28. Further Investigation of the Nature of the C-Li Bond. Structures of a Phenylthiomethyllithium Complex and of a Methylthiomethyllithium Complex

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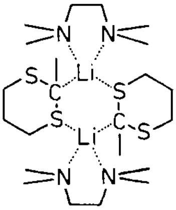
Summary

Phenylthiomethyllithium/*N,N,N′,N′*-tetramethylethylenediamine (TMEDA) (1:1) is shown by X-ray analysis to be dimeric in the crystalline state. The structural unit contains a six-membered ring in which each Li is bonded to the terminal C atom of one thioanisole and to the S atom of the other, as well as to the two N atoms of a TMEDA. Methylthiomethyllithium/TMEDA (1:1) is also dimeric, but the structural unit contains a four-membered ring in which each Li is bonded to two C atoms and to the two TMEDA N atoms. An error has been detected in an earlier published electron-density difference map for 2-lithio-2-phenyl-1, 3-dithiane/TMEDA/THF (1:1:1). The conclusion drawn then that this complex exists as a tight ion-pair in the crystal is now retracted.

Introduction. – In the course of our studies of the nature of the C-Li bond we have already reported on the crystal structures of two 2-lithio-1, 3-dithiane derivatives [1] [2]. The 2-methyl derivative occurs as a dimer **1** containing a central six-membered ring in which each Li atom is bonded to the two N atoms of a *N,N,N′,N′*-tetramethylethylenediamine molecule (TMEDA) as well as to C and S atoms of different dithianes [1]. In contrast, for the 2-phenyl derivative a monomeric structure **2** was found in which the Li atom is bonded to the two N atoms of a TMEDA molecule, to the O atom of a tetrahydrofuran molecule, and to the C atom only of a dithiane [2]. From the observed bond distances and angles around the substituted C atom and from electron-density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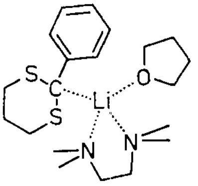
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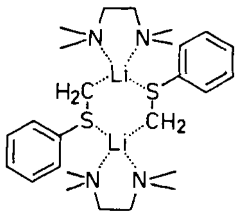
[1] Based in part on the doctoral dissertation of *R.A.*, ETH No. 7210.

difference maps, we interpreted the former structure as containing a polarized but essentially covalent C-Li bond, the latter as a contact ion-pair [2].

We now describe two new low-temperature crystal structures, those of phenylthiomethyllithium/TMEDA (1:1) and of methylthiomethyllithium/TMEDA (1:1). As might be expected from their 1:1 compositions both compounds are dimeric, the former containing a six-membered ring **3** similar to **1**, the latter a four-membered ring **4** where the Li is bonded to two carbanionoid centers but not to the S atom.



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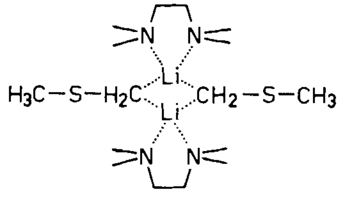

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We have also obtained an electron-density difference map for **3** which is similar to that of **1** in the region of the Li atom. More important, we have detected an error in the difference map described earlier for **2** which compels us to revise our previous interpretation [2] of these maps.

Table 1. *Atomic Coordinates and Vibration Parameters for Structure* **3** *with Standard Deviations in Units of the Last Significant Figure in Parentheses*

Atom	X	Y	Z	U_{11} (or U)	U_{12}	U_{33}	U_{12}	U_{13}	U_{23}
C(1)	0.6367(2)	0.3897(1)	0.7548(1)	0.0113(8)	0.0203(9)	0.0136(9)	0.0013(7)	– 0.0017(6)	0.0021(7)
C(2)	0.6478(2)	0.2962(1)	0.7833(1)	0.0199(9)	0.021(1)	0.0181(9)	0.0023(7)	– 0.0019(7)	0.0021(8)
C(3)	0.6707(2)	0.2716(1)	0.8874(2)	0.0224(9)	0.026(1)	0.024(1)	0.0026(8)	– 0.0016(8)	0.0089(8)
C(4)	0.6846(2)	0.3404(2)	0.9637(2)	0.0195(9)	0.040(1)	0.0142(9)	0.0017(8)	– 0.0020(7)	0.0084(9)
C(5)	0.6694(2)	0.4334(1)	0.9370(1)	0.0209(9)	0.035(1)	0.0141(9)	0.0004(8)	– 0.0020(7)	– 0.0016(9)
C(6)	0.6446(2)	0.4580(1)	0.8330(1)	0.0168(8)	0.0210(9)	0.0156(9)	0.0008(7)	– 0.0019(7)	0.0003(8)
C(7)	0.6378(2)	0.5419(1)	0.5984(1)	0.0213(9)	0.0185(9)	0.0180(9)	– 0.0013(7)	– 0.0055(7)	0.0056(8)
C(8)	0.3033(2)	0.2214(1)	0.6595(2)	0.025(1)	0.025(1)	0.033(1)	0.0063(8)	0.0022(9)	0.0081(9)
C(9)	0.1981(3)	0.2344(2)	0.4953(2)	0.041(1)	0.032(1)	0.029(1)	– 0.009(1)	– 0.005(1)	– 0.008(1)
C(10)	0.0642(2)	0.3121(1)	0.6592(2)	0.0171(9)	0.022(1)	0.030(1)	– 0.0019(8)	– 0.0009(8)	0.0009(9)
C(11)	0.0829(2)	0.3821(1)	0.7473(2)	0.0193(9)	0.024(1)	0.020(1)	0.0040(8)	0.0026(8)	0.0029(8)
C(12)	0.2256(2)	0.5190(2)	0.7852(2)	0.023(1)	0.042(1)	0.026(1)	0.0012(9)	– 0.0069(8)	– 0.013(1)
C(13)	0.0600(2)	0.5267(1)	0.6507(2)	0.0249(9)	0.023(1)	0.027(1)	0.0049(8)	– 0.0073(8)	0.0013(9)
Li(1)	0.3457(3)	0.4143(2)	0.5672(2)	0.022(1)	0.020(2)	0.019(1)	0.001(1)	– 0.005(1)	0.002(1)
N(1)	0.2210(2)	0.2835(1)	0.5944(1)	0.0216(8)	0.0195(8)	0.0176(8)	– 0.0010(6)	0.0001(6)	0.0000(7)
N(2)	0.1685(2)	0.4667(1)	0.6992(1)	0.0178(7)	0.0217(9)	0.0162(8)	0.0013(6)	– 0.0044(6)	– 0.0020(7)
S(1)	0.62272(5)	0.42031(3)	0.61724(3)	0.0186(2)	0.0176(2)	0.0106(2)	– 0.0007(2)	– 0.0044(1)	0.0009(2)
H(21)	0.642(2)	0.243(2)	0.723(2)	0.026(6)					
H(31)	0.674(3)	0.199(2)	0.909(2)	0.033(7)					
H(41)	0.707(3)	0.319(2)	1.042(2)	0.030(6)					
H(51)	0.676(2)	0.488(2)	0.996(2)	0.026(6)					
H(61)	0.637(2)	0.531(2)	0.812(2)	0.022(5)					
H(71)	0.750(3)	0.566(2)	0.617(2)	0.028(6)					
H(72)	0.540(2)	0.576(2)	0.652(2)	0.021(5)					
H(81)	0.413(3)	0.198(2)	0.608(2)	0.039(7)					
H(82)	0.228(3)	0.162(2)	0.688(2)	0.033(6)					
H(83)	0.333(3)	0.258(2)	0.729(2)	0.036(6)					
H(91)	0.125(3)	0.173(2)	0.515(2)	0.053(8)					
H(92)	0.139(3)	0.279(2)	0.446(2)	0.038(7)					
H(93)	0.313(3)	0.214(2)	0.447(2)	0.037(6)					
H(101)	0.001(3)	0.252(2)	0.699(2)	0.036(6)					
H(102)	– 0.006(3)	0.342(2)	0.605(2)	0.030(6)					
H(111)	0.150(2)	0.351(1)	0.803(2)	0.021(5)					
H(112)	– 0.033(3)	0.400(2)	0.795(2)	0.029(6)					
H(121)	0.129(3)	0.539(2)	0.851(2)	0.034(6)					
H(122)	0.285(3)	0.582(2)	0.750(2)	0.038(6)					
H(123)	0.310(3)	0.477(2)	0.819(2)	0.045(7)					
H(131)	0.008(3)	0.489(2)	0.591(2)	0.032(6)					
H(132)	0.125(3)	0.585(2)	0.609(2)	0.033(6)					
H(133)	– 0.037(3)	0.553(2)	0.713(2)	0.048(7)					

