4)2BI_3$	33.7	14.7	1.4	50.1
S_3N_3BI	34.8	15.2	3.9	46.0

Yield: maroon solid - 0.29 g 85 % (based on S_3N_3BI)

grey solid - 0.28 g 70 % (based on I_2)

orange crystals - 0.04g 57 % (based on S_4N_4)

Infra red spectra (nujol mull): maroon solid - see Table A1.3.

grey solid - no trace.

orange crystals - identical with S_4N_4

Mass spectra - see Table A1.4

M.p. No decomposition or melting below 105 °C. Iodine was given off above this temperature condensing at the top of the capillary. No melting below 300 °C.

A1.5.2 Reaction of S_4N_4 with BI_3 in molar ratio 3:4

$$3S_4N_4 \quad + \quad 4BI_3 \quad = \quad 4S_3N_3BI \quad + \quad 4I_2$$

S_4N_4 (0.15g, 0.8 mmole) was dissolved in dichloromethane (25 cm^3) in a two necked flask under a stream of nitrogen at room temperature (20 °C). The orange solution was cooled to -5 °C and maintained at this temperature (± 0.1 °C) in a Haake bath. A solution of boron tri-iodide (0.43 g, 1.08 mmole) in dichloromethane was added dropwise producing a maroon precipitate. This was filtered immediately at 0 °C and washed with dichloromethane (3 x 5 cm^3), dried under vacuum and stored under nitrogen in the absence of light. A dark grey lustrous solid was recovered by removal of solvent from the purple filtrate. Vacuum sublimation of this left a few orange crystals in the flask.

Yield: maroon precipitate - 0.23 g 77 % (based on S_3N_3BI)

grey solid - 0.25 g 89 % (based on I_2)

orange crystals - too little to measure.

Infra red spectra : maroon solid - identical with A1.5.2

grey solid - no trace

orange crystals - identical with S_4N_4.

A1.5.3 Thermolysis of product of reaction between S_4N_4 and BI_3

0.1 g of the maroon solid from the S_4N_4/BI_3 reaction was weighed into clean dry tube (8 mm diameter) which was drawn out and sealed (see Figure A1.10). The lower part of the tube AB was covered in aluminium foil and immersed in a silicone oil bath at 100 °C for 2 hours.

Figure A1.10

After removal from the oil bath the bulb was examined under the microscope. Three distinct layers were found:

(1) A very small number (5-10) of tiny orange crystals at the top of the tube.

(2) A mixture of shiny grey crystals and red-black crystals in the middle of the tube. Yield 0.42 g

(3) The residue in the bottom of the tube. Yield 0.51 g

A1.5.4 Reaction of $(PhCN_2S_2)_2$ with BI_3, molar ratio 1:2

$(PhCN_2S_2)_2$ (0.1 g 0.28 mmole) was dissolved in dichloromethane (15 cm^3) in a 50 cm^3 two necked flask under a stream of nitrogen at room temperature (20 °C) and then cooled to 0 °C in a Haake bath. This temperature was maintained during dropwise addition of a solution of boron tri-iodide (0.22 g, 0.56 mmole) in dichloromethane (5 cm^3). The mixture was stirred at 0 °C for thirty minutes when a dark red precipitate appeared dispersed in a deep purple red solution. This was filtered cold (0 °C), washed with dichloromethane (3 x 5 cm^3), dried under vacuum and stored under nitrogen in the absence of light. Dichloromethane was removed from the purple red filtrate under vacuum to leave a red brown solid with shiny grey crystals in it. The latter were removed by vacuum sublimation.

Yield: precipitate - 0.27 g 84 % based on $(PhCN_2S_2.BI_3)_2$

grey solid 0.01g

Elemental analysis: precipitate - N 5.4 %, S 13.2 %, I 69.8 %.

Calculated for $(PhCN_2S_2.BI_3)_2$ N 4.9 %, S 11.2 % I 66.5 %.

M.p. 128-130 °C

Infra red spectrum (nujol mull) see Table A1.5

A1.5.5 Reaction of $(PhCN_2S_2)_2$ with BI_3, molar ratio 1:1

$(PhCN_2S_2)_2$ (0.1 g, 0.28 mmol) was reacted with BI_3 (0.11 g, 0.28 mmol) using the conditions described in section A1.5.4. A dark red solid precipitated, dispersed in an orange red solution. The precipitate was filtered, washed with dichloromethane (3 x 5 cm^3), dried under vacuum and stored under nitrogen in the absence of light. Removal of the solvent from the filtrate left an orange red solid in the flask.

