

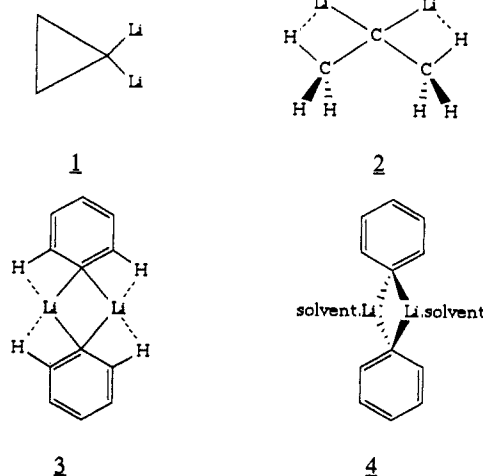
Planar Tetracoordinate Carbon Atoms Hidden in the Tetrameric Aggregate of (2,6-Dimethoxyphenyl)lithium

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Abstract: The crystal structure of the (2,6-dimethoxyphenyl)lithium tetramer is comprised of two interacting dimer units. This is shown both by the somewhat greater C-Li distances between rather than within the dimers and by differences in the corresponding ¹³C-Li coupling constants of the tetramer in toluene solution. While these dimer units fold as a result of their interaction, the local environment of C(ipso) approaches the planar tetracoordination predicted in 1981 for the isolated dimer on the basis of MNDO calculations.

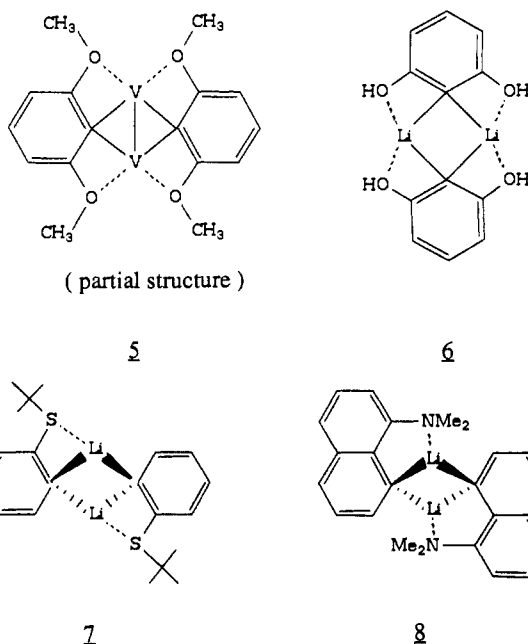
When two lithium atoms are attached to the same carbon atom, there is a remarkable increase in the stability of the planar versus the tetrahedral geometrical arrangement.¹ While CH₂Li₂ affords the simplest example,¹⁻⁵ 1,1-dilithiocyclopropane (**1**) was the first



molecule calculated to prefer planar tetracoordination at carbon.¹ 2,2-Dilithioethane (**2**) is an even simpler example.⁶ The bonding in such *gem*-dilithio species has been well-analyzed.¹⁻⁵ There is considerable ionic character (R₂C²⁻, 2 Li⁺), but some three-center π-bonding contributes preferentially to the stability of the planar singlet. Some additional stabilizing resulting from attractive CH...Li ("agostic") interaction in **2** also favors the planar form. The same factors are involved in the unsolvated phenyllithium dimer, which MNDO calculations indicate to prefer planar geometry **3** by 24.7 kJ/mol.⁷

However, solvation of lithium reverses this preference; the X-ray structure of [C₆H₅Li·TMEDA]₂⁸ as well as MNDO calculations on [C₆H₅Li·S]₂ with model solvent⁷ indicate **4**, the perpendicular ("tetrahedral") form, to be favored.

Although not recognized by the original authors,⁹ the first experimental example of planar tetracoordinate carbon¹⁰ was observed in the X-ray structure of a vanadium 2,6-dimethoxyphenyl complex, **5**. The effectiveness of oxygen-lithium chelation in stabilizing such planar tetracoordinate geometries was shown by MNDO calculations on **6**.⁷ The increase in the stability of the planar form (to 122 kJ/mol over the perpendicular arrangement) was indicated to be sufficient to persist when each



lithium was solvated. Hence, (2,6-dimethoxyphenyl)lithium dimer (as well as analogous systems employing the same principle of chelation to stabilizing planar arrangements) was proposed as a good candidate for the experimental verification of planar tetracoordinate carbon. Unfortunately, the first attempt of verification by X-ray analyses failed.^{11a} Evidently, partial hydrolysis had occurred during the preparation, and the crystal structure consisted of an aggregate containing a 6:1 ratio of (2,6-dimethoxyphenyl)lithium and Li₂O. Although interesting in its own right, the structure of this aggregate was not pertinent to the planar