Table 2. *Bond Distances* (in Å) *and Angles* (in degrees) *in Dimeric Phenylthiomethyllithium/TMEDA* (1:1 complex)

Li–C(7)	2.131(4)	C(7)–S	1.759(2)
Li–S	2.555(3)	C(1)–S	1.792(2)
Li–N(1)	2.148(4)		
Li–N(2)	2.133(3)	N(1)–C(8)	1.470(3)
		N(1)–C(9)	1.465(3)
C(1)–C(2)	1.394(3)	N(2)–C(12)	1.466(3)
C(1)–C(6)	1.391(3)	N(2)–C(13)	1.475(3)
C(2)–C(3)	1.392(3)	N(1)–C(10)	1.473(2)
C(5)–C(6)	1.397(3)	N(2)–C(11)	1.479(2)
C(3)–C(4)	1.390(3)	C(10)–C(11)	1.517(3)
C(5)–C(4)	1.387(3)		
		C(8)–N(1)–C(9)	109.2(2)
Li–C(7)–S	114.2(1)	C(8)–N(1)–C(10)	110.2(1)
C(7)–S–Li	92.7(1)	C(9)–N(1)–C(10)	109.7(2)
S–Li–C(7′)	109.7(1)	C(12)–N(2)–C(11)	109.4(1)
		C(13)–N(2)–C(11)	110.2(1)
C(7)–S–C(1)	110.7(1)	C(12)–N(2)–C(13)	108.9(2)
Li–S–C(1)	117.5(1)		
S–C(1)–C(2)	119.9(1)	Li–N(1)–C(10)	102.1(1)
S–C(1)–C(6)	121.0(1)	Li–N(2)–C(11)	103.8(1)
C(6)–C(1)–C(2)	119.0(2)	N(1)–C(10)–C(11)	111.5(2)
C(1)–C(2)–C(3)	120.6(2)	N(2)–C(11)–C(10)	111.4(1)
C(2)–C(3)–C(4)	120.1(2)	N(1)–Li–N(2)	86.2(1)
C(3)–C(4)–C(5)	119.7(2)		
C(4)–C(5)–C(6)	120.2(2)	Li–N(1)–C(8)	109.9(1)
C(5)–C(6)–C(1)	120.4(2)	Li–N(1)–C(9)	115.5(1)
		Li–N(2)–C(12)	117.1(1)
		Li–N(2)–C(13)	107.2(1)

Crystal Structure of Phenylthiomethyllithium/TMEDA (1:1) (3) at 95 K. – Monoclinic, $a = 8.507$, $b = 14.336$, $c = 12.432$ Å, $\beta = 78.62°$, $V = 1486$ Å^3, $Z = 4$ formula units $C_{13}H_{23}N_2SLi$, space group $P2_1/c$, $D_x = 1.10$ gcm^{-3}.

Atomic coordinates and vibration parameters are given in *Table 1*, selected interatomic distances and angles in *Table 2*. The structural units consist of centrosymmetric dimers, as shown in *Fig. 1*, containing a six-membered ring in which each Li is linked to the terminal C atom of one thioanisole fragment and to the S atom of the other. There is a general similarity to the corresponding central ring in the methyldithiane complex **1**, but there are also significant differences between the two structures. In **3** the Li-C distance is shorter (2.130 *vs.* 2.186 Å), the Li-S distance is longer (2.554 *vs.* 2.519 Å), the angle at the S atom is smaller (99.7 *vs.* 110.6°), and the angle at the C atom is larger (114.2 *vs.* 102.9°).

