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A study on the structures of the substituted (aminomethyl)lithium and (thiomethyl)lithium compounds

Abstract The structures of substituted (aminomethyl) lithium and (thiomethyl)lithium compounds have been examined. Geometric parameters, charge densities, bond orders, dipole moments and heats of formation for all the members of the two series of monomers and dimers of the units $LiCN(R)_2$ and $LiCSR$ where R=H, $CH_3(Me)$, $C_6H_5(Ph)$ have been calculated. The structures of the three complex compounds containing the same units; $[\{Li(CH_2SMe)(THF)\}_\infty]$, $[Li_2(CH_2SPh)_2(THF)_4]$ and $[Li_2(CH_2NPh_2)_2(THF)_3]$ have also been modeled. Geometry optimizations have been performed with the semi-empirical PM3 method. The molecular orbital calculations have been carried out by a self-consistent field method using the restricted Hartree–Fock formalism. Comparisons have been made with the corresponding properties of methyl lithium monomer and dimer. The results show that in all of the nitrogen-containing monomers, the C–Li bonds weaken and the Li–C–H(N) angles decrease due to the coordination of lithium with nitrogen. Substitution of hydrogen atoms by methyl or phenyl groups decreases the Li–N coordination. In the sulfur-containing compounds, sulfur behaves similarly to nitrogen but the changes are smaller because the $3p$ lone-pair orbital of sulfur is higher in energy than the $2p$ lone-pair of nitrogen. All the dimers of nitrogen/sulfur-containing methyl lithium derivatives form six-membered rings in which the Li–N(S) coordination is greater than the one in the corresponding monomers. Dimerization reactions have been found to be exothermic and the formation of all the dimers is favored. The results obtained for the three complex structures are comparable to the experimental results reported in the literature.

Keywords (Aminomethyl)lithium compounds · (Thiomethyl)lithium compounds · Organolithium compounds · Substituted methyl lithium monomers · Substituted methyl lithium dimers

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Introduction

Starting with the investigations of Köbrich and coworkers, [1] lithium carbenoids $LiCH_2X$ have gained considerable attention in the past two decades. The most interesting feature of these compounds is that they contain an electronegative atom or group X and a metal Li on the same carbon. Thus, they display a versatile reactivity depending upon the nature of the electronegative substituent X. Species with X=OR or NR_2 react as electrophiles with nucleophilic agents, whereas compounds with X=halogen behave as nucleophiles in their reactions. [2] The presence of two different groups of opposite polarity not only leads to an enhancement in their reactivities, but also facilitates their fragmentation reactions. As a consequence, lithium carbenoids are thermally unstable and can exist only at low temperatures. [3, 4]

(Halomethyl)lithium compounds are the most widely studied lithium carbenoids. However, functionalized methyl lithiums of the type $LiCH_2YR_n$ (Y=heteroatom, R=alkyl, aryl, H) also have carbenoid reactivities. [4, 5] The structures and reactivities of these compounds depend entirely on the nature of the heteroatom Y, which may be a neutral, coordinatively saturated heteroatom ($YR_n=SiR_4,...$), a neutral Lewis-basic heteroatom ($YR_n=NR_2$, PR_2, OR, SR, F, Cl,....) or a cationic heteroatomic center of these three groups ($YR_n=^+NR_3$, $^+PR_3$, $^+SR_2,...$). Functionalized methyl lithium compounds with Lewis-basic heteroatom centers are of great interest, due to the possible involvement of the heteroatom in the coordination at lithium leading to unusual structures and reactivities. Moreover, these compounds cover a wide range of

stability. In contrast to their interesting features, structural information about these compounds became available only in the last decade and is very limited. [2, 6, 7, 8, 9] Most of the functionalized methyl lithium compounds with heteroatom centers whose solid state structures are known are either TMEDA (N,N,N',N'-tetramethylethylenediamine) adducts or contain other nitrogen chelating ligands. It has been reported that they all form dimeric molecules either with four-membered Li_2C_2 rings in which there is no coordination of the heteroatom to lithium or with six-membered $Li_2C_2Y_2$ rings in which Y is coordinated to lithium. [2]

The solid state structures of substituted (thiomethyl)lithium compounds as tetrahydrofuran (THF) adducts have been reported by Steinborn et al. [2] They have determined the structures of [{Li(CH$_2$SMe)(THF)}$_\infty$] and [Li$_2$(CH$_2$SPh)$_2$(THF)$_4$] by single-crystal X-ray analysis. These two compounds are the first structurally characterized functionalized methyl lithium compounds LiCH$_2$YR$_n$ with a Lewis-basic heteroatomic center Y without chelating nitrogen donor ligands. The first compound was found to be a polymeric species with a ladder-like structure, containing planar four-membered rings and six-membered rings alternately arranged in a chair conformation and it is the only example of a polymeric complex LiCH$_2$YR$_n$, in which both characteristic structural features, a six-membered ring $Li_2C_2Y_2$ and a four-membered ring Li_2C_2, occur together. On the other hand, the TMEDA adduct [Li(CH$_2$SMe)$_2$(TMEDA)$_2$] is a dimer with a four-membered Li_2C_2 ring that is not exactly planar. The second compound has been determined to be a centrosymmetric dimer, which has a planar Li_2C_2 ring at the center with phenylthiomethyl ligands, but without sulfur coordination at lithium. The TMEDA adduct of this thiomethyl compound has shorter Li–C bonds indicating the formation of six-membered rings, $Li_2C_2Y_2$.

The structures of two (aminomethyl)lithium compounds of the type LiCH$_2$NRR´ containing nitrogen as the Lewis-basic heteroatom have been investigated experimentally by Steinborn et al. [6] [Li$_2$(CH$_2$NPh$_2$)$_2$(THF)$_3$] was found to be a dimer with a central four-membered ring in which the coordinations of the two lithium atoms are different from each other. One of the lithium atoms was determined to be tetrahedral, surrounded by two methylene carbon atoms and two oxygen atoms of THF molecules while the other lithium atom is trigonal planar coordinated by the two methylene carbon atoms and the oxygen atom of the THF molecule. It has also been pointed out that planar NC$_3$ units indicate an sp^2 hybridization of nitrogen. The structure of [Li$_4$(CH$_2$NC$_5$H$_{10}$)$_4$(THF)$_2$] has also been examined and found to contain a characteristic Li$_4$ tetrahedron, which is usual in organolithium chemistry, but unusual for functionalized methyl lithium compounds. (D. Steinborn, personal communication)

Very recently, another unusual structure of such organolithium compounds has been determined by Steinborn et al. [7] They have reported a single-crystal X-ray analysis of [Li$_4$(CH$_2$NMe$_2$)$_4$(THF)$_4$] and mentioned that this compound forms tetrameric molecules with a planar four-membered Li_2C_2 ring. The two lithium atoms of the ring are pentacoordinated by Li, N and three C atoms while the other two adopt tetrahedral coordination by C, N and two O atoms of the THF molecules. It is well known that tetranuclear organolithium compounds exhibit tetrahedral arrangements of lithium atoms. However, this organolithium compound does not have a tetrahedral structure.

