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Isolation and X-ray Crystal Structures of the Solvate Complexes [Li(Et$_2$O)benzyl]$_x$ and [Li(THF)$_2$mesityl]$_2$

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The organolithium monodentate ether solvates [Li(Et$_2$O)benzyl]$_x$, 1, and [Li(THF)$_2$mesityl]$_2$, 2, have been isolated and characterized by X-ray diffraction. The structure of 1 consists of infinite chains of alternating benzyl and lithium ions with lithium also coordinated to Et$_2$O. The geometry at lithium is approximately trigonal planar, provided only the ether oxygen and the close contacts to the CH$_2$ carbons of each benzyl group are considered. A somewhat weaker interaction with the adjacent ring carbon on each benzyl is also apparent. The structure of 2 consists of discrete centrosymmetric dimers of two lithium and two mesityl groups. The lithium atom is also coordinated to two THF molecules. The crystal data at 140 K are as follows. 1: a = 7.503 (3) Å, b = 13.811 (3) Å, c = 21.498 (6) Å, α = 103.50 (2)°, β = 93.93 (3)°, γ = 91.77 (2)°, Z = 8, space group $P\bar{1}$, R = 0.078. 2: a = 9.566 (3) Å, b = 9.488 (3) Å, c = 17.927 (6) Å, β = 102.69 (3)°, Z = 2, space group $P2_1/n$, R = 0.065.

Introduction

Recent years have seen a renewed interest in the reactivity, structure, and bonding in organolithium compounds. This has been reflected in a number of reviews which have detailed the large amount of structural and theoretical information now available.[1,2] Much of the X-ray structural data on crystalline compounds had dealt with either solvent-free compounds or their adducts with chelating bases such as TMEDA (*N,N,N',N'*-tetramethylethylenediamine) and related ligands. Such studies have provided much useful information. However, the degree of aggregation, and to a lesser extent other structural details, are expected to differ when these lithium reagents are dissolved in the commonly used ether solvents, i.e., Et$_2$O or THF. Very few structures of simple alkyl- or aryllithium solvates of these monodentate ethers have been published. These structures are important in order to establish the relationship between the solution and crystaline phases. Phenyllithium etherate, (PhLi·Et$_2$O)$_4$, is one of the few reported case where there clearly is a close relationship between the liquid phase and the ether solvate.[3–5] The paucity of information for other compounds arises primarily from a lack of X-ray structural data on monodentate ether complexes.

In this paper we describe the structures of two important lithium hydrocarbyl solvates having structures not previously seen for monodentate etherates. These are the benzyllithium monoetherate polymer [Li(Et$_2$O)benzyl]$_x$, 1, and the mesityllithium bis(tetrahydrofuranate) dimer [Li(THF)$_2$mesityl]$_2$, 2. Complex 1 shows a rare sandwich structure with alternating benzyl and lithium ions wherein lithium is also coordinated to ether. Complex 2 is the first instance of an X-ray structurally characterized dimeric lithium hydrocarbyl monodentate etherate complex.

Experimental Section

All manipulations were carried out under an N$_2$ atmosphere using standard Schlenk tube techniques. All solvents were distilled from drying agents and degassed three times immediately before use.

Benzyllithium Monoetherate, 1. Dibenzylmercury(II)[6] (3.8 g) was suspended in *n*-hexane (40 mL) at 0 °C. *n*-BuLi (13 mL of a 1.7 M solution in *n*-hexane) was added dropwise which caused the colorless crystals of HgBz$_2$ to dissolve with concomitant precipitation of benzyllithium as a yellow solid. After the solution was stirred for 2 h, the yellow solid was removed by filtration (crude yield 1.8 g, 92%) and washed with two 20-mL portions of *n*-hexane. The yellow solid was dissolved in Et$_2$O (40 mL), and subsequent cooling to −20 °C gave 1 as orange yellow crystals.

Mesityllithium Bis(tetrahydrofuranate), 2.[7] *n*-BuLi (20 mL of a 1.7 M solution in *n*-hexane) was added dropwise to 30 mL of a 0 °C solution comprised of 1:2 Et$_2$O/*n*-hexane and 2-bromomesitylene (8 g). The mixture became cloudy, and stirring was continued for 12 h. The white solid was removed by filtration and washed with two 20-mL portions of *n*-hexane. The crude product (yield ca. 85%) was redissolved in THF (20 mL) to give an orange solution. A 1:1 Et$_2$O/*n*-hexane mixture was added dropwise until a faint cloudiness appeared. Slow cooling to −20 °C gave a good crop of crystals of 2 suitable for X-ray studies.

