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THE CRYSTAL AND MOLECULAR STRUCTURE OF THE Li_2O COMPLEX OF 2,6-DIMETHOXYPHENYLLITHIUM, $(C_8H_9O_2Li)_6$ Li_2O *

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Summary

The 2,6-dimethoxyphenyllithium molecule has the crystallographic site symmetry $\bar{3}$. All lithium atoms of the six formula units of the complex are combined together with the Li_2O to form a long cluster, Li_8O, in the centre of the molecule. This cluster is composed of two Li_4 pyramids, each of which is connected to the oxygen atom via its Li_3 base in such a way that the oxygen atom has a nearly octahedral coordination with very short Li—O distances. The remaining six Li_3 faces of the Li_4 pyramides are occupied by the organic residues as in the tetramers of ethyllithium [1] and methyllithium [2]. The final $F_0 - F_c$ map suggests weak 4-centre bonds in each of the Li_4 pyramids and, as expected, between each of the metallated ring atoms, C(1), and the pyramid face to which it is attached. At the ring atoms C(1) and C(3) there are additional charges which extend in the sp^2 and p_z areas. The ring is planar but the C—C—C angles deviate systematically from 120°; the biggest deviation, of —8°, is found at C(1).

Introduction

It is well known that organolithium compounds form oligomers in solutions as well as in the gas and solid states. The oligomers were assumed at one time to be electron deficient compounds like the boranes or $[(CH_3)_2Be]_x$ or $[(CH_3)_3Al]_2$ [3]. The first quantum mechanical model was given by Weiss and Lucken [2]

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* This paper is dedicated to Professor R. Brill on the occasion of his 81st birthday.

for $(CH_3Li)_4$ and $(C_2H_5Li)_4$, after X-ray structure determinations had shown that tetrahedral Li_4 clusters are present in crystals of ethyllithium [1] and methyllithium [2]. A Li_6 octahedron was found in crystalline cyclohexyl lithium [4].

The three compounds just mentioned can be crystallized only from hydrocarbon solutions and not from basic solvents like ether. On the other hand, basic solvents are mostly used in chemical syntheses with organolithium reagents and it is well known that they influence the reactivity of these reagents. Therefore, it seemed desirable to look at the structure of an etherate. However, many efforts to obtain crystals of an ether complex of ethyl- or butyllithium were unsuccessful, and it seems that these substances are all either liquids or gels. Finally, we found in a paper by Wittig [5] the statement that 2,6-dimethoxyphenyllithium (= DMPL) can easily be crystallized from ether. This substance, of course, must in any case be an etherate since the organic residue itself contains two ether groups.

Experimental

According to the description of Wittig [5], good crystals could be grown from ether solution. A well shaped crystal of dimensions 0.43 × 0.6 × 0.6 mm was sealed in a thin walled glass capillary under pure argon for the X-ray work. The crystal was cooled to about 113 K by means of a cold nitrogen stream [6]. The space group is $R\bar{3}$ and the unit cell parameters, a = 11.613 Å, α = 61.20°, V = 1137 Å^3, n = 6, correspond to the density ρ_x = 1.306 g cm^{-3} if the Li_2O is included which was found during the structure determination.

2772 reflections were measured on a paper tape controlled Siemens diffractometer using nickel-filtered copper radiation. The comparison of symmetry related reflections after the correction for the Lorentz and polarization factors revealed a rather strong absorption effect of the glass capillary. Reflections measured at high χ angles, where both the primary and the reflected beams make small angles with the capillary axis, were considerably weaker than their symmetry equivalents measured at lower χ angles. In order to correct for this effect, a computer program was written [7] which, in a first step, calculates from the raw data the product μd where μ is the absorption coefficient of the glass and d is the thickness of the wall of the capillary. In a second step the program then applies the correction to the data and averages the symmetry related reflections so that a unique set of reflections results. In the present case a value for μd of 0.214 was found. As μ is known to be 90 cm^{-1} [8] for copper radiation, the thickness of the capillary wall, d, was about 0.024 mm. The averaging of symmetry related reflections after the corrections yielded a unique set of 1475 reflections, 11 of which were weaker than 1 σ. The "averaging error index" was

$$\Sigma \left| |F_0|^2 - \overline{|F_0|^2} \right| / \Sigma |F_0|^2 = 0.034$$

Structure determination

The phase problem was solved by direct methods using the program system X-RAY 70 [9]. An E-map showed the positions of all the lithium, carbon, and

TABLE 1

ATOMIC PARAMETERS OF THE COMPLEX $(DMPL)_6Li_2O$

Standard deviations in parentheses. Temperature factors given by $T = \exp[-2\pi^2(U_{11}a^{*2} + U_{22}b^{*2} + U_{33}c^{*2} + 2\,U_{12}hka^*b^* + 2\,U_{13}hla^*c^* + 2\,U_{23}klb^*c^*)]$.