Yield: precipitate 0.12 g, 38 % based on $(PhCN_2S_2.BI_3)$, orange red solid 0.035 g.

Infra red spectra: precipitate and orange-red solid - see Table A1.6.

A1.5.6 Reaction of $(PhCN_2S_2)_2$ with BI_3, molar ratio 1:4.

$(PhCN_2S_2)_2$ (0.05 g, 0.14 mmol) was reacted with BI_3 (0.22 g, 0.56 mmol) using the conditions described in A1.5.4. On addition of BI_3 the reaction mixture turned orange brown. A dark red solid was collected on filtration, washed with dichloromethane (2 x 5 cm^3) and dried under vacuum. Removal of the solvents from the filtrate gave a mixture of black and orange solids. The black solid was collected by vacuum sublimation leaving an orange residue.

Yield: dark red solid 0.08 g, 50 % based on $(PhCN_2S_2.BI_3)_2$
orange solid 0.03 g
black grey solid 0.04 g
Infra red spectra (nujol mull):
dark red solid identical with A1.5.4
orange solid would not mull
black grey solid no absorptions.

A1.5.7 Reaction of 9-borabicyclo(3.3.1)nonane (9-BBN) with 4-phenyl-1,2,3,5,dithiazole $(PhCN_2S_2)_2$ in tetrahydrofuran (THF).

9-BBN (0.12 g, 0.5 mmol) was dissolved in 5 cm^3 THF in a 50 cm^3 two necked flask under nitrogen at 18 °C. A solution of $(PhCN_2S_2)_2$ (0.18 g, 0.5 mmol) in THF (5 cm^3) was added dropwise and the reaction mixture stirred at 18 °C for 18 hours. Removal of THF under vacuum left a glass-like red solid.

Yield: 0.20 g 67 % based on $(PhCN_2S_2.9\text{-}BBN)_2$
M.p. 118-122 °C
Elemental analysis: N 8.4 %, S 19.7 %.

Calculated for $(PhCN_2S_2.9\text{-}BBN)_2$: N 9.3 %, S 21.2 %.

A1.5.8 Reaction of 9-BBN with S_4N_4 in dichloromethane.

S_4N_4 (0.184 g, 1 mmol) was dissolved in dichloromethane (30 cm^3) in a 100 cm^3 two necked flask under nitrogen. A solution of 9-BBN (0.244 g, 1 mmol) in dichloromethane (10 cm^3) was added dropwise at 20 °C stirring vigorously. After about one hour a dark red colouration had developed which became cloudy after a further 24 hours stirring at room temperature. Solvent was removed under vacuum to leave an orange solid.

Yield: 0.3 g 70 % (based on total reactants)
Elemental analysis: N 12.5 %, S 17.8 %, B 3.3 %
Calculated for $S_4N_4.(9\text{-}BBN)_2$: N 13.1 %, S 30.0 %, B 5.1 %
M.p. melted and resolidified at 120 °C, completely decomposed above 200 °C.
Infra red spectrum (nujol mull) see Table A1.7

A1.5.9 Reaction of S_4N_4 with 9-BBN in THF

S_4N_4 (0.184 g, 1 mmol) was dissolved in THF (20 cm^3) under nitrogen. A solution of 9-BBN (0.244 g, 1 mmol) in THF (10 cm^3) was added quickly, stirring vigorously, and the reaction mixture immediately turned very dark. A clear orange solution was obtained after stirring at 20 °C for 24 hours. Removal of solvent under vacuum left orange needles in the flask just above a very sticky residue. Attempts at recrystallisation from THF and dichloromethane were unsuccessful.

Infra red spectrum (nujol mull)

crystals	identical with product in A1.5.9.
residue	failed to form a mull.

Table A1.3 Infra red spectrum of $[S_4N_4.BI]_n$ (nujol mull) in wave no. cm^{-1}.

	Assignments	
$[S_4N_4.BI]_n$	S_4N_4	BI_3
1320 -1290 w.		
1168 w.		
980-950 w.		
935 w.	924 v.s.	
900-885 w.		
780 w.sh.		
740-715 m.	726 s.	724 s.

Table A1.4 Mass spectra for $[S_4N_4.BI]_n$ - major peaks.