As seen in *Fig. 1*, the central ring has a chair-like conformation with the phenyl groups equatorial; thus the aryl-S bond of each monomeric fragment is antiperiplanar to the C-Li bond. If this feature is attributed to an anomeric effect type of interaction involving the carbanionoid electron pair, we would expect the bond C(7)-S (1.759 Å) to be shortened and C(1)-S (1.792 Å) to be lengthened compared with CH_3-S-aryl molecules. This expectation seems to be borne out by the available information gleaned from the *Cambridge Structural Database* [3], from which we found CH_3-S distances of

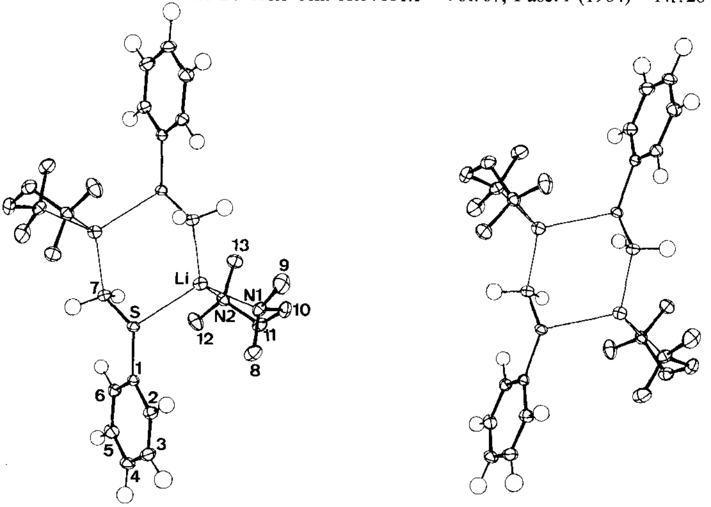

Fig. 1. *ORTEP* [27] *stereoview of a dimeric structural unit of phenylthiomethyllithium/TMEDA (1:1) showing atomic numbering.* For clarity, H atoms of the TMEDA molecules have been omitted. Vibrational ellipsoids are drawn at the 50% probability level.

1.773–1.831 Å, average 1.821 Å, and S-aryl distances of 1.750–1.790 Å, average 1.768 Å in eight CH_3-S-aryl structures with $R < 0.07$. Alternatively, one might be tempted to explain the shortness of the C(7)-S bond by invoking some degree of ylid character in this bond. However, the analogous argument applied to structure **1** would lead us to expect that of the two geminal C-S bonds, the one involving the Li-bonded S should be the shorter, which is not the case, it being actually a shade longer: 1.791(2) *vs.* 1.782(2) Å [1]. We intend to return to the dicussion of C-S bond distances in a forthcoming publication on the structure of sulfonium salts and ylids.

The C-C bonds of the phenyl group all lie within 0.005 Å of the average length of 1.392 Å, and little significance can be attached to the variations of the individual bonds from this average. Corrections for rigid-body and internal motion could easily account for the slight apparent contraction with respect to benzene itself (1.396 Å) [4]. On the other hand, the deviations of some of the bond angles from 120° are highly significant. Angular deviations on a substituted benzene ring, particularly that at the ipso C atom, have been correlated with substituent parameters such as *Taft*'s inductive parameter σ_I [5]. By interpolation, the bond angle of 119.0(2)° at C(1) in our structure would correspond to a σ_I very close to 0.19, the accepted value for the thiomethyl substituent [6].

Tetrahedral coordination at each Li is completed by a TMEDA molecule *(Fig. 1)*. The Li-N distances of 2.148(4) and 2.133(3)Å and the N-Li-N angle of 86.2(1)° are close to the values found in **1** and **2**. Indeed, the bond distances found for the TMEDA fragment in these three low-temperature crystal structure analyses are remarkably self-consistent, varying by not more than a few 10^{-3} Å from their mean values: 1.468(3)Å for the peripheral N-C bonds, 1.477(2)Å for the inside ones, and 1.515(2)Å for the central C-C bond. There would thus appear to be a significant shortening of the latter, compared with the standard value of 1.541 Å for C-C bonds in alkanes [7].²) It is

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²) Judging from a more recent compilation of structures of gas-phase molecules [8], this standard value may well be liable to downward revision by *ca.* 0.01 Å.

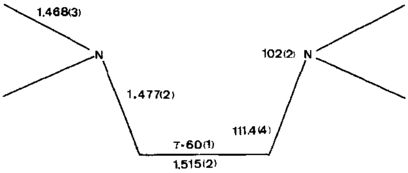

Fig. 2. *Standard dimensions for a TMEDA molecule, based on results of three low-temperature X-ray diffraction studies*

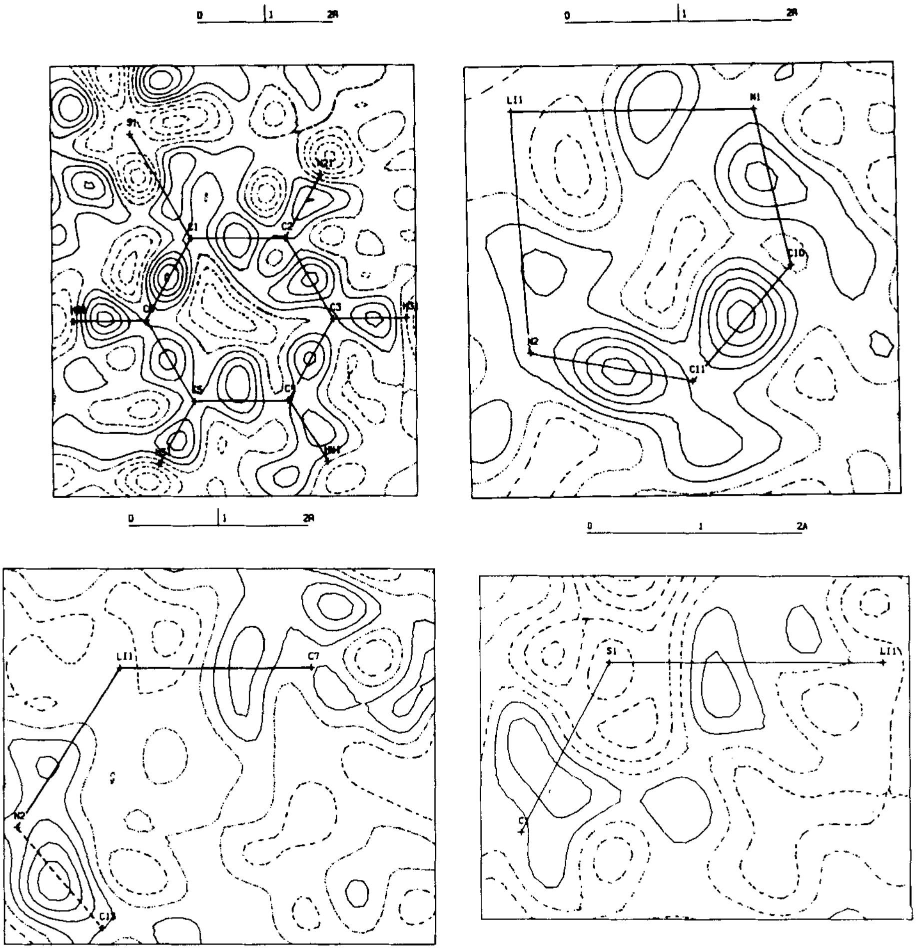

Fig. 3. *Several sections of the residual electron-density difference map for phenylthiomethyllithium/TMEDA dimer:* upper left, in the plane of the phenyl group; upper right, in the plane through N(1), N(2), and Li; lower left, in the plane through C(7), N(2), and Li; lower right, in the plane through C(1), S(1), and Li. Contours are drawn at intervals of 0.05 e. Å^{-3}, zero contour dotted, negative contours dashed.