X-ray Crystallographic Studies

Structure Determination and Refinement. Crystals of the title compounds were coated with a hydrocarbon oil to retard decomposition and mounted in the cold stream of a Syntex P2$_1$ diffractometer equipped with a locally modified Syntex LT-1 low-temperature device. No decay in the intensity of standard reflections was observed during data collection. Solution of the structures was accomplished by using direct methods. All crystallographic computing was carried out using SHELXTL, version 4, August 1983, installed on a Data General Eclips S/230 computer, except for the direct methods solution of the structure of [Li(Et$_2$O)benzyl]$_x$, which was carried out by using MULTAN, installed on a VAX 11/780 computer. Atomic scattering factors and anamalous dispersion corrections were from common sources.[8] Further details are in Table I. No absorption or extinction corrections were considered necessary. Structure refinement proceeded smoothly in both cases, with no residual as large as a hydrogen atom in the final difference Fourier maps. All non-hydrogen atoms were assigned anisotropic thermal parameters. Hydrogen atoms were refined by using a riding model in which an idealized C–H vector of 0.96 Å length was recalculated with each cycle of refinement. Isotropic hydrogen thermal parameters were fixed at 1.2 times the equivalent isotropic thermal parameter of the bonded carbon. Final blocked-cascade least-squares refinement (based on F) converged at R = 0.078 and R_w = 0.085 using 4677 reflections with $I > 2\sigma(I)$ for [Li(Et$_2$O)benzyl]$_X$ and at R = 0.065 and R_w = 0.089 using 3655 reflections with $I > 2\sigma(I)$

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Table I. Crystallographic Data and Summary of Data Collection and Structure Refinement for 1 and 2

	1	2
chemical formula	$C_{11}OLiH_{17}$	$C_{34}O_4Li_2H_{54}$
fw	172.19	540.65
cryst color and habit	yellow plates	colorless parallelpipeds
space group	$P\bar{1}$	$P2_1/n$
lattice consts		
a, Å	7.503 (3)	9.566 (3)
b, Å	13.811 (3)	9.488 (3)
c, Å	21.498 (6)	17.927 (6)
α, deg	103.50 (2)	
β, deg	93.93 (3)	102.69 (3)
γ, deg	91.77 (2)	
V, Å³	2158.6	1587.3
Z	8	2
radiation, λ	Cu Kα	Mo Kα
graphite monochromator	1.541 78 Å	0.710 69 Å
d_{calcd}, g cm^{-3}	1.06	1.13
cryst dimens, mm	0.12 × 0.45 × 0.50	0.20 × 0.20 × 0.35
μ, cm^{-1}	0.69	0.64
range of absorptn factors	1.01–1.03	1.01–1.02
diffractometer	Syntex P2$_1$	Syntex P2$_1$
scan type	ω, 2.0° range, 1.8° offset for background, 60° min^{-1}	1.5° offset for background, 30° min^{-1}
$2\theta_{max}$, deg	130	55
h,k,l collected	$h,\pm k,\pm l$	$h,\pm k,\pm l$
no. of refl measd	7269	4204
no. of independent refl	7250	4129
R(merge)	0.012	0.007
no. of parameters refined	493	253
R (based on F)	0.078	0.065

for [Li(THF)$_2$mesityl]$_2$. Atomic coordinates for 1 and 2 are given in Tables II and III.