The use of computational methods has been valuable in the determination of the unusual structures and reactivities of organolithium compounds. [10] Two parallel computational strategies have been developed for the understanding of the electronic structure and chemical bonding of such compounds: rigorous ab initio methods and semiempirical methods based on different approximate levels. [11] Semiempirical methods can still be used for chemically interesting large systems. Although approximations are involved; many calculations have proved that semiempirical methods can be used as predictive tools for the determination of the structures and reactivities of organolithium compounds. [10, 11, 12]

In this study, with the intention of determining and explaining the unusual structural features of organolithium compounds, we have examined the structures of the functionalized organomethyl lithium compounds containing S and N as the heteroatom. We present here the results of our calculations on all the members of the two series of monomers and dimers of the LiCN(R)$_2$ and LiCSR units where R=H, CH$_3$ (Me), C$_6$H$_5$ (Ph). Also, we have modeled the structures of the three complex compounds containing the aforementioned units; [{Li(CH$_2$SMe)(THF)}$_\infty$], [Li$_2$(CH$_2$SPh)$_2$(THF)$_4$] and [Li$_2$(CH$_2$NPh$_2$)$_2$(THF)$_3$] and have compared our findings with the experimental results reported in the literature. [2, 6]

Method of calculation

The molecular orbital calculations for all the molecules in this study were carried out by a self-consistent field method using the restricted Hartree–Fock formalism with the semiempirical PM3 method within the SPARTAN 5.1.1 package. [13] The most stable conformer for the monomers **m1**–**m7** in Fig. 1a and b, dimers **d1**–**d7** in Fig. 2a and b was determined by carrying out a conformer search. [14, 15] The complex structures **I**, **II** and **III** were built and fully optimized. Vibrational frequencies were calculated for the determination of all the structures as stationary points and true minima on the potential energy surfaces. All the stationary points were confirmed by the presence of positive vibrational frequencies. [16]
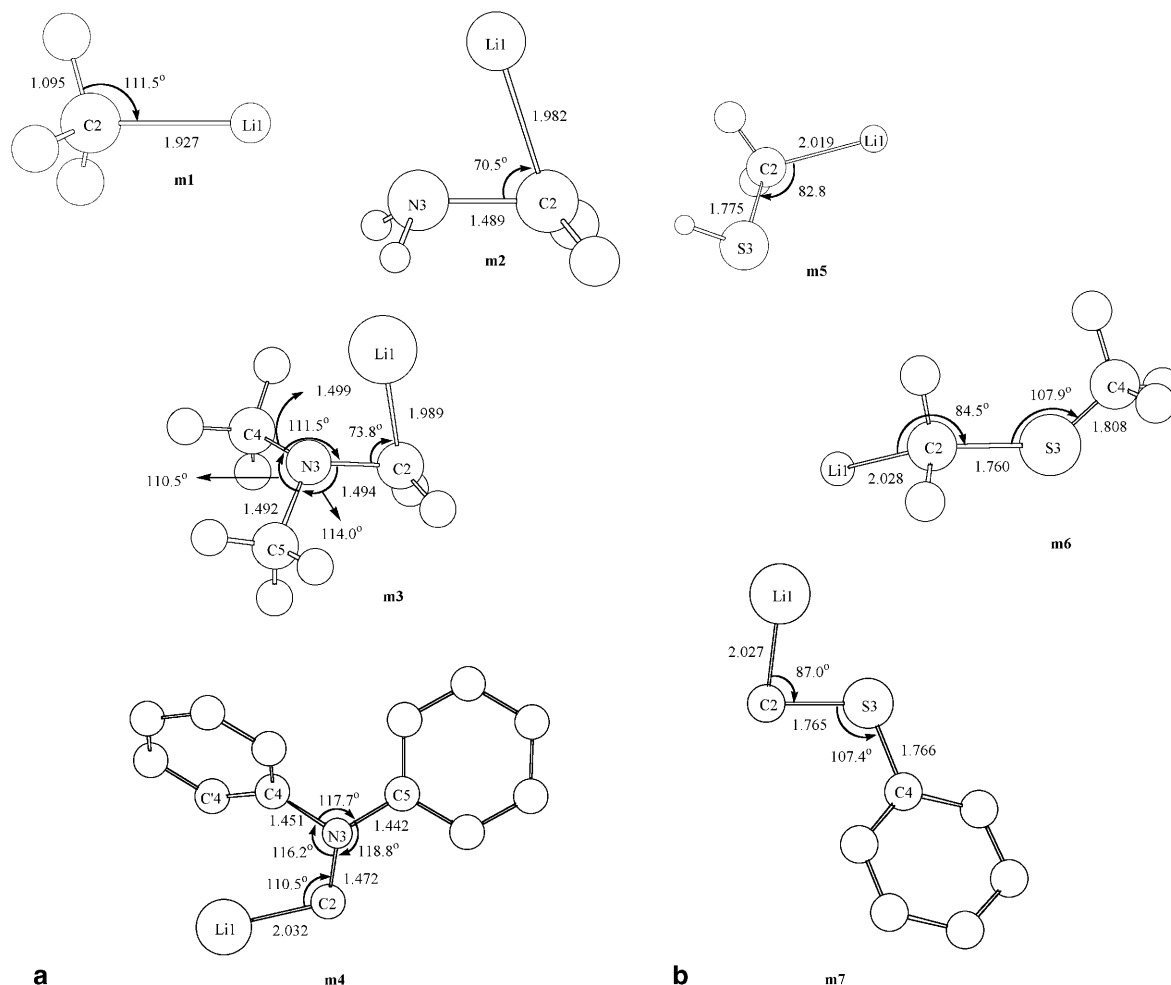
Fig. 1 a Optimized geometries of the monomers **m1**–**m4**. **b** Optimized geometries of the monomers **m5**–**m7**

Results and discussion

Monomers

Figure 1a and b shows the optimized structures together with the necessary geometric parameters obtained for the monomers investigated in this study. The heats of formation and dipole moments, charge densities and bond orders for the corresponding structures are presented in Tables 1, 2 and 3. We are concerned with structural and energetic changes that occur when one of the hydrogens in MeLi is replaced sequentially by $-NR_2$ and $-SR$ (R=H, Me, Ph).

Methyl lithium, MeLi (**m1**)

When one of the hydrogens of methane CH_4 is replaced by a lithium atom to form methyl lithium MeLi, the tetrahedral structure does not change; the C–Li bond length was calculated to be 1.927 Å. It is shorter than the experimental value, which is 2.100 Å. [10, 17] The only struc-

Table 1 Heats of formation (ΔH_f) and dipole moments (μ) for the monomers

	Structure	ΔH_f (kcal mol^{-1})	μ (D)
Methyl lithium	**m1**	25.6	5.19
N-containing	**m2**	24.8	3.62
compounds	**m3**	25.6	3.79
	m4	88.4	5.94
S-containing	**m5**	18.2	4.62
compounds	**m6**	13.8	4.60
	m7	47.1	5.75

tural change that occurs with the substitution of Li for a hydrogen atom in CH_4 is the widening of the Li–C–H angle, which was calculated to be 111.5°. This may be attributed to the electropositive nature of the lithium atom. As lithium is more electropositive than hydrogen, the C–Li bond is more ionic than the other bonds involving hydrogens.