unlikely that this apparent shortening in these low-temperature structures can be attributed to neglect of corrections for librational motion, as has been suggested to account for similar shortenings found in room-temperature analyses of other ethylenediamine complexes [9].

The bond angles within the TMEDA fragment also show remarkably little variation, and the N-C-C-N torsion angle is within a degree or so of 60°. Those bond angles and torsion angles involving the coordinated Li atom vary more. *Fig. 2* shows what we consider to be a set of standard dimensions for this important chelating agent. Appreciable deviations from the standard bond distances in *Fig. 2* may be regarded as indications of possible disorder in the crystal structure. An example will be seen in the analysis of compound **4**.

Residual Density Maps. – *Fig. 3* shows residual density maps $\Delta\rho = \rho_o - \rho_c$ in the plane of the phenyl group and in several planes containing the Li atom in the crystal structure of **3**. These maps depict that part of the experimental charge density not accounted for by the procrystal[3]), *i.e.* by a model consisting of a set of spherically averaged neutral atoms with the positional and vibrational parameters listed in *Table 1*. The overall quality of the maps can be judged from the appearance of $\Delta\rho$ in the phenyl group plane. Although this map evidently leaves much to be desired[4]), it does show fairly clear charge accumulations close to the midpoints of the C-C bonds and, to a lesser extent, in the C-H bonds as well.

The other sections in *Fig. 3* show diffuse peaks along the Li-N and Li-C bonds, much closer to the N and C atoms than to the Li, which is situated in a rather featureless region with $\Delta\rho$ close to zero. This is similar to the residual density described previously for **1** but quite different from that for **2**, where $\Delta\rho$ at the Li atom was strongly negative and where integration of $\Delta\rho$ over the region round the Li atom led to an apparent positive charge of 0.5–0.6 electrons [2]. We concluded then that 2-lithio-2-methyldithiane would seem to have a covalent, at most polarized, Li-C bond, whereas 2-lithio-2-phenyldithiane could be regarded as an example of a contact ion-pair complex. The present result would seem to indicate that **3** resembles **1** in having a polarized but essentially covalent Li-C bond, in contrast to the ionic bond in **2**.

Correction of an Error. – However, we now have to report that the $\Delta\rho$ map obtained earlier for **2** is erroneous because it was based on an incorrect form factor for the neutral Li atom[5]). When the calculations are repeated with the correct form factor the residual density in the region round the Li atom does not differ in any important

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[3]) A useful dictionary of terms and concepts used in charge density analysis is provided in a recent article by *Coppens* [10].

[4]) Compare, for example, with the $\Delta\rho$ map for tetrafluoroterephthalonitrile [11].

[5]) In the XRAY set of programs [12] form factors (f curves) for C, N, O, P, S, Cl and H are called automatically, but those for other atoms must be read in as input, either as a stored table of $f(\sin\theta/\lambda)$ values or as a set of coefficients from which the f values may be calculated. In the input for the analysis of crystal **2**, one of the coefficients for the neutral Li atom was given a wrong value, with the result that the f values fell off much too slowly with increase in $\sin\theta/\lambda$. Because of the reciprocal property of *Fourier* transforms this error leads to a fallacious concentration of charge close to the atomic center in ϱ_c. Least-squares refinements based on the erroneous f curve led to anomalously high vibrational parameters for the Li atom, 3–4 times larger than for the other atoms (already a danger sign!). However, because of the low scattering power of the Li atom (3 electrons out of 212 in the complex **2**) the refinements proceeded otherwise normally and converged to $R = 0.039$.

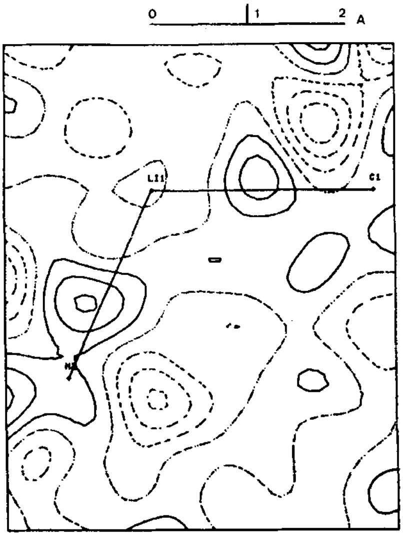

Fig. 4. *Corrected electron-density difference map through the atoms C(1), Li, and N(2) of the 2-lithio-2-phenyl-1,3-dithiane/TMEDA/THF (1:1:1) complex.* Contours are drawn at intervals of 0.05 e. Å^{-3}, zero contour dotted, negative contours dashed. Compare with the corresponding portion of *Fig. 2* in [2].

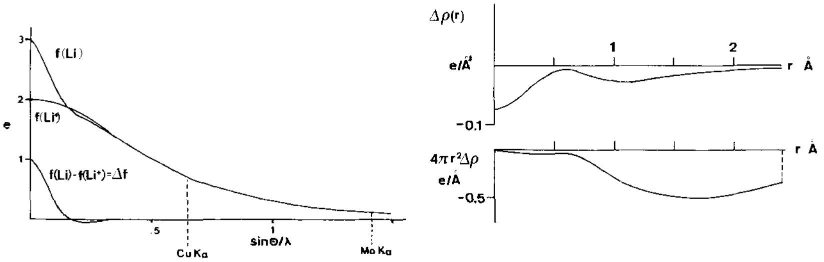

Fig. 5. Left: *atomic scattering curves* [28] *for Li and Li*$^+$. Right: $\Delta\varrho(\mathrm{r})$ *and* $4\pi \mathrm{r}^2\Delta\varrho(\mathrm{r})$ *calculated from* Δf. In order to make these functions roughly compatible with the conditions of our experiment ($B \sim 1$ Å^2, $\sin\theta/\lambda$ limit ~ 0.65 Å^{-1}) we computed the *Fourier* transform of $\Delta f \exp(-\sin^2\theta/\lambda^2)$ with an integration limit of $\sin\theta/\lambda = 0.7$ Å^{-1}.

way from the results obtained for **1** and **3**. *Fig. 4* shows a portion of the revised $\Delta\rho$ map for **2** in the C(1)-Li-N(1) plane; like the other maps it shows diffuse 'lone pair' like peaks close to the C and N atoms and is essentially featureless at the Li center.

