

FULL PAPER

## An Investigation of the Structural Diversities of Lithiated HMPA Complexes of *o*-Mercaptopyridine and Trithiocyanuric Acid: Syntheses, Crystal structures and Model Molecular Orbital Calculations

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**Abstract** Reaction of *o*-mercaptopyridine (*o*-MPH) and trithiocyanuric acid (TTCyH<sub>3</sub>) with one equivalent of Bu<sup>n</sup>Li in the presence of HMPA yields the mono-lithiated salts MPLi.HMPA (**1**) and TTCyH<sub>2</sub>Li.2HMPA (**2**) respectively, which have been characterised by NMR spectroscopy and X-ray crystallography. Reaction of three equivalents of Bu<sup>n</sup>Li with anhydrous TTCyH<sub>3</sub> in THF yields the tri-lithiated species TTCyLi<sub>3</sub>.4THF (**3**). In all three compounds the lithium centres have N,S-bridged coordination modes. Whereas **1** is dimeric in the solid state, **2** has an unusual monomeric structure and **3**, which is a very rare example of a structurally characterised tri-lithiated compound, has an unprecedented polymeric structure incorporating (NCSLi)<sub>n</sub> (*n* = 1, 2) rings. The structural diversities displayed by **1** and **2** have been probed, and thereby in part rationalised, by *ab initio* (6-31G\*/RHF, 6-31G\*\*/RHF and 6-31G\*/MP2 levels) MO calculations on both their thio-keto and thiol isomers and on their uncomplexed and complexed lithiated derivatives. In particular, the optimised structures predict and reproduce the N,S-bridging coordination modes found for lithium and explain why structure **1** is dimeric whereas **2** is monomeric.

**Keywords** *Ab initio* calculation, Isomerism, Lithium, Solid-state structure, Sulphur

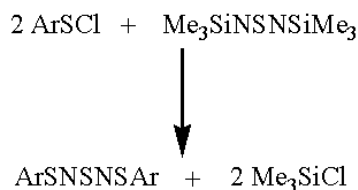
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Dedicated to Professor Paul von Ragué Schleyer on the occasion of his 70<sup>th</sup> birthday. In recognition of his outstanding contribution to the calculational study of Group 1 organometallic molecules and to organometallic chemistry as a whole.

### Introduction

We have been interested [1] in the preparation of novel materials in which redox-active functional groups are linked via a  $\pi$ -delocalised backbone which will facilitate through bond communication between redox active centres. Our synthetic strategy has been to utilise sulphur-nitrogen chains {i.e. small fragments of conducting poly(sulphur nitride) [2]} to provide the delocalised  $\pi$ -framework. Sulphur-nitrogen

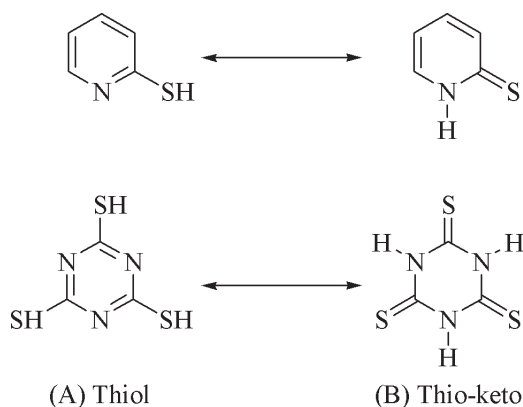
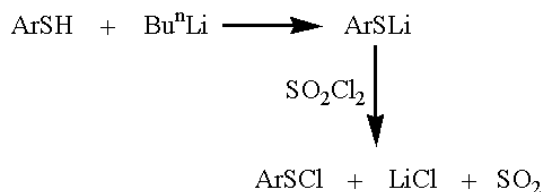
**Scheme 1** A general synthetic route to trithiadiazene chains

chains can be prepared easily using well established synthetic methodologies which generally involve condensation reactions of aromatic sulfenyl chlorides (usually prepared by chlorination of the corresponding thiol using either  $\text{Cl}_2$  or  $\text{SO}_2\text{Cl}_2$ ) with suitable reagents containing trimethylsilyl groups (Scheme 1).[1]

Whilst sulfenyl chlorides generally provide a convenient route to sulphur-nitrogen chains, in the case of reaction of *o*-mercaptopyridine (*o*-MPH) with excess  $\text{SO}_2\text{Cl}_2$ , the evolved HCl is coordinated by the N-donor base and, subsequently, solutions must be refluxed for up to 72 hours in order to remove the HCl.[3] These synthetic difficulties prompted us to investigate alternative routes to sulfenyl chlorides *via* lithiation of the mercaptan, thereby preventing the evolution of HCl (Scheme 2).

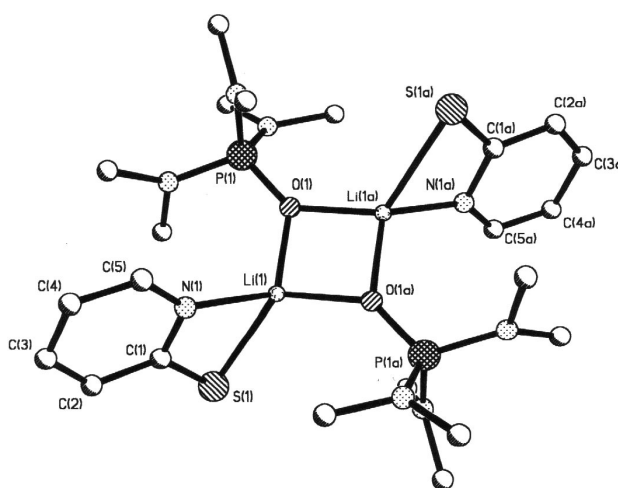
In addition, this methodology may also allow the selective conversion of thiols to sulfenyl chlorides in compounds containing several thiol functional groups, such as trithiocyanuric acid ( $\text{TTCyH}_3$ ). This would be highly advantageous, allowing mono-, di-, tri- and polyfunctional sulphur-nitrogen chains to be selectively prepared. Thus far we have reported the preparation of only *difunctional* chains derived from *m*-dimercaptobenzene.[4]

Whilst keto-enol tautomerism in *o*-pyridinols [5] and cyanuric [6,7] acid has been studied extensively, that in their

**Figure 1** Thio-keto/thiol tautomerism in *o*-MPH and  $\text{TTCyH}_3$ **Scheme 2** Preparation of a sulfenyl chloride via lithiation

sulphur analogues (Figure 1) has not been fully investigated. All that is known is that *o*-MPH [8] crystallises in the thio-keto form [Figure 1 (B)], forming centrosymmetric dimers *via* N–H...S hydrogen bonds with N...S distances of 3.276 Å. Further, a number of metal salts of  $\text{TTCyH}_3$  have been known since 1885 when Hofmann reported the syntheses of the first such species; however, these salts have not been properly characterised.[9] In addition, the preparation of  $\text{TTCyH}_3$  itself is *via* the tri-sodium salt, which is then converted to free  $\text{TTCyH}_3$  by treatment with excess hydrochloric acid.[6] Previously these alkali (and alkaline earth) metal salts have been represented with the metal ions sulphur-bound,[6] in spite of the fact that they have not been structurally characterised. While the derivatives of the heavier d-block metals Os [10] and, very recently, Au [11] are consistent with the presence of an anion of this tautomer [Figure 1 (A)] it has recently been reported that  $\text{TTCyH}_3$  itself affords extensive hydrogen-bonded networks upon recrystallisation from highly polar solvents. These networks demonstrate the favourability of the keto type.[7] Finally, cyanuric acid is known to exhibit keto-enol tautomerism, with the keto form being the most prevalent.[6,7]

In order to examine the feasibility of the conversion of thiols to sulfenyl chlorides *via* lithiated intermediates, the

**Figure 2** The dimeric structure of **1**. H atoms removed for clarity

lithiation of a series of mercaptans was investigated. This manuscript describes the isolation and characterisation of the mono-lithiated derivative of *o*-MPH, and the mono- and tri-lithiated derivatives of TTCyH<sub>3</sub>. The structural diversities displayed for these compounds and the thio-keto/thiol tautomerism observed for pure *o*-MPH and TTCyH<sub>3</sub> are probed, and thereby in part rationalised, by *ab initio* MO calculations.