After many years of controversy, the ionic character of the C–Li bond is now well known. [18, 19] The Mulliken population analysis of organolithium compounds has shown a polar but nevertheless predominantly covalent C–Li bonding. [20] In contrast, NPA (natural population analysis) and the AIM (atoms in molecules) topological density analyses have revealed an 80–90% ionic
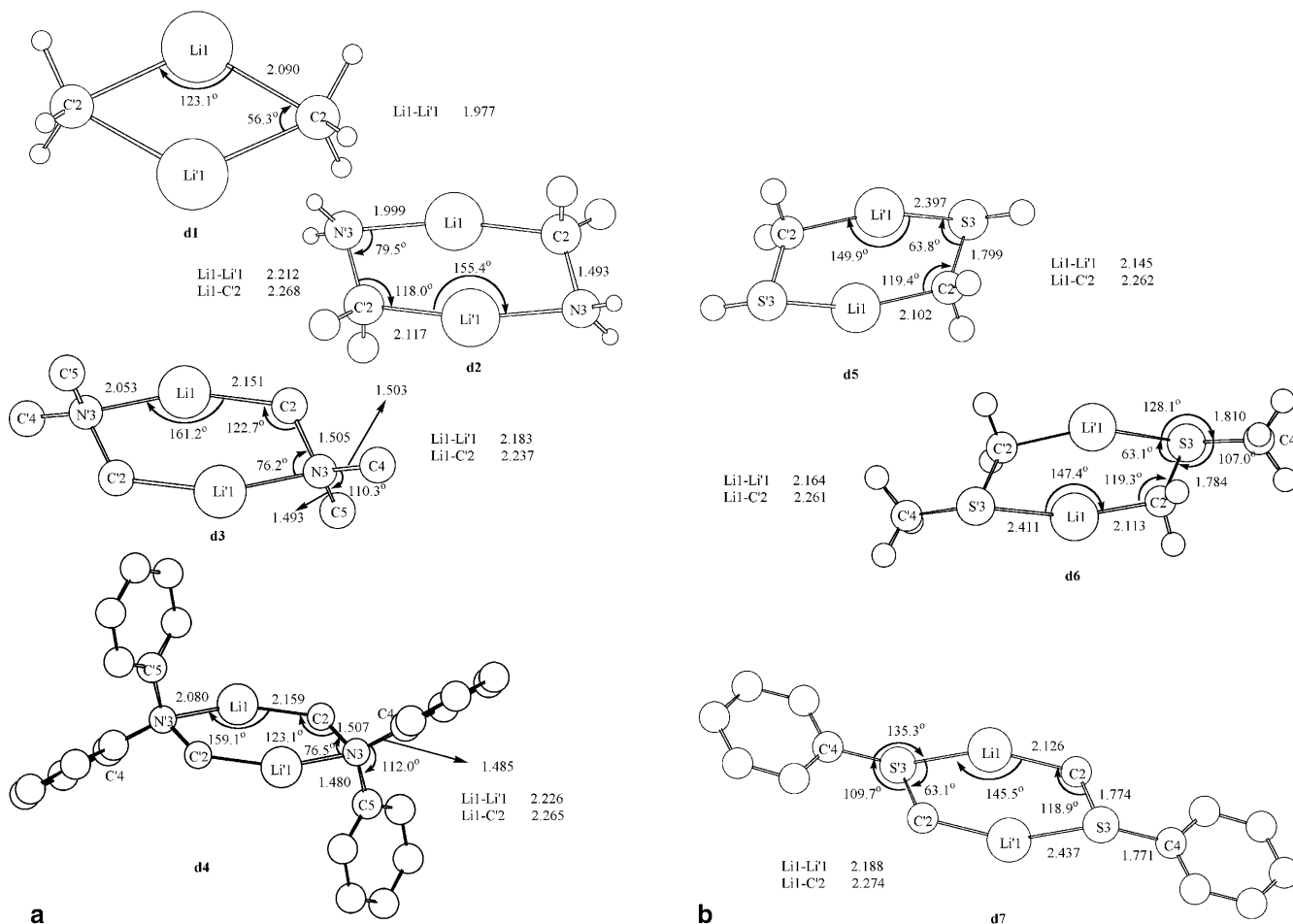
Fig. 2 a Optimized geometries of the dimers **d1–d4**. **b** Optimized geometries of the dimers **d5–d7**

Table 2 Mulliken charge distribution for the monomers

Methyl lithium	**m1**	Li1	0.376
		C2	−0.483
N-containing compounds	**m2**	Li1	0.283
		C2	−0.568
		N3	0.205
	m3	Li1	0.305
		C2	−0.505
		N3	0.097
		C4	−0.100
		C5	−0.133
	m4	Li1	0.369
		C2	−0.491
		N3	0.167
		C4	0.003
		C5	−0.043
S-containing compounds	**m5**	Li1	0.399
		S3	0.028
		C2	−0.530
	m6	Li1	0.416
		S3	0.012
		C2	−0.528
		C4	−0.227
	m7	Li1	0.439
		C2	−0.526
		S3	0.099
		C4	−0.182

Table 3 Bond orders for the monomers

Methyl lithium	**m1**	Li1C2	0.871
N-containing compounds	**m2**	Li1C2	0.693
		Li1N3	0.445
		C2N3	1.011
	m3	Li1C2	0.705
		Li1C4	0.016
		Li1N3	0.327
		C2N3	0.988
		N3C4	0.985
		N3C5	0.973
	m4	Li1C2	0.720
		Li1C4	0.035
		Li1C´4	0.134
		Li1N3	0.017
		C2N3	0.979
		N3C4	1.040
		N3C5	1.041
S-containing compounds	**m5**	Li1C2	0.681
		Li1S3	0.272
		C2S3	1.025
	m6	Li1C2	0.674
		Li1S3	0.233
		C2S3	1.031
		S3C4	0.915
	m7	Li1C2	0.671
		Li1S3	0.200
		C2S3	1.034
		S3C4	0.941

bonding contribution in the C–Li bond of MeLi. [21] The high dipole moment of MeLi, which was calculated to be 5.19 D in this study, also supports the ionic character of the C–Li bond. For all the monomers investigated, the lithium atom has much larger positive charge than all the other atoms (Table 2). Thus, electrostatic repulsions involving the lithium are greater than the ones involving hydrogens. The structural consequence is the widening of the Li–C–H angle to a value greater than that of the tetrahedral angle.

Nitrogen-containing methyl lithium derivatives

The presence of the nitrogen atom in all of the MeLi derivatives (**m2**, **m3**, **m4**) causes the C–Li bond to lengthen. As can be seen from the values given in Fig. 1a, the C–Li bond length in MeLi is 1.927 Å, but it increases to 1.982 Å in structure **m2**, to 1.989 Å in **m3** and to 2.032 Å in **m4**. Replacement of one of the hydrogens in MeLi by –NR_2 (R=H, Me, Ph) was also observed to decrease the Li–C–H(N) angle, which is 111.5° in MeLi (**m1**). It decreases to 70.5° in (NH_2)CH_2Li (**m2**) and to 73.8° in (Me)$_2N CH_2$Li (**m3**). But in **m4**, the presence of the two phenyl groups causes the same angle to increase almost to its original value in MeLi, 110.5°. All of these structural changes are due to the coordination of the nitrogen atom with the lithium.

In all three structures, the nitrogen atom has a lone-pair orbital, while the lithium atom has low-lying vacant 2p orbitals in contrast to the case for hydrogen. Therefore, the nitrogen atom acts as an electron donor to lithium. The calculated N–Li bond orders also support this finding. Furthermore, due to the coordination of lithium with nitrogen, the C–Li bonds were observed to weaken. As presented in Table 3, the bond order for the C–Li bond in MeLi was calculated to be 0.871. With the replacement of one of the hydrogens by –NR_2, it decreases to 0.693 in structure **m2**, to 0.705 in **m3** and to 0.720 in **m4**. It is also interesting to follow the trend in the Li–N bonds; as the Li–C bond order increases, the bond order for the Li–N decreases.