ATOM	X	Y	Z	U11 OR U	U22	U33	U12	U13	U23
O(0)	.50000	.50000	.50000	.0182(5)	.0182	.0182	-.0061(3)	-.0061	-.0061
O(6)	.5130(1)	.8096(1)	.6461(1)	.0292(6)	.0312(6)	.0410(6)	-.0086(4)	-.0114(5)	-.0173(5)
O(2)	.2081(1)	.6137(1)	.7062(1)	.0260(6)	.0284(6)	.0358(6)	-.0100(4)	-.0030(4)	-.0152(5)
C(60)	.5384(2)	.9060(2)	.6658(2)	.042(1)	.035(1)	.047(1)	-.0152(8)	-.0173(8)	-.0156(9)
C(20)	.0690(2)	.6099(2)	.7644(2)	.0263(9)	.037(1)	.060(1)	-.0117(8)	-.0045(7)	-.0235(9)
C(6)	.3765(2)	.8200(2)	.6616(1)	.0275(7)	.0251(7)	.0209(7)	-.0079(6)	-.0082(5)	-.0063(5)
C(1)	.3653(2)	.7095(1)	.6763(1)	.0259(7)	.0195(7)	.0185(6)	-.0059(5)	-.0051(5)	-.0060(5)
C(2)	.2263(2)	.7210(2)	.7148(2)	.0319(8)	.0232(7)	.0236(7)	-.0101(6)	-.0065(6)	-.0069(6)
C(3)	.1108(2)	.8292(2)	.7558(2)	.0252(8)	.0286(8)	.0347(8)	-.0078(6)	-.0036(6)	-.0132(6)
C(4)	.1334(2)	.9361(2)	.7554(2)	.0309(9)	.0254(8)	.0317(9)	-.0040(6)	-.0066(7)	-.0125(6)
C(5)	.2663(2)	.9351(2)	.7173(2)	.0355(8)	.0228(8)	.0248(8)	-.0085(6)	-.0091(6)	-.0081(6)
LI(0)	.6214(2)	.62143	.62143	.034(1)	.0339	.0339	-.0113(8)	-.0113	-.0113
LI(1)	.4508(3)	.4849(3)	.6810(3)	.030(1)	.024(1)	.027(1)	-.008(1)	-.010(1)	-.0075(9)
H(61)	.645(2)	.881(2)	.632(2)	.00(1)	.03(1)	.07(2)	-.010(8)	.002(9)	-.02(1)
H(62)	.504(2)	.996(2)	.605(2)	.11(2)	.02(1)	.02(1)	-.04(1)	.00(1)	-.006(9)
H(63)	.492(3)	.893(3)	.777(2)	.12(2)	.12(2)	.01(1)	-.02(2)	-.03(1)	-.01(1)
H(21)	.069(2)	.520(2)	.774(3)	.04(1)	.03(1)	.14(2)	-.01(1)	.00(1)	-.06(1)
H(22)	.026(2)	.600(3)	.882(2)	.07(2)	.10(2)	.03(1)	-.04(1)	.01(1)	-.05(1)
H(23)	.012(2)	.703(2)	.707(3)	.06(2)	.02(1)	.14(3)	.03(1)	-.06(2)	-.03(1)
H(3)	.015(2)	.830(2)	.775(2)	.02(1)	.01(1)	.08(2)	.015(9)	-.01(1)	-.001(9)
H(4)	.057(2)	1.011(2)	.777(2)	.04(1)	.07(2)	.05(1)	-.00(1)	-.04(1)	-.01(1)
H(5)	.272(2)	1.013(2)	.721(2)	.02(1)	.02(1)	.04(1)	-.015(8)	-.000(8)	-.017(9)