Does this new result mean that all three compounds **1–3** are to be regarded as having covalent polarized Li-C bonds? We think not. Rather, in contradiction to the view expressed in [2], we now think that the X-ray results leave the question of the ionic character of the Li-C bonds open. In fact, it is obviously going to be an exceedingly difficult matter to measure the charge of the Li atom by X-ray diffraction methods. For example, when the refinement for crystal **2** is repeated using the form factor for Li$^+$, the resulting atomic parameters are practically the same as those obtained with the (correct) form factor for neutral Li, and the $\Delta\rho$ maps are also practically indistinguishable. The problem is that the scattering powers of the neutral Li atom and of the mono-charged Li$^+$ cation are so very similar over most of the range of observability

(Fig. 5). The difference in scattering power amounts to 1.0 electron at $\sin\theta/\lambda = 0$ (where all electrons scatter in phase) but it fades off so rapidly that the two curves become practically indistinguishable for $\sin\theta/\lambda$ greater than about 0.17 Å^{-1}. The 2s electron cloud of the neutral Li atom is evidently so diffuse that its contribution to the scattering power of the atom becomes negligible at higher scattering angle. In fact, as *Fig. 5* shows, the 2s density is so diffuse that only a small fraction (less than 15%) of the charge can be said to be concentrated within a sphere of radius 1.1 Å (roughly half the Li-X bond distance); some 28% of the charge is still not contained within a sphere of radius 2.4 Å, extending well past the centers of the bonded atoms. If the radius of the Li atom in these compounds is taken to be about half the distance to its closest neighbors, then integration of the charge density of the neutral atom out to this limit would give an appreciable effective positive charge to the atom. If such a calculation were accepted as defining the atomic charge, the bonds formed by the Li atom would then appear to be ionic, whatever their actual nature.

Some of these difficulties have been discussed by *Streitwieser et al.* [13] in a different though related context. We now tend to agree with this author that 'operational criteria to distinguish charge transfer from polarization effects are difficult to devise, particularly within the limitations of working with real compounds' [14]6).

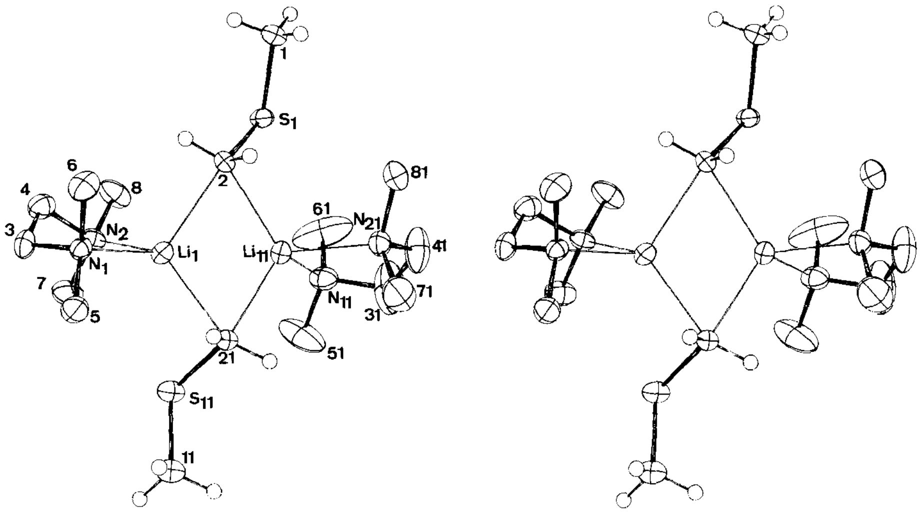

Fig. 6. *ORTEP* [27] *stereoview of a dimeric structural unit of methylthiomethyllithium*/TMEDA (1:1) showing atomic numbering. For clarity, H atoms of the TMEDA molecules have been omitted. Vibrational ellipsoids are drawn at the 50% probability level, but the H atoms are represented by circles of radius 0.1 Å. Note the large, drawn-out ellipsoids for some of the atoms of the primed TMEDA molecule, indicative of disorder.

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6) It is interesting that the results of the residual density studies for compounds **1**–**3** led to an NMR investigation which appeared to confirm the covalency of the C-Li bonds in **1** and **3** as well as the special status of **2** as a contact ion-pair complex. When the three compounds were marked with ^{6}Li and with ^{13}C at the carbanionoid center, a triplet was observed for the corresponding ^{13}C signal at −100° for **1** and **3** but not for **2** even on cooling to −130°. This evidence for ^{13}C-^{6}Li coupling in **1** and **3** and its absence in **2** was initially interpreted as confirmation of the covalent nature of the C-Li bonds in **1** and **3** but not in **2**. Other explanations, involving the difference between rates of exchange processes in dimeric **1** and **3** on the one hand, and in monomeric **2** on the other, are now considered to be more correct.

