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The crystal structure of [1-lithio-2-methoxybenzene]$_8$ · TMEDA

S. Harder, J. Boersma, L. Brandsma,

Department of Metal-mediated Synthesis, University of Utrecht, Padualaan 8, 3508 TB, Utrecht (The Netherlands)

and J.A. Kanters

Laboratory for Crystal and Structural Chemistry, University of Utrecht, Padualaan 8, 3508 TB, Utrecht (The Netherlands)

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Abstract

The structure of 1-lithio-2-methoxybenzene(2-methoxyphenyllithium) in the presence of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) has been determined by single crystal X-ray diffraction techniques. The compound crystallizes in the triclinic system with space group $P\bar{1}$. The cell dimensions are determined as follows: a 9.035(1), b 11.896(1), c 15.219(2) Å, α 92.55(1), β 92.03(1) and γ 110.11(1)°. The structure was refined by least-squares techniques to $R(F)$ 6.1% and $R(wF)$ 3.9%. The structure consists of two centrosymmetrically related tetrameric units of lithiomethoxybenzene connected to each other by a bridging TMEDA ligand which has a center of inversion in the middle of the C–C bond. The nature of the highly asymmetric tetrameric unit is discussed and compared to that of other organolithium compounds with intramolecular coordination through an ether function.

Introduction

The crystal structures of organolithium compounds have been reviewed recently [1]. In the review, the structures were subdivided into a few standard forms, in which the carbanions are either four-center-two-electron bonded or three-center-two-electron bonded. Most of the structures determined are of solvent containing species, e.g. [PhLi · Et$_2$O]$_4$ [2] and [PhLi · TMEDA]$_2$ [3]. In recent years several solvent-free structures involving intramolecular coordination have been determined; for example, these of the tetrameric species **1** [4], **2** [5] and **3** [6] and the dimeric compound **4** [7]. All these compounds contain a heteroatom-containing substituent

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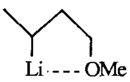

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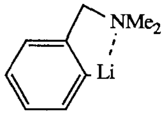

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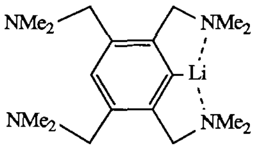

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which fills the open coordination sites by forming a five-membered chelate ring. Recently we described the structure of the dimeric [2-lithiophenyl-t-butylsulfide]$_2$ · [TMEDA], in which the intramolecular coordination involves a four-membered ring [8]. Now we report the structure of 1-lithio-2-methoxybenzene, which also contains a four-membered intramolecular ring.

Experimental

X-ray data collection

Crystals were obtained by treating methoxybenzene in hexane at 40–50 °C with one equivalent of butyllithium in the presence of two equivalents of *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) and then cooling the solution to room temperature. The ^{1}H NMR spectrum revealed that the crystals contained one TMEDA molecule per eight 1-lithio-2-methoxybenzene molecules. A suitable crystal with

Table 1

Physical constants and experimental crystal data for the structure determination of 1-lithio-2-methoxybenzene

Molecular formula	$C_{62}H_{72}Li_8N_2O_8$
Molecular weight	1028.79
Crystal system	triclinic
Space group	$P\bar{1}$
Z	1
Cell dimensions	a 9.035(1) Å
	b 11.896(1) Å
	c 15.219(2) Å
	α 92.55(1) °
	β 92.03(1) °
	γ 110.11(1) °
	V 1532(0) Å^3
$F(000)$	546
ρ(calcd)	1.115 g cm^{-3}
Temperature	295 K
Radiation	Cu-K_α (1.54184 Å)
2θ scan range	0–140 °
Scan method	$\omega-2\theta$ with ω $(1.33+0.15 \tan \theta)°$
Standard reflections	1 −1 4 and 3 −1 −1
Decay	0.9%
Index range	$-11 \leq h \leq 11$, $0 \leq k \leq 14$ and $-18 \leq l \leq 18$
No. of measured unique reflections	5667
No. of observed reflections, $I > 2.5\sigma(I)$	2795
Linear absorption coefficient	5.2 cm^{-1}

dimensions 0.5 × 0.4 × 0.3 mm was sealed under nitrogen in a Lindemann glass capillary. An Enraf–Nonius CAD 4 diffractometer was used and the cell constants were determined from a least-squares fit of the setting angles of 12 reflections with θ range 12.9–18.6 °. Details of the data collection are given in Table 1.