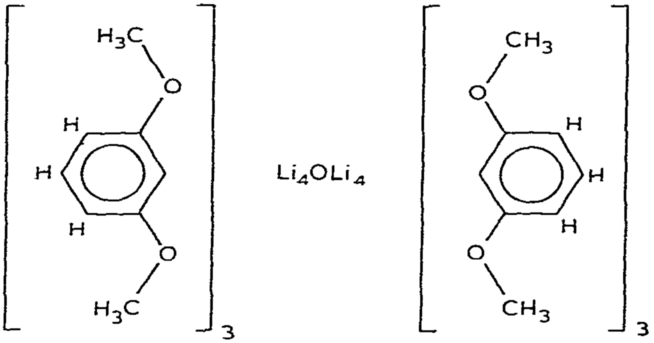
oxygen atoms. In the light of the comments by Wittig [5], it was expected that the crystals should contain only DMPL and possibly solvent molecules. From the peaks in the E-map it was obvious that the organolithium compound forms a hexamer, $DMPL_6$, with crystallographic symmetry $\bar{3}$, and the lithium atoms clustered around the centre in the form of an octahedron. Two additional peaks on the threefold axis, a rather high one at the centre and a lower one outside the Li_6 octahedron, could not be explained at this stage. They were thought to be spurious and were not included in the initial refinement. The latter stopped, however, at $R = 0.16$ and a $F_0 - F_c$ synthesis showed that the two unidentified peaks had not vanished. They were sharp maxima. The one at the central position ($\bar{3}$) showed a density of 9 $e/\text{Å}^3$. The other one outside the Li_6 octahedron had a density maximum of 2.5 $e/\text{Å}^3$.

It was clear that these peaks indicated additional atoms not belonging to solvent molecules. Since we had carried out the synthesis of the substance carefully using pure reagents and dry argon as a protective gas, it was difficult to believe that anything other than ether molecules or argon could be present. But when the heights of the additional peaks, the symmetry of their positions, and their distances from the atoms of the hexamer were taken into account, we had to conclude that one unit of Li_2O had been included in the hexamer. This must be due to slight contamination with traces of water and a strong tendency to form the present complex. Therefore the yield of crystals can be increased by using phenyllithium solution contaminated with Li_2O for the metallation of the 2,6-dimethoxy-benzene.

With the inclusion of the Li_2O entity, the refinement was straightforward. The positions of all the hydrogen atoms were taken from a $F_0 - F_c$ map and all atoms were refined with anisotropic vibration parameters. As expected for low temperature data, towards the end of the refinement the temperature parameters of some hydrogen atoms became negative and had to be reset. The final error indices were $R_{F2} = 0.068$, $R_F = 0.057$. In the calculations the form factor tables for neutral atoms and bonded hydrogen atoms from the International Tables IV [10] were used. The atomic parameters are listed in Table 1. Tables of structure factors are available from the author.

Discusision

The structure consists of isolated molecules, one of which is shown in the stereoscopic view in Fig. 1. The eight lithium atoms and the central oxygen atom form a Li_8O cluster inside the molecule. The cluster can be interpreted as two Li_4 pyramids, each of them attached via its Li_3 base to the single oxygen atom, so that the oxygen has a nearly octahedral coordination. The organic residues occupy the remaining six free Li_3 faces of the two Li_4 pyramids. Formally, the structure of the molecule may be written as



The presence of the Li_4 sub-clusters and the connection of the organic residues to their faces resembles the arrangements found in ethyllithium [1] and methyllithium [2]. A difference is, however, that the oligomers in the latter two structures are connected via rather short contacts, whereas in the present structure there are isolated molecules.

Some interesting details about the bonding can be derived from the atomic distances, bonding angles, and the final $F_0 - F_c$ synthesis. Fig. 2 shows the lower left part of Fig. 1 with atomic distances and angles added. The central

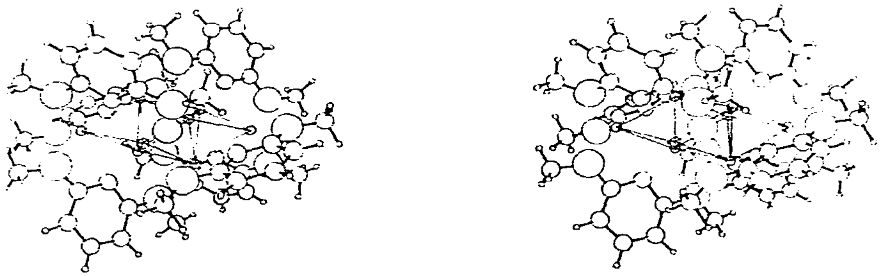


Fig. 1. Stereoscopic ORTEP [11] view of the complex $(DMPL)_6Li_2O$. The threefold axis is approximately horizontal.

