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LOW TEMPERATURE STUDY OF THE STRUCTURE OF CRYSTALLINE ETHYLLITHIUM *

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Summary

Comparison with the room temperature structure shows that the Li_4 clusters in the tetramer units of crystalline ethyllithium tend to increase their symmetry at low temperature. This, and the fact that 4-centre bond peaks $C—Li_3$ are observed in difference maps, suggest some covalent bonding inside the tetramers. Comparison to the structure of the Li_2O complex of 2,6-dimethyllithium reveals how this bonding changes in an environment of basic groups. The latter system might be representative of the lithium clusters assumed to act as reaction centres for organolithium compounds in basic solvents.

Introduction

After X-ray structure determinations had shown that tetrahedral lithium clusters exist in ethyllithium [1] and methyllithium [2], Weiss and Lucken [2] concluded from the first quantum mechanical calculations that the clusters are essentially stabilized by 4-centre bonds between the metallated carbon atoms and the triangular cluster faces to which they are coordinated. In contrast, other authors concluded from quantum mechanical [3] and electrostatic calculations that covalent character is absent in these compounds [4]. An experimental study of the bonding in ethyllithium seemed to us be of interest in this situation.

Experimental

Diffractometer measurements at 113 K were carried out with X-rays as well as with neutrons. Because of the latter, ethyllithium was prepared with the iso-

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

topes ^2H and ^7Li of high purity. Single crystals of this composition were used for all experiments in order to make possible good X—N syntheses.

While the X-ray measurements led to good results, three attempts to collect neutron diffraction data of comparable quality were unsuccessful. The reason for this is probably that the larger crystals which are necessary for neutron diffraction work were damaged by mechanical strain when they were cooled. The rather extreme type of layer structure with chemical bonding only inside the layers and Van der Waals contacts of methyl groups between the layers facilitate gliding of one layer on the surface of the adjoining one. As a consequence the crystal plates are extremely sensitive to bending, which by experience is also the main problem when a single crystal is transferred into and fastened in a capillary for diffraction experiments. A temperature gradient in the crystal must result in a bending of the layers since the contraction of the lattice is mainly due to a reduction of the distance of the layers. The unit cell parameters found at 113 K are $a = 7.123(1)$, $b = 8.291(2)$, $c = 17.738(5)$ Å, while the room temperature values [1] are 7.24, 8.27, and 18.11 Å, respectively.

Many of the reflection profiles measured by neutron diffraction showed shoulders and tails which were not found in studies of the crystals at room temperature with X-rays. It is assumed, therefore, that the crystals are split into a small number of fragments during the cooling process.

This hypothesis is supported by the experience with the single crystal which was used for the X-ray measurements. It was a plate of dimensions 0.5 × 1.2 × 0.2 mm, which was sealed in a thin walled capillary under pure argon. A cold nitrogen apparatus [5] was used for its cooling. The crystal gave good reflection profiles at low temperature, but after several interruptions of the cooling caused by failures of the mains power supply, some profiles became broad and split similar to those in the neutron diffraction experiments. This was the reason for terminating the X-ray measurements at $\sin\theta/\lambda = 0.95$ Å^{-1} where strong reflections could still be measured at 113 K.

A total of 12814 reflections was measured on a paper tape controlled Siemens diffractometer using zirconium-filtered molybdenum radiation. Most of the measurements were carried out in the "5-value mode" of the Siemens diffractometer, the rest was measured as step scan profiles with the step width 0.05°. During the data reduction 42 forbidden reflections were eliminated which had been measured as a check. After sorting of symmetry related reflections, 255 dubious measurements were discarded and the remaining 12517 structure amplitudes combined to a unique set of 3528 values. The error index for the averaging was

$$\Sigma ||F_0|^2 - |F_0|^2| / \Sigma |F_0|^2 = 0.027$$

The standard deviations of the averaged structure factors were calculated from the variance around the average. As a lower limit for these standard deviations the estimate $(\Sigma_i 1/\sigma_i^2)^{-1/2}$ was set, where the σ_i are the standard deviations of the individual measurements based on the counter statistics. For the few structure factors which had been measured only once, the standard deviation was calculated as $(\sigma_i^2 + (CF_0^2)^2)^{1/2}$. An estimate of $C = 0.007$ was obtained from the averaging of measurements greater than 10σ and is based on 3185 measurements. In practice $C = 0.01$ was applied.