Solution and refinement of the structure

Direct methods in the space group $P\bar{1}$ using the programm SHELX-86 [9] led to location of the carbon and oxygen atoms in the four ring systems and of the

Table 2

Fractional coordinates of the non-hydrogen atoms

Atom	*x*	*y*	*z*
O(1)	0.5950(3)	0.2351(2)	0.4022(2)
O(2)	0.9669(3)	0.0103(2)	0.2565(1)
O(3)	1.0989(3)	0.4850(2)	0.3760(2)
O(4)	1.0607(3)	0.4701(2)	0.1760(2)
N(5)	0.5606(3)	0.1450(2)	0.0757(2)
Li(1)	0.7348(6)	0.1974(5)	0.1825(3)
Li(2)	0.7746(6)	0.2053(5)	0.3558(3)
Li(3)	0.9887(6)	0.1793(5)	0.2659(4)
Li(4)	0.9566(6)	0.3903(5)	0.2794(4)
C(11)	0.5737(5)	0.3096(3)	0.3372(3)
C(12)	0.6956(4)	0.3393(3)	0.2781(2)
C(13)	0.6769(4)	0.4180(3)	0.2164(2)
C(14)	0.5501(5)	0.4602(3)	0.2120(3)
C(15)	0.4350(5)	0.4237(4)	0.2714(3)
C(16)	0.4445(5)	0.3470(4)	0.3360(3)
C(17)	0.4718(4)	0.1845(3)	0.4607(2)
C(21)	0.8016(4)	−0.0423(4)	0.2584(2)
C(22)	0.7269(4)	0.0417(3)	0.2718(2)
C(23)	0.5635(4)	−0.0118(3)	0.2780(2)
C(24)	0.4820(4)	−0.1351(4)	0.2702(2)
C(25)	0.5667(5)	−0.2094(3)	0.2543(2)
C(26)	0.7274(5)	−0.1656(3)	0.2477(2)
C(27)	1.0649(4)	−0.0603(3)	0.2507(2)
C(31)	1.1073(4)	0.3951(4)	0.4307(3)
C(32)	1.0236(4)	0.2793(4)	0.3951(2)
C(33)	1.0315(4)	0.1916(4)	0.4505(3)
C(34)	1.1173(5)	0.2154(5)	0.5325(3)
C(35)	1.1971(5)	0.3326(5)	0.5616(3)
C(36)	1.1950(4)	0.4247(4)	0.5116(3)
C(37)	1.1841(4)	0.6075(3)	0.4020(2)
C(41)	1.0671(4)	0.3787(4)	0.1157(3)
C(42)	0.9870(4)	0.2652(4)	0.1428(2)
C(43)	0.9931(4)	0.1751(4)	0.0822(3)
C(44)	1.0712(5)	0.1967(5)	0.0040(3)
C(45)	1.1485(6)	0.3113(5)	−0.0160(3)
C(46)	1.1492(5)	0.4063(4)	0.0400(3)
C(47)	1.1313(5)	0.5913(3)	0.1561(2)
C(51)	0.5609(3)	0.0280(3)	0.0379(2)
C(52)	0.6074(4)	0.2379(3)	0.0116(2)
C(53)	0.4062(4)	0.1359(3)	0.1093(2)

Table 3

Selected bond distances (Å), bond angles (degrees) and the Li coordination geometry