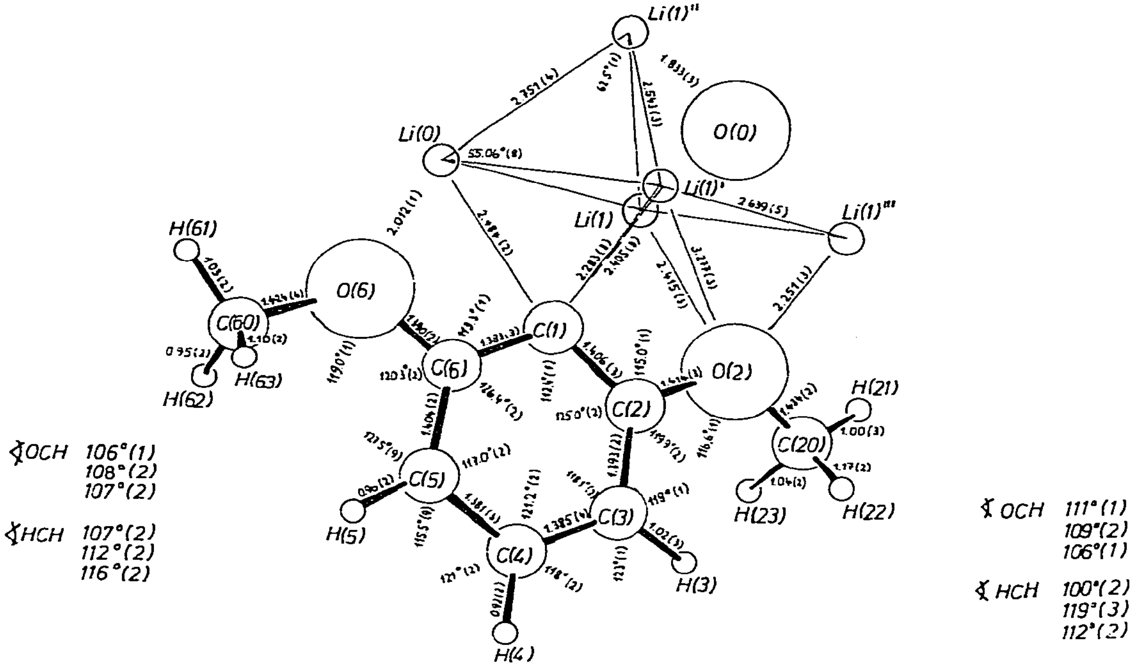


Fig. 2. Lower left part of Fig. 1 with some interatomic distances and bonding angles added. The standard deviations (in brackets) are in units of the last decimal place of the values.

oxygen atom is remarkably close to the six lithium atoms surrounding it. The Li—O distance of 1.833 Å is much shorter than those in Li_2O (2.00 Å) and LiOH (1.97 Å) [12]. The coordination of the oxygen atom is not a regular octahedron, but slightly elongated parallel to the threefold axis. The distances Li(1)—Li(1)′ within the pyramid bases (2.543 Å) are about 0.1 Å shorter than the lateral distances Li(1)—L(1)‴ of 2.639 Å.

Similarly, the Li_4 pyramids deviate from tetrahedra by an elongation along the threefold axis. The edges of type Li(1)—Li(0) are about 0.2 Å longer than the edges at the pyramid base.

From a comparison of the structures of ethyl- and methyllithium one may conclude that the Li_4 tetrahedra can be deformed to a considerable extent without changing their average Li—Li distance (2.55 and 2.56 Å, respectively). But in the present cluster the range of Li—Li distances is shifted by about 0.1 Å to larger values. The average edge length for the Li_4 pyramids is 2.647 Å and for all edges of the Li_8O cluster it is 2.643 Å.

The comparison with methyl- and ethyl-lithium reveals also a similar lengthening of the C—Li distances in the 4-centre bonds C—Li_3 in the DMPL complex. The relevant distances are 2.28 Å in methyl- and 2.30 Å in ethyl-lithium, whereas 2.391 Å (average of C(1)—Li(0), C(1)—Li(1), and C(1)—Li(1)′ in Fig. 2) is found in $DMPL_6$ Li_2O.