## Results and discussion

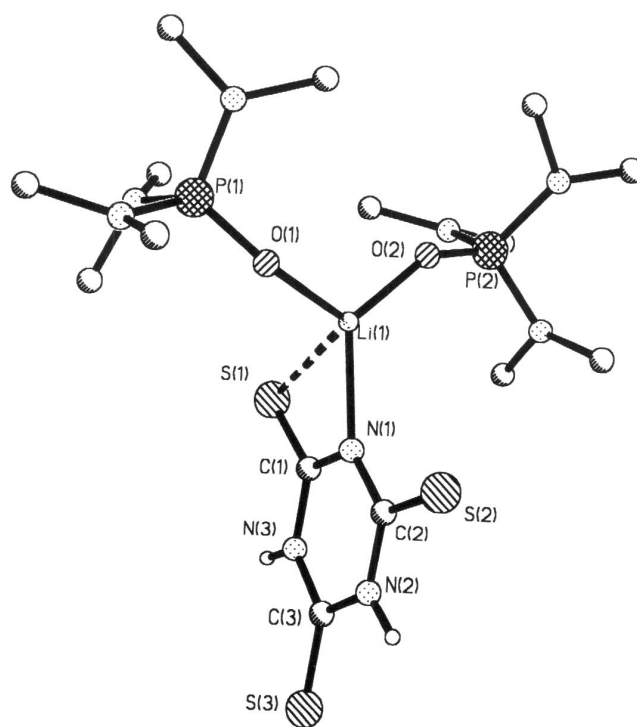
Reaction of *o*-MPH with Bu<sup>n</sup>Li in a 1:1 molar ratio in the presence of HMPA [= hexamethylphosphoramide, (Me<sub>2</sub>N)<sub>3</sub>P=O] yielded the mono-lithiated product, *o*-MPLi.HMPA (**1**) which was characterised by NMR spectroscopy and X-ray crystallography. The <sup>1</sup>H NMR spectrum of **1** showed signals characteristic of the aromatic ring and a doublet centred at δ 2.52 attributable to HMPA. Integration of the aromatic and HMPA resonances in the <sup>1</sup>H NMR spectrum indicated a 1:1 *o*-MPLi:HMPA ratio. In the solid state **1** has a bridged dimeric structure (Figure 2), the four-coordinate lithium centre taking up a *pseudo*-tetrahedral arrangement, bonding to both a nitrogen and a sulphur atom of the anionic ring [Li(1)–N(1) and Li(1)–S(1), 2.038(5) and 2.468(4) Å, respectively] and to the oxygen atoms of two bridging HMPA molecules [Li(1)–O(1) and Li(1)–O(1a), 1.942(5) and 1.926(5) Å, respectively]. Just as for the crown ether complex (*o*-MPLi)<sub>2</sub>·(18-crown-6) [12] the C–S bond distance in **1** [1.727(2) Å] is intermediate between a C–S single and a C=S double bond.[13] The C–C distances in the *o*-MPLi ring are in the range 1.366(4) to 1.408(4) Å, indicative of delocalised bonding.

Surprisingly, despite the availability of the tri-sodium salt, TTCyNa<sub>3</sub>·*n*H<sub>2</sub>O, we at first found that reaction of TTCyH<sub>3</sub> with *three* equivalents of the strong base Bu<sup>n</sup>Li yielded only the mono-lithiate.[14] Treatment of TTCyH<sub>3</sub> with *one* equivalent of Bu<sup>n</sup>Li in the presence of HMPA gave the mono-lithiated product as its HMPA adduct, TTCyH<sub>2</sub>Li·2HMPA (**2**), which was characterised by NMR spectroscopy and X-ray crystallography.[14] Unlike **1**, **2** is monomeric in the solid state (Figure 3). It has a structure which has not previously been observed for any solid-state lithiated species incorporating HMPA. Usually, lithiation of an organic acid (RH) in the presence of HMPA affords a complex of type (RLi.HMPA)<sub>2</sub>, as in **1**, or (RLi.HMPA)<sub>4</sub> in which either R<sup>−</sup> or O (of HMPA) centres bridge Li<sup>+</sup> cations.[15] The unique nature of **2** may be accounted for in terms of the electron withdrawing capability of the TTCyH<sub>2</sub><sup>−</sup> anion, enough electron density being removed from the lithium for it to require the stabilisation of *two terminal* HMPA molecules.

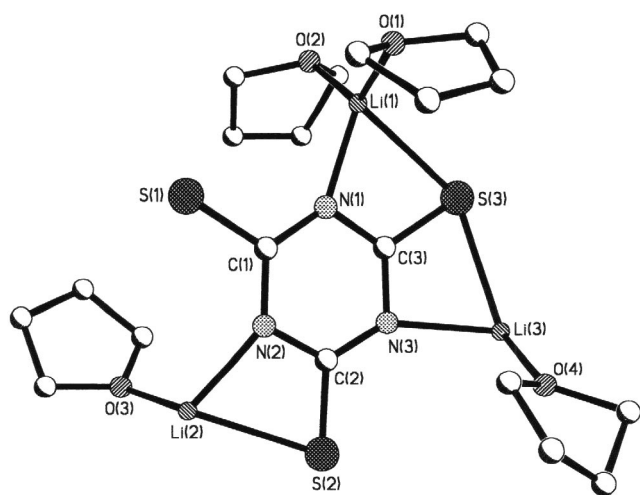
In **2** the lithium is four coordinate, taking up a *pseudo*-tetrahedral arrangement. It bonds strongly to a nitrogen atom and weakly to a sulphur atom of the TTCyH<sub>2</sub><sup>−</sup> anion ring [Li(1)–N(1) and Li(1)–S(1), 2.079(11) and 2.959(12) Å respectively], and to the oxygen atoms of two HMPA molecules [Li(1)–O(1) and Li(1)–O(2), 1.856(11) and 1.858(11) Å re-

spectively]. The Li–S bond in **2** is long in comparison with those in **1** and with previously reported structures in which Li–S bonds were categorically [16] identified (wherein Li–S distances were in the range 2.412 to 2.518 Å). The weakness of the Li–S interaction is confirmed by the essentially equivalent carbon-sulphur distances [1.668(6), 1.673(6) and 1.654(6) Å, for C(1)–S(1), C(2)–S(2) and C(3)–S(3), respectively] all of which are characteristic of C=S double bonds.[11] Hence **2** exists in the thio-keto form [Figure 1 (B)] with the two remaining hydrogen atoms being nitrogen-bound, making it the analogue of the keto form of cyanuric acid. Molecules of **2** associate in the solid state *via* N–H⋯S interactions forming zig-zag chains; the N⋯S distances are in the range 3.283–3.386 Å (*cf.* 3.276 Å for dimers of *o*-MPH). The presence of the thio-keto form is further substantiated by the <sup>1</sup>H NMR (d<sup>6</sup>-DMSO) spectrum of **2** in which the two remaining TTCyH<sub>2</sub><sup>−</sup> hydrogen atoms are relatively deshielded [δ 12.23 (2H)], since they lie in the plane of the trithiocyanuric acid anion ring. The <sup>1</sup>H NMR spectrum of the starting material, TTCyH<sub>3</sub>, showed a peak at δ 13.69 in d<sup>6</sup>-DMSO, also consistent with the thio-keto form [Figure 1 (B)].