C(11)–C(16)	1.385(7)	C(31)–C(36)	1.403(6)
C(11)–C(12)	1.406(6)	C(31)–C(32)	1.397(6)
C(12)–C(13)	1.401(5)	C(32)–C(33)	1.389(6)
C(13)–C(14)	1.401(6)	C(33)–C(34)	1.410(6)
C(14)–C(15)	1.370(6)	C(34)–C(35)	1.375(8)
C(15)–C(16)	1.391(6)	C(35)–C(36)	1.366(7)
O(1)–C(11)	1.408(5)	O(3)–C(37)	1.424(4)
O(1)–C(17)	1.432(4)	O(3)–C(31)	1.405(5)
C(21)–C(26)	1.386(6)	C(41)–C(42)	1.384(6)
C(21)–C(22)	1.397(6)	C(41)–C(46)	1.383(6)
C(22)–C(23)	1.401(5)	C(42)–C(43)	1.399(6)
C(23)–C(24)	1.394(6)	C(43)–C(44)	1.394(6)
C(24)–C(25)	1.373(6)	C(44)–C(45)	1.355(8)
C(25)–C(26)	1.373(6)	C(45)–C(46)	1.383(7)
O(2)–C(27)	1.417(5)	O(4)–C(41)	1.409(5)
O(2)–C(21)	1.409(5)	O(4)–C(47)	1.413(4)
C(51)–C(51) [a]	1.524(4)		
N(5)–C(53)	1.473(5)		
N(5)–C(51)	1.483(4)		
N(5)–C(52)	1.468(4)		
C(11)–C(12)–C(13)	112.0(3)	C(21)–C(22)–C(23)	112.7(3)
C(12)–C(11)–C(16)	126.5(4)	C(22)–C(23)–C(24)	124.4(3)
C(12)–C(13)–C(14)	124.4(3)	C(23)–C(24)–C(25)	118.1(4)
C(13)–C(14)–C(15)	119.1(4)	C(24)–C(25)–C(26)	121.9(3)
C(14)–C(15)–C(16)	120.6(4)	C(21)–C(26)–C(25)	117.1(4)
C(11)–C(16)–C(15)	117.3(4)	C(22)–C(21)–C(26)	125.9(4)
O(1)–C(11)–C(16)	120.9(4)	O(2)–C(21)–C(26)	121.0(4)
O(1)–C(11)–C(12)	112.6(4)	O(2)–C(21)–C(22)	113.1(3)
C(11)–O(1)–C(17)	119.6(3)	C(21)–O(2)–C(27)	121.6(3)
C(31)–C(32)–C(33)	112.4(3)	C(41)–C(42)–C(43)	112.0(3)
C(32)–C(33)–C(34)	124.3(4)	C(42)–C(43)–C(44)	124.2(4)
C(33)–C(34)–C(35)	118.9(5)	C(43)–C(44)–C(45)	119.4(5)
C(34)–C(35)–C(36)	120.7(4)	C(44)–C(45)–C(46)	120.6(5)
C(31)–C(36)–C(35)	117.6(4)	C(41)–C(46)–C(45)	117.1(4)
C(32)–C(31)–C(36)	126.0(4)	C(42)–C(41)–C(46)	126.7(4)
O(3)–C(31)–C(32)	113.2(4)	O(4)–C(41)–C(42)	112.4(4)
O(3)–C(31)–C(36)	120.8(4)	O(4)–C(41)–C(46)	120.8(4)
C(31)–O(3)–C(37)	119.5(3)	C(41)–O(4)–C(47)	119.4(3)
N(5)–C(51)–C(51) [a]	114.9(3)		
C(51)–N(5)–C(52)	111.5(3)		
C(51)–N(5)–C(53)	111.9(2)		
C(52)–N(5)–C(53)	110.2(3)		
Li(1)–C(12)	2.307(6)	Li(2)–C(12)	2.311(6)
Li(1)–C(22)	2.329(6)	Li(2)–C(22)	2.184(6)
Li(1)–C(42)	2.255(7)	Li(2)–C(32)	2.166(7)
Li(1)–N(5)	2.136(6)	Li(2)–O(1)	1.927(6)
Li(3)–C(22)	2.376(7)	Li(4)–C(12)	2.223(7)
Li(3)–C(32)	2.207(7)	Li(4)–C(32)	2.427(7)
Li(3)–C(42)	2.176(7)	Li(4)–C(42)	2.580(7)
Li(3)–O(2)	1.950(6)	Li(4)–O(3)	1.951(7)
		Li(4)–O(4)	1.971(7)

Table 3 (continued)