TABLE 1

STRUCTURAL PARAMETERS OF ETHYLLITHIUM AT 113 K

Standard deviations in parenthesis. 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
C(01)	.47816(5)	.10127(4)	.09005(2)	.0263(1)	.0177(1)	.0142(1)	-.0017(1)	.00505(9)	.00005(9)
C(11)	.01832(4)	.10198(4)	.41033(2)	.0260(1)	.0181(1)	.0107(1)	-.0012(1)	.00150(9)	.00189(8)
C(02)	.43343(3)	.14812(3)	.17254(2)	.01265(9)	.01258(8)	.0122(1)	.00010(7)	-.00120(7)	-.00047(7)
C(12)	.06244(3)	.14841(3)	.32776(2)	.01223(8)	.00839(7)	.0112(1)	.00150(7)	.00263(6)	-.00140(7)
LI(01)	.12906(6)	.10622(7)	.19612(3)	.0142(2)	.0131(2)	.0192(3)	.0005(2)	-.0011(1)	.0011(2)
LI(11)	.36729(6)	.10607(7)	.30332(3)	.0149(2)	.0124(2)	.0173(2)	-.0016(2)	.0005(1)	.0006(2)
H(01)	.3666(5)	.1186(5)	.0510(2)	.018(2)	.079(3)	.006(1)	-.000(2)	.008(1)	-.014(1)
H(11)	.1327(5)	.1179(4)	.4376(2)	.050(2)	.020(1)	.000(1)	.001(1)	.004(1)	.0015(9)
H(02)	.5183(5)	-.0108(6)	.0821(2)	.046(2)	.031(2)	.011(1)	.009(2)	-.004(2)	.000(2)
H(12)	-.0116(5)	.0112(6)	.4132(2)	.049(2)	.024(2)	.018(2)	.008(2)	.028(2)	.007(2)
H(03)	.5271(5)	.1594(4)	.0687(2)	.051(2)	.019(2)	.004(1)	.006(2)	-.003(1)	-.009(1)
H(13)	-.0970(4)	.1711(5)	.4369(2)	.018(2)	.078(3)	.019(2)	.026(2)	.008(1)	.003(2)
H(04)	.5600(4)	.1488(3)	.1999(2)	.032(2)	.006(1)	.003(1)	.005(1)	.006(1)	-.002(1)
H(14)	-.0602(4)	.1523(4)	.2950(2)	.004(1)	.049(2)	.026(2)	.008(2)	.010(1)	.012(2)
H(05)	.3825(5)	.2653(4)	.1701(2)	.032(2)	.001(1)	.026(2)	-.006(1)	.001(1)	.000(1)
H(15)	.1127(4)	.2525(4)	.3260(2)	.014(1)	.048(2)	.003(1)	-.010(1)	.005(1)	.004(1)

Refinement

Although the space group *Pcan* (D_{2h}^{14}) used in the room temperature study [1] does not follow the conventional definition, it will be used in the present paper too, in order to facilitate the comparison.

Several weighting schemes were tried in an effort to use at least part of the neutron diffraction measurements for the refinement of the structural parameters. In all trials, however, the results proved to be inferior to those obtained from the X-ray data. Therefore, the rest of the present study was based on the X-ray data only. The refinement was carried out with the program system X-RAY 76 [6] using the conventional isolated atom model. The form factors for bonded hydrogen atoms [7] were used. The full matrix refinement was based on F^2 and the symmetry constraint which had been imposed on the tetramer units in the room temperature work [1] was released. The weights were taken to be $1/\sigma^2$ where σ is the standard deviation of F^2 derived in the data reduction.

In the final stage of the refinement anisotropic temperature parameters were introduced for all hydrogen atoms. As expected for low temperature data, most of them tended to become "not positive definite". It was possible, however, to fit vibration ellipsoids to the hydrogens which did not leave too much background around these atoms in the difference synthesis. The error index reduced to $R(F^2) = 0.056$. The atomic parameters are compiled in Table 1. Tables of structure factors can be obtained from the author.