E.I.	%HT.base	C.I.	%HT.base	Assignments
573.19	0.69	572.95	1.58	
571.22	1.62	570.93	3.68	
569.28	1.02	568.98	2.60	
		446.40	0.85	
444.52	1.71	444.41	1.78	
442.53	0.83	442.41	1.11	
		321.89	4.47	
		317.7	11.54	
255.98	2.36			S_8
253.89	51.30	253.86	98.13	I_2
191.91	4.49			S_6
		182.97	6.37	
		168.90	15.39	
159.84	2.64			S_5
149.03	7.64			
		141.89	36.74	
127.87	23.10			
126.84	32.18	126.80	5.87	I
91.87	12.64			S_2N_2
71.01	4.31			
69.00	7.55			
64.01	8.80			S_2
63.02	5.60			
61.99	5.69			
57.13	11.25			

Table A1.5 Infra red spectrum of $[PhCN_2S_2]_2/BI_3$ molar ratio 1:2.

	Assignments	
$[PhCN_2S_2]_2/BI_3$	$[PhCN_2S_2]_2$	BI_3
1597 w.		
1148 m.	1138 m.	
1024 m.	1024 m.	
922 m.	923 w.	
893 m.	900 w.	
830 s.	834 s.	
772 m.	778 s.	
723 m.	724 m.sh.	724 s.
684 v.s.	685 s.	680 s.
540 s.		

Table A1.6 Infra red spectra of the products of the reaction of $[PhCN_2S_2]_2$ and BI_3 in molar ratio 1:1.

		Assignments	
Maroon solid	Orange crystals	$[PhCN_2S_2]_2$	BI_3
1597 w.	1590-1620 w.		
	1550 w.		
	1270 w.		
1148 m.			
	1135 w.	1138 m.	
1024 m.	1020 m.	1024 m.	
	970 w.		
922 m.	925 v.w.	923 w.	
893 m.			
830 s.	825-835 w.		
	790 m.		
772 m.	770 m.		
723 m.		728 s.	
684 v.s.	690 m.	685 s.	680 s.
	655 w.		
	520 w.		
540 s.	455 m.		

Table A1.7 Infra red spectrum of 9BBN/S_4N_4

	Assignments	
9BBN/S_4N_4	9BBN	S_4N_4
3310 w.		
3225 w.		
1340 w.		
1296 w.	1300 w.	
1235 w.		
1215 w.	1210 s.	
1178-1160m		
1112 m.	1106 m.	
1082 w.		
975 w.		
966 w.		
930 w.		
908 m.	916 s,	
820 m.		
724 m.	720 m.	726 s.
700 m.		700 v.s.
545 m.		545 v.s.

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APPENDIX 2

REACTIONS OF SULPHURATED LITHIUM BOROHYDRIDE WITH DONOR LIGANDS.

A2.1 INTRODUCTION

Two papers by Lalancette and co-workers describe the reactions of alkali metal borohydrides with solid sulphur.[1,2] The products resulting from these reactions, the so-called sulphurated borohydrides, MBH_2S_3, are reported to be insoluble solids, the only solvent in which it was possible to dissolve $NaBH_2S_3$ being hexamethylphosphoramide, $O=P(NMe_2)_3$, (HMPA).

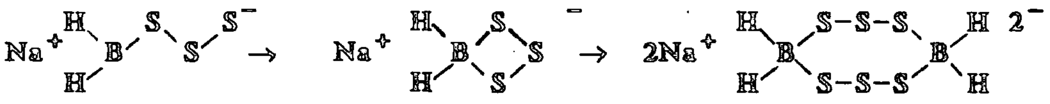
This particular feature of the compounds was the basis of our interest, since, by comparison with lithium structures already studied, it seemed possible that the dissolution of $NaBH_2S_3$ in HMPA was due to the formation of a soluble complex with HMPA chelating to the sodium atom. If, by varying the chelating ligand used, a crystalline complex could be formed, it might yield more information about the structure of these compounds and their role in reducing reactions.

The reaction described by Lalancette and co-workers involves the addition of anhydrous THF to a solid mixture of one mole alkali metal borohydride and three moles of sulphur. A few drops of solvent initiate the reaction and a brisk gas evolution is reported to start immediately, according to equation 1.

$$NaBH_4 + 3S \longrightarrow NaBH_2S_3 + H_2$$

Equation 1

Evidence for the proposed structure came partially from measurements of the hydrogen evolved during the reaction. Their plot of this against the number of moles of sulphur available in the reaction mixture showed that for one mole of hydride it remained constant at one mole of hydrogen when at least three moles of sulphur ($\frac{3}{8}\,S_8$) are available in the reaction mixture. Elemental analysis indicated a formulation $NaBH_2S_3$. The infra red spectrum showed a B-S absorption at 930 cm^{-1} but no indication of S-H absorptions. They proposed the following structural scheme:



An intimate mixture of sodium borohydride and sulphur is marketed by Aldrich Chem. Co. as Lalancette's reagent, which, on addition of tetrahydrofuran, becomes a powerful reducing agent.