In **m3**, the difference between the bond lengths of the two N3–C4 and N3–C5 bonds indicates a small interaction between the carbon atom (C4) of one of the methyl groups and the lithium atom. The N3–C4 bond which is closer to the lithium atom was found to be longer than N3–C5, while the C4–N3–C5 angle is tetrahedral. In **m4**, the C–Li bond has the highest bond order, indicating that there is almost no coordination between lithium and nitrogen. The two phenyl groups in structure **m4** were found to lie in the planes perpendicular to each other. The one that is *syn* to lithium interacts with it by donating its π-electrons. The bond orders for the Li1–C´4 and Li1–C4 atom pairs were calculated to be 0.134 and 0.035 respectively, whereas in structure **m3**, the bond order for the Li1–C4 bond was 0.016 (Table 3), indicating only a very small interaction between the carbon atom and the lithium atom.

The presence of the nitrogen atom in structures **m2** and **m3** causes a decrease in the polarity of the molecule, which may be due to the N–Li coordination which decreases the positive charge on the lithium atom. But, in **m4**, due to the presence of two phenyl rings, the coordination of the nitrogen with the lithium atom is too small to cause a decrease in the positive charge of the lithium and thus the dipole moment increases almost to its original value 5.94 D.

Sulfur-containing methyl lithium derivatives

A comparison of the structures in Fig. 1a and b reveals a lengthening of the C–Li bond in shifting from methyl lithium (**m1**) to its sulfur-containing derivatives (**m5**, **m6**, **m7**). In structure **m5**, –SH substitution increases the C–Li bond length from its original value, 1.927 Å in MeLi, to 2.019 Å, to 2.028 Å in **m6** and to 2.027 Å in **m7**. Furthermore, it was also observed that the Li–C–H(S) angle decreases with sulfur substitution, but the angles involving sulfur are wider than those with nitrogen. In structure **m5**, the Li–C–S angle was calculated to be 82.8° whereas the same angle, Li–C–N in structure **m2** is 70.5°. The same trend was observed in structure **m6** for which the calculated Li–C–S angle is 84.5°, wider than the one in the analogous nitrogen-containing compound. But, in structure **m7**, the same angle is narrower (87.0°) than the one in structure **m4**.

The above structural changes may be attributed to the coordination of the sulfur atom with lithium. The sulfur atom has lone-pairs; thus it can donate electrons to the lithium atom in a similar way to nitrogen. But the lone-pair orbital of sulfur is a high-lying 3p orbital, higher in energy than the 2p lone-pair orbital of nitrogen. Therefore, the interaction between the lone-pair orbital of sulfur with the vacant p orbitals of the lithium is weaker than that of the nitrogen atom. The bond orders also reflect this weak S–Li interaction. The S–Li bond order was calculated to be 0.272 for structure **m5**, whereas for the analogous nitrogen-containing compound, structure **m2**, the Li–N bond order was found to be 0.445. The same trend was observed in structures **m3** and **m6**. However, for structure **m7**, an opposite trend was observed; the Li–S bond order is higher than the Li–N bond order in the corresponding structure **m4**, because of the presence of the phenyl group.

The effects of the methyl and phenyl substituents in the sulfur-containing methyl lithium derivatives are similar to those in the nitrogen-containing compounds. Replacement of the hydrogen atom bonded to the sulfur in structure **m5** by a methyl or a phenyl group causes a slight decrease in the S–Li coordination. The S–Li bond order, which is a measure of this coordination, was calculated to be 0.272 in structure **m5**, but it decreases to 0.233 in structure **m6** and to 0.200 in structure **m7**. The widening of the S–C–Li angle in the last two structures also supports this finding.

Charge densities of the atoms (Table 2) indicate that charge distribution occurs mainly between the carbon

and the lithium atoms. The nitrogen and sulfur atoms carry small positive charges due to their coordination with lithium. In all of the nitrogen-containing compounds, the nitrogen atom is four-bonded and is positively charged. The sulfur atom has a smaller positive charge, because of the weaker coordination with lithium.

Dimers

Because of the electron-deficient character of the C–Li bonds, alkyllithium derivatives do not exist as monomers, but as higher aggregated species in which lithium is associated with more than one carbon. [21] Dimers of methyl lithium derivatives form either four-membered Li_2C_2 or six-membered $Li_2C_2X_2$ (X=N or S) rings. [2] Therefore, we have modeled both four-membered and six-membered rings for the dimers. The result is that the two different dimeric forms converge to the same, unique structure. In the structures **d2**–**d7**, the Li–C bonds are around 2.100 Å. We consider these structures as six-membered, rather than four-membered rings, because the C–Li bonds in the hypothetical four-membered

Table 4 Heats of formation (ΔH_f), dipole moments (μ) and dimerization energies for the dimers

	Structure	ΔH_f (kcal mol^{-1})	μ (D)	Dimerization energies (kcal mol^{-1})
Methyl lithium	**d1**	–7.6	0.06	–58.8
N-containing compounds	**d2**	–7.4	0.00	–57.0
	d3	–0.1	0.00	–51.1
	d4	132.3	0.00	–44.5
S-containing compounds	**d5**	–21.2	0.00	–57.6
	d6	–27.8	0.00	–55.4
	d7	41.7	0.00	–52.5

structures are longer (~2.2 Å) than the ones in the six-membered structures. We have examined the structural and energetic changes that occur with the substitution of –NR$_2$ and –SR(R=H, Me, Ph) for the two hydrogens in methyl lithium dimer.

Methyl lithium dimer

Methyl lithium dimer, **d1**, contains a four-membered Li$_2$C$_2$ ring and has C$_2$ symmetry. The dimerization energy was calculated to be –58.8 kcal mol^{-1}; thus dimerization is exothermic and the formation of the dimer is favored (Table 4). Dimerization causes the C–Li bonds to lengthen; the C2–Li1 bond length increases from 1.927 Å in the monomer to 2.090 Å in structure **d1**. The decrease in the C–Li bond orders (Table 5) from 0.871 in **m1** to 0.469 in **d1** also supports the weakening of the C–Li bonds. This can be explained by the fact that each lithium atom in structure **d1** forms two bonds with the two carbon atoms of the four-membered ring. Furthermore, a slight coordination between the two lithium atoms was also observed. The bond order for Li1–Li´1 was calculated to be 0.142 and the distance between the two lithium atoms is 1.977 Å.The Li1–C2–Li´1 angle is 56.3°, while the C´2–Li1–C2 angle is 123.1°. In **d1**, the Mulliken charge distribution (Table 6) shows that the two lithium atoms carry positive charges of the same magnitude as in the monomer, while the negative charge on the carbon atoms is almost twice the one in the MeLi monomer, due to the multicentered bonds of the lithium atoms.