In order to investigate the initially observed formation of mono-lithiated TTCyH<sub>2</sub>Li in preference to the tri-lithiate, irrespective of the number of equivalents of Bu<sup>n</sup>Li added, *ab initio* MO geometry optimisations were carried out with the 6-31G\* basis set at the MP2 level.[17] These calculations showed that multiple lithiations of trithiocyanuric with Bu<sup>n</sup>Li should be favourable, with ΔE = -78.1, -77.6 and -78.4 kcal



**Figure 3** The monomeric structure of **2**. HMPA H atoms removed for clarity



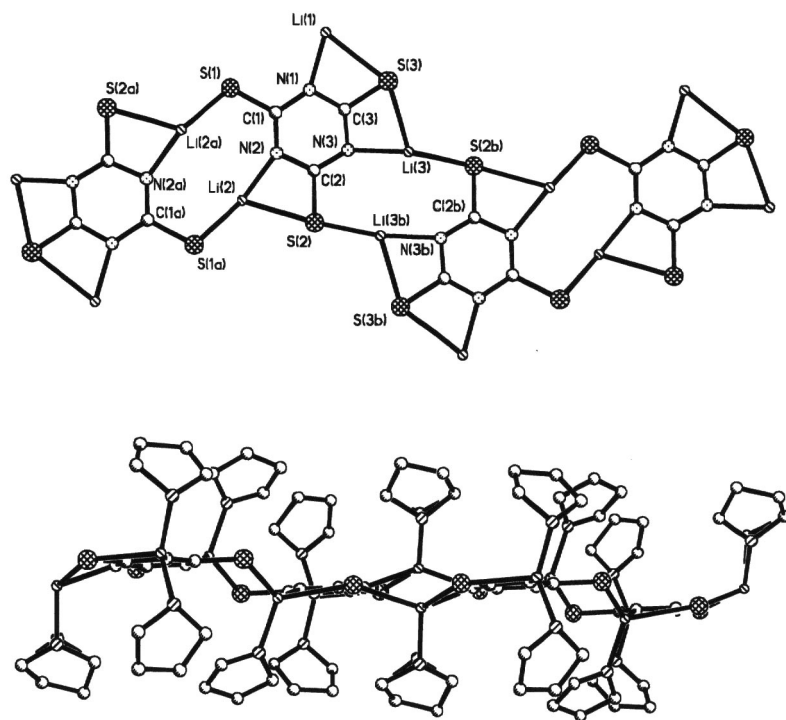
**Figure 4** Asymmetric unit of **3** showing atom labelling scheme. H atoms and minor THF disorder omitted for clarity

mol<sup>-1</sup> (1 kcal = 4.184 kJ) for mono-, di- and tri-lithiation, respectively (where, for example for mono-lithiation,  $\Delta E$  is calculated as the difference in energy between the lowest energy optimised structure of TTCyH<sub>3</sub> plus an optimised structure of Bu<sup>n</sup>Li, and the lowest energy optimised structure of TTCyH<sub>2</sub>Li plus an optimised structure of Bu<sup>n</sup>H). This knowledge led us to re-examine the lithiation process and it transpired that the extent of lithiation of TTCyH<sub>3</sub> is very dependent on the amount of water of crystallisation present in

the TTCyH<sub>3</sub> starting material (as judged by <sup>1</sup>H NMR spectroscopy). Thus, reaction of finely ground TTCyH<sub>3</sub> (dried *in vacuo*) with three equivalents of Bu<sup>n</sup>Li in THF yielded the tri-lithiated product TTCyLi<sub>3</sub>·4THF (**3**), which was characterised by NMR spectroscopy and X-ray crystallography. Whilst there are many synthetic organic reaction schemes which cite the intermediacy of polyolithiated derivatives of organic molecules,[18] there are very few examples of structurally characterised di- and, especially, tri-lithiated compounds. The tri-lithiated derivatives of RSi(NHSiMe<sub>3</sub>)<sub>3</sub> (R = Me, <sup>t</sup>Bu or Ph) [19, 20] are all discrete dimers in the solid state; and the tri-lithiated derivative of 2,6-dimethylphenol forms discrete solid-state tetramers.[21] In contrast **3** has a unique polymeric structure formed *via* a series of NCSLi-containing rings of various sizes.

The asymmetric unit of **3** is shown in Figure 4. One lithium centre [Li(1)] bears two THF solvent molecules, whilst the other two metal centres have one such molecule each [slightly disordered in the case of the THF attached to Li(3)]. In addition, each lithium is bonded to a N atom of the trithiocyanuric ring [Li(1)–N(1) 1.978(9) Å, Li(2)–N(2) 2.012(8) Å, Li(3)–N(3) 2.080(9) Å] and to an *exo*-S atom of the trianion [Li(1)–S(3) 2.616(9), Li(2)–S(2) 2.566(7), Li(3)–S(3) 2.549(10) Å]. These latter, Li–S distances are considerably shorter than that found for mono-lithiate **2** [2.959(12) Å] and are much more akin to distances found in lithiated thiols, wherein Li–S distances are in the range 2.412–2.518 Å.[16] The stronger Li–S bonding in **3** leads to C–S bond lengths [C(1)–S(1) 1.715(4), C(2)–S(2) 1.724(4) and C(3)–S(3) 1.714(4) Å] which are greater than those found in TTCyH<sub>3</sub>·HMPA [1.654(6), 1.668(6) and 1.673(6) Å] where the TTCyH<sub>3</sub> is present es-

**Figure 5** (a) Formation of the pseudo one-dimensional polymer of **3** via horizontal ring laddering. THF molecules omitted for clarity. (b) A side-on view of polymeric **3**, with THF molecules included. H atoms and minor THF disorder omitted for clarity





**Table 1** Ab initio calculated energies [absolute energies in au ( $\gg 4.36 \times 10^{-18}$  J), relative energies in kcal mol<sup>-1</sup> of thio-keto and thiol isomers of *o*-MPH and its uncomplexed and HMPA-complexed monolithiated derivatives. Basis sets: [a] 6-31G\*/RHF, [b] 6-31++G\*\*/RHF, [c] 6-31G\*/MP2

Species	Absolute energy	Relative energy
<b>MP.I</b> (thiol)[a]	-644.206478	+0.80
<b>MP.II</b> (thio-keto)[a]	-644.207828	0.00
<b>MP.I</b> (thiol)[b]	-644.225250	+0.40
<b>MP.II</b> (thio-keto)[b]	-644.225913	0.00
<b>MP.I</b> (thiol)[c]	-645.117314	+0.65
<b>MP.II</b> (thio-keto)[c]	-645.118347	0.00
<b>MP.III</b> (H transfer)[a]	-644.137141	–
<b>MP.III</b> (H transfer)[b]	-644.158798	–
<b>MP.III</b> (H transfer)[c]	-645.069558	–
<b>MP.IV</b> (Li)[a]	-651.149975	–
<b>MP.V</b> (Li.HMPA)[a]	-1467.847144	-31.6 (cf. <b>MP.IV</b> )
<b>MP.VI</b> (Li.HMPA <sub>2</sub> )[a]	-2284.515507	-13.6 (cf. <b>MP.V</b> )
<b>MP.VII</b> (dimer of <b>MP.IV</b> )[a]	-1302.350470	-31.7 (cf. <b>MP.IV</b> )
<b>MP.VIII</b> (dimer of <b>MP.V</b> )[a]	-2935.715204	-13.1 (cf. <b>MP.V</b> )

**Table 2** Ab initio calculated energies [absolute energies in au ( $\gg 4.36 \times 10^{-18}$  J), relative energies in kcal mol<sup>-1</sup> of thio-keto and thiol isomers of TTCyH<sub>3</sub> and its uncomplexed and HMPA-complexed monolithiated derivatives. Basis sets: [a] 6-31G\*/RHF, [b] 6-31G\*/MP2