C(12)-Li(1)-C(22)	103.7(2)	C(12)-Li(2)-C(22)	108.3(2)
C(12)-Li(1)-C(42)	108.9(3)	C(12)-Li(2)-C(32)	111.2(3)
C(12)-Li(1)-N(5)	111.4(3)	C(12)-Li(2)-O(1)	66.4(2)
C(22)-Li(1)-C(42)	103.4(3)	C(22)-Li(2)-C(32)	109.8(3)
C(22)-Li(1)-N(5)	113.5(3)	C(22)-Li(2)-O(1)	117.0(3)
C(42)-Li(1)-N(5)	115.1(2)	C(32)-Li(2)-O(1)	131.4(3)
C(22)-Li(3)-C(32)	101.8(3)	C(12)-Li(4)-C(32)	105.2(3)
C(22)-Li(3)-C(42)	104.3(3)	C(12)-Li(4)-C(42)	100.9(2)
C(22)-Li(3)-O(2)	64.6(2)	C(12)-Li(4)-O(3)	123.6(3)
C(32)-Li(3)-C(42)	122.0(3)	C(12)-Li(4)-O(4)	116.7(3)
C(32)-Li(3)-O(2)	121.3(3)	C(32)-Li(4)-C(42)	99.9(2)
C(42)-Li(3)-O(2)	116.6(3)	C(32)-Li(4)-O(3)	63.5(2)
		C(32)-Li(4)-O(4)	135.6(3)
		C(42)-Li(4)-O(3)	134.8(3)
		C(42)-Li(4)-O(4)	59.6(2)
		O(3)-Li(4)-O(4)	101.7(3)
Li(1)-Li(2)	2.642(6)	Li(2)-Li(1)-Li(3)	56.4(2)
Li(1)-Li(3)	2.660(8)	Li(2)-Li(1)-Li(4)	57.2(2)
Li(1)-Li(4)	2.790(8)	Li(3)-Li(1)-Li(4)	57.5(2)
Li(2)-Li(3)	2.504(8)	Li(1)-Li(2)-Li(3)	62.2(6)
Li(2)-Li(4)	2.603(8)	Li(1)-Li(2)-Li(4)	64.3(2)
Li(3)-Li(4)	2.624(8)	Li(3)-Li(2)-Li(4)	61.8(2)

[a] Symmetry code: $1-x, -y, -z$.

nitrogen and carbon atoms of the half-TMEDA molecule. Isotropic least-squares block refinement with SHELX-76 [10] converged to an R value of 18.0%, and the four missing Li atoms were located from a subsequent Fourier difference map. Hydrogen atoms were placed at idealized calculated C(sp^2) and C(sp^3) positions 1.0 Å from their C atoms and were refined riding on their C atoms with an overall variable temperature factor. Anisotropic full-matrix refinement yielded residual indices of $R(F)$ * 6.1% and $R(wF)$ * 3.9%. The overall temperature factor of the H atoms refined to 0.135 Å^2. The average shift to error ratio (Δ/σ) was < 0.001. Maximum and minimum electron densities were 0.25 and -0.22 eÅ^{-3}, respectively. Neutral atom scattering factors [11] were used for all atoms. Final positional parameters of the non hydrogen-atoms are listed in Table 2, and selected bond distances, bond angles, torsion angles, and details of the geometry of the Li coordination are in Table 3. Anisotropic thermal parameters, hydrogen atom positions, and observed and calculated structure factors as well as a complete listing of all bond distances, bond angles and torsion angles are available from the authors. Geometric calculations and illustrations were performed with the EUCLID package [12].

Results and discussion

The structure of the title compound, illustrated in Fig. 1, consists of two tetrameric aggregates of 1-lithio-2-methoxybenzene linked together by a TMEDA

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* $R(F)=\Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R(wF)=\sqrt{\{\Sigma[w\times(|F_o|-|F_c|)^2]/\Sigma[w\times F_o^2]\}}$