Nitrogen-containing dimers

Dimerization energies for the nitrogen-containing derivatives were found to be of the same order of magnitude

Table 5 Bond orders for the dimers

Methyl lithium	**d1**	Li1Li´1	0.142				
		Li1C2	0.469				
N-containing compounds	**d2**	Li1Li´1	0.097	S-containing compounds	**d5**	Li1Li´1	0.105
		Li1C´2	0.217			Li1C´2	0.272
		Li1C2	0.595			Li1C2	0.523
		Li1N3	0.019			Li1S3	0.031
		Li1N´3	0.534			Li1S´3	0.395
		C2N3	1.005			C2S3	1.007
	d3	Li1Li´1	0.115		**d6**	Li1Li´1	0.107
		Li1C´2	0.260			Li1C´2	0.282
		Li1C2	0.546			Li1C2	0.496
		Li1N3	0.016			Li1S3	0.029
		Li´1N3	0.403			Li1S´3	0.355
		C2N3	0.960			C2S3	1.013
	d4	Li1Li´1	0.117		**d7**	Li1Li´1	0.103
		Li1C´2	0.260			Li1C´2	0.286
		Li1C2	0.552			Li1C2	0.464
		Li1N3	0.016			Li1S3	0.029
		Li1N´3	0.391			Li1S´3	0.319
		C2N3	0.970			C2S3	1.029
		Li´1C5	0.024				
		N3C5	0.960				

Table 6 Mulliken charge distributions for the dimers

Methyl lithium	**d1**	Li1	0.394
		C2	−0.812
N-containing compounds	**d2**	Li1	0.088
		C2	−0.474
		N3	0.307
	d3	Li1	0.128
		C2	−0.417
		N3	0.171
	d4	Li1	0.076
		C2	−0.399
		N3	0.266
S-containing compounds	**d5**	Li1	0.192
		C2	−0.450
		S3	0.133
	d6	Li1	0.220
		C2	−0.455
		S3	0.107
	d7	Li1	0.261
		C2	−0.461
		S3	0.186

as that for MeLi dimer, except for structure **d4**. In structure **d2** because of dimerization, the Li–N coordination in the same unit decreases. The bond order was calculated to be 0.019, whereas it is 0.445 in the monomeric species. The widening of the Li1–C2–N3 angle from 70.5° in the monomer to 118.0° in the dimer also reflects this finding. Instead, each lithium atom coordinates with the adjacent nitrogen atom of the second unit. The bond order for Li1–N´3 is 0.534, greater than the original value in the monomer. The Li–N coordination in the dimer causes a decrease in the C–Li bond orders, it decreases from 0.693 in structure **m2** to 0.595 in structure **d2**. The C–Li bond length is 1.982 Å in structure **m2**, whereas it is 2.117 Å in structure **d2**. Moreover, the two lithium atoms coordinate with each other. The bond order for Li1–Li´1 is 0.097, less than the one in MeLi dimer, **d1**. The distance between the two lithium atoms is 2.212 Å whereas it is 1.977 Å in MeLi dimer, **d1**. There is a slight interaction between the lithium atom of one monomeric unit with the carbon atom of the second unit. The bond order for this interaction was calculated to be 0.217, almost half of the bond order for the other Li1–C2 bond.

In **d3**, replacement of the hydrogens in structure **d2** by –CH$_3$ groups further decreases the Li–N coordination in the same unit. The bond order for Li1–N3 is 0.016. The widening of the Li1–C2–N3 angle to 122.7° also supports this finding. In structure **d3**, each lithium atom coordinates with the adjacent nitrogen atom of the second unit. The bond order for this coordination was calculated to be 0.403, smaller than the corresponding value in structure **d2**. This indicates that –CH$_3$ groups cause a decrease in Li–N coordination in structure **d3**, due to the interaction between the –CH$_3$ groups and the lone-pairs of the nitrogen atoms. The decrease in the Li–N coordination weakens the C–Li bonds. The bond order for C2–Li1 in structure **d3** was calculated to be 0.546 and is smaller than the one in **d2**. However, the coordination

between the two lithium atoms increases. The bond order for Li1–Li´1 was calculated to be 0.115. The Li1–N´3–C´2 angle is smaller than the one in structure **d2**.

In **d4**, the two phenyl rings lie in perpendicular planes. Phenyl substitution decreases the Li–N coordination in the same unit; the bond order is 0.016. The Li1–C2–N3 angle is wider than the one in structure **d3**, 123.1°. Each lithium atom of the dimer coordinates with the adjacent N atom of the second unit. But the coordination is less than the one in the methyl substituted compound, structure **d3**. The bond order for Li1–N´3 coordination was calculated to be 0.391. This decrease in the Li–N coordination causes the C–Li bonds in structure **d4** to strengthen compared to the ones in structure **d3**. The coordination between the two lithium atoms is slightly greater than the one in structure **d3**. Each lithium also interacts with the carbon atom of the phenyl ring *syn* to itself; the bond order for Li´1-C5 was calculated to be 0.024. Thus, we may conclude that methyl or phenyl substitution for the hydrogen atoms in structure **d2** causes a decrease in Li–N coordination, but Li1–Li´1 coordination remains unchanged.

The Mulliken charge distribution for the dimers, given in Table 6 shows that N atoms decrease the positive charges on the two lithium atoms, as compared to structure **d1**, due to coordination. The charge distribution occurs mainly among the carbon and nitrogen atoms of the dimeric units, while both of the lithium atoms act almost as neutral. This effect is more pronounced in structure **d2** for which the Li–N coordination was observed to be the highest.

Sulfur-containing dimers

Dimerization energies for the sulfur-containing dimers are of the same order of magnitude as the ones obtained for the analogous N-containing derivatives. The geometric parameters show the same trend for the three sulfur-containing dimers investigated as for the nitrogen-containing dimers. Dimerization causes the Li–S coordination in the same unit to decrease. The bond order for this coordination was calculated to be 0.031 for structure **d5**, smaller than the value for the corresponding monomer **m5**, 0.272. Due to this decrease in the Li–S coordination, the Li1–C2–S3 angle widens. It is 119.4° in the dimer **d5**, and 82.8° in the monomer. Each lithium atom of the dimer coordinates with the adjacent sulfur atom of the second unit. The bond order for Li1–S´3 was calculated to be 0.395, smaller than the value for the corresponding N-containing compound, **d2**, but greater than the original value for the monomer, **m5**, which is 0.272. Due to the increased Li–S coordination in the dimer, the Li–C bonds are weaker than the ones in the monomer. The Li1–C2 bond order was calculated to be 0.681 in structure **m5**, but it decreases to 0.523 in structure **d5**. The two lithium atoms of the dimer coordinate with each other. The bond order for the Li1–Li´1 coordination was

calculated to be 0.105, greater than the corresponding one in the N-containing compound, but smaller than the one in the MeLi dimer (**d1**). Due to the coordination between the two lithium atoms, the Li1–S´3–C´2 angle is 63.8°, smaller than the corresponding angle in the N-containing compound **d2**. It was also observed that there is a slight interaction between the lithium atom of one unit and the carbon atom of the second unit. The Li1–C´2 bond order was calculated to be almost half of the Li1–C2 bond order, similar to the one in the N-containing analog **d2**.

In **d6**, substitution of the methyl groups for the hydrogens in **d5** was observed to decrease the Li–S coordination, due to the interaction between the methyl groups and sulfur atoms. The Li1–S´3 bond order was calculated to be 0.355 for structure **d6**, whereas it is 0.395 for **d5**. This decrease in the Li–S coordination causes the Li–C bonds to weaken. The bond order for C2–Li1 in structure **d6** was calculated to be 0.496 smaller than its value in structure **d5**. The lengthening of the C–Li bonds to 2.113 Å is a result of this weakening. As a result of the lengthening of the Li–S and Li–C bonds, the distance between the two lithium atoms increases from 2.145 Å in structure **d5** to 2.164 Å in structure **d6**. However, the Li1–Li´1 coordination increases slightly. The bond order for this coordination was calculated to be 0.107, slightly greater than its value in structure **d5**, which is 0.105. The consequence is the narrowing of the Li1–S´3–C´2 angle to 63.1°. The Li–S and Li1–Li´1 coordinations were found to be weaker than the ones in the nitrogen-containing analog, **d3**.