Results and comparison to the room temperature structure

The crystallographical symmetry 211 of the tetramer units is supplemented by an approximate chemical twofold axis 121 as in the room temperature structure [1]. This can be seen from the atomic parameters in Table 1, in which the atoms are sorted in pairs related by that chemical axis.

The most obvious change with respect to the room temperature structure is an average shift of all atoms of the asymmetric unit along the *a* axis by $\Delta x = -0.0387$, which corresponds to -0.28 Å. The same shift applies also to the

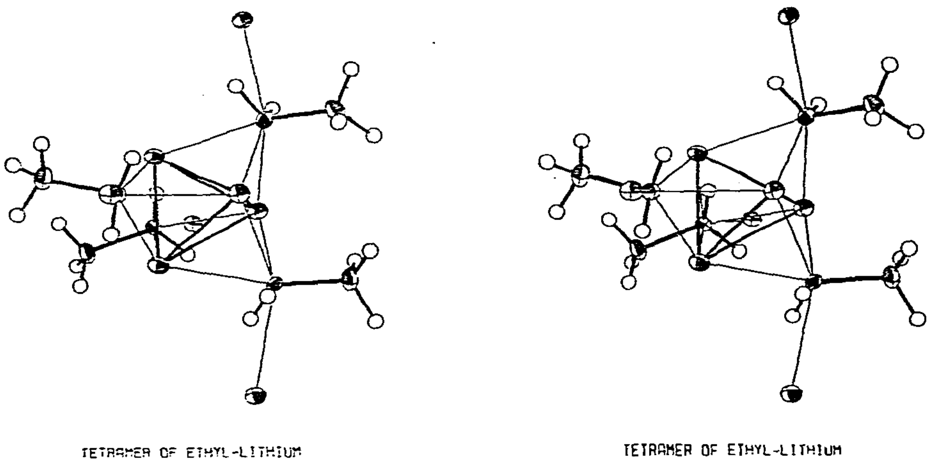
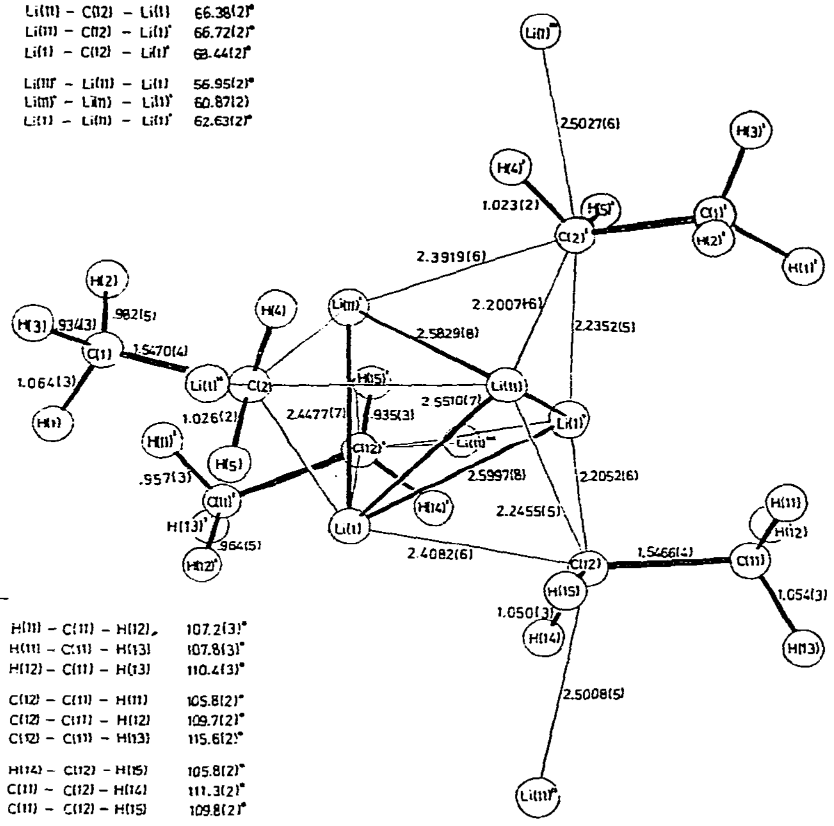


Fig. 1. ORTEP [8] picture of one tetrameric unit of ethyllithium and the four closest lithium atoms belonging to neighbouring clusters. The carbon and lithium atoms are represented by 50% probability ellipsoids, the hydrogen atoms by spheres of diameter 0.2 Å. The C—Li contacts are marked by thin lines, the Li—Li contacts in the cluster by somewhat thicker lines, C—C and C—H bonds as sticks. The crystallographic axis 211 is approximately vertical.