The following sections describe a short preliminary investigation of the above system, particularly the lithium compound, with chelating ligands to establish the possibility of obtaining crystalline derivatives whose structures could be determined by X-ray analysis.

A2.2 RESULTS AND DISCUSSION

A2.2.1 Preparation of sulphurated lithium borohydride

The initial preparation was a repeat of that reported by J. M. Lalancette et al.[1] They described the preparation of sulphurated sodium borohydride but the paper indicates that this method is also applicable to lithium, potassium and tetraethylammonium borohydrides. We found that as soon as a few drops of tetrahydrofuran touched the stirred solids a violent reaction took place distributing solid throughout the reflux condenser. Addition of solvent had obviously caused a rapid local reactiom in the mixture liberating hydrogen. For subsequent preparations the method was modified and solid sulphur added to a slurry of lithium borohydride in THF. No cooling of the flask contents was necessary, the effervescence accompanying the reaction being only moderate. Despite washing with petroleum ether and prolonged vacuum drying the product remained somewhat sticky, possibly still containing THF which would be likely to co-ordinate to the lithium. The infra red spectrum (see Table A2.1 p.219) shows a B–H stretch at 2420 cm^{-1} and a B–H bend at 1040–1050 cm^{-1}. An absorption at 915–925 cm^{-1} could possibly be assigned to B–S. The nature of the product made analysis difficult and it was used as prepared for subsequent reactions.

A2.2.2 Reactions of sulphurated lithium borohydride with TMEDA.

Addition of a four molar excess of TMEDA to the sulphurated lithium borohydride and refluxing gave a yellow–brown solid dispersed in a dark orange slightly oily solution. Clear orange crystals were isolated from the solution, on cooling, and these were expected to have the formula LiH_2BS_3.TMEDA. However, no boron was found either by elemental analysis or ^{11}B n.m.r. in $^2H_8$ toluene solution which seems to indicate the break up of the borohydride unit. ^7Li n.m.r. in $^2H_8$ toluene indicated only one lithium environment in solution and it is possible that the complex is a lithium sulphide rendered soluble by the co-ordinating ligands THF and TMEDA. A good infra red spectrum of the crystals was obtained (see Table A2.2 p.210) and comparison with spectra obtained for the sulphurated lithium borohydride and TMEDA allowed some absorptions to be assigned but many others are still uncertain.

Examination under the microscope showed many well-formed crystals that could be suitable for structure determination. Preliminary examination using oscillation techniques will be carried out to find single crystals for a full X-ray analysis.

A2.2.3 Reaction of sulphurated lithium borohydride with pyridine.

This reaction has so far produced only a dark red oily product and modifications of the preparative method are needed.

A2.3 CONCLUSIONS

This is undoubtedly an area for further investigation. As discussed in the introduction a powdered mixture of sodium borohydride and sulphur is marketed as Lalancette's reagent for use as a reducing agent on occasions when sodium borohydride itself is unreactive.

The preliminary work we have carried out has shown that there are handling difficulties associated with the use of a mixture of powdered reactants. In addition the composition of the sulphurated borohydride prepared is, as yet, uncertain leading to difficulties in its subsequent use.

The initial preparation of sulphurated lithium borohydride has been modified to obtain a controllable reaction. However, certain aspects are still unsatisfactory and in need of further modification in order to obtain a product that is easier to handle and analyse. Reactions of this product with a donor ligand such as TMEDA and pyridine have so far been only briefly investigated. The sulphurated lithium borohydride/TMEDA system has produced orange crystals of a complex that may be a lithium sulphide co-ordinated with TMEDA and THF, though the evidence is not conclusive. The compound is still to be investigated by X-ray analysis.

A2.4 EXPERIMENTAL

A2.4.1 Reaction of lithium borohydride with sulphur.[1]

Lithium borohydride (4.36 g, 0.20 mol) was mixed with solid sulphur (19.20 g, 0.60 mol) in a 250 cm^3 two-necked flask fitted with a reflux condensor, dropping funnel (containing THF (50 cm^3)) and nitrogen inlet. The flask was immersed in a cold water bath. Addition of a few drops (2 cm^3) of THF to the stirred solids caused a violent reaction in which a mixture of solids blocked the relux condenser. This experiment was abandoned.