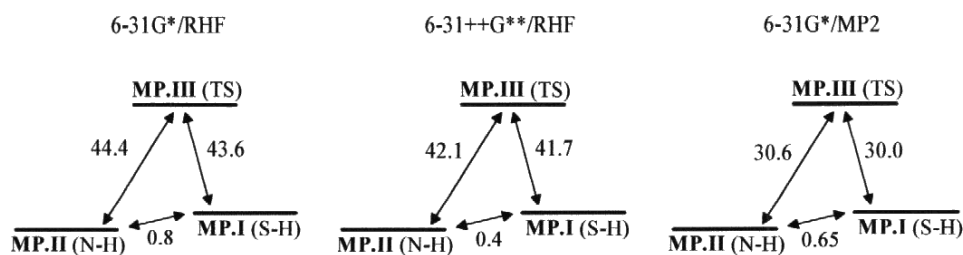
Species	Absolute energy	Relative energy
<b>TTC.I</b> (all N-H)[a]	-1471.267343	0.00
<b>TTC.II</b> (2 N-H)[a]	-1471.238826	+17.90
<b>TTC.III</b> (1 N-H)[a]	-1471.225468	+26.30
<b>TTC.IV</b> (all S-H)[a]	-1471.235330	+20.10
<b>TTC.I</b> (all N-H)[b]	-1472.490839	0.00
<b>TTC.II</b> (2 N-H)[b]	-1472.460144	+19.30
<b>TTC.III</b> (1 N-H)[b]	-1472.443517	+29.70
<b>TTC.IV</b> (all S-H)[b]	-1472.449580	+25.90
<b>TTC.V</b> (H transfer)[a]	-1471.175947	–
<b>TTC.V</b> (H transfer)[b]	-1472.418667	–
<b>TTC.VI</b> (H transfer)[a]	-1471.156970	–
<b>TTC.VI</b> (H transfer)[b]	-1472.396619	–
<b>TTC.VII</b> (H transfer)[a]	-1471.158345	–
<b>TTC.VII</b> (H transfer)[b]	-1472.394321	–
<b>TTC.VIII</b> (Li)[a]	-1478.212304	0.00
<b>TTC.IX</b> (Li)[a]	-1478.189000	+14.60
<b>TTC.X</b> (Li)[a]	-1478.180578	+19.90
<b>TTC.XI</b> (Li transfer)[a]	-1478.208046	+2.67 (cf. <b>TTC.VIII</b> )
<b>TTC.XII</b> (Li.HMPA)[a]	-2294.916025	-35.8 (cf. <b>TTC.VIII</b> )
<b>TTC.XIII</b> (Li.HMPA <sub>2</sub> )[a]	-3111.592190	-18.4 (cf. <b>TTC.XII</b> )
<b>TTC.XIV</b> (dimer of <b>TTC.VIII</b> )[a]	-2956.485818	-38.4 (cf. <b>TTC.VIII</b> )
<b>TTC.XV</b> (dimer of <b>TTC.XII</b> )[a]	-4589.856815	-15.5 (cf. <b>TTC.XII</b> )

carried out at 6-31G\*/RHF, 6-31++G\*\*/RHF and 6-31G\*/MP2 basis set levels. The relative energies (Figure 7) suggest that the transfer is not facile, although introduction of correlation energy (MP2 level) does lower the activation energy. The 6-31G\*/RHF structure of **MP.III** shows the presence of a four-membered C–S–H–N ring in which both the SH and NH bonds are each longer than in **MP.I/MP.II** respectively by ~0.35 Å. The angles within the four-membered C–S–H–N ring in **MP.III** show that the N–H bond has been notably displaced and this is borne out by the calculated N–H distance of 1.349 Å. The C–S and C–N bond lengths in **MP.III** are almost midway between their corresponding values in **MP.I** and **MP.II**. The remaining pyridine ring bond lengths

are almost the same as those for **MP.I**, *i.e.* belonging to a fully-delocalised system.

Calculations show that lithiation of *o*-MPH is favourable with  $\Delta E = -80.4$  kcal mol<sup>-1</sup> for reaction with Bu<sup>n</sup>Li ( $\Delta E$  is calculated as the difference in energy between the lowest energy optimised structure of *o*-MPH plus an optimised structure of Bu<sup>n</sup>Li, and the lowest energy optimised structure of *o*-MPLi plus an optimised structure of Bu<sup>n</sup>H, 6-31G\*/RHF basis set). The optimised lithiate structure, (Figure 6, **MP.IV**) is reminiscent of the transition state for hydrogen transfer, **MP.III**, and is obtained whether the Li centre is placed originally on the nitrogen (thio-keto) or on the sulphur (thiolato) centre. In each case the lithium adopts a bridging position

**Figure 7** Representation of transition state (**MP.III**) energies in kcal mol<sup>-1</sup>



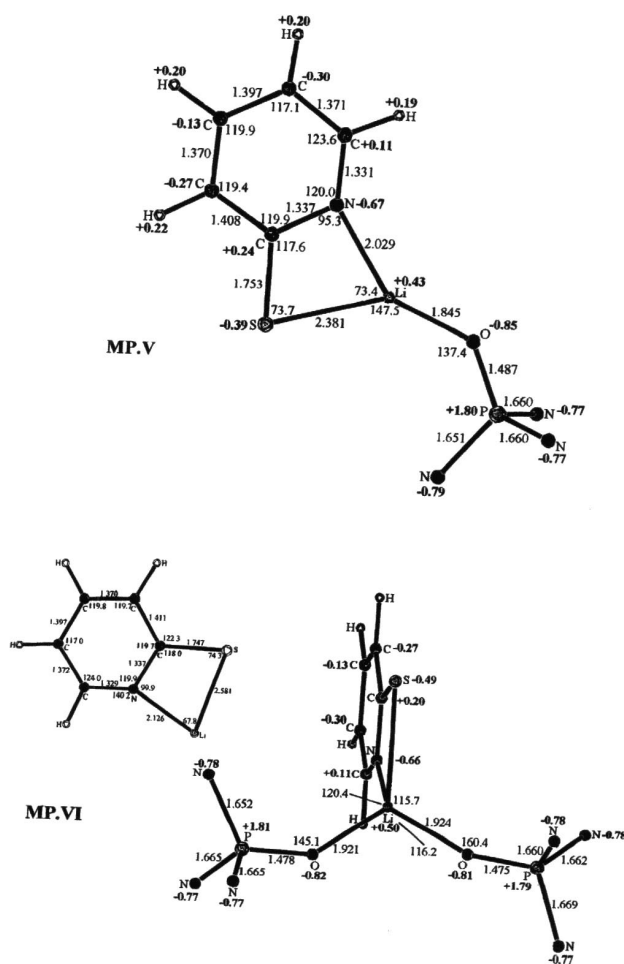
between the two heteroatoms, as found in the solid-state structure of **1**. While the calculated bond lengths in **MP.IV** lie between those for **MP.I** and **MP.II**, they are closer to those of **MP.II**. The calculated Li–N and Li–S distances of 1.967 and 2.273 Å respectively, which involve only a two-coordinate lithium centre, are considerably shorter than those in **1** (cf. 2.038 and 2.468 Å), which incorporate four-coordinate lithium. However, the metal centre in **MP.IV** is clearly in a position to expand its coordination number by the attachment of donors (e.g. solvation with experimentally provided HMPA) or by intermolecular association.

Two solvated monomers, **MP.V** ( $\equiv$ **MP.IV**.HMPA) and **MP.VI** ( $\equiv$ **MP.IV**.2HMPA) (Figure 8), were examined. Structure **MP.V** was optimised to give a molecule which possesses a mirror plane coincident with the mercaptopyridine ring. Formation of the Li–O bond upon complexation of **MP.IV** causes the Li–N and Li–S bonds to lengthen and weaken, to 2.029 and to 2.381 Å respectively. The electron donation to mercaptopyridine is 0.16e, the main beneficiaries of this being the sulphur and to a lesser extent the lithium centre. Coordination of a second HMPA molecule at Li in **MP.VI** causes a further lengthening of the Li–N and Li–S bonds to 2.126 and 2.581 Å respectively. A stabilisation energy of -31.6 kcal mol<sup>-1</sup> is observed for the addition, to **MP.IV**, of one equivalent of the Lewis base HMPA (**MP.V**) with a further -13.6 kcal mol<sup>-1</sup> gained from coordination of a second equivalent of HMPA (**MP.VI**).

Two models for the dimerisation of mono-lithiated *o*-MPH were considered (Figure 9). While **MP.VII** is a dimer of uncomplexed *o*-MPLi (**MP.IV**) incorporating two inter-monomer Li–S bonds, **MP.VIII** is a dimer of the mono-HMPA complex **MP.V** featuring a central four-membered (LiO)<sub>2</sub> ring. A comparison of **MP.VII** with monomer (**MP.IV**) shows that the greatest change to occur on dimerisation is the lengthening of the intra-molecular Li–S bonds to 2.607 Å. This, and the angles at Li (188.8°) and S (130.6°), indicate a relaxation of the ring strain in the NCSLi system. This is reflected in the very negative energy of dimerisation (-31.7 kcal mol<sup>-1</sup>). A comparison of **MP.VIII** with the monomeric structure **MP.V** shows that the Li–N and Li–S bonds have lengthened to 2.109 and 2.518 Å, respectively. These values are in reasonable agreement with those observed for **1** in the solid state. The calculated dimerisation energy of **MP.V** to **MP.VIII** is -13.1 kcal mol<sup>-1</sup>.