The two phenyl rings of structure **d7** lie in parallel planes. Each lithium atom of the dimer coordinates with the adjacent sulfur atom, but the coordination is smaller than the one of the methyl substituted compound, **d6**. The bond order for Li1–S´3 was calculated to be 0.318, whereas it is 0.355 in structure **d6**. Moreover, the Li1–Li´1 coordination and the Li1–C2 bond order were also found to be smaller than their values in structure **d6**, because of the interactions between the lone-pair orbitals of the sulfur atoms and the π-orbitals of the phenyl rings. The decrease in the S3–C4 distance from 1.810 Å in structure **d6** to 1.771 Å in structure **d7** also supports this finding. Thus, phenyl substitution for the methyl group in structure **d6** further decreases the Li–S coordination in the dimer. The Mulliken charge distribution indicates that S atoms decrease the positive charges on the two Li atoms as compared to structure **d1**, in the same way as N atoms do.

Complex compounds

Structure I [Li₂(CH₂NPh₂)₂(THF)₃]

This compound has been prepared and characterized by Steinborn and his coworkers [6] through the reaction of *n*-butyl lithium with the appropriate tributyltin derivative in *n*-hexane. They have reported the formation of the
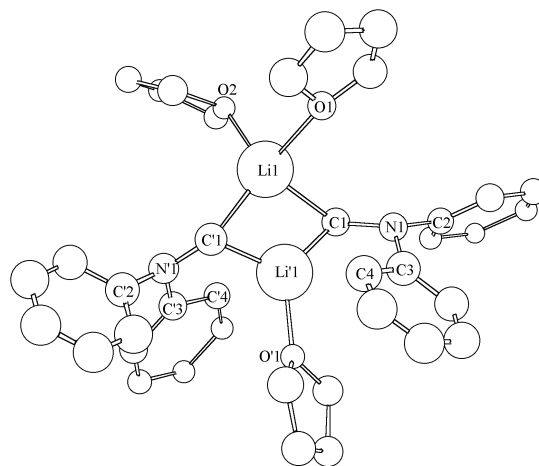

Fig. 3 Optimized geometry of structure **I**

Table 7 Selected distances (Å) and angles (°) for structure **I**

Li1–Li´1	2.465[a] (2.420)[b]	Li1–C1	2.379 (2.246)
Li1–C´1	2.344 (2.235)	Li´1–C1	2.217 (2.170)
Li´1–C´1	2.223 (2.160)	Li1–O1	2.119 (1.988)
Li1–O2	2.080 (1.975)	Li´1–O´1	2.024 (1.935)
Li´1–C4	2.767 (2.712)	Li´1–C´4	2.841 (2.710)
C1–N1	1.484 (1.497)	N1–C3	1.438 (1.434)
N1–C2	1.473 (1.392)	N´1–C´1	1.483 (1.486)
N´1–C´3	1.445 (1.424)	N´1–C´2	1.463 (1.409)
Li1–C1–Li´1	64.8 (66.4)	Li1–C´1–Li´1	65.3 (66.7)
C1–Li1–C´1	120.2 (116.4)	C1–Li´1–C´1	109.2 (110.5)
C1–Li1–O1	107.6 (106.6)	O1–Li1–O2	104.3 (104.3)
O2–Li1–C´1	111.2 (106.8)	C1–Li1–O2	120.3 (112.4)
C´1–Li1–O1	114.5 (116.2)	C´1–Li´1–O´1	125.3 (124.0)
C1–Li´1–O´1	114.5 (119.5)	C1–N1–C3	120.6 (114.7)
C3–N1–C2	115.0 (120.5)	C1–N1–C2	112.5 (122.4)
C´1–N´1–C´3	117.5 (116.9)	C´3–N´1–C´2	115.8 (119.8)
C´1–N´1–C´2	115.0 (122.3)		

[a] This work
[b] X-ray results [6]

compound to require a small amount of THF as a polar aprotic solvent and a recrystallization process from an *n*-hexane–THF solution, which produces discrete dimers. Figure 3 shows the optimized structure of this compound obtained through our PM3 calculations. The selected geometric parameters are presented in Table 7 together with Steinborn's X-ray results. [6] The calculated bond orders and charge densities are given in Tables 8 and 9.

Structure **I** has no Li–N coordination. Therefore, six-membered rings do not form, instead a four-membered Li₂C₂ ring with diphenylaminomethyl ligands and THF molecules forms. The two carbon atoms of the ring are bonded to the nitrogen atoms and each nitrogen has two phenyl groups as the substituents; whereas THFs are bonded to the lithium atoms. One of the lithiums has two THF molecules, while the second lithium is bonded to only one THF. So, structure **I** is asymmetric and the geometric parameters of the two subunits are not equivalent.

All the bond lengths and angles given in Table 7 show that the PM3 geometry obtained in this work is compara-

Table 8 Bond orders for structure **I**

Li1–Li´1	0.113	Li1–O1	0.257
Li1–C1	0.297	Li1–O2	0.267
Li´1–C1	0.478	Li´1–O´1	0.288
Li1–C´1	0.330	N1–C2	0.966
Li´1–C´1	0.459	N1–C3	1.074
C1–C´1	0.007	N´1–C´2	1.000
C1–N1	0.973	N´1–C´3	1.052
C´1–N´1	0.980		

Table 9 Mulliken charge distribution for structure **I**

Li1	0.133	N1	0.118
Li´1	–0.023	N´1	0.133
C1	–0.372	C2	–0.070
C´1	–0.363	C3	00.008
O1	–0.186	C´2	–0.073
O2	–0.171	C´3	–0.001
O´1	–0.156		

ble to the experimental one reported by Steinborn et al. [6] The central four-membered Li_2C_2 ring was found to be almost planar. The calculated dihedral angles Li1–C´1–Li´1–C1 and C´1–Li´1–C1–Li1 are +6.4° and –6.4° respectively. Li1 has a tetrahedral structure and is coordinated by the oxygen atoms of the two THF molecules and the two carbon atoms of the methylene groups. The calculated value of 109.2° for the C´1–Li1–C1 angle also supports this finding. The other lithium atom Li´1 is bonded to the two methylene carbons and to the oxygen atom of one THF molecule. Li´1 has a trigonal planar structure. The sum of the three angles; C´1–Li´1–C1= 120.2°, C1–Li´1–O´1=114.5°, C´1–Li´1–O´1=125.3° is 360.0°.

All the C–Li bonds of the Li_2C_2 ring are almost equivalent to each other, 2.217–2.379 Å. They are longer than the corresponding ones in the dimer (**d4**) and the monomer (**m4**). The C–Li bonds in structure **I** are weaker than the ones in structures **d4** and **m4**. The bond orders are in the range of 0.297–0.478, whereas the bond order for the C–Li bonds in structure **d4** is 0.552. Furthermore, two of the C–Li bonds of the ring, C1–Li1 and C´1–Li1, are longer and weaker than Li´1–C bonds, because of the difference in the coordination numbers of the two lithium atoms. The coordination number for Li1 is 4, whereas the one for Li´1 is 3. In structure **I**, the Li1–Li´1 distance was found to be 2.465 Å, greater than the corresponding one in structure **d4** (2.226 Å), due to a weaker interaction between the lithium atoms for which the bond order was found to be 0.113, instead of 0.117 in structure **d4**. The C´1–C1 distance is much greater than the Li1–Li´1 distance, because of the repulsive interactions between the two carbon atoms. Thus the C´1–Li1–C1 angle (109.2°) is wider than the Li1–C´1–Li´1 angle of the Li_2C_2 ring (65.3°).