A2.4.2 Reaction of lithium borohydride and sulphur in THF.

Sulphur (6.403 g, 0.20 mol) was added, in small amounts, via a banana joint, to a stirred slurry of $LiBH_4$ (1.453 g, 0.067 mol) in THF (50 cm^3) in a 500 cm^3 two-necked flask fitted with a reflux condenser and nitrogen inlet. Each addition of sulphur produced effervescence, but the reaction was not sufficiently exothermic to cause reflux. After the effervescence had subsided the contents of the flask were warmed (60-70 °C) and then stirred overnight at room temperature (20 °C). Removal of THF under vacuum left a yellow-brown sticky product. This was washed vigorously with degassed petroleum ether (70 cm^3, b.p. 40-60 °C) and the washings removed with a syringe. The product was dried under vacuum but some solvent seemed very tenaciously held.

Infra red spectrum see Table A2.1

A2.4.3 Reaction of sulphurated lithium borohydride with TMEDA.

TMEDA (40.27 cm^3, 31 g, 0.267 mol) and toluene (30 cm^3) were added to the sulphurated lithium borohydride

(0.067 mol) in a Schlenk under nitrogen and stirred. It was heated to 60 °C and the yellow-brown solid was filtered off, washed with toluene (10 cm^3) and dried under vacuum. Orange crystals precipitated from the filtrate after leaving in the freezer overnight (-10 °C). These were filtered, washed with cold toluene (3 x 5 cm^3) and dried under vacuum. The filtrate was returned to the freezer and left for several days. A further crop of well facetted rectangular orange crystals were obtained, filtered, washed with ice-cold hexane (3 x 5 cm^3), dried under vacuum and stored under nitrogen.

Elemental analysis: Amorphous solid, N 8.3 %, H 6.5 %, C 23.7 %.

orange crystals, N 12.1 %, S 20.2 %, B 0 %, C 31.8 %, H 7.9 %, Li 2.9 %

Calculated for $LiBH_2S_3$.TMEDA, N 12.1 %, S 41.4 %, B 4.7 %, Li 3.0 %, C 31.0 %, H 7.8 %.

Infra red spectrum see Table A2.2

^{11}B n.m.r. in $^2H_8$ toluene - no resonance.

^7Li n.m.r. in $^2H_8$ toluene - δ = -0.0260 ppm

A2.4.4 Reaction of sulphurated lithium borohydride with pyridine.

$LiBH_4$ (1.453 g, 0.067 mol) was slurried in THF (50 cm^3) and stirred briskly under nitrogen. Solid sulphur

(6.403 g, 0.20 mol) was added from a banana joint at room temperature over twenty minutes. The mixture was stirred for 1 hour at 40 °C, and THF removed under vacuum to leave a pale yellow sticky residue. Four molar proportions of pyridine were added (21.10 g, 21.60 cm^3, 0.27 mol) to give a dark red very oily product. Cooling to −10 °C for several days produced no solid.

Table A2.1 Infra red spectrum of sulphurated lithium borohydride (thin film).

Wave no. cm^{-1}	Assignment
2970 s.	
2880 s.	
2420 s.	B-H stretch
2360 m.sh.	
1460 m.	
1448 m.	
1370 w.	
1340 w.	
1292 w.	
1238-1266 w.	
1178-1200 w.	
1040-1050 s.	B-H bend
970 m.	
915-925 m.	B-S?
890 m.	
660-680 m.	

Table A2.2 Infra red spectrum of sulphurated lithium borohydride/TMEDA (nujol mull) - in wave no. cm^{-1}.

	Assignments	
$LiBH_2S_3$/TMEDA	TMEDA	$LiBH_2S_3$
2350-2380 w.		2360
2280 s.		
2220 s.		
1282 s.	1280 m.sh.	1292 w.
1260 w.sh.	1262 s.	1238-1266 w.
1250 m.		
1175 m.		1175-1200 w.
1154 s.	1152 m.	
1125 s.	1137 m.	
1092 w.	1096 m.	
1070 s.		
1035 s.	1032 s.	
1020 vs.		
948 vs.	932 w.	915-925 m.
862 w	870 w	
790 vs.	782 vw.	
773 m.		
722 m.		
588 m.		
510 vs		
462 m		

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APPENDIX 3

RESEARCH COLLOQUIA, SEMINARS, LECTURES, AND CONFERENCES

(A) Lectures and Seminars organised by the Department of Chemistry during the period 1984–1987.