The phenyl ring is planar to within ±0.01 Å, and the C—C bond lengths do not vary by more than this from their (quite normal) average of 1.392 Å. But the angles within the ring deviate seriously and systematically from 120° (see

Fig. 2). The biggest change, of almost −8°, is found at the metallated ring atom C(1). Towards the opposite side of the ring the deviations alternate in sign and become gradually smaller. The angle at C(4) deviates by +1° only. It is obvious from Fig. 2 that the angle changes are more pronounced in the left side of the ring, C(1)—C(6)—C(5)—C(4), than in the right side, C(1)—C(2)—C(3)—C(4). This is probably a consequence of the asymmetry in the connection of the organic residue to the cluster. Along with C(1), which is bonded to the pyramid face Li(0)—Li(1)—Li(1)′, the ether atom O(6) appears to have the shortest contact to the cluster, i.e. 2.012 Å to Li(0). It belongs to the left half of the ring in Fig. 2, where the deviations of the ring angles are bigger. The attractive forces between Li(0) and O(6) may be responsible for the reduced angle C(1)—C(6)—O(6) of 113.3° compared to the angle C(1)—C(2)—O(2) of 115.5°, for the elongation of the pyramids, and for the asymmetry of the 4-centre bond Li(0)—Li(1)—Li(1)′—C(1) which appears to be shifted from the centre of the pyramid face towards Li(1).

Further details of the bonding can be extracted from the final $F_0 - F_c$ synthesis. Of course, the least squares refinement of the conventional model tends to compensate bonding effects in the charge distribution by small shifts in the positional and vibrational parameters of the atoms and it is well known that this applies most generally to terminal bonds and lone pairs. This is confirmed

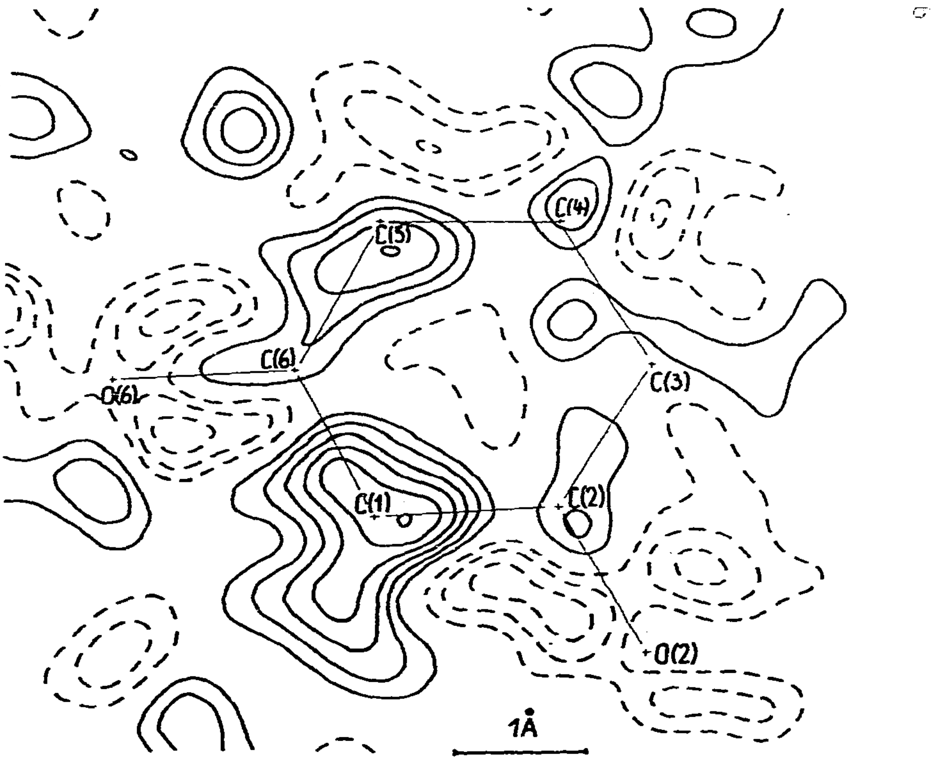


Fig. 3. $F_0 - F_c$ section in the ring plane. Contour interval 0.05 e/Å^3, full lines positive contours, broken lines negative contours. Zero contours omitted.