Table 3. *Atomic Coordinates and Vibration Parameters for Structure* **4** *with Standard Deviations in Units of the Last Significant Figure in Parentheses*

Atom	X	Y	Z	U_{11} (or U)	U_{22}	U_{33}	U_{12}	U_{13}	U_{33}
C(1)	1.0975(4)	0.0893(3)	0.0350(2)	0.021(2)	0.043(2)	0.027(1)	-0.004(2)	0.001(1)	-0.006(1)
C(2)	0.8277(3)	0.1167(2)	0.1526(2)	0.018(1)	0.023(1)	0.022(1)	-0.002(1)	-0.004(1)	-0.001(1)
C(3)	0.4228(4)	0.0165(2)	0.1605(2)	0.033(2)	0.023(2)	0.031(2)	-0.007(1)	-0.013(1)	-0.001(1)
C(4)	0.5304(5)	-0.0464(3)	0.1584(3)	0.038(2)	0.027(2)	0.030(2)	-0.001(2)	-0.004(2)	-0.003(1)
C(5)	0.3571(4)	0.1605(3)	0.1995(3)	0.025(2)	0.040(2)	0.035(2)	0.009(2)	-0.011(1)	-0.011(2)
C(6)	0.5350(5)	0.1315(2)	0.0658(2)	0.047(2)	0.031(2)	0.024(1)	-0.003(2)	-0.012(1)	0.007(1)
C(7)	0.4809(5)	-0.0783(3)	0.3207(3)	0.041(2)	0.031(2)	0.036(2)	-0.001(2)	0.001(2)	0.005(2)
C(8)	0.7081(4)	-0.0875(3)	0.2242(3)	0.029(2)	0.027(2)	0.062(3)	0.005(2)	0.002(2)	0.003(2)
C(11)	0.3023(4)	0.1910(3)	0.4829(3)	0.029(2)	0.056(3)	0.044(2)	0.000(2)	0.002(2)	-0.022(2)
C(21)	0.5671(4)	0.1869(2)	0.3539(2)	0.020(2)	0.032(2)	0.022(1)	-0.001(1)	-0.003(1)	-0.006(1)
C(31)	0.937(1)	0.2032(6)	0.4236(6)	0.103(7)	0.093(6)	0.076(5)	-0.043(6)	-0.067(6)	0.033(5)
C(41)	0.9926(7)	0.2590(4)	0.3526(4)	0.072(4)	0.056(3)	0.065(3)	-0.025(3)	-0.049(3)	0.012(3)
C(51)	0.7720(6)	0.1017(6)	0.4853(3)	0.040(3)	0.167(7)	0.031(2)	-0.005(4)	-0.007(2)	0.037(3)
C(61)	0.9798(9)	0.0602(5)	0.3802(4)	0.136(7)	0.107(6)	0.032(2)	0.078(5)	-0.025(3)	-0.001(3)
C(71)	0.8230(6)	0.3538(3)	0.3231(5)	0.043(3)	0.028(2)	0.093(4)	0.003(2)	0.001(3)	-0.018(2)
C(81)	0.9980(5)	0.2982(3)	0.2007(3)	0.041(2)	0.046(2)	0.042(2)	-0.021(2)	0.000(2)	-0.006(2)
Li(1)	0.6151(6)	0.0936(4)	0.2400(4)	0.026(3)	0.022(2)	0.022(2)	0.000(2)	-0.006(2)	-0.004(2)
Li(11)	0.7899(6)	0.1667(4)	0.2953(4)	0.025(3)	0.025(3)	0.025(2)	-0.005(2)	-0.006(2)	-0.004(2)
N(1)	0.4708(3)	0.1034(2)	0.1601(2)	0.024(1)	0.019(1)	0.020(1)	-0.001(1)	-0.005(1)	-0.0009(9)
N(2)	0.5815(3)	-0.0405(2)	0.2429(2)	0.022(1)	0.021(1)	0.024(1)	0.002(1)	0.000(1)	0.005(1)
N(11)	0.8744(3)	0.1247(2)	0.4036(2)	0.031(2)	0.042(2)	0.025(1)	0.004(1)	-0.007(1)	0.001(1)
N(21)	0.9070(3)	0.2797(2)	0.2914(2)	0.023(1)	0.023(1)	0.034(1)	-0.002(1)	-0.006(1)	-0.004(1)
S(1)	0.98796(9)	0.07248(6)	0.14982(5)	0.0207(4)	0.0293(4)	0.0178(3)	0.0031(4)	-0.0032(3)	-0.0014(3)
S(11)	0.4380(1)	0.12224(6)	0.42326(6)	0.0272(5)	0.0322(5)	0.0254(4)	0.0020(4)	-0.0008(3)	-0.0006(4)
H(101)	1.054(5)	0.068(3)	-0.007(3)	0.03(1)					
H(102)	1.184(6)	0.059(4)	0.034(4)	0.08(2)					
H(103)	1.103(5)	0.148(3)	0.022(4)	0.05(1)					
H(111)	0.230(5)	0.153(3)	0.523(3)	0.04(1)					
H(112)	0.273(7)	0.223(4)	0.441(4)	0.08(2)					
H(113)	0.333(6)	0.228(4)	0.523(4)	0.06(2)					
H(201)	0.841(5)	0.174(3)	0.130(3)	0.03(1)					
H(202)	0.802(5)	0.087(3)	0.107(3)	0.04(1)					
H(211)	0.596(5)	0.225(3)	0.396(4)	0.04(1)					
H(212)	0.528(5)	0.220(3)	0.313(3)	0.05(1)					
H(301)	0.387(5)	0.004(3)	0.111(4)	0.05(1)					
H(302)	0.358(6)	0.008(4)	0.221(4)	0.06(2)					
H(311)	0.860	0.237	0.474	*					
H(312)	1.018	0.185	0.454	*					
H(401)	0.486(6)	-0.102(4)	0.154(4)	0.05(2)					
H(402)	0.617(6)	-0.035(4)	0.099(4)	0.06(2)					
H(411)	1.015	0.317	0.383	*					
H(412)	1.085	0.232	0.311	*					
H(501)	0.325(5)	0.143(3)	0.260(3)	0.04(1)					
H(502)	0.388(6)	0.224(4)	0.191(4)	0.05(2)					
H(503)	0.282(5)	0.153(3)	0.167(3)	0.05(1)					
H(511)	0.702(8)	0.143(5)	0.485(5)	0.10(3)					
H(512)	0.812(7)	0.093(4)	0.533(5)	0.08(2)					
H(513)	0.72(1)	0.052(8)	0.458(9)	0.18(5)					
H(601)	0.472(5)	0.133(3)	0.028(3)	0.04(1)					
H(602)	0.607(5)	0.090(3)	0.035(3)	0.04(1)					
H(603)	0.566(5)	0.190(3)	0.069(3)	0.05(1)					
H(611)	1.026	0.054	0.436	*					
H(612)	0.935	0.001	0.369	*					
H(613)	1.057	0.078	0.319	*					
H(701)	0.380(7)	-0.042(4)	0.329(4)	0.05(2)					
H(702)	0.546(5)	-0.071(3)	0.369(3)	0.04(1)					
H(703)	0.472(7)	-0.146(4)	0.305(5)	0.04(8)					
H(711)	0.791(7)	0.365(4)	0.277(4)	0.08(2)					
H(712)	0.769(6)	0.339(4)	0.381(4)	0.07(2)					
H(713)	0.886(7)	0.401(4)	0.328(4)	0.10(2)					
H(801)	0.766(7)	-0.074(4)	0.184(5)	0.07(2)					
H(802)	0.693(6)	-0.149(4)	0.213(4)	0.06(2)					
H(803)	0.75(1)	-0.081(6)	0.284(7)	0.10(4)					
H(811)	1.062(5)	0.349(3)	0.198(3)	0.03(1)					
H(812)	1.054(8)	0.245(5)	0.175(5)	0.06(2)					
H(813)	0.941(8)	0.305(5)	0.161(5)	0.07(2)					