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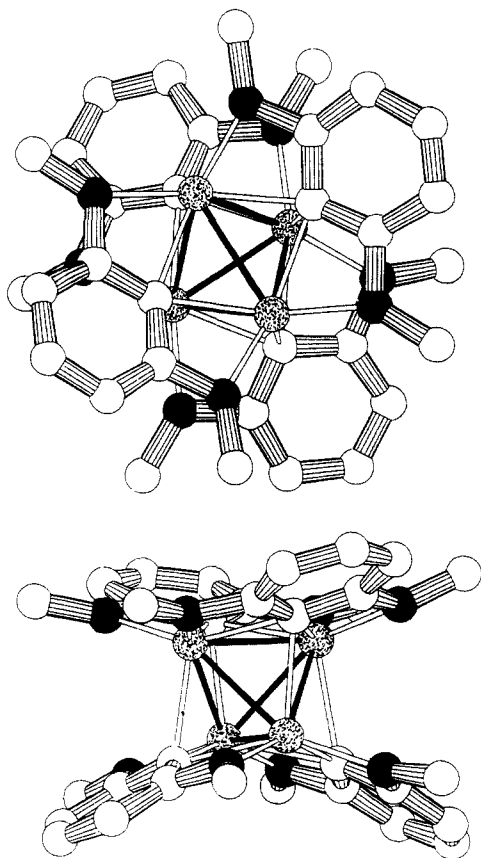


Figure 1. Plot of the asymmetric part of the unit cell containing two tetrameric aggregates. The oxygen atoms are indicated by black spheres and the lithium atoms by speckled spheres. The lithium tetrahedra are indicated by black Li-Li contacts.

tetracoordinate carbon problem.

Other organolithium complexes with one chelating substituent (7^{12} and 8^{13}) show some tetrahedral-planar distortion of the tetracoordinate carbon atom bonded to lithium. We have now been able to prepare Li_2O -free (2,6-dimethoxyphenyl)lithium crystals, and its X-ray structure and NMR behavior in solution are the subject of this paper. During the course of this work, we learned that Dietrich's group also had obtained X-ray results on the same Li_2O -free compound at 117 K.^{11b}

Results

X-ray Study of (2,6-Dimethoxyphenyl)lithium. X-ray diffraction data for crystalline (2,6-dimethoxyphenyl)lithium were collected, and the structure was solved (detailed information in the Experimental Section). The asymmetric part of the unit cell contains two tetrameric aggregates of (2,6-dimethoxyphenyl)lithium (Figure 1), which are turned at 90° to one another and show no significant structural differences. The molecule and atom numbering are given schematically in parts a and b of Figure 2, respectively. The fractional coordinates and equivalent thermal parameters of the non-hydrogen atoms are given in Table I. Bond distances and angles are given in Table II and are similar to those for other aryllithium compounds.¹⁴ The tetrameric aggregate contains a pseudo 4-fold inversion axis, so every lithium atom has approximately the same coordination geometry as is given in Table III. Every oxygen atom is coordinated to one lithium atom, and every C(ipso) atom has three short contacts to lithium atoms, so

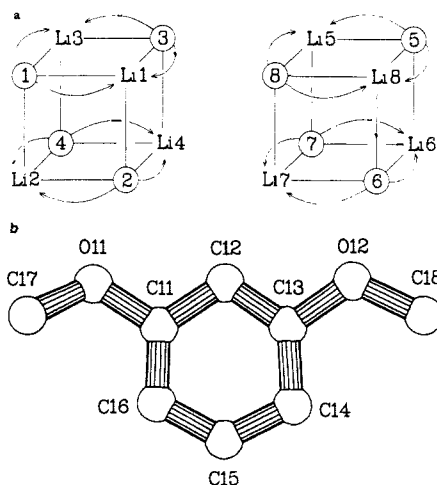


Figure 2. (a) Schematic representation of the molecule numbering. The numbers for the 2,6-dimethoxyphenyl molecules are circled. (b) Systematic atom numbering for molecule 1. The first number indicates the molecule and the second the atom.

the C(ipso) atoms are all five-coordinated. The C-Li and O-Li bond distances are in the normal range. The average Li-Li distance of 2.70 (1) Å is longer than those found in other tetrameric organolithium compounds with intramolecular Li-O coordination, e.g. 2.485 Å for 1-lithio-3-methoxypropane,¹⁵ 2.495 Å for 2-lithio-4-methoxybutane,¹⁶ and 2.637 Å for (2-methoxyphenyl)lithium.¹⁷ The C-O-C angles are all very close to 120° , ranging from $118.7 (5)^\circ$ to $122.7 (5)^\circ$ (average $120.4 (5)^\circ$). As in (2-methoxyphenyl)lithium,¹⁷ appreciable electron donation from the O 2p orbitals to C(ipso) is expected due to the mesomeric effect, which should be decreased by eventual O-Li chelation. We consider the tetramer to consist of two "planar" dimeric units joined to one another via the interactions of electron-rich C(ipso) p orbitals to lithium atoms of the other dimeric unit. We discriminate between the C-Li("in plane") and C-Li("out of plane") bonds since their average lengths differ significantly. The C-Li(in plane) bond distances range from 2.253 (9) to 2.338 (9) Å (average 2.285 (9) Å), and the C-Li(out of plane) bond lengths are in the 2.310 (9)-2.396 (9)-Å range (average 2.349 (9) Å). The Li-Li distances within and between the dimers also are different. The Li-Li distances within the dimers range from 2.71 (1) to 2.78 (1) Å (average 2.74 (1) Å) and between the dimeric units range from 2.62 (1) to 2.71 (1) Å (average 2.68 (1) Å). Effective chelation in each dimethoxyphenyl moiety is responsible for the long Li-Li distances within the dimeric unit.