Due to the interactions of the THF molecules with the phenyl groups, the Li1–O bonds were found to be slightly longer than the Li´1–O´1 bond. The bond orders for the two Li1–O bonds (0.257 and 0.267) are smaller than the one for the Li´1–O´1 bond (0.288). When these val-

ues are compared to the C–Li bond orders of the Li_2C_2 ring (0.4), it may be suggested that the electrons are almost equally delocalized among the Li–C and Li–O bonds.

NC_3 units were found to be quasiplanar; the sum of the angles C1–N1–C3, C1–N1–C2 and C2–N1–C3 angles is 348.1°. This finding indicates sp^2 hybridization of the nitrogen atoms. The interplanar angles between the NC_3 units and the Li_2C_2 ring, calculated to be 25.9° and 43.8°, are somewhat smaller than the experimental ones, 63.6° and 65.8°, and show that there is no interaction between the lone-pair orbitals of the nitrogens with the methylene carbons. In structure **I**, Li1–N1, Li1–N´1 distances are 3.601 Å and 3.374 Å respectively. Although Li´1 interacts with the nitrogens more than Li1 does, (Li´1–N1=3.110 Å, Li´1–N´1=3.187 Å), these features suggest that there is no Li–N coordination either. In structure **d4**, the Li–N distance is 2.080 Å and the calculated bond order is 0.391. Due to the presence of the THF molecules bonded to the lithium atoms, the N–Ph bonds in structure **I** are stronger and shorter than the corresponding bonds in structure **d4**, because of the contribution of the nitrogens to the phenyl groups. The calculated bond orders are around 1.1 for structure **I**, whereas the N–Ph bond order in structure **d4** is 0.960.

The Mulliken charge distribution for structure **I** shows that the charge distribution mainly occurs among the carbon and nitrogen atoms of the units, while the oxygens are negatively charged. Due to their coordination numbers, the two lithium atoms are differently charged. Li1 is positively charged while the other lithium atom carries a small negative charge, –0.023.

Structure **II** [{Li(CH$_2$SMe)(THF)}$_\infty$]

The solid structure of [{Li(CH$_2$SMe)(THF)}$_\infty$] has first been synthesized by Steinborn and his coworkers [2] through the transmetallation of Bu$_3$SnCH$_2$SMe with *n*-butyllithium in *n*-hexane. They have obtained the above mentioned compound by a recrystallization process from an *n*-hexane–THF solution and determined its structure by single crystal X-ray analysis. Some selected geometric parameters, bond orders and charge densities for structure **II** (Fig. 4) are presented in Tables 10, 11 and 12.

Structure **II** is composed of alternating four-membered Li_2C_2 and six-membered $Li_2C_2S_2$ rings arranged alternately. The four-membered Li_2C_2 rings were found to be planar in agreement with the experimental X-ray results, the dihedral angle Li1–C7–Li6–C2 was calculated to be 5.5°. The Li–C bond lengths are equivalent to each other, around 2.276 Å but they are slightly longer than the corresponding bonds in structure **d6**. The calculated bond orders for the same bonds in structures **II** and **d6** are 0.350 and 0.496 respectively, which may be due to the crowded environment in structure **II**.

Structure **II** is similar to the dimeric species, and there are no phenyl substituents on the heteroatom sulfur.

Fig. 4 Optimized geometry of structure **II**
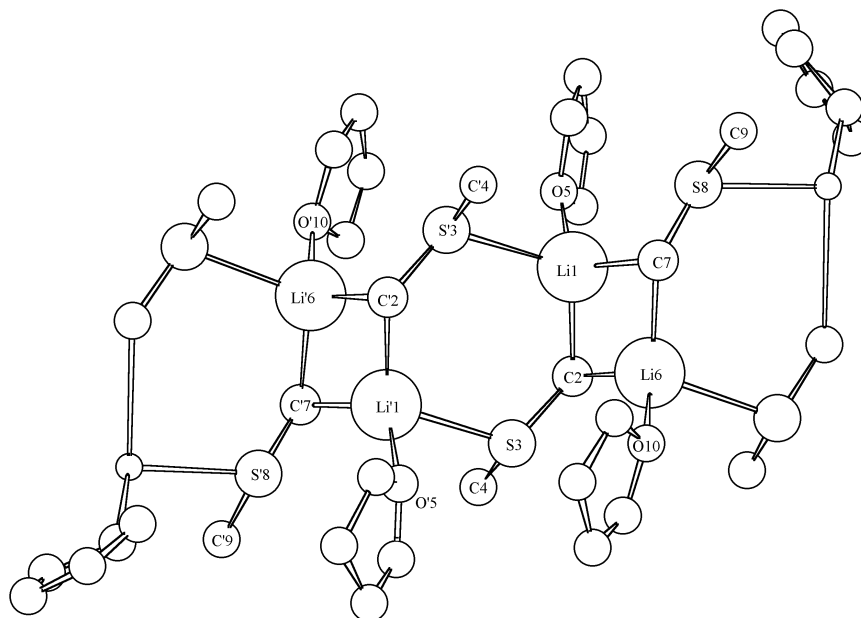
Table 10 Selected distances (Å) and angles (°) for structure **II**

C´2–S´3	1.770[a] (1.769)[b]	S´3–C´4	1.821 (1.814)
Li1–C2	2.276 (2.225)	C7–Li6	2.280 (2.256)
Li1–O5	2.223 (1.982)	Li1–S´3	2.630 (2.531)
Li1–Li6	2.555 (2.499)		
C´2–S´3–C´4	105.6 (106.7)	C2–Li1–C7	111.5 (112.2)
Li1–C2–Li6	68.3 (67.8)	Li´1–C´2–S´3	119.1 (128.0)
Li6–C2–S3	97.9 (103.2)	C2–Li1–O5	102.3 (100.3)
C7–Li1–O5	125.9 (114.8)	S´3–Li1–C2	114.6 (116.6)
S´3–Li1–O5	92.2 (101.0)	C´2–S´3–Li1	118.9 (105.2)

[a] This work
[b] X-ray results [2]

Table 11 Bond orders for structure **II**

Li1–Li´1	0.006	Li6–C2	0.397
Li1–Li6	0.110	Li6–C7	0.336
Li1–C2	0.350	S8–C9	0.885
Li1–S´3	0.375	Li6–O10	0.266
C2–S3	1.021	Li´1–O´5	0.214
Li1–O5	0.227	Li1–S8	0.075
S3–C4	0.907	Li6–S3	0.048
Li1–C7	0.392		

Table 12 Mulliken charge distribution for structure **II**

C´2	−0.399	O5	−0.171
Li´1	0.022	O´5	−0.178
S3	0.150	C9	−0.252
C2	−0.398	S8	0.160
Li1	0.007	C7	−0.409
S´3	0.157	Li6	0.026
C´4	−0.277	O10	−0.163
C4	−0.276		

Therefore, a six-membered structure is the expected one. However, it has adjacent four-membered and six-membered rings. In order to rationalize the formation of four-membered rings instead of six-membered ones, we modeled a hypothetical structure by bonding an extra hydrogen atom to each of the sulfur atoms in structure **d7**. The heat of formation for this structure was calculated to be 108.4 kcal mol^{-1}, greater than the calculated one for structure **d7**, 41.7 kcal mol^{-1}. Thus, we may conclude that the formation of adjacent six-membered rings is not favored.