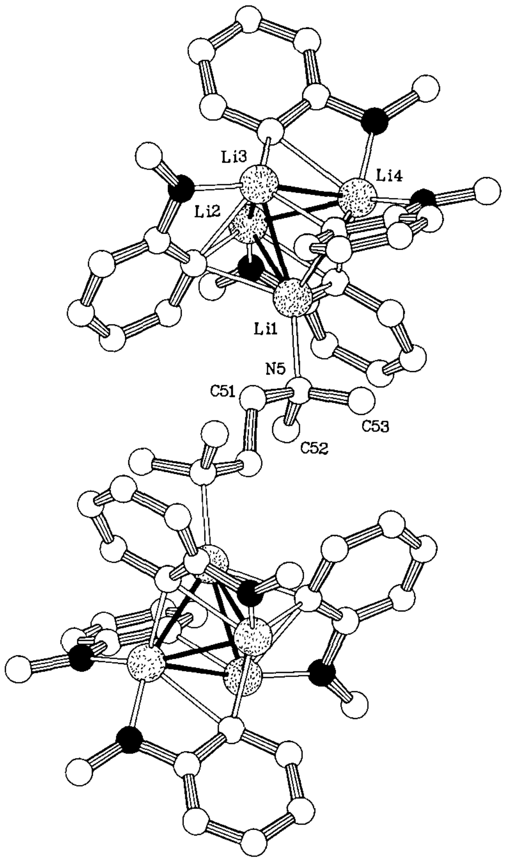

Fig. 1. Perspective view of the complete complex, involving two centrosymmetrically related tetrameric aggregates of lithiomethoxybenzene bridged by a TMEDA ligand (of which the atom numbering is shown). For clarity the hydrogen atoms have been omitted, and the lithium atoms are indicated by the large speckled spheres with atom numbers.

ligand, which possesses a center of inversion in the middle of the C–C bond. Figure 2 gives a clearer picture of one of the tetrameric units. At first sight this tetrameric cluster looks like a propeller, but the methoxyphenyl anion (3) destroys the pseudo threefold axis. As a consequence of this asymmetry, the four Li atoms in the cluster have different coordination spheres, as shown in Table 3; those of Li(2) and Li(3) resemble each other.

The Li atom in organolithium compounds is often tetracoordinate, but exceptions are common [1]. In the tetrameric cluster, the twelve C–Li bonds and four O–Li bonds should be sufficient for coordinative saturation, and therefore participation of one N donor atom of TMEDA must result in five-coordination at one of the Li atoms. As one can see from Fig. 2, Li(4) possesses five contacts (3 C–Li and 2 O–Li), but two of the C–Li contacts are rather long and therefore Li(4) must be regarded as three-coordinate. In Fig. 3 the projections of the lithium-bonded C atoms on the triangular Li planes are illustrated, and these pictures make clear the extremely asymmetric bonding of all C(*ipso*) atoms, especially C(32) and C(42). The

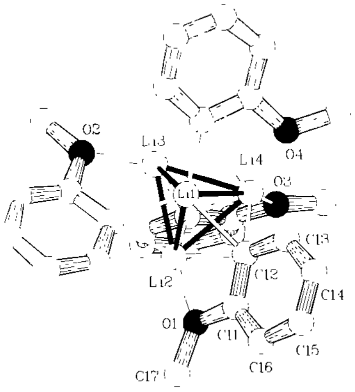

Fig. 2. Perspective view of a tetrameric aggregate. The coordinating TMEDA ligand and the hydrogen atoms have been omitted for clarity. The N atom of TMEDA which is coordinated to Li(1) lies above the plane of projection. The atom numbering is shown for molecule 1; the first number gives the molecule number and the second the atom number. For molecules 2, 3 and 4 only the O atoms are numbered, but the numbering sequence is the same as in molecule 1.

four-center-two-electron bond of C(32) and C(42) can be better regarded as a three-center-two-electron bond. The same type of bonding of the methoxyphenyl anion is found in the structure of 1-copper-2-methoxy-benzene [13]. The asymmetric bonds of C(32) and C(42) directly influence the O(3) and O(4) coordination to Li(4)