by the present $F_0 - F_c$ synthesis. The limitation of the data to the copper range favours this kind of correlation effect, and so one should expect only charge details, which are less correlated to the parameters of the model. It is not surprising, therefore, that the $F_0 - F_c$ synthesis is in general rather flat. There are only three peaks above 0.2 $e/Å^3$. The highest and the lowest indicate broadly smeared charges at C(1) and C(5), respectively. Both can be seen in Fig. 3 which shows a section in the plane of the ring. The sp^2 orbital at C(1), engaged in the 4-centre bond to the cluster, is clearly visible as a tail. But there is obviously still more charge left at C(1) itself, with tails extending along the bonds to C(6) and C(2). It is understandable that such a roughly trigonal charge distribution should be poorly correlated with any atomic parameters, either positional nor vibrational, and therefore cannot be compensated by the model. For π-type charges, i.e. charges above and below the ring plane, one might expect some correlation to the out of plane component of the vibrational tensor. But Fig. 3 shows that at least some elongation of the charge cloud perpendicular to the ring plane has survived the refinement, and suggests an increased population of the $p_z{}^2$ region of C(1). The asymmetry of this π-type charge with respect to the ring plane is not significant, but it is interesting to state that

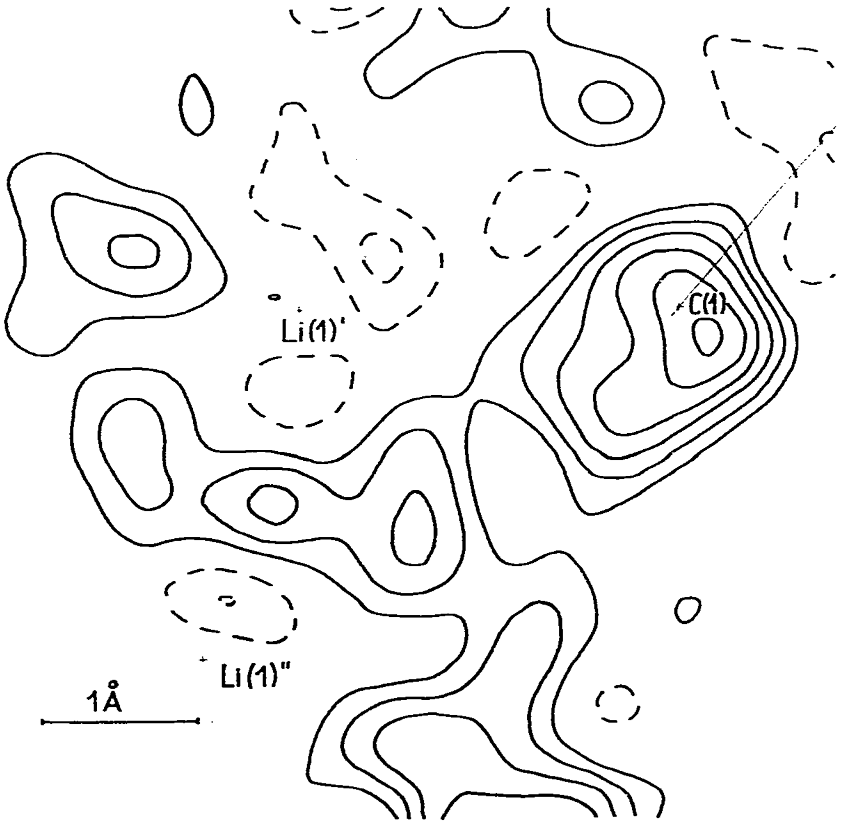


Fig. 4. $F_0 - F_c$ section through C(1), approximately perpendicular (85°) to the ring plane. The intersection with the ring plane is marked by a line. Contours as in Fig. 3.