The tetramer is built from two dimeric units, which are not planar but are folded back from one another (angles between the aryl ring planes in these dimer moieties range from 44.7° to 62.1°). This is due to short contacts (ranging from 3.20 to 3.35 Å) between the oxygen atoms and the carbon atoms ortho from C(ipso) belonging to the other dimeric unit. Nevertheless, the C(ipso) atoms can be regarded as having an approximately planar tetracoordinated environment (the twist angles between the planes C-C(ipso)-C' and Li-C(ipso)-Li' are in the range of $6.0 (4)^\circ$ - $16.8 (4)^\circ$ (average 11.1°)).

NMR Study of (2,6-Dimethoxyphenyl)lithium. Crystals of (2,6-dimethoxyphenyl)lithium (isotopically enriched with ^6Li , spin $I = 1$) dissolve readily in toluene- d_8 or in tetrahydrofuran- d_8 (THF- d_8). At low temperatures, the splitting pattern of the ^{13}C NMR signal ($J_{^{13}\text{C}-^6\text{Li}}$) of the lithiated carbon atom of organolithium compounds depends on the number of attached lithium atoms.^{18,21} Hence, the multiplicity indicates the degree of ag-

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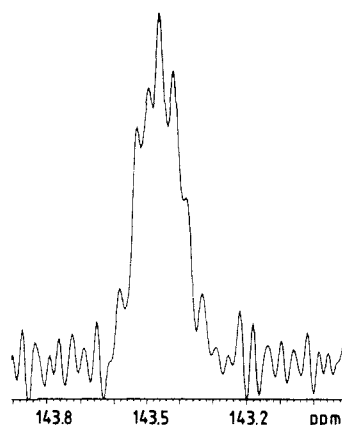
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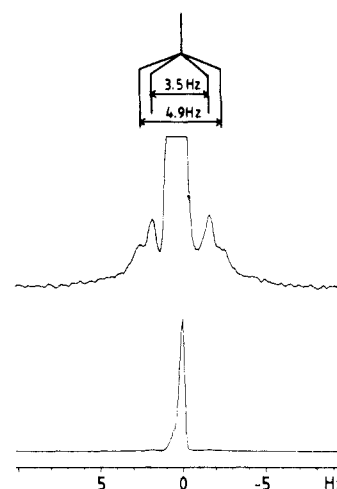
Table I. Fractional Coordinates of the Non-Hydrogen Atoms with Their Equivalent Thermal Parameters (\AA^2)

atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}^a	atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	U_{eq}^a
O(11)	0.5864 (3)	0.5245 (3)	0.5949 (2)	0.104 (2)	C(35)	0.3234 (6)	0.2277 (5)	0.8526 (4)	0.131 (3)
O(12)	0.6888 (3)	0.6111 (2)	0.7786 (2)	0.101 (2)	C(36)	0.3796 (6)	0.2851 (5)	0.8835 (3)	0.109 (3)
O(21)	0.1899 (2)	0.5194 (2)	0.7334 (2)	0.094 (2)	C(37)	0.5126 (5)	0.4106 (4)	0.9364 (3)	0.133 (3)
O(22)	0.4685 (3)	0.7403 (2)	0.6103 (2)	0.086 (1)	C(38)	0.3206 (6)	0.3137 (4)	0.6527 (3)	0.138 (3)
O(31)	0.4875 (3)	0.4389 (2)	0.8739 (2)	0.096 (2)	C(41)	0.4755 (5)	0.7504 (4)	0.8154 (3)	0.075 (2)
O(32)	0.3721 (3)	0.3743 (2)	0.6884 (2)	0.095 (2)	C(42)	0.4079 (4)	0.6689 (3)	0.8165 (2)	0.065 (2)
O(41)	0.5398 (3)	0.7849 (2)	0.7534 (2)	0.089 (2)	C(43)	0.3340 (5)	0.6410 (4)	0.8764 (3)	0.083 (2)
O(42)	0.2577 (3)	0.5644 (3)	0.8757 (2)	0.099 (2)	C(44)	0.3298 (6)	0.6834 (5)	0.9335 (3)	0.109 (3)
O(51)	0.1751 (3)	0.0017 (2)	0.8139 (2)	0.103 (2)	C(45)	0.4051 (8)	0.7605 (6)	0.9268 (4)	0.126 (4)
O(52)	0.0980 (4)	0.1538 (3)	0.6182 (2)	0.133 (2)	C(46)	0.4789 (6)	0.7972 (4)	0.8692 (4)	0.105 (3)
O(61)	0.0333 (3)	-0.1644 (2)	0.7829 (2)	0.102 (2)	C(47)	0.6198 (4)	0.8660 (4)	0.7440 (3)	0.117 (3)
O(62)	-0.2640 (3)	0.0126 (3)	0.8856 (2)	0.115 (2)	C(48)	0.1855 (6)	0.5187 (5)	0.9339 (3)	0.155 (3)
O(71)	-0.3082 (3)	0.1284 (3)	0.7387 (2)	0.108 (2)	C(51)	0.2130 (5)	0.0195 (4)	0.7461 (4)	0.094 (3)
O(72)	-0.0243 (4)	-0.0611 (3)	0.6401 (2)	0.107 (2)	C(52)	0.1334 (4)	0.0682 (4)	0.7148 (3)	0.076 (2)
O(81)	-0.0340 (3)	0.1364 (3)	0.8969 (2)	0.105 (2)	C(53)	0.1748 (6)	0.0960 (5)	0.6487 (4)	0.106 (3)
O(82)	0.1168 (4)	0.2808 (2)	0.7002 (2)	0.124 (2)	C(54)	0.2815 (8)	0.0708 (7)	0.6150 (5)	0.152 (5)
Li(1)	0.4699 (6)	0.5001 (5)	0.6815 (4)	0.073 (2)	C(55)	0.352 (1)	0.0185 (9)	0.6476 (7)	0.209 (8)
Li(3)	0.5345 (7)	0.5382 (5)	0.7918 (4)	0.076 (2)	C(56)	0.3207 (6)	-0.0070 (5)	0.7136 (5)	0.145 (4)
Li(2)	0.4786 (6)	0.6876 (5)	0.7048 (4)	0.071 (2)	C(57)	0.2431 (5)	-0.0569 (4)	0.8535 (3)	0.150 (4)
Li(4)	0.3149 (6)	0.5544 (5)	0.7782 (4)	0.073 (2)	C(58)	0.1272 (7)	0.1908 (5)	0.5527 (3)	0.193 (4)
Li(6)	-0.0196 (7)	-0.0425 (5)	0.7299 (4)	0.077 (2)	C(61)	-0.0492 (5)	-0.1587 (4)	0.8402 (3)	0.086 (3)