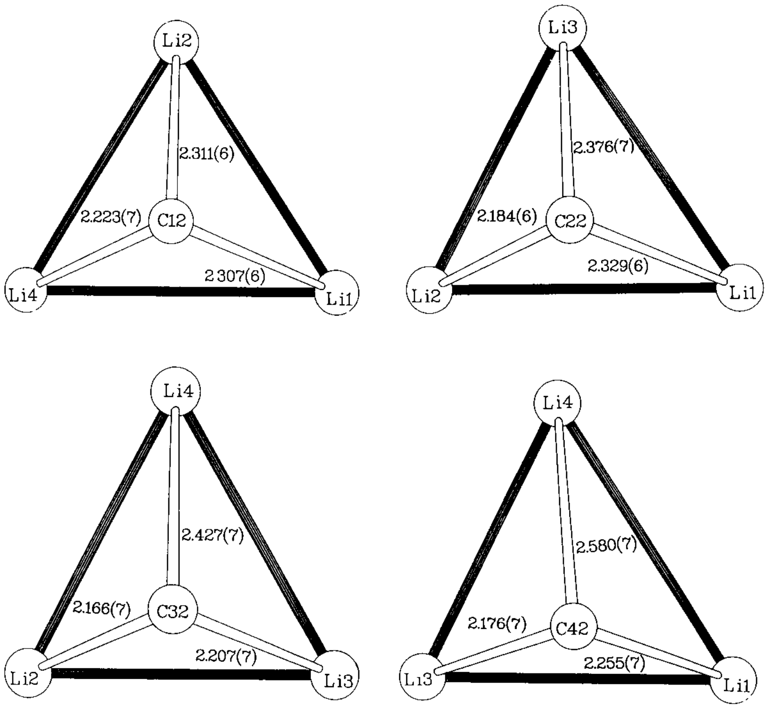

Fig. 3. Plots perpendicular to the four planes of the Li tetrahedron showing the asymmetry of the C–Li bond systems.

because the shift of the aryl rings of the molecules 3 and 4 causes the angle C(31)–O(3)–Li(4) of 101.5(3)° and the angle C(41)–O(4)–Li(4) of 106.6(3)° to be slightly greater then the angles C(11)–O(1)–Li(2) and C(21)–O(2)–Li(3), 98.1(3)° and 99.7(3)°, respectively.

The aryl rings are planar (maximum deviation from the least-squares plane 0.01 Å), but are distorted in a way which is common for aryl rings bonded to electropositive metals (smaller angles around the C(*ipso*) atoms which results in larger neighbouring angles in the aryl rings).

For each anion the torsion angles around the C(ring)–O bond differ slightly from 0 or ±180° (maximum deviation is 8.3(5)°, and the average absolute deviation is 4.7(4)°), which means that the phenyl ring, the methoxy group and the Li atom bonded to it are approximately in the same plane. An earlier analysis of the Cambridge Crystallographic Database [14] revealed that Li cations bonded to ether anions have a tendency to lie on the C–O–C bisector. But as the C–O–C angles in these searched structures were not 120° (range: 108.4–117.1° (average 111.2°)) there is no evidence for sp^2 hybridization, and the Li cations are assumed to lie between the lone pairs of the O atom in these structures. The C–O–C angles in the present structure are all close to 120°, so it seems justified to regard the O atoms as being sp^2 hybridized.

The trigonal pyramid of Li atoms (marked with black bonds) is distorted to some extent; the Li–Li distances vary from 2.504(8) to 2.790(8) Å (average: 2.637(8) Å) and the Li–Li–Li angles from 56.4(2) to 64.3(2)°. Average Li–Li distances in comparable tetrameric organolithium complexes with an intramolecular O–Li coordination are 2.485 Å for **1** and 2.495 Å for **2**. The only Li–Li distance in the present, complex that approaches these average values is that between Li(2) and Li(3) (2.504(8) Å). The Li–Li distances seem to depend on the coordination at the two Li atoms involved. The longest Li–Li distance (2.790(8) Å) is that between Li(1), bonded to the Lewis base (TMEDA), and Li(4), which possess three coordination. Since ethers are better Lewis bases than tertiary amines [15], it can be concluded that Li(1) is slightly less coordinatively saturated then Li(2) and Li(3) and so it seems that internuclear Li–Li distances may increase as the coordination number falls. This is supported by the interatomic distances Li(1)–Li(2), Li(1)–Li(3), Li(4)–Li(2) and Li(4)–Li(3), which are also rather long. MNDO calculations on a regular methyllithium tetramer, with each Li atom coordinated to an O atom of a water molecule, showed that the Li–Li distances are increased by increasing the the Li–O distance [4].

It would be interesting to compare this structure with that of the corresponding TMEDA-free analogue, for which no structural data are known yet. This should give information about the change in structure that this organolithium reagent undergoes when a molecule with a potential electron-donating atom (which could be an electrophilic reagent, e.g. ethylene oxide) coordinates to it.

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