Structural Description

[Li(Et$_2$O)benzyl]$_x$, 1. The asymmetric unit contains two [Li(Et$_2$O)benzyl]$_2$ formula units, each of which comprises a portion of two parallel, noninteracting chains propagated in the a direction. These are depicted in Figure 1, together with the atom numbering scheme. The unit cell contains four sections of chain since another pair of chains are related to the first two by a center of symmetry. This packing is illustrated in Figure 2. Within one chain the Li–Li separation alternates 4.420 (7) and 4.403 (7) Å, and within the other it alternates 4.357 (7) and 4.381 (7) Å. The shortest contacts between chains are ca. 2.44 Å between phenyl hydrogen atoms. Each chain is constructed of alternating lithium cations and benzyl anions. In addition, one molecule of diethyl ether is coordinated to each lithium. The arrangement of atoms looking down a chain axis is shown in Figure 3. Two dominant factors determine the chain structure: donation of benzyl π-electron density to Li(1) and Li(2)' above and below the benzyl plane and trigonal-planar geometry at each lithium. These two factors prevent the adjacent benzyl rings in the chain from stacking in a parallel fashion. Rather, the angles between adjacent ring normals range from 58.3° to 63.7°. On the basis of an examination of Li and C internuclear separations, it appears that the primary interaction occurs between the terminal CH$_2$ group and lithium. These distances range from 2.189 (8) to 2.229 (8) Å. The distances to the adjacent ring carbon atom are significantly greater and show large variations. For each Li there is one distance between 2.404 (8) and 2.458 (8) Å. The opposite distance is considerably longer, ranging between 2.686 (8) and 2.875 (8) Å. Distances between lithium and the ortho ring carbon atoms are longer still and are in the same range of distances as between lithium and the ether α-carbons (3 Å). This is not the whole story, however. While the results show that the Li–C distance is 0.8 Å longer for the ortho carbon than for the terminal CH$_2$ carbon, the C–C distances within the ring, not surprisingly, reveal extensive
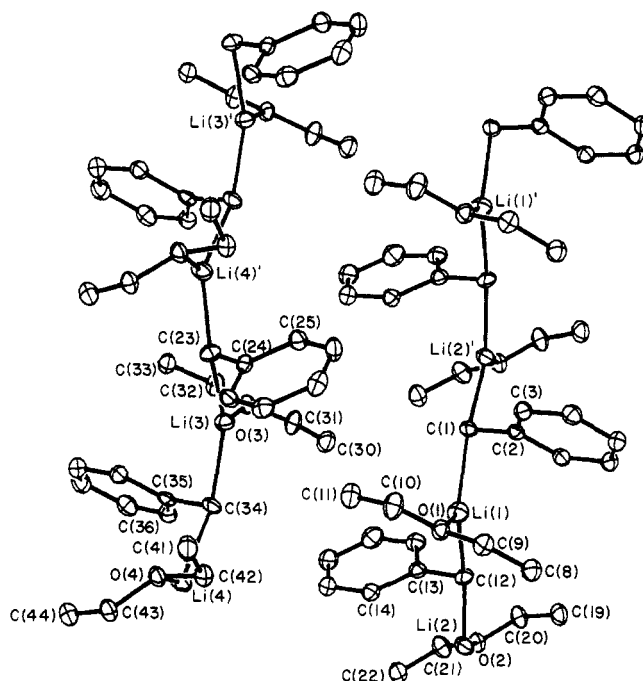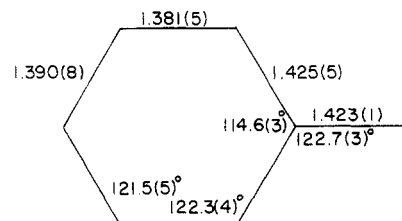

Figure 1. Computer generated drawing illustrating the chain structure of 1.

perturbation. Average C–C distances and angles for the four benzyl rings are pictured (mean deviations in parentheses). If only the three shortest bonds to lithium are

taken into account, a planar array of atoms is found. Figure 4 illustrates one such arrangement. Although it

Table II. Atom Coordinates (×10⁴) and Thermal Parameters (Å² × 10³) for [Li(Et₂O)benzyl]ₓ, 1