Li(5)	-0.0254 (7)	0.1563 (6)	0.7006 (4)	0.083 (2)	C(62)	-0.1066 (4)	-0.0722 (3)	0.8383 (2)	0.071 (2)
Li(7)	-0.1925 (7)	0.0685 (6)	0.7927 (4)	0.078 (2)	C(63)	-0.1982 (5)	-0.0713 (4)	0.8918 (3)	0.086 (3)
Li(8)	0.0215 (6)	0.0682 (5)	0.8176 (4)	0.075 (2)	C(64)	-0.2235 (7)	-0.1468 (6)	0.9432 (3)	0.136 (4)
C(11)	0.6694 (5)	0.5673 (4)	0.6194 (3)	0.078 (2)	C(65)	-0.1582 (9)	-0.2289 (6)	0.9434 (4)	0.157 (5)
C(12)	0.6346 (4)	0.5788 (3)	0.6858 (3)	0.074 (2)	C(66)	-0.0687 (7)	-0.2396 (5)	0.8917 (4)	0.116 (3)
C(13)	0.7213 (5)	0.6118 (4)	0.7106 (4)	0.092 (3)	C(67)	0.1048 (5)	-0.2471 (4)	0.7764 (4)	0.151 (3)
C(14)	0.8336 (5)	0.6426 (4)	0.6744 (4)	0.108 (3)	C(68)	-0.3472 (6)	0.0342 (5)	0.9394 (3)	0.184 (4)
C(15)	0.8533 (6)	0.6314 (5)	0.6096 (5)	0.130 (4)	C(71)	-0.2624 (5)	0.0890 (4)	0.6820 (3)	0.088 (3)
C(16)	0.7758 (6)	0.5933 (4)	0.5804 (3)	0.116 (3)	C(72)	-0.1599 (4)	0.0432 (3)	0.6857 (2)	0.072 (2)
C(17)	0.6206 (6)	0.4770 (6)	0.5401 (3)	0.179 (4)	C(73)	-0.1214 (5)	-0.0070 (4)	0.6339 (3)	0.082 (3)
C(18)	0.7651 (5)	0.6488 (4)	0.8122 (3)	0.140 (3)	C(74)	-0.1732 (7)	-0.0093 (5)	0.5810 (3)	0.122 (3)
C(21)	0.2283 (4)	0.5808 (4)	0.6730 (3)	0.072 (2)	C(75)	-0.2699 (9)	0.0436 (6)	0.5800 (4)	0.147 (5)
C(22)	0.3342 (4)	0.6626 (3)	0.6682 (2)	0.064 (2)	C(76)	-0.3198 (6)	0.0942 (4)	0.6296 (4)	0.116 (3)
C(23)	0.3668 (4)	0.6906 (4)	0.6116 (3)	0.068 (2)	C(77)	-0.4138 (5)	0.1787 (4)	0.7432 (4)	0.157 (4)
C(24)	0.3064 (6)	0.7124 (4)	0.5614 (3)	0.090 (3)	C(78)	0.0289 (5)	-0.1183 (4)	0.5932 (3)	0.135 (3)
C(25)	0.2051 (6)	0.6611 (5)	0.5700 (3)	0.106 (3)	C(81)	-0.0862 (4)	0.2154 (4)	0.8629 (3)	0.089 (3)
C(26)	0.1625 (4)	0.5954 (4)	0.6250 (3)	0.094 (3)	C(82)	-0.0866 (4)	0.2052 (4)	0.7999 (3)	0.074 (2)
C(27)	0.0864 (4)	0.4636 (4)	0.7453 (3)	0.128 (3)	C(83)	-0.1309 (4)	0.2858 (4)	0.7667 (4)	0.090 (3)
C(28)	0.5249 (5)	0.8014 (4)	0.5531 (3)	0.142 (3)	C(84)	-0.1783 (5)	0.3665 (5)	0.7939 (5)	0.124 (4)
C(31)	0.4267 (4)	0.3747 (4)	0.8477 (3)	0.077 (2)	C(85)	0.1763 (7)	0.3681 (6)	0.8575 (5)	0.168 (5)
C(32)	0.4197 (4)	0.4101 (3)	0.7830 (2)	0.066 (2)	C(86)	0.1302 (6)	0.2948 (5)	0.8947 (4)	0.131 (3)
C(33)	0.3667 (4)	0.3428 (4)	0.7553 (3)	0.075 (2)	C(87)	-0.0068 (8)	0.1425 (5)	0.9559 (3)	0.197 (4)
C(34)	0.3153 (4)	0.2539 (4)	0.7881 (4)	0.100 (3)	C(88)	-0.1649 (7)	0.3546 (4)	0.6585 (4)	0.192 (5)