ANGLES

Li(1) - C(2) - Li(11)	66.82(2)°	Li(11) - C(12) - Li(1)	66.38(2)°
Li(1) - C(2) - Li(11)'	66.98(2)°	Li(11) - C(12) - Li(1)'	66.72(2)°
Li(11) - C(2) - Li(11)'	68.30(2)°	Li(1) - C(12) - Li(1)'	68.44(2)°
Li(1)' - Li(1) - Li(11)	56.74(2)°	Li(11)' - Li(11) - Li(1)	56.95(2)°
Li(1)' - Li(1) - Li(11)'	60.63(2)°	Li(11)' - Li(11) - Li(1)'	60.87(2)
Li(11) - Li(1) - Li(11)'	62.19(2)°	Li(1) - Li(11) - Li(1)'	62.63(2)°



ANGLES

H(1) - C(1) - H(2)	104.6(3)°	H(11) - C(11) - H(12)	107.2(3)°
H(1) - C(1) - H(3)	103.3(3)°	H(11) - C(11) - H(13)	107.8(3)°
H(2) - C(1) - H(3)	102.1(3)°	H(12) - C(11) - H(13)	110.4(3)°
C(2) - C(1) - H(1)	115.4(1)°	C(12) - C(11) - H(11)	105.8(2)°
C(2) - C(1) - H(2)	115.7(2)°	C(12) - C(11) - H(12)	109.7(2)°
C(2) - C(1) - H(3)	114.1(2)°	C(12) - C(11) - H(13)	115.6(2)°
H(4) - C(2) - H(5)	107.2(2)°	H(14) - C(12) - H(15)	105.8(2)°
C(1) - C(2) - H(4)	105.5(1)°	C(11) - C(12) - H(14)	111.3(2)°
C(1) - C(2) - H(5)	105.3(2)°	C(11) - C(12) - H(15)	109.8(2)°

Fig. 2. Right part of Fig. 1 showing atom labels, interatomic distances and bond angles of the low temperature structure. Primed lables refer to atoms generated from the asymmetric unit by the crystallographic site symmetry 211 of the tetramer (x; $-y$; $1/2 - z$). Two or more primes indicate other crystallographic symmetry transformations.

chemical axis 121 for which the approximate transformation 0.4190 $- x; y$; $1/2 - z$ had been derived in the room temperature study [1]. For the low temperature structure the transformation becomes approximately 0.4964 $- x; y$; 0.5000 $- z$.

Other characteristic changes can best be demonstrated by means of interatomic distances and bond angles. As a survey, Fig. 1 shows a stereoscopic view of one tetrameric unit together with those lithium atoms of neighbour clusters which are in close contact to the methylene groups. The latter contacts constitute the two-dimensional network connecting the tetramers within the layers. Figs. 2 and 3 show the atomic lables, distances, and angles for low and room temperature structures, respectively.

Comparison of Figs. 2 and 3 shows that almost all Li—Li and Li—C distances become shorter at low temperature. This means that the electron deficient bonding system is slightly temperature dependent. This is not surprising since the deviation of the tetramers in ethyllithium from a regular symmetry is an