19.10.84	Dr. A. Germain (Languedoc, Montpelier) "Anodic Oxidation of Perfluoro Organic Compounds in Perfluoroalkane Sulphonic Acids"
24.10.84	Prof. R. K. Harris (Durham) "N.M.R. of Solid Polymers"
25.10.84	Dr. W. J. Feast (Durham) "Synthesis of Conjugated Polymers. Why and How?"
28.10.84	Dr. R. Snaith (Strathclyde) "Exploring Lithium Chemistry: Novel Structures, Bonding, and Reagents"
1.11.84	Prof. B. J. Aylett (Queen Mary College, London) "Silicon - Dead Common or Refined".
7.11.84	Prof. W. W. Porterfield (Hampden-Sydney College, USA) "There is no Borane Chemistry (only Geometry)"
7.11.84	Dr. H. S. Munro (Durham) "New Information from ESCA Data"
21.11.84	Mr. N. Everall (Durham) "Picosecond Pulsed Laser Raman Spectroscopy"
22.11.84	Prof. D. T. Clark (I.C.I. New Science Group) "Structure, Bonding, Reactivity and Synthesis as Revealed by ESCA".
27.11.84	Dr. W. J. Feast (Durham) "A Plain Man's Guide to Polymeric Organic Metals"

28.11.84	Dr. T. A. Stephenson (Edinburgh) "Some Recent Studies in Platinum Metal Chemistry"
29.11.84	Prof. C. J. M. Stirling (University College of North Wales) "Molecules Taking the Strain"
5.12.84	Mr. P. J. Lux (Durham) "I.R. and G.C. Studies of the Interaction of CH_3OH with High Silica Zeolites".
5.12.84	Prof. R. D. Chambers (Durham) "The Unusual World of Fluorine".
12.12.84	Dr. K. B. Dillon (Durham) "^{31}P NMR Studies of some Anionic Phosphorus Complexes"
11. 1.85	Emeritus Prof. H. Suchitzky (Salford) "Fruitful Fissions of Benzofuroxanes and Isobenzimidazoles (Umpolung of o-phenylenediamine)"
24. 1.85	Dr. A. K. Covington (Newcastle) "Chemistry with Chips"
31. 1.85	Dr. M. L. H. Green (Oxford) "Naked Atoms and Negligee Ligands"
7. 2.85	Prof. A. Ledwith (Pilkington Bros) "Glass as a High Technology Material"
13. 2.85	Dr. G. W. J. Fleet (Oxford) "Synthesis of some Alkaloids from Carbohydrate"
14. 2.86	Dr. J. A. Salthouse (Manchester) "Son et Lumiere"
19. 2.85	Dr. D. J. Mincher (Durham) "Stereoselective Synthesis of some Novel Anthracyclinones Related to the Anti-cancer Drug Adriamycin and to the Steffimycin Antibiotics"
21. 2.85	Prof. P. M. Maitlis, FRS (Sheffield) "What Use is Rhodium?"

27. 2.85	Dr. R. E. Mulvey (Durham) "Some Unusual Lithium Complexes"
6. 3.85	Dr. P. J. Kocienski (Leeds) "Some Synthetic Applications of Silicone-Mediated Annulation Reactions"
7. 3.85	Dr. P. W. Atkins (Oxford) "Magnetic Reactions"
7. 3.85	Dr. P. J. Rodgers (I.C.I. plc Agricultural Division, Billingham) "Industrial Polymers from Bacteria"
12. 3.85	Prof. K. J. Packer (B.P. Ltd./East Anglia) "NMR Investigations of the Structure of Solid Polymers"
14. 3.85	Prof. A. R. Katritzky F.R.S. (Florida) "Some Adventures in Heterocylcic Chemistry"
20. 3.85	Dr. M. Poliakoff (Nottingham) "New Methods for Detecting Organometallic Intermediates in Solution"
28. 3.85	Prof. H. Ringsdorf (Mainz) "Polymeric Liposomes as Models for Biomembranes and Cells"
24. 4.85	Dr. M. C. Grossel (Bedford College, London) "Hydoxypyridine Dyes - Bleachable One-Dimensional Metals"
25. 4.85	Major S. A. Shackelford (U.S. Air Force) "In situ Mechanistic Studies on Condensed Phase Thermochemical Reaction Processes: Deuterium Isotope Effects in HMX Decomposition, Explosives and Combustion"
1. 5.85	Dr. D. Parker (I.C.I. plc, Petrochemical and Plastics Division, Wilton) Application of Radioisotopes to Industrial Research"
7. 5.85	Prof. G. E. Coates (formerly of Wyoming, USA) "Chemical Education in England and America: Successes and Deficiencies"
8. 5.85	Prof. D. Tuck (Windsor. Ontario) "Lower Oxidation State Chemistry of Indium"