$$^a U_{eq} = 1/3(\sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j)$$

**Figure 3.** ^{13}C NMR signal of the lithiated carbon atom of (2,6-dimethoxyphenyl)lithium (toluene- d_8 , -90°C) with slight resolution enhancement (Gauss filter).

gregation. In toluene- d_8 at -90°C the C(ipso) signal (Figure 3) in (2,6-dimethoxyphenyl)lithium shows splitting that deviates from the regular septet pattern expected for a ^{13}C atom coupled with three equivalent lithium atoms, e.g. as in isopropyllithium.¹⁹ This splitting is consistent with the magnetic nonequivalence of the

**Figure 4.** ^6Li NMR signal of (2,6-dimethoxyphenyl)lithium (toluene- d_8 , -90°C) with slight resolution enhancement (Gauss filter): spinning speed 20 Hz, upper row magnified 50-fold.

lithium atoms attached to C(ipso) in the solid-state structure of (2,6-dimethoxyphenyl)lithium. Hence, the tetrameric structure found by X-ray analysis is retained in an apolar solvent (toluene). This conclusion is corroborated by ^6Li NMR spectroscopy: in the solid state structure each lithium atom has two equivalent (in

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Table II. Selected Bond Distances (Å) and Angles (deg)^a

X =	1	2	3	4	5	6	7	8
Distances								
CX1-CX2	1.402 (8)	1.371 (7)	1.388 (7)	1.378 (7)	1.374 (8)	1.360 (7)	1.379 (8)	1.353 (8)
CX2-CX3	1.355 (8)	1.377 (7)	1.386 (7)	1.378 (7)	1.37 (1)	1.395 (7)	1.372 (7)	1.372 (8)
CX3-CX4	1.42 (1)	1.391 (9)	1.381 (8)	1.403 (9)	1.39 (1)	1.358 (9)	1.384 (9)	1.38 (1)
CX4-CX5	1.36 (1)	1.37 (1)	1.37 (1)	1.36 (1)	1.33 (2)	1.36 (1)	1.36 (1)	1.34 (1)
CX5-CX6	1.36 (1)	1.356 (9)	1.36 (1)	1.37 (1)	1.35 (2)	1.38 (1)	1.37 (1)	1.36 (1)
CX6-CX1	1.376 (9)	1.392 (8)	1.391 (9)	1.391 (9)	1.40 (1)	1.41 (1)	1.41 (1)	1.403 (9)
CX1-OX1	1.382 (7)	1.398 (7)	1.391 (1)	1.380 (7)	1.384 (9)	1.398 (7)	1.389 (7)	1.413 (7)
CX7-OX1	1.394 (8)	1.415 (6)	1.402 (7)	1.435 (6)	1.433 (7)	1.416 (7)	1.422 (7)	1.360 (8)
CX3-OX2	1.409 (9)	1.391 (6)	1.391 (7)	1.400 (7)	1.395 (9)	1.388 (7)	1.386 (8)	1.383 (9)
CX8-OX2	1.41 (7)	1.398 (7)	1.424 (7)	1.399 (8)	1.362 (7)	1.406 (8)	1.398 (7)	1.427 (8)
Angles								
CX1-CX2-CX3	112.2 (4)	112.3 (4)	112.5 (4)	113.0 (4)	112.5 (6)	113.6 (4)	112.4 (5)	112.3 (5)
CX2-CX3-CX4	127.4 (7)	126.1 (5)	125.7 (6)	125.9 (5)	124.4 (7)	123.4 (6)	125.7 (6)	125.5 (8)
CX3-CX4-CX5	113.5 (6)	116.1 (5)	116.8 (6)	115.2 (6)	120.0 (1)	119.5 (7)	117.1 (6)	117.2 (7)
CX4-CX5-CX6	124.7 (7)	122.8 (6)	122.3 (6)	124.0 (7)	120.0 (1)	121.9 (7)	123.3 (8)	122.7 (8)
CX5-CX6-CX1	116.7 (6)	116.5 (5)	117.4 (6)	116.1 (6)	119.2 (8)	114.9 (7)	115.0 (7)	115.7 (7)
CX6-CX1-CX2	125.2 (5)	126.0 (5)	124.9 (5)	125.5 (6)	124.1 (8)	126.4 (6)	126.3 (5)	126.4 (6)
OX1-CX1-CX2	113.8 (5)	112.4 (4)	112.6 (5)	112.8 (5)	112.1 (5)	113.7 (5)	112.0 (5)	113.5 (5)
OX1-CX1-CX6	121.0 (5)	121.6 (4)	122.5 (5)	121.7 (5)	123.7 (7)	119.9 (5)	121.7 (5)	120.1 (6)
CX1-OX1-CX7	118.7 (5)	120.5 (4)	122.0 (4)	120.2 (4)	119.2 (4)	122.1 (5)	119.5 (5)	121.5 (5)
OX2-CX3-CX2	111.4 (6)	112.0 (5)	111.8 (4)	113.1 (5)	112.4 (6)	113.1 (5)	113.1 (5)	111.9 (5)
OX2-CX3-CX4	121.2 (6)	121.9 (5)	122.4 (5)	121.0 (5)	123.2 (7)	123.4 (6)	121.1 (5)	122.5 (6)
CX3-OX2-CX8	119.8 (4)	120.7 (4)	118.8 (4)	121.0 (5)	120.2 (6)	120.6 (5)	122.7 (5)	119.9 (4)

^aX indicates the molecule number.

Table III. Coordination Geometry of the Li Atoms (Bond Distances, Å; Angles, deg)