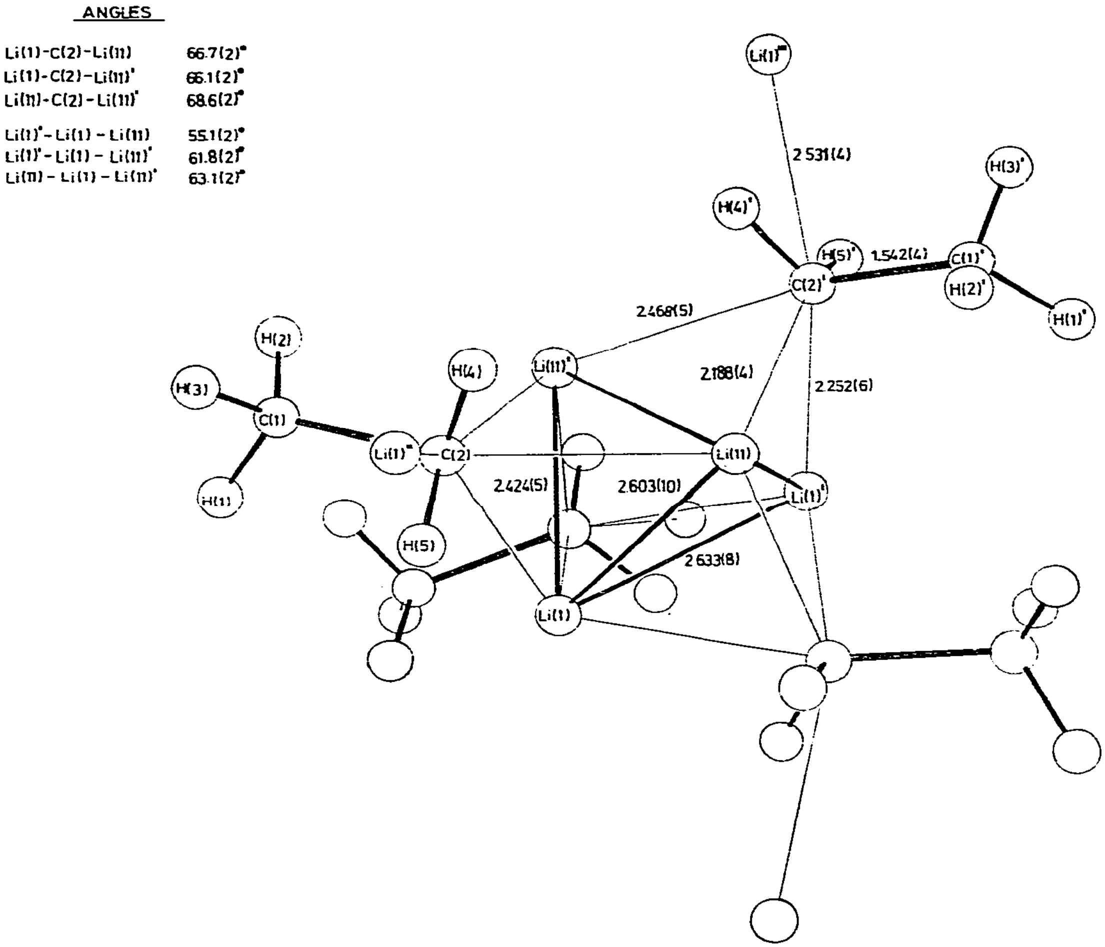


Fig. 3. Same as Fig. 2 with distances and angles of the room temperature structure [1].

independent proof for the flexibility of that bonding system. On the other hand the tendency to increase the symmetry of the 4-centre C—Li_3 bonds as well as of the Li_4 clusters at low temperature is obvious from Figs. 2 and 3. It is confirmed by shifts of the extremal values of the distances C—Li and Li—Li—Li towards their average values. This implies that the electron deficient bond system does not contract uniformly.at low temperature, and the shortest of the relevant distances are, in fact, widened. Thus, the distance C(2)—Li(11)′ of 2.188 Å at room temperature is increased to 2.2007 or 2.2052 Å (chemical equivalent C(12)—Li(1)′) and the shortest edge Li(1)—Li(11)′ of the cluster is lengthened from 2.424 Å at room temperature to 2.4477 Å at 113 K.