Crystal Structure of Methylthiomethyllithium/TMEDA (1:1) (4) at 113 K. – Monoclinic, $a = 10.254$, $b = 15.874$, $c = 15.144$ Å, $\beta = 74.45°$, $V = 2375$ Å^3, $Z = 8$ formula units $C_8H_{21}N_2SLi$, space group $P2_1/c$, $D_x = 1.03$ gcm^{-3}.

Atomic coordinates and vibration parameters are given in *Table 3*, selected interatomic distances and angles in *Table 4*. The structural units consist of dimers with an approximate twofold rotation axis passing through the middle of a four-membered

Table 4. *Bond Distances* (in Å) *and Angles* (in degrees) *in Dimeric Methylthiomethyllithium/TMEDA* (1:1 complex). The dimer has an approximate dyad axis, and values for the primed atoms follow those for the unprimed ones.

Li(1)–C(2)	2.256(6)	C(2)–S(1)	1.777(4), 1.778(3)
Li(1)–C(21)	2.227(7)	C(1)–S(1)	1.819(3), 1.808(5)
Li(11)–C(2)	2.236(7)		
Li(11)–C(21)	2.241(7)	N(1)–C(5)	1.471(5), 1.439(6)
		N(1)–C(6)	1.472(4), 1.460(10)
Li–N(1)	2.153(8), 2.156(8)	N(2)–C(7)	1.471(5), 1.460(6)
Li–N(2)	2.155(6), 2.151(7)	N(2)–C(8)	1.458(5), 1.468(5)
		N(1)–C(3)	1.464(5), 1.471(10)
Li–N(1)–C(3)	102.2(3), 100.5(4)	N(2)–C(4)	1.510(6), 1.474(8)
Li–N(1)–C(4)	97.7(3), 102.6(3)	C(3)–C(4)	1.481(6), 1.392(10)
N(1)–Li–N(2)	87.3(3), 86.8(3)	N(1)–C(3)–C(4)	112.8(3), 119,4(7)
		N(2)–C(4)–C(3)	111.5(3), 116.1(6)
Li–N(1)–C(5)	114.0(3), 112.6(4)		
Li–N(1)–C(6)	111.8(3), 117.1(3)	C(5)–N(1)–C(6)	107.8(3), 110.7(5)
Li–N(2)–C(7)	119.5(3), 112.7(3)	C(5)–N(1)–C(3)	110.5(3), 107.2(5)
Li–N(2)–C(8)	111.9(3), 113.7(3)	C(6)–N(1)–C(3)	110.6(3), 107.9(6)
		C(7)–N(2)–C(8)	110.1(3), 108.5(4)
C(1)–S–C(2)	107.2(3), 107.3(3)	C(7)–N(2)–C(4)	109.0(3), 111.8(4)
		C(8)–N(2)–C(4)	107.3(3), 107.2(4)
Li(1)–C(2)–Li(11)	66.5(4), 66.9(4)		
C(2)–Li–C(21)	108.9(3), 109.1(3)	H(201)–C(2)–H(202)	104.2(40), 109.2(45)
		H(201)–C(2)–S	108.9(25), 105.8(28)
Li–Li	2.463(9)	H(202)–C(2)–S	103.3(25), 108.6(29)
S(1)–C(2)–Li(1)	133.7(3)		
S(1)–C(2)–Li(11)	94.8(3)		
S(11)–C(21)–Li(1)	92.8(3)		
S(11)–C(21)–Li(11)	132.1(3)		

ring built from two Li atoms and two methylenic C atoms *(Fig. 6)*. The ring is approximately equilateral (C-Li, 2.23–2.26 Å) but the diagonals differ greatly in length, with Li ... Li = 2.46 Å and C ... C = 3.65 Å. In fact, the Li-C-Li angle is only about 66°. The ring is also markedly nonplanar, being folded by 22° about the Li ... Li line; it thus has approximate C_{2v} symmetry.

Each ring C atom is bonded to five atoms: two H, two Li, and one S, but the carbanionoid fragments do not lie symmetrically with respect to the mirror-planes of the ring *(Fig. 6)*. Fortunately, the H atoms have been located accurately enough to provide a reasonably detailed picture of the steric relationships at C(2) and C(21). Each of the four H atoms H(201), H(202), H(211), and H(212) lies about 2.35–2.4 Å from one Li (considerably further from the other), forming a slightly acute ($\approx$ 85°) H-C-Li angle. The C-S bond obviously also lies quite asymmetrically with respect to the two Li atoms, forming an approximately 90° S-C-Li angle with one, a 135° angle with the other. Indeed, the shorter S ... Li distance in each case is less than 3 Å [S(1) ... Li(11), 2.97; S(11) ... Li(1), 2.92 Å], closely similar to the 'non-bonded' S ... Li distances of 2.92 and 3.02 Å in monomeric **2**, and not so very much longer than the 'bonded' S-Li distances of *ca.* 2.55 Å in **3**. Thus, each Li atom in dimeric **4** has seven neighbors within a distance of 2.4 Å (2 N at 2.15 Å, 2 C at 2.25 Å, 2 H at 2.35 Å and 1 Li at 2.45 Å) as well as a S atom at 2.95 Å – a convincing illustration, if one were needed, of *Schleyer*'s dictum [15] that lithium prefers to interact simultaneously with as many atoms as possible.

The H–C–H and H–C–S bond angles at the two carbanionoid centers are all quite close to the tetrahedral angle (see *Table 4*) so it seems justified to regard these centers as approximately sp^3 hybridized and to take the direction of the lone-pair orbital as lying along the negative resultant of the three normalized vectors along the C–H and C–S bonds. This direction is found to lie within 10° of the Li–C–Li angle bisector for both carbanionoid centers.

