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Preliminary communication

Dilithiation of *N*,*N*′-diphenylthiourea, PhNHC(=S)NHPh, in HMPA: the unexpected structure of the product, $[\mathrm{PhN\overline{LiC({=}N}Ph)SLi\cdot 2HMPA}]_2$, and supporting ab initio MO calculations on model systems

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Abstract

Ab initio calculations on mono- and di-lithiated derivatives of thiourea predict that Li atom(s) will bridge N and S centres, leading to lengthening of the C=S bond and shortening of one or both of the C=N bonds in thiourea. The synthesised complex of dilithiated diphenylthiourea, $[\mathrm{PhN\overline{LiC({=}N}Ph)SLi\cdot 2HMPA}]_2$ (**1**) displays many of the structural features suggested by theory, having been shown by X-ray crystallography to contain monomeric units with S–Li and N(μ_2-Li)N bonds, these monomers then being linked by N: → Li coordinations.

We report a study of lithiated thiourea-type molecules. Our reasons for such a study were: (i) Lithiated organics with nearby (α or β or γ) heteroatoms, $\sim$XLi $\cdot$ $(\mathrm{C})_{0,1,2}\mathrm{X}'$ $\sim$ often show involvement of X′ with Li, either intra- or inter-molecularly (X,X′ being combinations of C, O, N) [1 *]; however, the role of S as X′, of interest vis-à-vis Li in "hard–soft" acid–base terms, remains largely unexplored. (ii) Although complexes with α-CLi–S $\sim$ units have been examined {e.g., $\overline{\mathrm{S(CH_2)_2S{-}C}}$-(R)Li (R = Me [2a]), Ph [2b], RS–CH$_2$Li (R = Me, Ph [2c]) and 2-Bu^{t}SC$_6$H$_4$Li [2d], whose S atoms either ignore Li or bond datively, S: → Li} as have some sulfonyl

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* Reference numbers with asterisks indicate notes in the list of references.

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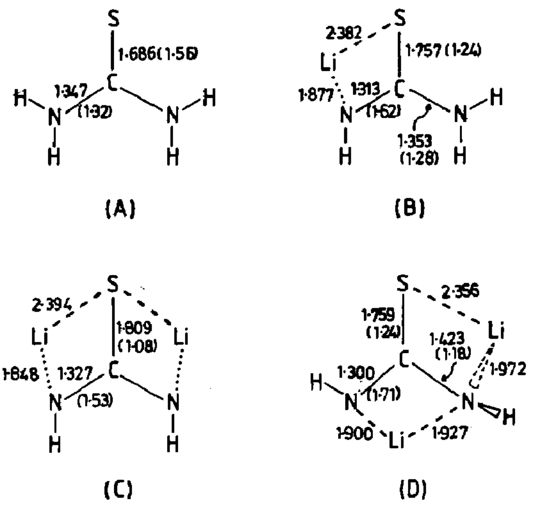

Fig. 1. Ab initio optimised geometries (6–31 G level with *d* orbitals included for S atoms only; relative energies cited in the text for these and other models derive from 6–31 G calculations done without *d* orbital inclusion). (**A**) thiourea; (**B**) monolithiated thiourea; (**C**) and (**D**) dilithiated thiourea. Bond lengths are in Å, and appropriate bond indices are shown in parentheses.

species (e.g., $\mathrm{PhS(=O)\cdot C(Ph)MeLi}$ [2e] and $\mathrm{PhS(=O)(=NSiMe_3)CH(SiMe_3)Li}$ [2f] which show O: → Li, not S: → Li, interactions), complexes containing the C=S unit have not; the presence of this unit α to an NLi centre (so X = N, X′ = S) could allow $\mathrm{N}\,\underline{\cdots}\,\mathrm{C}\,\underline{\cdots}\,\mathrm{S}$ delocalised bonding to Li. For these reasons we first investigated structural features by performing MO calculations on thiourea and its lithiated derivatives. The intriguing results obtained were followed by dilithiation of *N,N′*-diphenylthiourea in HMPA [$\mathrm{O{=}P(NMe_2)_3}$] and the crystal structure of the product, $[\mathrm{PhN\overline{LiC(=N}Ph)SLi\cdot 2HMPA}]_2$ (**1**) revealed many of the features suggested by theory.

Ab initio MO calculations (6–31 G basis set [3]) were performed on thiourea (Fig. 1, **A**), then on models for its monolithiate. Of the latter, the preferred structure has Li bridging between a S and a N centre (Fig. 1, **B**); structures with an N–Li bond directed away from S and with Li bridging both N atoms were less stable by 22.7 and 15.8 kcal $\mathrm{mol^{-1}}$, respectively. In **B**, the Li–S distance is too short to be classed as an additional intramolecular coordination (cf. in crystalline $\mathrm{(2\text{-}Bu^tSC_6H_4Li)_2\cdot TMEDA}$, S: → Li 2.712(5) Å [2d]), and is much more compatible with a direct Li–S bond (i.e., one formed by lithiation of S–H species, e.g., 2.478(4) Å in $\mathrm{[PhC(=O)SLi\cdot TMEDA]_2}$ [4a], 2.412(6) Å in $o\text{-}\mathrm{MeC_6H_4SLi\cdot 3Pyr}$ [4b], and 2.454(11) Å in $\mathrm{2,4,6\text{-}Bu^t_3C_6H_2SLi\cdot 3THF}$ [4c]). In confirmation of this, comparison of **A** and **B** (Fig. 1) shows that the C–S bond lengthens (and its bond index, a measure of the bond order, falls) on lithiation, while the C–N bond involved with the Li shortens and strengthens: thus the anion is best formulated as $[\mathrm{HN}\,\underline{\cdots}\,\mathrm{C}(\underline{\cdots}\,\mathrm{S})\underline{\cdots}\,\mathrm{NH_2}]^-$.