Discussion of bonding details

As the X-ray data contain many high order reflections whose intensities were measured with considerable accuracy, it can be expected that the chemical bonding does not interfere much with the conventional refinement of the atomic parameters, except of course, with respect to the hydrogen atoms. The difference synthesis confirms this. It shows only four peaks above 0.25 $e\text{Å}^{-3}$ within the volume of the asymmetric unit. The peak densities are in the range between 0.34 and 0.41 $e\text{Å}^{-3}$. Two peaks represent the C—C bonds in the two ethyl groups of the asymmetric unit and the remaining peaks mark two 4-centre C—Li_3 bonds. To my knowledge, these are the first localized 4-centre bonds so far revealed by means of diffraction studies. Sections through the ethyl groups and through these peaks are shown in Figs. 4 and 5. Fig. 6 gives a section through the centre of the cluster where no peak is indicated. The peaks at the left and right hand side in Fig. 6 are due to the 4-centre bonds mentioned above. The section passes through the atoms Li(11) and Li(1)′ which are marked on the map.

From Figs. 4 and 5 it is obvious that the 4-centre bond peaks have about the same density as the C—C bond peaks and are about the same distance from their carbon atoms. This leads to the conclusion that the overlap of the carbon sp^3 orbital with lithium orbitals must be comparable to the overlap between the two sp^3 orbitals in the C—C bond. If the overlap were absent , i.e. in case of purely ionic C—Li interaction, each metallated carbon sp^3 orbital would be occupied by a lone pair. But such a lone pair peak should be much closer to the carbon atom than is observed in Figs. 4 and 5. Less than half of the observed distance would be expected in a X-N synthesis [12], and there is little hope of resolving such a peak in a $F_0 - F_c$ synthesis because of its correlation to a (small) shift of the carbon atom. Figs. 4 and 5 support, therefore, the quantum chemical interpretation of Weiss and Lucken [2] who predicted 4-centre bonds of the type C—Li_3.

The electron deficient bond system will certainly not be purely covalent, because of the considerable electronegativity difference between carbon and lithium. From this electronegativity difference Pauling [9] estimated 43% ionic character for bonds between carbon and lithium.

An independent argument for covalent, i.e. oriented, bonding forces is the tendency of the tetramers to increase the symmetry of the 4-centre bonds and the clusters at low temperature, which was mentioned in the preceding para-

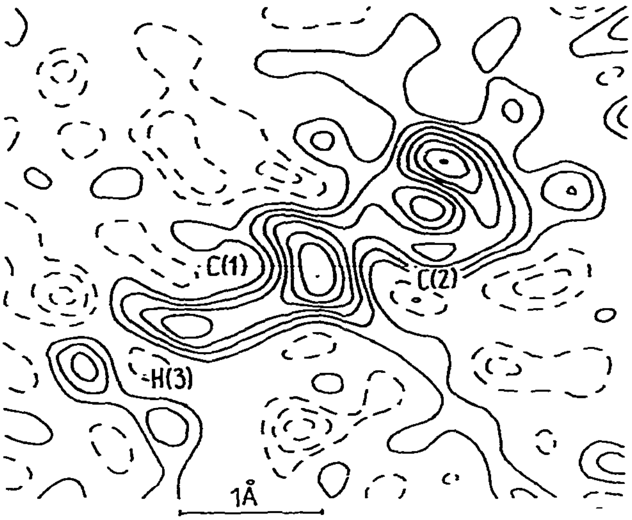


Fig. 4. $F_o - F_c$ synthesis section through the atoms H(3)—C(1)—C(2). The contour interval is 0.05 $e/Å^3$; dashed lines: negative contours; full lines: positive contours; zero contour omitted.

graph. Usually, the tendency for symmetry changes of structures is in the opposite direction, i.e. towards decreasing symmetry at low temperatures, because the thermal movement tends to introduce isotropic disorder. Thus in the case of purely ionic bonding one would expect this "normal" tendency. But with a flexible electron deficient bonding system deformations seem to be released at low temperature. For the difference density study in particular, it is advantageous that the asymmetric unit of the structure contains two formula units of ethyllithium, because each result is obtained twice independently, which allows an internal check (cf. Figs. 4 and 5).