The dimerisation of **MP.IV** to **MP.VII** (-31.7 kcal mol<sup>-1</sup>) is similar in energy to the coordination of one HMPA to **MP.IV**, to give **MP.V** (-31.1 kcal mol<sup>-1</sup>). The latter is clearly

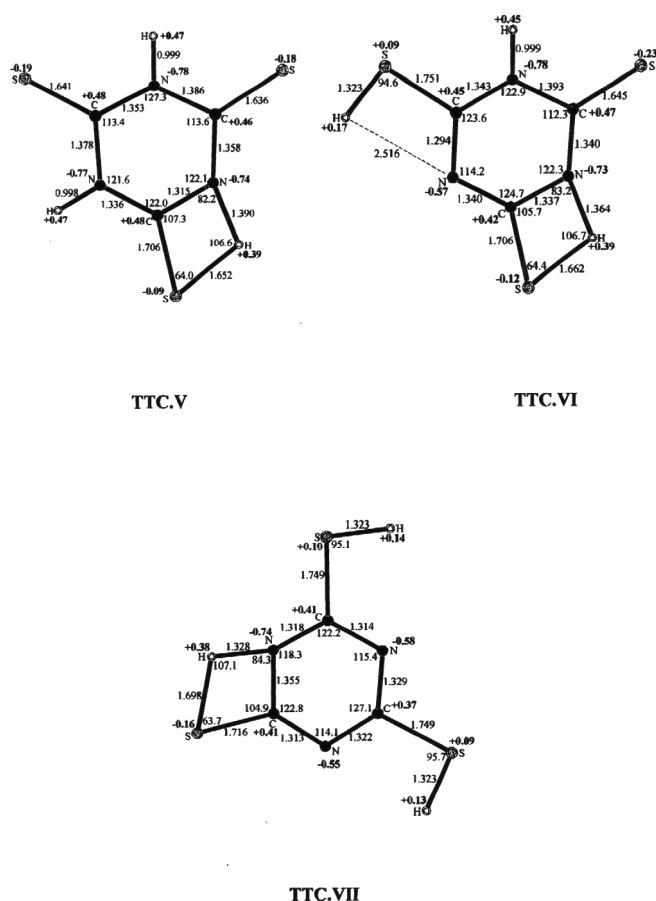
more favourable in the experimental system as **MP.V**, containing a three-coordinate lithium, can then gain extra stabilisation by either coordinating to another HMPA molecule (**MP.VI**) (-13.6 kcal mol<sup>-1</sup>) or dimerising (**MP.VIII**) (-13.1 kcal mol<sup>-1</sup>). The slight favourability of the former process is reflected by the observed solid-state structure of **1**.



**Figure 8** Diagrams showing bond lengths, bond angles and charges within the calculated structures (6-31G\*/RHF level) of HMPA complexes of lithiated *o*-MPH. HMPA methyl groups removed for clarity



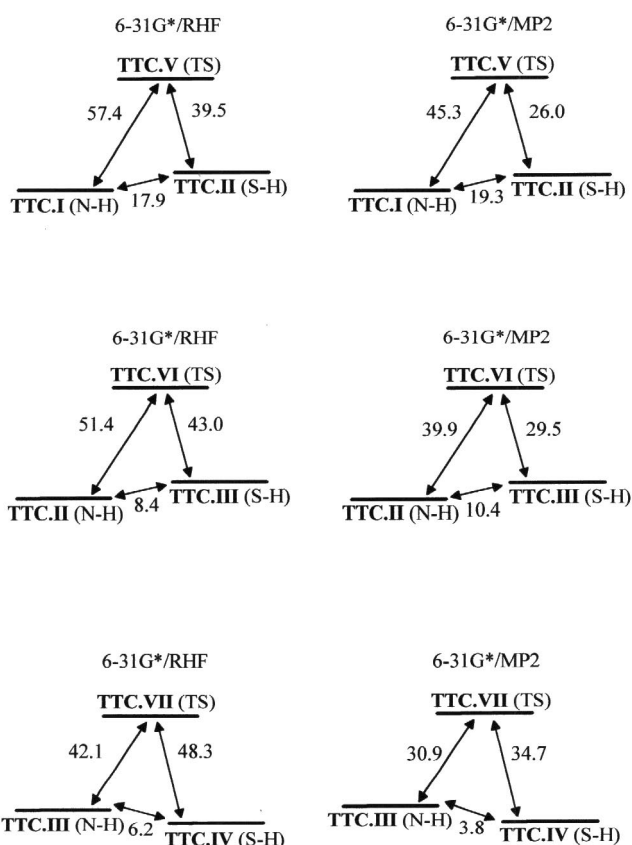




**Figure 11** Diagrams showing bond lengths, bond angles and charges within the calculated transition-state structures (6-31G\*/RHF level) for H-transfer within  $\text{TTCyH}_3$

tions from the  $\text{sp}^2$  optimum of  $120^\circ$ , coupled with the lengthening of the hydrogen bonds, are probably responsible for the observed energy barrier to rearrangement.

Calculations show the favourability of lithiation of  $\text{TTCyH}_3$  with  $\text{Bu}^n\text{Li}$  such that  $\Delta E = -78.1 \text{ kcal mol}^{-1}$  for mono-lithiation and  $-77.6$  and  $-78.4 \text{ kcal mol}^{-1}$  for the subsequent two lithiations respectively [where, for example, for mono-lithiation,  $\Delta E$  is calculated as the difference in energy between the lowest energy optimised structure of  $\text{TTCyH}_3$  plus an optimised structure of  $\text{Bu}^n\text{Li}$ , and the lowest energy optimised structure of  $\text{TTCyH}_2\text{Li}$  plus an optimised structure of  $\text{Bu}^n\text{H}$ , 6-31G\*/MP2 basis set]. Mono-lithiation was examined in two ways; by lithiating an NH group (**TTC.I**→**TTC.VIII**, **TTC.II**→**TTC.IX** and **TTC.III**→**TTC.X**) and by lithiating an SH group (**TTC.II**→**TTC.VIII**, **TTC.III**→**TTC.IX** and **TTC.IV**→**TTC.X**). Three unique mono-metallated models **TTC.VIII**, **TTC.IX** and **TTC.X** (Figure 13) were obtained, Lithiation not apparently altering the order of the thio-keto/thiol equilibrium. Hence, the thio-keto conformation **TTC.VIII** (as observed in the solid-state structure of **2**) is the most stable, although the energy differ-

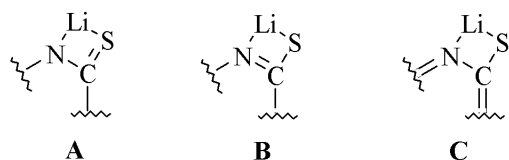


**Figure 12** Representation of transition state (for **TTC.V**, **TTC.VI** and **TTC.VII**) energies in  $\text{kcal mol}^{-1}$

ences between isomers are smaller than those between **TTC.I** to **TTC.IV**.

In **TTC.VIII** a lithium centre is bridging a sulphur and a nitrogen atom. The Li–N and Li–S distances of 1.943 and 2.446 Å respectively, involving only two coordinate lithium, are considerably shorter than those in the solid-state structure of **2** which contains four-coordinate lithium. However, the Li in this calculated structure is in a position to expand its coordination number by the attachment of donors (*e.g.* solvation with experimentally provided HMPA) or by intermolecular association. The other bond lengths are in close agreement with those observed in the structure of **2**. Those within the four-membered NCSLi ring suggest that it is best described as an intermediate between A and B-types (Scheme 3).