atom	x	y	z	U^a
O(1)	7203 (4)	6979 (2)	3838 (1)	28 (1)
O(2)	11817 (4)	8109 (2)	1196 (1)	30 (1)
O(3)	3455 (4)	3136 (2)	1133 (1)	28 (1)
O(4)	8740 (3)	1971 (2)	3684 (1)	28 (1)
C(1)	4079 (5)	7452 (3)	2577 (2)	29 (1)
C(2)	4120 (5)	8325 (3)	3087 (2)	25 (1)
C(3)	3384 (5)	8341 (3)	3679 (2)	28 (1)
C(4)	3460 (5)	9182 (3)	4174 (2)	30 (1)
C(5)	4274 (5)	10081 (3)	4117 (2)	32 (1)
C(6)	5001 (5)	10096 (3)	3546 (2)	31 (1)
C(7)	4946 (5)	9252 (3)	3043 (2)	27 (1)
C(8)	8365 (6)	8647 (3)	4315 (2)	35 (1)
C(9)	7532 (6)	7714 (3)	4436 (2)	32 (1)
C(10)	6436 (7)	6066 (3)	3939 (2)	41 (2)
C(11)	6245 (6)	5300 (3)	3325 (2)	40 (2)
C(12)	9084 (5)	7606 (3)	2476 (2)	29 (1)
C(13)	8978 (5)	6719 (3)	1978 (2)	27 (1)
C(14)	9743 (5)	5819 (3)	2059 (2)	31 (1)
C(15)	9665 (6)	4972 (3)	1564 (2)	39 (2)
C(16)	8889 (6)	4956 (3)	962 (2)	42 (2)
C(17)	8130 (6)	5815 (4)	868 (2)	45 (2)
C(18)	8160 (5)	6678 (3)	1355 (2)	34 (1)
C(19)	10674 (6)	9693 (3)	1666 (2)	39 (2)
C(20)	10955 (6)	8961 (3)	1054 (2)	39 (2)
C(21)	12183 (6)	7423 (3)	615 (2)	39 (2)
C(22)	13035 (6)	6533 (3)	769 (2)	41 (2)
C(23)	1743 (5)	2504 (3)	2481 (2)	32 (1)
C(24)	2069 (5)	3197 (3)	3084 (2)	26 (1)
C(25)	1285 (5)	4147 (3)	3225 (2)	32 (1)
C(26)	1560 (6)	4810 (3)	3814 (2)	38 (2)
C(27)	2640 (6)	4580 (3)	4309 (2)	37 (2)
C(28)	3419 (5)	3661 (3)	4191 (2)	32 (1)
C(29)	3156 (5)	2994 (3)	3603 (2)	30 (1)
C(30)	4670 (6)	4764 (3)	1662 (2)	38 (2)
C(31)	4080 (6)	4072 (3)	1028 (2)	39 (2)
C(32)	2805 (6)	2439 (3)	552 (2)	38 (2)
C(33)	2118 (6)	1500 (3)	701 (2)	34 (1)
C(34)	6759 (5)	2709 (3)	2373 (2)	30 (1)
C(35)	6646 (5)	1819 (3)	1878 (2)	27 (1)
C(36)	7252 (5)	1764 (3)	1261 (2)	31 (1)
C(37)	7077 (6)	917 (3)	776 (2)	37 (2)
C(38)	6268 (6)	32 (3)	869 (2)	38 (2)
C(39)	5680 (5)	53 (3)	1466 (2)	34 (1)
C(40)	5840 (5)	909 (3)	1955 (2)	29 (1)
C(41)	7591 (6)	2577 (3)	4746 (2)	37 (2)
C(42)	8558 (6)	2827 (3)	4202 (2)	32 (1)
C(43)	9734 (5)	1195 (3)	3875 (2)	31 (1)
C(44)	10040 (6)	415 (3)	3283 (2)	34 (1)
Li(1)	6801 (9)	7338 (5)	3018 (3)	34 (2)
Li(2)	11644 (9)	7754 (5)	2031 (4)	34 (2)
Li(3)	4022 (9)	2802 (5)	1953 (3)	31 (2)
Li(4)	9153 (9)	2287 (5)	2867 (3)	32 (2)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Atom Coordinates (×10⁴) and Temperature Factors (Å² × 10³) for [Li(THF)₂mesityl]₂, 2

atom	x	y	z	U^a
O(1)	2943 (1)	9770 (1)	1046 (1)	29 (1)
O(2)	1416 (1)	7161 (1)	446 (1)	29 (1)
C(1)	-842 (2)	9914 (2)	868 (1)	20 (1)
C(2)	-471 (2)	10896 (2)	1485 (1)	20 (1)
C(3)	-853 (2)	10710 (2)	2188 (1)	22 (1)
C(4)	-1631 (2)	9541 (2)	2336 (1)	22 (1)
C(5)	-2022 (2)	8563 (2)	1747 (1)	22 (1)
C(6)	-1640 (2)	8739 (2)	1043 (1)	20 (1)
C(7)	386 (2)	12203 (2)	1395 (1)	26 (1)
C(8)	-2031 (2)	9341 (2)	3095 (1)	32 (1)
C(9)	-2104 (2)	7592 (2)	450 (1)	26 (1)
C(10)	4188 (2)	9909 (2)	727 (1)	30 (1)
C(11)	5038 (2)	11143 (2)	1151 (1)	33 (1)
C(12)	4473 (2)	11280 (3)	1880 (1)	47 (1)
C(13)	3449 (2)	10034 (2)	1843 (1)	39 (1)
C(14)	1666 (2)	6501 (2)	1197 (1)	39 (1)
C(15)	2683 (2)	5293 (2)	1174 (1)	34 (1)
C(16)	3526 (2)	5817 (2)	602 (1)	35 (1)
C(17)	2389 (2)	6559 (2)	20 (1)	31 (1)
Li	1025 (3)	9278 (3)	347 (2)	25 (1)