Li1-O11	2.028 (9)	O11-Li1-O32	111.2 (4)	O32-Li1-C12	152.2 (4)
Li1-O32	2.060 (8)	O11-Li1-C32	146.9 (4)	O32-Li1-C22	100.7 (3)
Li1-C32	2.253 (9)	O11-Li1-C12	65.3 (3)	C32-Li1-C12	102.8 (4)
Li1-C12	2.277 (9)	O11-Li1-C22	103.6 (4)	C32-Li1-C22	109.4 (3)
Li1-C22	2.344 (8)	O32-Li1-C32	64.3 (3)	C12-Li1-C22	107.0 (3)
Li2-O41	2.027 (8)	O41-Li2-O22	115.6 (4)	O22-Li2-C42	151.8 (4)
Li2-O22	2.030 (9)	O41-Li2-C22	151.6 (4)	O22-Li2-C12	100.0 (4)
Li2-C22	2.271 (9)	O41-Li2-C42	63.9 (3)	C22-Li2-C42	102.3 (3)
Li2-C42	2.295 (9)	O41-Li2-C12	101.9 (3)	C22-Li2-C12	106.0 (3)
Li2-C12	2.378 (9)	O22-Li2-C22	64.2 (3)	C42-Li2-C12	107.7 (4)
Li3-O31	2.003 (9)	O31-Li3-O12	117.2 (4)	O12-Li3-C32	153.9 (4)
Li3-O12	2.050 (9)	O31-Li3-C12	150.3 (4)	O12-Li3-C42	99.8 (3)
Li3-C12	2.28 (1)	O31-Li3-C32	64.8 (3)	C12-Li3-C32	101.5 (3)
Li3-C32	2.290 (9)	O31-Li3-C42	101.0 (4)	C12-Li3-C42	108.2 (3)
Li3-C42	2.377 (9)	O12-Li3-C12	63.4 (3)	C32-Li3-C42	105.4 (4)
Li4-O21	2.021 (8)	O21-Li4-O42	113.6 (4)	O42-Li4-C22	149.7 (4)
Li4-O42	2.043 (9)	O21-Li4-C42	149.7 (4)	O42-Li4-C32	102.3 (4)
Li4-C42	2.267 (8)	O21-Li4-C22	63.7 (3)	C42-Li4-C22	101.8 (3)
Li4-C22	2.316 (9)	O21-Li4-C32	102.1 (3)	C42-Li4-C32	107.8 (3)
Li4-C32	2.326 (8)	O42-Li4-C42	64.8 (3)	C22-Li4-C32	107.8 (3)
Li5-O82	2.013 (9)	O82-Li5-O52	114.5 (4)	O52-Li5-C82	150.2 (5)
Li5-O52	2.028 (9)	O82-Li5-C82	64.3 (3)	O52-Li5-C72	100.8 (4)
Li5-C82	2.26 (1)	O82-Li5-C52	152.2 (5)	C82-Li5-C52	102.6 (4)
Li5-C52	2.28 (1)	O82-Li5-C72	101.0 (4)	C82-Li5-C72	108.8 (4)
Li5-C72	2.34 (1)	O52-Li5-C52	64.0 (3)	C52-Li5-C72	106.5 (4)
Li6-O72	1.954 (9)	O72-Li6-O61	112.6 (4)	O61-Li6-C72	150.7 (4)
Li6-O61	2.027 (8)	O72-Li6-C62	146.9 (5)	O61-Li6-C52	102.5 (4)
Li6-C62	2.270 (9)	O72-Li6-C72	64.9 (3)	C62-Li6-C72	100.8 (4)
Li6-C72	2.304 (9)	O72-Li6-C52	103.4 (4)	C62-Li6-C52	109.5 (4)
Li6-C52	2.32 (1)	O61-Li6-C62	64.7 (3)	C72-Li6-C52	106.4 (3)
Li7-O62	1.992 (9)	O62-Li7-O71	113.5 (4)	O71-Li7-C62	148.7 (5)
Li7-O71	2.05 (9)	O62-Li7-C72	145.2 (5)	O71-Li7-C82	102.9 (4)
Li7-C72	2.279 (9)	O62-Li7-C62	64.3 (3)	C72-Li7-C82	109.3 (4)
Li7-C82	2.31 (1)	O62-Li7-C82	105.1 (4)	C72-Li7-C62	99.5 (3)
Li7-C62	2.338 (9)	O71-Li7-C72	63.8 (3)	C82-Li7-C62	107.7 (4)
Li8-O81	2.023 (9)	O81-Li8-O51	115.5 (4)	O51-Li8-C82	151.4 (4)
Li8-O51	2.030 (8)	O81-Li8-C52	150.2 (4)	O51-Li8-C62	101.4 (3)
Li8-C52	2.29 (1)	O81-Li8-C82	64.5 (3)	C52-Li8-C82	101.5 (4)
Li8-C82	2.290 (9)	O81-Li8-C62	103.0 (4)	C52-Li8-C62	106.4 (3)
Li8-C62	2.396 (8)	O51-Li8-C52	63.7 (3)	C82-Li8-C62	106.4 (3)

plane) and one different (out of plane) carbon bonding partners. Accordingly, in the ⁶Li NMR spectrum the main singlet (involving the major ¹²C isotopomer) is accompanied by two pairs of ¹³C

satellites in a 2:1 ratio (¹J_{13C-6Li} = 3.5 and 4.9 Hz, respectively). The magnitude of these ¹³C-⁶Li coupling constants is characteristic for Li bonded to three carbon atoms.²⁰

Table IV. Crystal Data

chemical formula	C ₈ H ₉ O ₂ Li
space gp	P1
Z	16
cell param	
a, Å	11.9358 (1)
b, Å	13.6832 (1)
c, Å	20.9962 (1)
α, deg	80.99 (1)
β, deg	77.90 (1)
γ, deg	89.36 (1)
V, Å ³	3310.7 (2)
D _{calcd.} , g/cm ³	1.156
μ(Cu Kα), cm ⁻¹	6.1

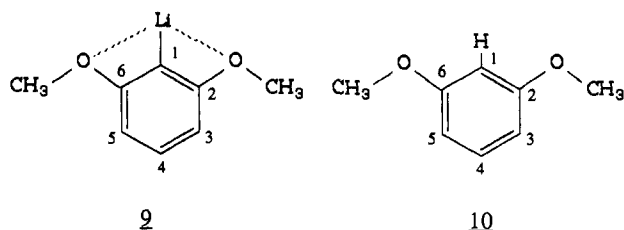
Table V. ¹³C Chemical Shifts of (2,6-Dimethoxyphenyl)lithium (9) and 1,3-Dimethoxybenzene (10) in Different Solvents at -90 °C^a

	THF-d ₈		toluene-d ₈	
	9	10	9	10
1	147.9	100.3	143.5	100.2
2,6	168.8	161.6	169.0	161.1
3,5	101.5	106.2	101.8	106.0
4	126.4	130.5	129.2	130.3
OCH ₃	54.1	55.2	54.2	54.2

^a δ(TMS) in ppm. The chemical shifts of 1,3-dimethoxybenzene were measured under the same conditions, since they are based on weak impurity signals of the hydrolysis product.