A comparison of **TTC.VIII**, **TTC.IX** and **TTC.X** indicates that as the thiol content increases the C–S and N–Li bond lengths increase while the Li–S one decreases. While this would indicate that chelate ring B is becoming more dominant, it does not concur with the observation that the C–N bond length also increases. An interesting feature of



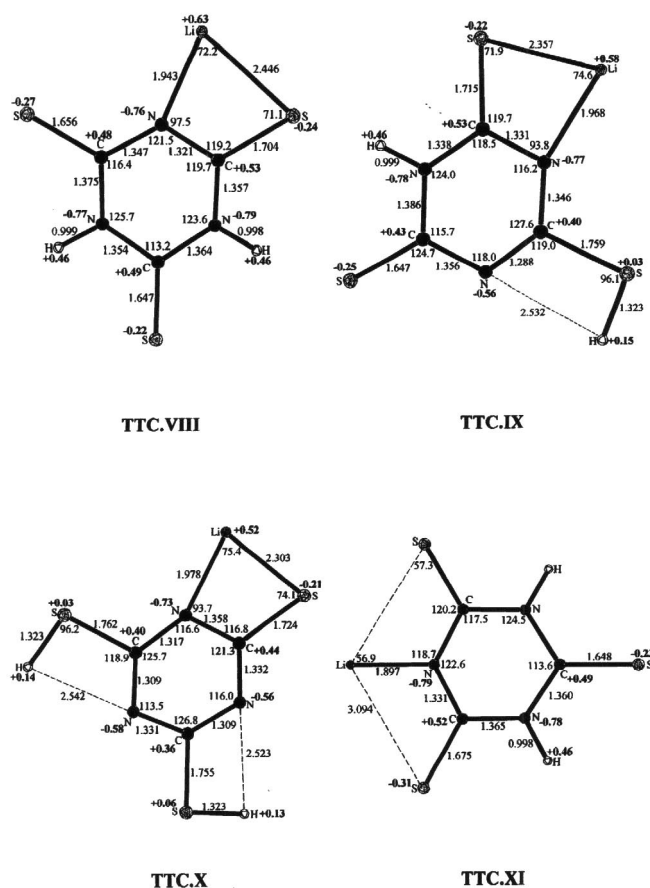
**Scheme 3** Representations of structure types A, B and C

**TTC.VIII** is the 'leaning' of the N–Li interaction towards the C–S bond (as observed in the solid-state structure of **2**) resulting in an Li–N–C angle of  $97.5^\circ$ . Thus the lithium is attracted to only one of its neighbouring sulphur atoms. Examination of a model in which the lithium is thought of as being bound to nitrogen and equally attracted to both its neighbouring sulphurs (**TTC.XI**) (Figure 13) shows it to be higher in energy than **TTC.VIII**, and it turns out to be a transition state for lithium transfer between two sulphur atoms. In **TTC.XI** the Li–S bonds are very long and weak and therefore easily broken. Both the N–Li and C=S bonds are much stronger than in **TTC.VIII**. Hence, lithium transfer is facile with  $\Delta E = 2.67$  kcal mol<sup>-1</sup>.

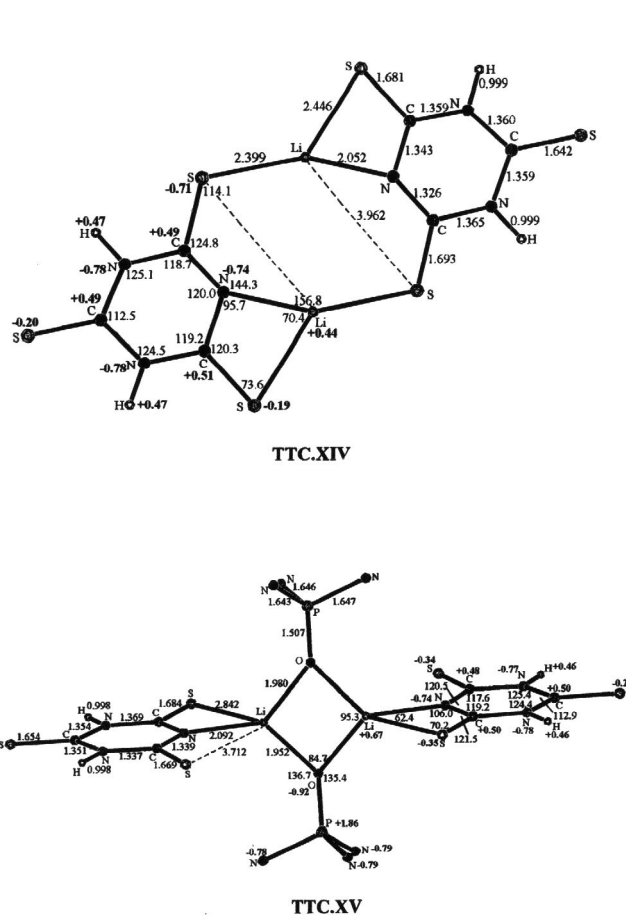
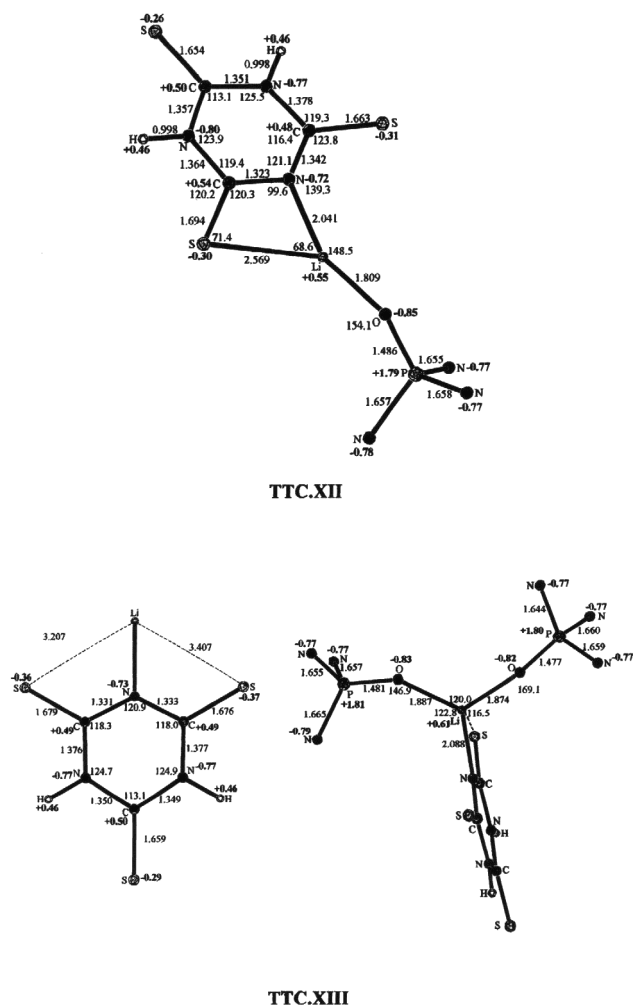
Two solvated monomers **TTC.XII** ( $\equiv$ **TTC.VIII**.HMPA) and **TTC.XIII** ( $\equiv$ **TTC.VIII**.HMPA<sub>2</sub>) (Figure 14) were examined theoretically. **TTC.XII** has no symmetry (unlike its mercaptopyridine counterpart). The plane of the **TTC.VIII** portion is slightly tilted from an obvious mirror plane. If symmetry constraints are imposed, *i.e.* if constrained to a mirror plane, the loss in stabilisation energy is a mere 0.16 kcal mol<sup>-1</sup>. Coordination of the lithium by HMPA causes a lengthening in Li–N and Li–S interactions, with a consequent decrease in C–S bond length. Overall, 0.16e of charge is transferred from the HMPA to the anion ring in **TTC.VIII** and this mainly resides on the Li- and the S-centres. Coordination of lithium by two HMPA molecules (**TTC.XIII**) has the effect of lengthening the Li–S bond to 3.207 Å such that the Li-centre is linked to the anion portion *via* a Li–N bond (2.088 Å) only. The neighbouring C–S bonds are 1.676 Å and 1.679 Å (*cf.* 1.704 Å and 1.656 Å in **TTC.VIII**) indicating that the Li–S interactions present are weak. The two HMPA molecules bonded to lithium by Li–O bonds of length 1.887 Å and 1.874 Å have their PNMe<sub>2</sub> moieties arranged in an almost staggered fashion. A total charge of 0.28e has been transferred to the **TTC.VIII** portion (0.14e from each of the HMPA molecules). A comparison with the parent compound reveals that the three S atoms are the main beneficiaries of this donation. A stabilisation energy of -35.8 kcal mol<sup>-1</sup> is observed for the addition of one equivalent of the Lewis base HMPA (**TTC.XII**) with a further -18.4 kcal mol<sup>-1</sup> obtained from coordination of a second equivalent (**TTC.XIII**). The calculated structure of **TTC.XIII** is very similar to that observed for **2** in the solid state, in which the sulphur atom of the TTCyH<sub>2</sub><sup>-</sup> anion is only weakly bonded to the lithium [Li–S = 2.959(12) Å].