The most stable optimised structure for dilithiated thiourea has each Li bridging between N and S atoms (Fig. 1, **C**); a structure with one Li so positioned and the other on the second N but directed away from S, and one with two such exclusively N–Li bonds are less stable, by 19.6 and 51.9 kcal $\mathrm{mol^{-1}}$, respectively. However, a model with one Li bridging S and an N and the other bridging the N atoms (Fig. 1,

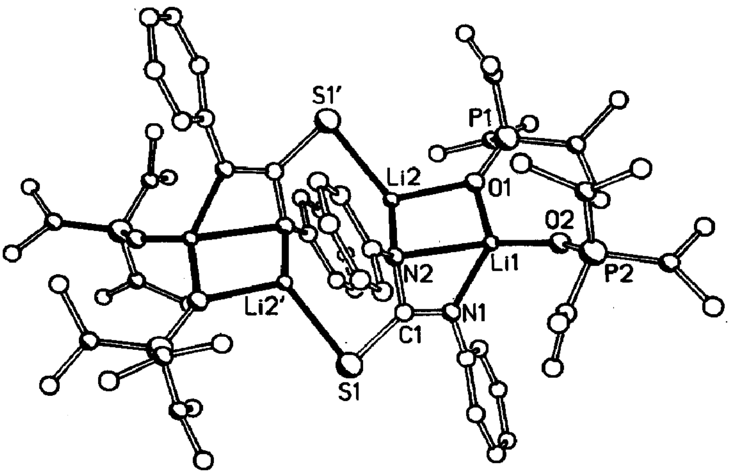

Fig. 2. Molecular structure of 1, with labelling of important atoms. Bonds to Li atoms filled, others open. Crystal data for 1: $C_{50}H_{92}Li_4N_{16}O_4P_4S_2$, $M = 1197.2$, monoclinic, $P2_1/n$, a 14.628(1), b 12.934(1), c 17.859(2) Å, β 93.77(1)°, V 3371.6 Å^3, $Z = 2$, $R = 0.064$ for 2451 unique observed reflections ($2\theta_{max}$ 115°, Cu-K_α radiation).

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

D) is only 14.7 kcal mol^{-1} higher in energy than **C**. Again, comparison of the bond distances and indices in **A** with those in **C** and **D** reveals structural modification within the thiourea moiety, $[HN{=\!=}C(-S){=\!=}NH]^{2-}$ in **C** and $[HN{=\!=}C({=\!=}S){=\!=}NH]^{2-}$ in **D**.

To test these predictions, Bu^{n}Li (5 mmol) was added to *N,N'*-diphenylthiourea (2.5 mmol) in hexane (5 ml), toluene (8 ml), and HMPA (5 mmol). Chilling of the resulting yellow oil gave pale yellow crystals of **1** *. An X-ray diffraction study revealed that **1** is dimeric (Fig. 2), with a central $(\overline{LiNCS})_2$ ring outside of which, fused on either side, are smaller, co-fused $(\overline{LiNLiO})$ and $(\overline{NCNLi})$ rings. The central Li atoms (Li2, Li2') apart, each half of **1** has a Li atom (e.g., Li1) bridging the two N atoms (e.g., N1, N2) of its thiourea moiety; it bears a terminal HMPA ligand (Li–O2, 1.842(11) Å) and bridges to a large-ring Li (e.g., Li1 to Li2) through a second HMPA (Li–O1, 1.946(10) and 1.971(12) Å). As in **C** and **D**, the Li–S distances in **1** (2.426(11) Å) are appropriate for direct bonds [4]. Moreover, the C–S bonds are single (1.722(6) Å), with one C–N bond of each anion also single (e.g., C1–N2, 1.431(7) Å) but the other double (e.g., C1–N1, 1.289(7) Å) (cf. values found for **D**). Thus the two monomers of **1** are actually joined by N: → Li coordinations (e.g., N2: → Li2, 2.046(12) Å), aided by μ_2-HMPA molecules, i.e., in Fig. 2, Li1 and Li2' (not Li2) belong formally to the same monomer. Within each monomer, the outer Li (e.g. Li1) interacts, HMPA ligands apart, directly with the N singly bonded to the central C (e.g., N2–Li1, 2.241(12) Å) and datively with the N doubly bonded to this C (e.g., N1: → Li1, 1.980(11) Å).

Optimised structures **C** and (particularly) **D** thus predict well most of the features found in **1**; that they do not do so completely reflects the dimeric nature of

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* For **1**: m.p. 138–141°C, yield of first batch 70%; satisfactory analyses (C, H, Li, N, P) were obtained.

crystalline **1**, since the Li bridging S and N in **D** is in the monomer of **1**, bonded exclusively to S, so leaving the N-centre free to effect association. However, all these results show that S–Li bonding is somewhat favoured, perhaps implying that "hard-soft" concepts do not pertain to very ionic systems, but perhaps, rather, reflecting the greater energy of C=N than of C=S bonds.

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