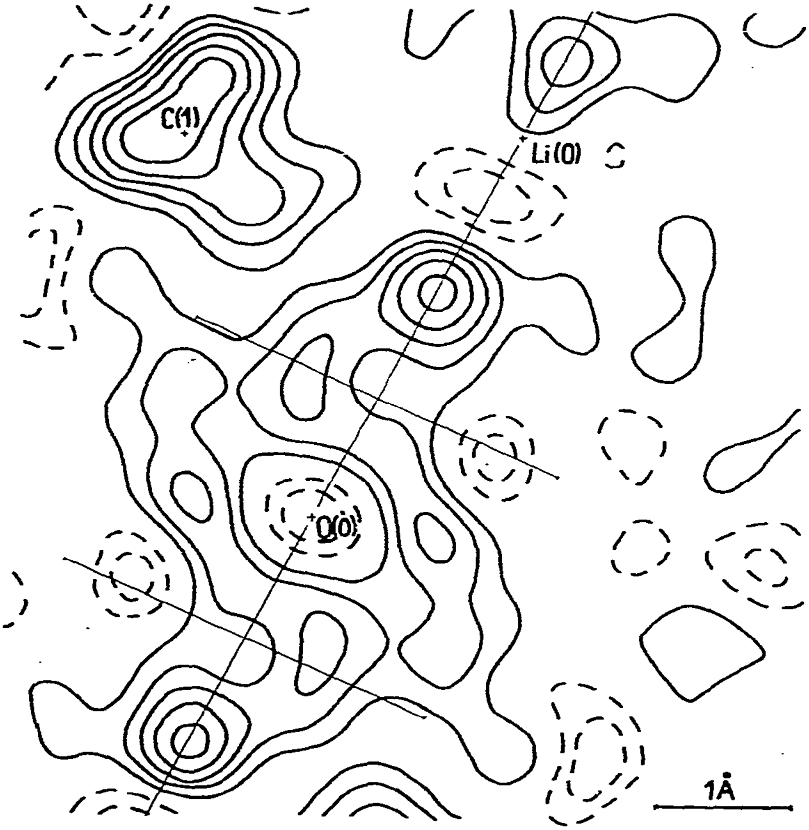


Fig. 5. $F_0 - F_c$ section along the threefold axis and through C(1). The intersections with the planes of the Li_3 bases of the two Li_4 pyramids above and below of O(0) are the threefold axis are marked by lines. Contours as in Fig. 3.

the maximum is on that side of the ring plane where the shortest C—Li contact occurs, namely C(1)—Li(1).

Regarding the negative charge of the phenyl ring, one would expect from electronic considerations that it would be concentrated at the *o*- and *p*-positions with respect to the methoxy groups, i.e. at C(1), C(3), and C(5). Apart from the charge at C(1), only that at C(3) is indicated in the difference density map. It is in the right half of the ring in Fig. 2 where the angular distortions are smaller.

A maximum of about 0.25 *e*/Å is observed approximately in the centre of the Li_4 pyramid. It is displayed in the section in Fig. 5 which contains the threefold axis and passes through C(1). This peak suggests at least a weak 4-centre bond inside each of the Li_4 sub-clusters.

Concluding remarks

The present compound contains a new type of cluster, Li_8O, with the oxygen as a basic hetero atom included very tightly in the centre. In the succeeding paper [13] the bonding is discussed further and compared to that in crystalline ethyllithium.

The DMPL complex proved to be very suitable for accurate electron density studies since it is easy to obtain crystals of good quality and shape for diffraction work. Therefore, low temperature measurements taken to as high orders as possible are planned with the perdeuterated compound in combined X-ray and neutron diffraction studies.

References

1 H. Dietrich, Acta Cryst., 16 (1963) 681.
2 E. Weiss and E.A.C. Lucken, J. Organometal. Chem., 2 (1964) 197.
3 R.E. Rundle, J. Phys. Chem., 61 (1957) 45.
4 R. Zerger, W. Rhine and G. Stucky, J. Amer. Chem. Soc., 96 (1974) 6048.
5 G. Wittig, in W. Foerst (Ed.), Neuere Methoden der präparativen organischen Chemie, Vol. 1, 4. edition, Verlag Chemie, Weinheim, 1963, p. 476.
6 H. Dietrich, Messtechnik, 76 (1968) 303; H. Dierks and H. Dietrich, Messtechnik, 78 (1970) 184.
7 Simplified version of the capillary correction in ref. 8.
8 H. Dierks and H. Dietrich, Z. Krist., 128 (1969) 259.
9 X-Ray 70, System of Crystallographic Programs, Computer Science Centre, University of Maryland, 1970.
10 International Tables for X-Ray Crystallography, Vol. IV, Kynoch Press, Birmingham, 1974.
11 C.K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Tennessee, 1967.
12 H. Dachs, Z. Kristallogr., 112 (1959) 60.
13 H. Dietrich, J. Organometal. Chem., 205 (1981) 291.