In THF-d₈ solution the C(ipso) signal remains unsplit even at -90 °C. This is probably due to intermolecular exchange, which is still rapid enough to cancel out ¹³C-⁶Li coupling.²¹ In addition the ⁶Li NMR spectrum of (2,6-dimethoxyphenyl)lithium at -90 °C is a singlet without ¹³C satellites. Hence, NMR does not reveal the aggregation state in THF. However, cryoscopic measurements²² of crystals of (2,6-dimethoxyphenyl)lithium dissolved in THF (0.15 mm) show a monomer to be present (measured aggregation number, *n* = 1.03 (5)). Thus, as is found in many other cases²² THF, because of its effective small bulk and good donor character, is able to dissociate (2,6-dimethoxyphenyl)lithium.

Table V compares the ¹³C chemical shifts of (2,6-dimethoxyphenyl)lithium, 9, and its neutral precursor, 10, both in toluene



and in THF. As was observed in monomeric and tetrameric phenyllithium the C(ipso) resonance (C1) of (2,6-dimethoxyphenyl)lithium is shifted downfield in the monomer. However, whereas in phenyllithium Δδ(monomer - tetramer) = 20.5 ppm,²⁰ the corresponding difference in (2,6-dimethoxyphenyl)lithium is much smaller (Δδ(monomer - tetramer) = 4.4 ppm). This suggests that the change in the C(ipso) environment in going from the tetramer to the monomer is smaller in (2,6-dimethoxyphenyl)lithium than in phenyllithium. This seems reasonable in view of the presence of the chelating methoxy groups in the former; these ameliate the effect of the donor solvent.

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Conclusion

In the solid state as well as in apolar solvents (2,6-dimethoxyphenyl)lithium is a tetramer. The X-ray structure shows this tetramer to be comprised of two dimeric subunits distinguished by different C-Li and Li-Li distances within and between the dimers. The observation of different coupling constants ($J_{^{13}\text{C}-^6\text{Li}}$ (in plane) and $J_{^{13}\text{C}-^6\text{Li}}$ (out of plane)) supports this distinction. Li(in plane) atoms are bonded to C(ipso) via the sp²-orbital and Li(out of plane) atoms via the electron-rich p orbital perpendicular to the ring plane. While in the tetrameric aggregate the C(ipso) atoms are pentacoordinated, C(ipso) can be considered to have a planar tetracoordinate environment in the dimeric subunit.

Experimental Section

(2,6-Dimethoxyphenyl)lithium can be prepared easily in diethyl ether according to the procedure of Wittig.²³ Large colorless platelike crystals are obtained by recrystallization from diethyl ether, but reflections with $\theta > 40^\circ$ (Cu Kα radiation) are scarce for most of the crystals (probably due to disorder). After many attempts, one moderately suitable crystal was found and mounted in a capillary on an Enraf-Nonius CAD4 diffractometer ($\lambda(\text{Cu K}\alpha) = 1.54184 \text{ \AA}$). The lattice parameters were determined by refining the setting angles of 16 reflections with θ in the range of 10–20°. Crystal data are given in Table IV; 6789 independent reflections were collected at $T = 295 \text{ K}$ within the Cu sphere of θ to 50° ($-11 \leq h \leq 11$, $-13 \leq k \leq 13$, $0 \leq l \leq 20$) of which 5002 reflections with $I \geq 2.5\sigma(I)$ were considered to be observed. The standard reflections (-4,0,1), (1,4,-3), and (0,3,5) were recorded to ensure the stability and position of the crystal (decay 2%). Intensities were corrected for Lorentz and polarization effects.

The structure was solved by direct methods using SHELX-86²⁴ with 507 *E* values larger than 1.2. Weighted least-squares refinement (using SHELX-76²⁵) including all carbon and oxygen atoms with anisotropic thermal parameters, lithium atoms with isotropic thermal parameters and hydrogen atoms, fixed at ideal geometry, with two fixed overall isotropic thermal parameters (0.10 Å² for the ring bonded hydrogen atoms and 0.15 Å² for the O-C bonded hydrogen atoms) converged to $R(F) = 0.0657$ and $R(wF) = 0.0695$ with $w = 1/\sigma^2(F)$ and 755 parameters. Anisotropic thermal parameters for the carbon atoms in the methoxy groups and the carbon atoms in the rings positioned at the outside of the tetramers are large. This is probably due to the high thermal motion of these atoms or static disorder in the crystal concerning these atoms. This may account for the trouble in finding a good crystal for this X-ray study.

Scattering factors were taken from Cromer and Mann.²⁶ Geometry calculations and illustrations were carried out with the EUCLID package.²⁷ All calculations in the initial state of structure solution and isotropic refinement were performed on the CYBER-855 of the University of Utrecht. Calculations in the anisotropic stages of refinement were performed on a VAX/VMS.

NMR spectra were recorded on a Jeol GX400 spectrometer (9.4 T) with 5-mm tubes. ¹³C NMR chemical shifts are referenced to the solvent signals: (toluene-d₈) *p*-C 125.2 ppm; (THF-d₈) α -C 67.4 ppm.

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Supplementary Material Available: Tables of anisotropic thermal parameters, fractional coordinates, bond distances and angles, and torsion angles (14 pages); listing of observed and calculated structure factors (16 pages). Ordering information is given on any current masthead page.

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