Two models for the dimerisation of TTCyH<sub>2</sub>Li were considered (Figure 15); **TTC.XIV**, a dimer of TTCyH<sub>2</sub>Li (**TTC.VIII**), incorporated two new inter-monomer Li–S bonds with an imposed centre of symmetry while **TTC.XV**, a dimer

of the mono-HMPA complex **TTC.XII**, contained a four-membered (LiO)<sub>2</sub> ring with an imposed centre of symmetry. Comparison of **TTC.XIV** with the monomer **TTC.VIII** shows that dimerisation has no effect on the original intra-monomer Li–S bond lengths (3.962 Å). This structure is best thought of as two monomers combining *via* the formation of two short Li–S(=C) bonds to give an eight-membered ring. Upon dimerisation the C=S bonds involved in the formation of the new eight-membered NCSLi ring lengthen (*cf.* **TTC.VIII**). The lithium atoms are now three-coordinate and the original Li–N and Li–S bonds have lengthened upon aggregation. The main effect of dimerisation on the charge distribution is the reduction of the positive charges on the Li atoms coupled with the lessening of the negative charges on the neighbouring sulphur atoms. The stabilisation energy is -38.4 kcal mol<sup>-1</sup> [*cf.* -31.7 kcal mol<sup>-1</sup> for (*o*-MPH)<sub>2</sub>]. The structure of **TTC.XV** shows that the central, planar four-membered (LiO)<sub>2</sub> ring consists of two different Li–O bonds (1.952 Å and 1.980 Å) and the larger of the two ring angles ( $95.3^\circ$ ) occurs at Li. The TTCyH<sub>2</sub>Li moieties lie almost perpendicular to this ring and are joined to it by Li–N bonds of 2.092 Å and Li–S ones of



**Figure 13** Diagrams showing bond lengths, bond angles and charges within the calculated structures (6-31G\*/RHF level) of TTCyH<sub>2</sub>Li



**Figure 14** Diagrams showing bond lengths, bond angles and charges within the calculated structures (6-31G\*/RHF level) of HMPA complexes of  $\text{TTCyH}_2\text{Li}$ . HMPA methyl groups removed for clarity

**Figure 15** Diagrams showing bond lengths, bond angles and charges within the calculated structures (6-31G\*/RHF level) of dimeric  $\text{TTCyH}_2\text{Li}$  and its HMPA complex. HMPA methyl groups removed for clarity

2.842 Å. This Li–S bond length is particularly long in comparison to the corresponding bonds in **TTC.XII** (2.569 Å) and in **TTC.VIII** (2.446 Å). The corresponding C–S bond is proportionally shorter and the C–N bond longer. The HMPA molecules each donate 0.17e of charge density to the three S atoms and the stabilisation energy for this dimerisation is  $-15.5 \text{ kcal mol}^{-1}$ .

Unlike that of *o*-MPH the dimerisation of  $\text{TTCyH}_2\text{Li}$  (without the Lewis base) is favoured over the solvation of the monolithiated species with one equivalent of HMPA. However, the solvated species can then either gain another equivalent of HMPA or dimerise gaining further stabilisation. Unlike the *o*-MPLi system, solvation of  $\text{TTCyH}_2\text{Li.HMPA}$  with a second equivalent of Lewis base ( $-18.4 \text{ kcal mol}^{-1}$ ) is energetically favoured over dimerisation ( $-15.5 \text{ kcal mol}^{-1}$ ). This confirms that the monomeric structure observed for **2** in the solid

state is more energetically favourable than the dimeric crystal structure observed for **1**.

## Conclusion

Both *o*-MPH and  $\text{TTCyH}_3$  have been found to adopt the thio-keto form in the solid state. Theoretical studies have confirmed that these thio-keto isomers are more energetically favourable than their thiol analogues, although in *o*-MPH the energy difference between the two isomers is significantly lowered by virtue of the stabilisation gained from the extra delocalisation present in the thiol isomer. Calculations have shown that on lithiation an optimised structure with the lithium atom bridging between N and S centres is obtained, regard-

less of whether formally the thio-keto or thiol isomer was lithiated. That this N,S-bridged structure is also energetically favoured over the possible S,N,S-bridged structure in  $\text{TTCyH}_2\text{Li}$  is in agreement with the solid-state structures of **1** and **2**, in both of which this N,S-bridged motif is observed. The tendency of these mono-lithiated compounds to increase the coordination number of lithium *via* solvation and/or dimerisation has been rationalised. Calculations have shown that solvation with one equivalent of HMPA followed by either solvation with a second equivalent or dimerisation is energetically favoured over dimerisation of the unsolvated monomer. This is borne out experimentally by the observation that compounds **1** and **2** both incorporate HMPA. Calculations show that solvation of  $\text{TTCyH}_2\text{Li}$  with two equivalents of HMPA, which gives the monomeric species observed for **2**, is energetically favoured over the dimerisation process observed for the corresponding *o*-mercaptopyridine species, **1**.

The  $\text{TTCyLi}_3$  species, **3**, is a very rare example of a structurally characterised tri-lithiated organic molecule, and it is the first example of such a species to contain S–Li bonds and to be poly- rather than oligomeric. Extensive aggregation is seen to be a consequence of trianion formation itself, and is aided by the presence of two types of electronegative centre (S and N) within the organic precursor,  $\text{TTCyH}_3$ .

Having thoroughly probed, both experimentally and theoretically, the metallated species formed from the lithiation of thiols it now remains to convert these lithiated compounds to the respective sulfenyl chlorides. If the mono- and tri-lithiated derivatives of  $\text{TTCyH}_3$  can be successfully and selectively converted so, it will greatly facilitate the preparation of new mono- and trifunctional sulphur-nitrogen chains.

## Experimental

All reactions and manipulations were carried out under an inert atmosphere of dry nitrogen or argon, using standard double manifold and glove-box techniques. Solvents were distilled off suitable drying agents prior to use. C, H and N analyses were carried out using an Exeter CE-440 elemental analyser. Lithium analyses were carried out on a Perkin-Elmer 3100 Atomic Absorption Spectrophotometer. NMR data were collected on a Bruker AM-400 FT NMR spectrometer. Melting points were determined using a standard Griffin melting point apparatus. HMPA (Aldrich) was dried over molecular sieve (13X or 4Å) for at least 24 hours before use; *o*-MPH and  $\text{TTCyH}_3$  (Aldrich) were used without further purification.

### Preparation of $\text{MPLi.HMPA}$ (**1**)

$\text{Bu}^n\text{Li}$  (1.6ml, 1.6M in hexanes, 2.5mmol) was added dropwise to a stirred solution of *o*-MPH (0.28g, 2.5mmol) in toluene (10ml) at  $-50^\circ\text{C}$ . Warming to room temperature gave a yellow precipitate which, upon addition of HMPA (0.45ml, 2.5mmol) and toluene (1ml) and with gentle heating, afforded

a yellow solution. Storage at room temperature for 24 h yielded crystals of **1**, m.p.  $126\text{--}130^\circ\text{C}$ , yield 34.5%.  $^1\text{H}$  NMR (400 MHz, 298 K,  $d^6$ -DMSO):  $\delta$  7.80 (d, 1H),  $\delta$  6.92 (d, 1H),  $\delta$  6.82 (dd, 1H),  $\delta$  6.30 (dd, 1H),  $\delta$  2.52 (d, 18H, HMPA), and.  $^7\text{Li}$  NMR (155 MHz, 298 K,  $d^6$ -DMSO, ref. PhLi):  $\delta$   $-0.10$  (s). Found: C, 44.5; H, 7.4; N, 18.5. Calc.: C, 44.6; H, 7.4; N, 18.9%.