^{a} Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table IV. Selected Internuclear Distances (Å) for [Li(Et₂O)benzyl]ₓ, 1^a

Li(1)–C(1)	2.218 (8)	Li(1)–C(2)	2.458 (9)
Li(1)–C(12)	2.206 (9)	Li(1)–C(13)	2.844 (9)
Li(2)–C(12)	2.229 (8)	Li(2)'–C(2)	2.780 (9)
Li(2)'–C(1)	2.207 (8)	Li(2)–C(13)	2.404 (9)
Li(3)–C(23)	2.195 (8)	Li(3)–C(24)	2.875 (9)
Li(3)–C(34)	2.206 (8)	Li(3)–C(35)	2.420 (9)
Li(4)'–C(23)	2.204 (8)	Li(4)'–C(24)	2.450 (8)
Li(4)–C(34)	2.189 (8)	Li(4)–C(35)	2.686 (9)
Li(1)–O(1)	1.948 (8)	C(1)–C(2)	1.426 (5)
Li(2)–O(2)	1.978 (9)	C(12)–C(13)	1.423 (5)
Li(3)–O(3)	1.947 (8)	C(23)–C(24)	1.421 (5)
Li(4)–O(4)	1.947 (8)	C(34)–C(35)	1.412 (5)

^{a} Primed atoms are at symmetry position $x - 1, y, z$.

Table V. Selected Angles (deg) for [Li(Et₂O)benzyl]ₓ, 1

Li(1)–C(1)–Li(2)'	168.5 (4)	C(12)'–Li(2)'–O(2)'	124.2 (4)
Li(1)–C(12)–Li(2)	170.8 (4)	C(1)–Li(2)'–O(2)'	120.2 (4)
Li(3)–C(23)–Li(4)'	169.4 (3)	C(23)–Li(3)–O(3)	116.5 (3)
Li(3)–C(34)–Li(4)	165.0 (4)	C(23)–Li(3)–C(34)	119.0 (4)
C(1)–Li(1)–O(1)	122.3 (4)	C(34)–Li(3)–O(3)	124.5 (4)
C(1)–Li(1)–C(12)	117.4 (4)	C(23)–Li(4)'–(4)'	127.7 (4)
C(12)–Li(1)–O(1)	120.3 (4)	C(23)–Li(4)'–C(34)'	117.4 (4)
C(12)'–Li(2)'–C(1)	115.6 (4)	C(34)'–Li(4)'–O(4)'	114.0 (3)

Angle of Li–C Line to the Normal of the Bonded C₇ Plane (esd 0.4°)

Li(1)–C(1)	11.4	Li(3)–C(23)	15.4
Li(2)'–C(1)	9.8	Li(4)'–C(23)	16.8
Li(1)–C(12)	15.0	Li(3)–C(34)	12.6
Li(2)–C(12)	13.2	Li(4)–C(34)	10.7

might be expected that the angle between the line of the Li–C(1) bond and the normal to the C(1) to C(7) plane would be close to 0°, such is not the case. Rather, a deviation of 11.4 (4)° is calculated, and this is typical for the other interacting pairs. These angles, together with selected bond distances and angles, are collected in Tables IV and V. A complete listing of distances and angles, calculated hydrogen atom coordinates, anisotropic thermal parameters, and structure factor amplitudes is available as supplementary material.

[Li(THF)₂mesityl]₂, 2. The structure consists of centrosymmetric dimers, as illustrated in Figure 5. There are no short intermolecular contacts. The Li₂C₂ rhombus is characterized by nearly equal LiC bond distances of 2.271 (3) and 2.279 (3) Å, and acute angle at carbon of 66.4 (1)°, and a Li⋯Li distance of 2.490 (5) Å. The aryl groups are canted from perpendicular to the Li₂C₂ plane by an angle of 2.3 (1)°. The geometry about lithium is approx-

imately tetrahedral and consists of interactions to two THF oxygens and two mesityl carbons. Within the mesityl groups, the C–C bonds involving the coordinated carbon atom are longer than the remaining C–C bonds in the ring. These bonds average 1.428 (4) Å vs. 1.396 (2) Å for the others. There is an unusually wide angle of 136.0 (1)° at O(1) which can be attributed to a close intramolecular H contact of 2.26 (3) Å between hydrogens on C(13) and C(7). Bond distances and angles for this structure are presesnted in Tables VI and VII. Tables of calculated hydrogen atom coordinates, anisotropic thermal parameters, and structure factor amplitudes are available as supplementary material.