8. 5.85	Prof. D. Williams (U.C.W., Aberwystwyth) "Liquid Crystalline Polymers"
9. 5.85	Prof. R. K. Harris (Durham) "Chemistry in a Spin: Nuclear Magnetic Resonance"
14. 5.85	Prof. J. Passmore (New Brunswick, Canada) "The Synthesis and Characterisation of some Novel Selenium-Iodine Cations, aided by 77-Se NMR Spectroscopy"
15. 5.85	Dr. J. E. Packer (Auckland, New Zealand) "Studies of Free Radical Reactions in Aqueous Solution Using Ionising Radiation"
17. 5.85	Prof. I. D. Brown (McMaster University, Canada) "Bond Valence as a Model for Inorganic Chemistry"
21. 5.85	Dr. D. L. H. Williams (Durham) "Chemistry in Colour"
22. 5.85	Dr. M. Hudlicky (Blacksburg, USA) "Preferential Elimination of Hydrogen Fluoride from Vicinal Bromofluorocompounds"
22. 5.85	Dr. R. Grimmett (Otago, New Zealand) "Some Aspects of Nucleophilic Substitution in Imidazoles"
4. 6.85	Dr. P. S. Belton (Food Research Institute, Norwich) "Analytical Photoacoustic Spectroscopy"
13. 6.85	Dr. D. Woolins (Imperial College, London) "Metal-Sulphur-Nitrogen Complexes"
14. 6.85	Prof. Z. Rappoport (Hebrew University, Jerusalem) "The Rich Mechanistic World of Nucleophilic Vinylic Substitution"
19. 6.85	Dr. T. N. Mitchell (Dortmund) "Some Synthetic and NMR-Spectroscopic Studies of Organic Compounds"
26. 6.85	Prof. G. Shaw (Bradford) "Synthetic Studies on Imidazole Nucleosides and the Antibiotic Coformycin"

23. 1.86	Prof. Sir Jack Lewis (Cambridge) "Some More Recent Aspects in the Cluster Chemistry of Ruthenium and Osmium Carbonyls"
29. 1.86	Dr. J. H. Clark (York) "Novel Fluoride Ion Reagents"
30. 1.86	Dr. N. J. Phillips (Loughborough) "Laser Holography"
12. 2.86	Dr. J. Yarwood (Durham) "The Structure of Water in Liquid Crystals"
12. 2.86	Dr. O. S. Tee (Concordia University, Montreal, Canada) "Bromination of Phenols"
13. 2.86	Prof. R. Grigg (Queen's, Belfast) "Thermal Generation of 1,3-Dipoles"
19. 2.86	Prof. G. Procter (Salford) "Approaches to the Synthesis of Some Natural Products"
20. 2.86	Dr. C. J. F. Barnard (Johnson Matthey Group) "Platinum Anti-Cancer Drug Development"
26. 2.86	Ms. C. Till (Durham) "ESCA and Optical Emission Studies of the Plasma Polymerisation of Perfluoroaromatics"
27. 2.86	Prof. R. K. Harris (Durham) "The Magic of Solid-State NMR"
5. 3.86	Dr. D. Hathway (Durham) "Herbicide Selectivity"
5. 3.86	Dr. M. Schroder (Edinburgh) "Studies on Macrocyclic Compounds"
6. 3.86	Dr. B. Iddon (Salford) "The Magic of Chemistry"
12. 3.86	Dr. J. M. Brown (Oxford) "Chelate Control in Homogeneous Catalysis"
14. 3.86	Dr. P. R. R. Langridge-Smith (Edinburgh) "Naked Metal Clusters - Synthesis, Characterisation, and Chemistry"