Each lithium atom has a tetrahedral structure and is coordinated by two methylene carbons, the sulfur and the oxygen atoms of one THF molecule. The S´3–Li1–C2 and C2–Li1–C7 angles, which were calculated to be 114.6° and 111.5° respectively, support this finding. The Li1–C7–Li6 and Li1–C2–Li6 angles of the four-membered ring are narrower than the C2–Li1–C7 and C7–Li6–C2 angles, because of the repulsive interaction between the carbon atoms. In contrast, there is a weak interaction between the lithium atoms with a bond order of 0.110, which causes the Li1–Li6 distance to be shorter than the distance between the carbons of the four-membered ring in structure **II**.

The adjacent unit $Li_2S_2C_2$ is six-membered. All the Li–S and C–S bonds of this unit have the same features as the ones in the corresponding dimer, **d6**. However, the interaction between the sulfur and lithium atoms on nonadjacent units is very weak as shown by the bond order of 0.075. Moreover, the C´2–S´3–Li1 angle is wider (118.9°) than the one in structure **d6** (63.1°), because of the presence of four-membered rings adjacent to the six-membered unit.

The Mulliken charge distribution for structure **II** (Table 12) shows that the charge distribution occurs mainly among the methylene carbons and the sulfur at-
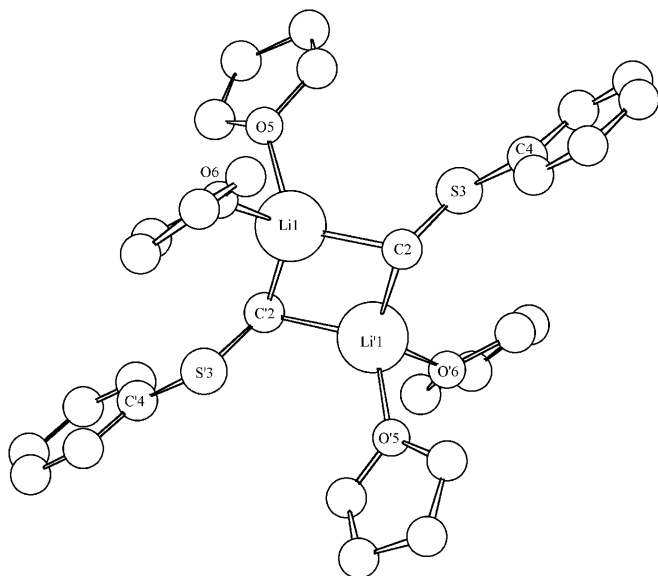
Fig. 5 Optimized geometry of structure **III**

Table 13 Selected distances (Å) and angles (°) for structure **III**

C2–S3	1.757[a] (1.780)[b]	S3–C4	1.770 (1.762)
C2–Li´1	2.289 (2.220)	C2–Li1	2.294 (2.270)
Li´1–O´6	2.111 (1.960)	Li´1–O´5	2.071 (1.960)
Li1–Li´1	2.610 (2.550)		
C2–S3–C4	109.1 (109.3)	C´2–Li1–C2	110.5 (111.1)
Li1–C2–Li´1	69.4 (68.9)	Li´1–C2–S3	104.1 (106.4)
C2–Li´1–O´6	120.8 (114.4)	C2–Li´1–O´5	109.1 (113.6)
C´2–Li´1–O´6	108.1 (110.0)	C´2–Li´1–O´5	119.8 (109.0)
O6–Li1–O5	87.6 (98.0)		

[a] This work
[b] X-ray results [2]

Table 14 Bond orders for structure **III**

Li1–Li´1	0.106	Li1–O6	0.267
Li1–C2	0.360	C2–S3	1.050
Li´1–C2	0.370	S3–C4	0.921
Li1–O5	0.265		

Table 15 Mulliken charge distribution for structure **III**

Li1	0.059	C4	–0.200
C2	–0.405	O6	–0.168
S3	0.085	O5	–0.169

oms. The oxygen atoms of THF molecules bonded to the lithiums carry small negative charges while lithium atoms act as neutral.

*Structure **III** [Li$_2$(CH$_2$SPh)$_2$(THF)$_4$]*

Structure **III** has been synthesized by Steinborn et al. [2] through the analogous transmetallation reaction carried out for structure **II** by using a phenyl substituted tributyl tin derivative. The structure of the compound has also been determined by single-crystal X-ray analysis, [2] the results of which are presented in Table 13, together with the PM3 results obtained in this work.

The optimized geometry of structure **III** is shown in Fig. 5. It is a centrosymmetric dimer composed of a four-membered Li$_2$C$_2$ ring with phenylthiomethyl ligands and four THF molecules, two on each lithium atom. The Li$_2$C$_2$ ring was found to be planar; the dihedral angle Li1–C´2–Li´1–C2 was calculated to be –2.6° and the sum of the internal angles, C´2–Li1–C2=110.5°, Li1–C2–Li´1=69.4°, is 359.8°. The Li–C bond lengths, 2.289 and 2.294 Å, are significantly greater than the corresponding ones in the monomer **m7** and dimer **d7**, but they are almost the same as the ones in structure **II**. Li–C bonds with a bond order (Table 14) of 0.360 are weaker than the ones in structure **d4**, due to the repulsion between the phenyl ring on sulfur and the THF rings on lithium. There is a weak interaction between the two lithium atoms, whose bond order was calculated to be 0.106, having the same order of magnitude as the corresponding one in structure **II**. The C´2–Li1–C2 angle is wider than the Li1–C2–Li´1 angle, because of the repulsive interactions between the carbon atoms.

The lithium atoms are tetrahedrally coordinated with two methylene carbons and two oxygen atoms belonging to two different THF molecules. The magnitude of the angle C´2–Li1–C2 also reflects this behavior. However the O6–Li1–O5 angle is narrower, due to the orientation of the two THF rings on the same lithium atom. They were found to be quasiperpendicular to each other, minimizing the repulsive interaction between the two THF units. There is no coordination between the lithium atoms and the sulfur atoms in structure **III**, because of the presence of the THF molecules. Thus, a four-membered structure is the expected one. The C–S and S–Ph bonds were found to be similar to the ones in the corresponding dimer, structure **d7**. The Mulliken charge (Table 15) distribution shows that the lithium and sulfur atoms carry small positive charges while the carbon and the oxygen atoms of THF molecules are negatively charged.

Conclusions

The principal conclusions of the present study can be summarized as follows:

1. In the nitrogen-containing methyl lithium derivatives, the C–Li bonds weaken and the Li–C–H(N) angles decrease due to the coordination of lithium with nitrogen. Replacement of hydrogens by methyl or phenyl groups decreases the N–Li coordination.
2. In the sulfur-containing methyl lithium derivatives, sulfur behaves similarly to nitrogen but the changes are somewhat smaller. The lone-pair orbital of sulfur is a high-lying 3*p* orbital, higher in energy than the 2*p* lone-pair orbital of nitrogen.
3. The dimers of nitrogen/sulfur-containing methyl lithium derivatives have been modeled by starting with both four- and six-membered rings but a unique struc-

ture which contains six-membered rings has been determined.

4. Dimerization reactions have been found to be exothermic and the formation of all the dimers is thus favored.

5. In N-containing dimers the coordination of lithium with the adjacent nitrogen is greater than the one in the corresponding monomers, but dimerization causes a decrease in the C–Li bond orders. The Li–Li interaction decreases due to the Li–N coordination.

6. The same trend is followed for sulfur-containing dimers.

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