Discussion

The relationship between the structure of organolithium reagents in the solid and solution phases has generated
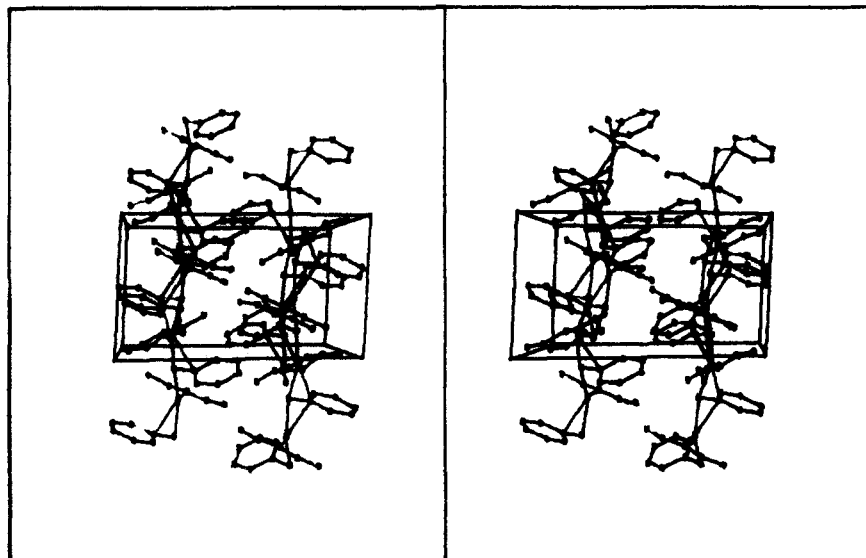
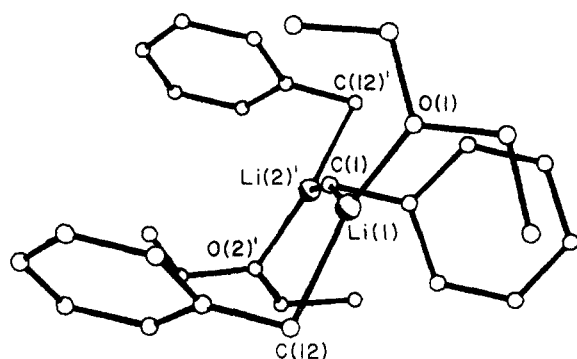**Figure 2.** Stereoview of 1 showing packing in the unit cell.

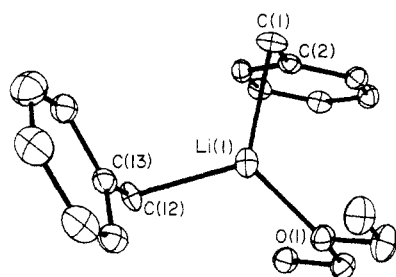
Figure 3. View of 1 down chain axes.
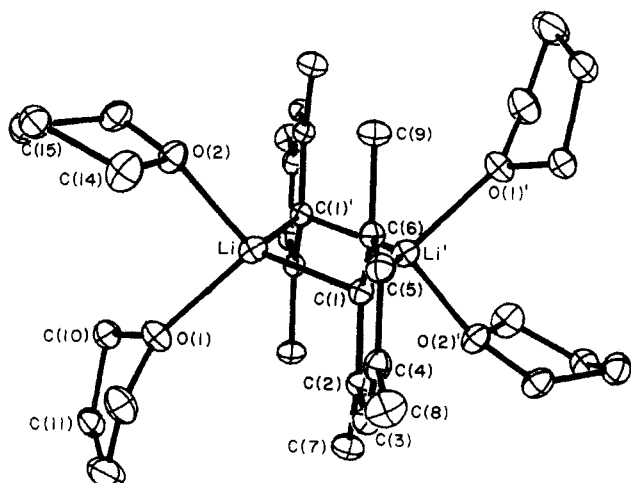

Figure 4. View of 1 showing the geometry at lithium.

Figure 5. Computer-generated representative drawing of 2.