9. 6.86	Prof. R. Schmutzler (Braunschweig, W.Germany) "Mixed Valence Diphosphorus Compounds"
23. 6.86	Prof. R. E. Wilde (Texas Technical University USA) "Molecular Dynamic Processes from Vibrational Bandshapes"
16.10.86	Prof. N. N. Greenwood (Leeds) "Glorious Gaffes in Chemistry"
23.10.86	Prof. H. W. Kroto (Sussex) "Chemistry in Stars, Between Stars and in the Laboratory"
29.10.86	Prof. E. H. Wong (New Hampshire, USA) "Coordination Chemistry of P-O-P Ligands"
5.11.86	Prof. Dopp (Duisberg) "Cyclo-Additions and Cylco-Reversions Involving Capto-Dative Alkenes"
6.11.86	Dr. R. M. Scrowston (Hull) "From Myth and Magic to Modern Medicine"
13.11.86	Prof. Sir Geoffrey Allen (Unilever Research) "Biotechnology and the Future of the Chemical Industry"
20.11.86	Dr. A. Milne and Mr. S. Christie (International Paints) "Chemical Serendipity - A Real Life Case Study"
26.11.86	Dr. N. D. S. Canning (Durham) "Surface Adsorption Studies of Relevance to Heterogeneous Ammonia Synthesis"
27.11.86	Prof. R. L. Williams (Metropolitan Police Forensic Science) "Science and Crime"
3.12.86	Dr. J. Miller (Dupont Central Research, USA) "Molecular Ferromagnets: Chemistry and Physical Properties"
8.12.86	Prof. T. Dorfmuller (Bielefeld) "Rotational Dynamics in Liquids and Polymers"
22. 1.87	Prof. R. H. Ottewill (Bristol) "Colloid Science: A Challenging Subject"

28. 1.87	Dr. W. Clegg (Newcastle) "Carboxylate Complexes of Zinc Charting a Structural Jungle"
4. 2.87	Prof. A. Thompson (East Anglia) "Metalloproteins and Magneto-optics"
5. 2.87	Dr. P. Hubberstey (Nottingham) "Demonstration Lecture on Various Aspects of Alkali Metal Chemistry"
11. 2.87	Dr. T. Shepherd (Durham) "Pteridine Natural Products: Synthesis and Use in Chemotherapy"
12. 2.87	Dr. P. J. Rodgers (I.C.I. Billingham) "Industrial Polymers from Bacteria"
17. 2.87	Prof. E. H. Wong (New Hampshire, USA) "Symmetrical Shapes from Molecules to Art and Nature"
19. 2.87	Dr. M. Jarman (Institute of Cancer Research) "The Design of Anti-Cancer Drugs"
4. 3.87	Dr. R. Newman (Oxford) "Change and Decay: A Carbon-13 CP/MAS NMR Study of Humification and Coalification Processes"
5. 3.87	Prof. S. V. Ley (Imperial College, London) "Fact and Fantasy in Organic Synthesis"
9. 3.87	Prof. F. G. Bordwell (Northeastern University USA) "Carbon Anions, Radicals, Radical Anions and Radical Cations"
11. 3.87	Dr. R. D. Cannon (East Anglia) "Electron Transfer in Polynuclear Complexes"
12. 3.87	Dr. E. M. Goodyear (Cranfield Institute of Technology) "Alternative Fuels for Transport"
17. 3.87	Prof. R. F. Hudson (Kent) "Aspects of Organophosphorus Chemistry"
18. 3.87	Prof. R. F. Hudson (Kent) "Homolytic Rearrangements of Free-Radical Stability"

3. 4.87	Prof. G. Ferguson (Guelph, Canada) "X-ray Crystallography for the Organic Chemist"
6. 5.87	Dr. R. Bartsch (Sussex) "Low Co-ordinated Phosphorus Compounds"
7. 5.87	Dr. M. Harmer (I.C.I. Chemicals and Polymer Group) "The Role of Organometallics in Advanced Materials"
11. 5.87	Prof. S. Pasynkiewicz (Technical University, Warsaw) "Thermal Decomposition of Methyl Copper and its Reactions with Trialkylaluminium"
27. 5.87	Dr. M. Blackburn (Sheffield) "Phosphonates as Analogues of Biological Phosphate Esters"
24. 6.87	Prof. S. M. Roberts (Exeter) "Synthesis of Novel Anti-Viral Agents"
26. 6.87	Dr. C. Krespan (E. I. Dupont de Nemours) "Nickel(0) and Iron(0) as Reagents in Organofluorine Chemistry"

B. Conferences attended during 1984-1987

September 1984	Intraboron 4 , Durham
September 1985	Intraboron 5 , Killen
April 1986,	R.S.C. Annual Congress, Warwick.
June 1986,	University of Strathclyde Inorganic Meeting.
July 1987,	R.S.C. Platinum Metals Conference, Sheffield.
September 1987	Intraboron 7 , Ross Priory, Strathclyde University.