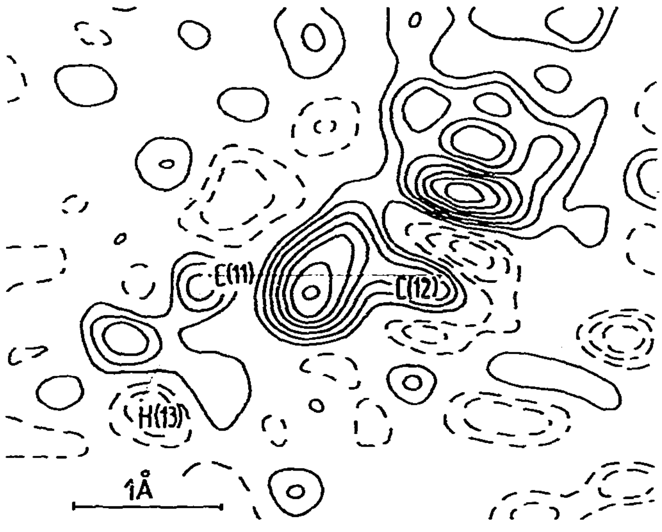


Fig. 5. $F_o - F_c$ synthesis section through the atoms H(13)—C(11)—C(12). Contours as in Fig. 4.

Fig. 6. $F_0 - F_c$ synthesis section through the atoms Li(11)—L(1)' and the centre of the cluster. The intersections of the two lateral tetrahedron faces with the map are marked by thin dashed lines. Contours as in Fig. 4.

Finally, a comparison can be made of the results derived in the preceding paper [10] with those for the Li_2O complex of 2,6-dimethoxyphenyllithium (I) can be made. It was shown that the latter structure contains tetrahedral Li_4 sub-clusters to the faces of which the metallated carbon atoms are bonded by 4-centre bonds in the same way as described above for ethyllithium. But the situation of the sub-clusters in I differs in several aspects from that of the clusters in ethyllithium: one face of each Li_4 sub-cluster is occupied by an oxygen atom via very short Li—O contacts. Moreover, each of the three lithium atoms of that face has two additional contacts to ether oxygen atoms, and the fourth lithium atom of the cluster has three contacts to ether oxygen atoms. This coordination of the cluster by donor atoms obviously replaces the connections between the tetramers in ethyl- or methyl-lithium and is equivalent to solvation of the cluster by basic solvent molecules like ether. Therefore, if the state of the electron-deficient bonding is changed by solvation, compound I may be regarded as a model for the organolithium complexes which are assumed [11] to form the reaction centres in basic solvents.

There are substantial changes in the distances Li—C and Li—Li as well as in the charge distribution. As the diffraction data of the two compounds were collected at the same temperature (113 K), the results can be compared directly. The average values for the C—Li distances around the 4-centre bonds are 2.281 and 2.391 Å for ethyllithium and I, respectively. The average edge length Li—Li of the Li_4 clusters increases from 2.530 Å in ethyllithium to 2.647 Å in I. This increase in the interatomic distances in the electron deficient bond system by more than 0.1 Å is large compared to their temperature dependence of about 10^{-4} Å/K. The latter number is based on the room temperature average lengths C—Li of 2.303 and Li—Li of 2.553 Å in ethyllithium.

Although the absence of high order structure factors in the study of I limits its resolution, comparison of the difference densities, Figs. 4 and 5, to Fig. 3 of ref. 10 reveals that there are 4-centre C—Li_3 bonds of the same type in both substances. A fundamental difference is the 4-centre peak found in the Li_4 sub-clusters of I (cf. Fig. 5 of ref. 10), which has no equivalent in ethyllithium (see Fig. 6).

It seems that the expansion of the skeleton of the electron deficient bond system and the contraction of electron density in the Li_4 sub-clusters can be interpreted mainly as a solvation effect of the many donor atoms around the clusters. The effect may be amplified in the special case of I by the availability of the ether groups in the organic residue and the acidity of the metallated position of the dimethoxybenzene. Because of the latter, the 4-centre C—Li_3 bond in I would be expected to have more ionic character than those in ethyllithium. This is supported by the additional charges found on C(1) and C(5) of the ring (cf. Fig. 5 of ref. 10).

The presence of Li_4 tetrahedra in I and the 4-centre bonds to carbon suggest that they may be stabilized as sub-units in the manner described by Weiss and Lucken [2] for methyl- and ethyllithium.

Acknowledgements

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