Table VI. Internuclear Distances (Å) for [Li(THF)$_2$mesityl]$_2$, 2^a

Li–C(1)	2.271 (3)	C(15)–C(16)	1.521 (3)
Li–C(1)′	2.279 (3)	C(16)–C(17)	1.506 (2)
Li–O(1)	2.036 (3)	C(17)–O(2)	1.446 (2)
Li–O(2)	2.044 (3)	C(1)–C(2)	1.431 (2)
Li⋯Li′	2.490 (5)	C(2)–C(3)	1.397 (2)
O(1)–C(10)	1.436 (2)	C(3)–C(4)	1.393 (2)
C(10)–C(11)	1.529 (2)	C(4)–C(5)	1.394 (2)
C(11)–C(12)	1.525 (3)	C(5)–C(6)	1.399 (2)
C(12)–C(13)	1.528 (3)	C(6)–C(1)	1.424 (2)
C(13)–O(1)	1.426 (2)	C(2)–C(7)	1.515 (2)
O(2)–C(14)	1.455 (2)	C(4)–C(8)	1.506 (2)
C(14)–C(15)	1.509 (3)	C(6)–C(9)	1.517 (2)

^{a} Primed atoms are at symmetry position $-x$, $1 - y$, $-z$.

Table VII. Internuclear Angles (deg) for [Li(THF)$_2$mesityl]$_2$, 2

C(1)–Li–C(1)′	113.6 (1)	C(3)–C(4)–C(8)	121.7 (1)
O(1)–Li–C(1)	111.7 (1)	C(5)–C(4)–C(8)	121.4 (1)
O(1)–Li–C(1)′	112.4 (1)	C(5)–C(6)–C(9)	116.8 (1)
O(1)–Li–O(2)	92.8 (1)	C(1)–C(6)–C(9)	119.7 (1)
C(1)–Li–O(2)	111.7 (1)	Li–O(1)–C(10)	119.3 (1)
C(1)′–Li–O(2)	112.8 (1)	O(1)–C(10)–C(11)	105.6 (1)
Li–C(1)–Li′	66.4 (1)	C(10)–C(11)–C(12)	104.0 (2)
Li–C(1)–C(2)	114.1 (1)	C(11)–C(12)–C(13)	103.9 (2)
Li–C(1)–C(6)	113.0 (1)	C(12)–C(13)–O(1)	104.7 (2)
Li′–C(1)–C(2)	118.3 (1)	C(13)–O(1)–Li	136.0 (1)
Li′–C(1)–C(6)	112.7 (1)	C(10)–O(1)–C(13)	104.7 (1)
C(1)–C(2)–C(3)	123.1 (1)	Li–O(2)–C(14)	119.6 (1)
C(2)–C(3)–C(4)	121.8 (1)	O(2)–C(14)–C(15)	106.2 (2)
C(3)–C(4)–C(5)	116.9 (1)	C(14)–C(15)–C(16)	102.2 (2)
C(4)–C(5)–C(6)	121.6 (1)	C(15)–C(16)–C(17)	102.2 (1)
C(5)–C(6)–C(1)	123.4 (1)	C(16)–C(17)–O(2)	105.6 (1)
C(6)–C(1)–C(2)	113.1 (1)	C(17)–O(2)–Li	118.0 (1)
C(1)–C(2)–C(7)	119.9 (1)	C(14)–O(2)–C(17)	108.9 (1)
C(3)–C(2)–C(7)	117.0 (1)		

considerable interest.[1,4,5] The structural characteristics of their crystalline monodentate ether complexes, in particular, represent the closest approach to the solvated species in which a fully detailed picture is possible. At present the X-ray structures of only a few complexes of simple organolithium reagents, involving only monodentate ethers, are known. These are the complexes (PhLi·Et$_2$O)$_4$,[3] (PhLi·Et$_2$O)$_3$LiBr,[3] (LiCH(CH$_2$)$_2$)$_2$(LiBr)$_2$·4Et$_2$O,[9] (LiC≡C-t-Bu·THF)$_4$,[10] and [1,1,3,3-bis(2,2′-biphenylene)-

(9) Schmidbaur, H; Schier, A.; Schubert, U. *Chem. Ber.* **1983**, *116*, 1938.

propene]lithium etherate.[11] It is interesting to note that (PhLi·Et$_2$O)$_4$ and (LiC≡C-t-Bu·THF)$_4$ are, at present, the only known organolithium monodentate ether solvates where the structures have very similar X-ray crystal structures to the proposed Et$_2$O solution phase structures. The structure of (LiBr·Et$_2$O)$_4$ is also tetrameric in both the solid[13] and solution phases.[14] In a wider context X-ray structures of many other ether solvate lithium complexes (involving Li–N, Li–O, and Li–P bonded species) have been published.[1,2]