Similar four-membered rings with C bonded to two Li atoms have been found previously in several other dimeric structures listed in *Table 5*. In particular, the molecular dimensions found for the $(\text{phenyllithium-TMEDA})_2$ structure [17] are very close to those found here, the similarity extending to the marked nonplanarity of the ring. The other three examples contain planar, centrosymmetric rings. Four-membered rings with similar dimensions (C–Li, 2.28–2.35 Å, Li ... Li, 2.51–2.71 Å) also occur in the distorted cubic tetrameric structure of $(\text{phenyllithium}\cdot Et_2O)_4$ and the closely related one of $(\text{phenyllithium}\cdot Et_2O)_3\cdot LiBr$ [20].

Some of the bond distances in the two TMEDA moieties in **4** differ markedly from those in the standard unit defined in *Fig. 2*. These differences are particularly pronounced for the primed TMEDA unit, where, for example, the central C–C bond is more than 0.1 Å shorter than its standard value. These differences are almost certainly due to disorder, *i.e.* to partial occupancy of several neighboring sites for the atoms in question. This interpretation is supported by the anomalously large vibrational parameters associated with some of the atoms of the primed TMEDA moiety *(Table 6)*. Clearly, the relatively low density of the crystals ($D_x = 1.03$ gcm^{-3} compared with 1.10 gcm^{-3} for **3**) speaks for a less efficient packing of the structural units.

Doubtless, residual density maps for this crystal would be of interest for comparison with the results for crystals **1–3**. However, in view of the indications of disorder,

Table 5. *Dimensions of Four-Membered Rings in Several Dimeric Organolithium Molecules.* Distances in Å, angles in degrees.

	Li–C	Li...Li	C–Li–C	Li–C–Li	Ref.
$(\text{Bicyclo[1.1.0]butyllithium. TMEDA})_2$	2.23	2.74	104	76	[16]
$(\text{Phenyllithium. TMEDA})_2$	2.208, 2.278	2.49	105.6	67.4	[17]
$(\text{Phenylethynyllithium. TMPDA})_2$	2.132, 2.164	2.56	106.7	73.3	[18]
$(\text{8-Dimethylamino-1-naphthyllithium. } Et_2O)_2$	2.232, 2.224	2.366	115.8	64.2	[19]
$(\text{Methylthiomethyllithium. TMEDA})_2$	2.227, 2.256	2.463	108.9, 109.1	66.5, 66.9	this work

Table 6. *Isotropic Vibrational Parameters* U_{eq} ($Å^2$) *and Torsion Angles* τ (deg) *for the Central Part of the TMEDA Units in Four Low-Temperature Crystal Structures*

			U_{eq}			
	T(K)	τ	N	C	C	N
4	113	63	0.021	0.029	0.032	0.022
		48	0.033	0.091	0.064	0.027
3	93	59	0.020	0.023	0.021	0.020
2	93	60	0.018	0.021	0.021	0.016
1	93	61	0.019	0.023	0.021	0.019

the interpretation of the $\Delta\rho$ maps would be associated with even greater uncertainties than in the case of the other compounds. We therefore choose to avoid this problem for the present.

Discussion. – The question, why **1** and **3** form cyclic dimers with six-membered rings while **4** forms a cyclic dimer with a four-membering ring, seems interesting, but we do not have a convincing answer⁷). Presumably, the energy differences are quite small. Nevertheless, it will doubtless soon be explained by semi-empirical or *ab initio* calculations that for **1** and **3** the six-membered ring has a lower energy than the four-membered, with the opposite result holding for **4**.

Experimental Part

Both compounds are air-sensitive. All manipulations on the crystals were therefore performed in a dry N_2 or Ar atmosphere. For the X-ray measurements, single crystals were mounted in thin-walled glass capillaries with hexadecane as adhesive. Measurements were made with an ENRAF-*Nonius CAD 4* diffractometer equipped with a graphite monochromator (Mo*Kα* radiation, $\lambda = 0.71069$ Å) and cooling device. The calculations were made with program suites MULTAN 80 [22], XRAY [12], and SHELX 76 [23].

Preparation of **3** [24]. To 1 g (8 mmol) thioanisole in 3 ml (20 mmol) neat TMEDA was injected 5.1 ml (8 mmol) BuLi at −20°. After stirring for 15 min the white precipitate was dissolved by warming to 45° and adding excess TMEDA. On cooling the yellowish solution to r.t., clear colorless crystals separated out and the supernatant solution was removed with a syringe.

Crystal Structure Analysis of **3**. With the crystal held at 93 K, 3229 independent reflections (2221 with $I > 3\sigma_I$) were recorded out to $\sin\theta/\lambda \sim 0.64$ Å^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares analysis. All H atoms were located in a difference synthesis. After further refinement using a modified weighting scheme [25] with $r = 4.3$ Å^2, a final cycle was calculated with C–H bond lengths fixed at 1.08 Å ($R = 0.034$). The residual density maps (*Fig. 3*) have $\sigma(\Delta\rho) \sim 0.035$ e.Å^{-3}.

Preparation of **4** [26]. To a stirred solution of 1.0 ml Me_2S (14 mmol) in 4.0 ml TMEDA (27 mmol) under Ar at −30° was added 6.3 ml of a BuLi solution in TMEDA (1.6 M, 10 mmol). After stirring for 1 h at 0° and 1.5 h at r.t., 4 ml TMEDA and 6 ml hexane were added. The mixture was then cooled immediately to −40° and then over 2 h to −60° and kept at −60° for 22 h. After removal of supernatant the crystals were washed with 2 × 4 ml isopentane and dried in high vacuum.

Crystal Structure of **4**. The measurements were made with the crystal held at 113 K. Intensities were recorded for 5718 independent reflections (3703 with $I > 3\sigma_I$) out to $\sin\theta/\lambda \sim 0.67$ Å^{-1}. The structure was solved by direct methods and refined by full-matrix least-squares analysis. Some of the H atoms of the TMEDA fragments were not located from difference syntheses but were positioned from stereochemical considerations. The final refinement cycles using modified weights with $r = 6$ Å^2 [25] gave $R = 0.067$.

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⁷) In the ^{13}C-NMR spectra of ^{13}C/^{6}Li-labelled **1** and **3** in Me_2O the signals due to the carbanionoid C atoms show a clear triplet splitting on cooling to temperatures around −100°, indicating at overwhelming preference for the six-membered ring structures for these compounds also in solution [21]. For **2** and the *n*-butyl analog of **4** the corresponding spectra show sharp singlets down to −130°.

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