### Preparation of $\text{TTCyH}_2\text{Li.2HMPA}$ (**2**)

$\text{Bu}^n\text{Li}$  (0.8ml, 1.6M in hexanes, 1.25mmol) was added dropwise to a stirred solution of  $\text{TTCyH}_3$  (0.22g, 1.25mmol) and HMPA (1ml, 5.5mmol) in toluene (15ml) at  $-50^\circ\text{C}$ . Warming to room temperature gave a pale green precipitate which, upon addition of toluene (5ml) and THF (3ml) and with heating, afforded a yellow solution. Storage at room temperature for 24 h yielded yellow crystals of **2**, mp  $204\text{--}208^\circ\text{C}$ , yield, 40%.  $^1\text{H}$  NMR spectroscopy (400 MHz, 298K,  $d^6$ -DMSO),  $\delta$  12.23 (s, 2H),  $\delta$  2.52 (d, 18H, HMPA).  $^7\text{Li}$  NMR spectroscopy (155 MHz, 298K,  $d^6$ -DMSO, ref. PhLi),  $\delta$   $-0.23$  (s). Found: C, 33.28; H, 7.01; N, 23.19; Li, 1.29. Calc.: C, 33.27; H, 7.02; N, 23.29; Li, 1.29%.

### Preparation of $\text{TTCyLi}_3.4\text{THF}$ (**3**)

$\text{Bu}^n\text{Li}$  (4.8ml, 1.6M in hexanes, 7.50mmol) was added dropwise to a stirred solution of thoroughly dried and powdered  $\text{TTCyH}_3$  (0.44g, 2.50 mmol) in THF (15ml) at  $-50^\circ\text{C}$ . THF was removed *in vacuo* until a turbid solution was produced, and this was then heated affording a clear yellow solution. Storage at room temperature for 24 h yielded pale yellow crystals of **3**, m.p.  $>300^\circ\text{C}$ , yield 31%.  $^1\text{H}$  NMR spectroscopy (400 MHz, 298K,  $d^6$ -DMSO),  $\delta$  1.77–1.78 (4H, THF),  $\delta$  3.39–3.76 (4H, THF).  $^7\text{Li}$  NMR spectroscopy (155 MHz, 298K,  $d^6$ -DMSO, ref. PhLi),  $\delta$  0.91 (s). Found: C, 43.55; H, 5.86; N, 10.15. Calc. for  $\text{C}_{15}\text{H}_{24}\text{Li}_3\text{N}_3\text{O}_3\text{S}_3$  ( $\text{TTCyLi}_3 \cdot 3\text{THF}$ , one THF molecule being lost on isolation with drying *in vacuo*): C, 43.80; H, 5.84; N, 10.22%.

### Crystal data for **1**

$\text{C}_{11}\text{H}_{22}\text{LiN}_4\text{OPS}$ ,  $M_r = 296.30$ , white block  $0.60 \times 0.50 \times 0.40$  mm in size, monoclinic, space group  $P2_1/n$ ,  $a = 7.4840(10)$ ,  $b = 14.383(8)$ ,  $c = 15.0480(10)$  Å,  $\beta = 91.10(2)$ ,  $V = 1607.4(9)$  Å<sup>3</sup>,  $Z = 4$ ,  $D_c = 1.224$  Mg m<sup>-3</sup>,  $\mu(\text{Mo-K}\alpha) = 0.297$  mm<sup>-1</sup>,  $F(000) = 632$ . Data were collected by the  $\omega$ - $2\theta$  scan method on a Rigaku AFC7-R four circle diffractometer at 150K with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å).  $5.46 < 2\theta < 54.98^\circ$ ,  $0 \leq h \leq 9$ ,  $0 \leq k \leq 18$ ,  $-19 \leq l \leq 17$ . 3856 reflections of which 3606 were independent ( $R_{int} = 0.0517$ ) and used in all calculations. The structure was solved [24] by direct methods and refined [25] by full-matrix least squares on  $F^2$  with anisotropic displacement parameters for all non-hydrogen atoms. H-atoms were added in geometrically idealised positions and refined using a riding model. Final  $R(F)$

= 0.0527 for 3595 reflections [ $I > 2\sigma(I)$ ];  $wR(F^2) = 0.1627$  for all data; 178 parameters; goodness of fit = 1.043. Maximum peak and hole in final Fourier difference map +0.654 and -0.336 e  $\text{\AA}^{-3}$  respectively.

#### Crystal data for 2

$C_{15}H_{38}LiN_9O_2P_2S_3$ ,  $M_r = 541.60$ , yellow block of 0.6×0.5×0.5 mm in size, orthorhombic, space group  $P2_12_12_1$ ,  $a = 9.744(2)$ ,  $b = 12.823(3)$ ,  $c = 22.978(5)$   $\text{\AA}$ ,  $V = 2871.0(11)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.253$  Mg  $\text{m}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 0.398$   $\text{mm}^{-1}$ ,  $F(000) = 1152$ . Data were collected by the  $\omega$  scan method on a Rigaku AFC5-R four circle diffractometer at 200K (below 180K a phase change was observed) with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$   $\text{\AA}$ ),  $5.26 < 2\theta < 55.00^\circ$ ,  $0 \leq h \leq 12$ ,  $-1 \leq k \leq 16$ ,  $0 \leq l \leq 29$ , 4023 reflections of which 3982 were independent ( $R_{int} = 0.0757$ ) and used in all calculations. The structure was solved by direct methods [24] and refined [25] by full-matrix least squares on  $F^2$  with anisotropic displacement parameters for all non-hydrogen atoms except where HMPA carbon atoms were disordered over several sites. H-atoms were added in geometrically idealised positions and refined using a riding model. Final  $R(F) = 0.0632$  for 3987 reflections [ $I > 2\sigma(I)$ ];  $wR(F^2) = 0.2067$  for all data; 304 parameters; goodness of fit = 1.051. Maximum peak and hole in final Fourier difference map +0.438 and -0.354 e  $\text{\AA}^{-3}$  respectively.

#### Crystal data for 3

$C_{19}H_{32}Li_3N_3O_4S_3$ ,  $M_r = 483.48$ , colourless block 0.40×0.30×0.25 mm in size, monoclinic, space group  $P2_1/n$ ,  $a = 11.027(5)$ ,  $b = 19.081(4)$ ,  $c = 12.181(2)$   $\text{\AA}$ ,  $\beta = 91.47(2)^\circ$ ,  $V = 2562.1(13)$   $\text{\AA}^3$ ,  $Z = 4$ ,  $D_c = 1.253$  Mg  $\text{m}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 0.317$   $\text{mm}^{-1}$ ,  $F(000) = 1024$ . Data were collected by the  $\omega$ - $2\theta$  scan method on a Rigaku AFC7-R four circle diffractometer at 180K with graphite monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71069$   $\text{\AA}$ ),  $7.22 < 2\theta < 55.02^\circ$ ,  $0 \leq h \leq 14$ ,  $0 \leq k \leq 24$ ,  $-15 \leq l \leq 15$ , 6169 reflections of which 5878 were independent ( $R_{int} = 0.0408$ ) and used in all calculations. The structure was solved [26] by direct methods and refined [27] by full-matrix least squares on  $F^2$  with anisotropic displacement parameters for all non-hydrogen atoms (except where atoms were found to be disordered and refined isotropically). H-atoms were added in geometrically idealised positions and refined using a riding model. Final  $R(F) = 0.0855$  for 5878 reflections [ $I > 2\sigma(I)$ ];  $wR(F^2) = 0.2716$  for all data; 267 parameters; goodness of fit = 1.043. Maximum peak and hole in final Fourier difference map +1.506 and -0.722 e  $\text{\AA}^{-3}$  respectively.

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**Supplementary material available** Crystallographic data for compounds 1-3.

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