Our objective in this work was to extend the range of known organolithium etherate complexes and to describe new structural types if possible. Our interest in benzyllithium arose as a result of our studies of crown ether salts of free carbanions.[15] Its structure in solution has been reported to be a contact ion pair with lithium also coordinated to ether molecules.[16] However it is not clear if this type of structure is maintained at higher concentrations where oligomerization would be favored. We believe that the structure of 1 represents the limiting situation wherein each lithium ion interacts with a second benzyl group forming a chain structure. The steric bulk of the π-bonding benzyl groups allows coordination of only one ether molecule, and the polymeric structure of 1 is the result. Support for this view also comes from recent conductivity studies in which agglomerates involving chains of alternating Li$^+$ and R$^-$ ions have been proposed to account for conductivities at higher concentrations.[16a]

The crystallographic results for [Li(Et$_2$O)benzyl]$_x$, 1, resemble those already reported for [Li(triethylenediamine)benzyl]$_x$,[17a] 3, and [{(LiTMEDA)$_2$}{(2-CH$_2$C$_6$H$_4$)$_2$}],[17b] 4, in certain important aspects. The mode of interaction between the carbanion's π cloud and the lithium cation is similar. This interaction has also been recently reinterpreted in terms of an ionic model.[18] The basic repeating unit in [Li(triethylenediamine)benzyl]$_x$ consists of a lithium cation, a benzyl anion, and two half triethylenediamine molecules. Its polymeric chain is propagated because there are two donor nitrogen atoms in triethylenediamine. Thus each lithium interacts with two nitrogen atoms and one benzyl anion. In contrast each lithium in 1 and 4 interacts with one ether oxygen atom or two nitrogens and two benzyl anions. This means that the π-orbital of the benzyl group interacts with a lithium above and below the molecular plane. Nevertheless, the strength of the Li$^+$benzyl$^-$ interaction diminishes very little, as the Li–C distances in each structure is comparable and in the range expected for complexes involving Li–C bridging.[1,2] The structure of another benzyl–Li compound has also been published recently. This concerns the species [Li(TMEDA)$_2$]-[(TMEDA)Li(benzyl)$_2$Mg(benzyl)$_2$]; however, there is only a limited structural resemblance to the polymer 1.[19] There is a resemblance between the coordination sphere of Li$^+$ in 1 and [1,1,3,3-bis(2,2'-biphenylene)propene]lithium etherate.[11] In the latter, the Li$^+$ is coordinated to an ether molecule and has a π-interaction with two aromatic rings. In this case the lithium may be regarded as having trigonal-planar geometry if vectors to the center of each phenyl ring and the oxygen atom are considered. Another feature of interest in the structure of 1 concerns the α-carbon atom geometry in each benzyl. The geometry is approximately trigonal bipyramidal, in agreement with the structural prediction for CH$_3$Li$_2$$^+$ by Schleyer and co-workers.[20] The only other X-ray structures for polymeric lithium hydrocarbyls are of the species [LiCH(SiMe$_3$)$_2$]$_x$[21a] and [Li(TMEDA)C$_3$H$_5$]$_x$.[21b]

The dimeric structure seen in 2 is mainly a consequence of steric effects. The steric requirements of two ortho methyl groups prevent tetramer formation. This steric interference is apparent in the close contact between hydrogen atoms of the ortho methyl group and THF. A strong resemblance can be seen between the structure of [Li(THF)$_2$mesityl]$_2$ and [Li(TMEDA)Ph]$_2$[22] which has very similar lithium carbon and lithium–lithium distances. Nevertheless there is an important difference in that 2 is dimeric for steric reasons whereas [Li(TMEDA)Ph]$_2$ is dimer because of the stronger coordinating ability of the bidentate TMEDA (cf. (PhLi·Et$_2$O)$_4$[3]). At present there is little information on the structure of mesityllithium in solution.[23] In the light of the above results, it can be anticipated that it will prove it to be dimeric in the solution phase also.

In summary our results support the view that the X-ray crystal structures of Et$_2$O or THF solvates of organolithium complexes closely resemble their structures at least in concentrated (ca. 1–2 M) solutions of the same solvent. Lower degrees of aggregation may be formed in dilute solutions (<0.1 M) or at lower temperatures.[1] However much more structural data are needed before this theory can be shown to have widespread validity.

Supplementary Material Available: Tables of anisotropic thermal parameters, bond distances and angles, and hydrogen coordinates (57 pages). Ordering information is on any current masthead page.

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