X-Ray Crystal Structure of Tetrameric 3-Lithio-1-methoxybutane

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3-Lithio-1-methoxybutane is tetrameric in benzene and crystallizes as the chelated *meso*-tetramer whose increased C–Li and decreased Li–Li distances reflect the size of the organic group.

Any attempt to understand the enhanced reactivity exhibited by Lewis base adducts of alkyl-lithium tetramers in certain reactions[1] requires the knowledge of structure and bonding in these species. So far ^{7}Li n.m.r. has revealed the tetrahedral nature of alkyl-lithiums dissolved in diethyl ether.[2] More detailed information about the structures of alkyl-lithium ether adducts[3] has remained unavailable owing to the failure to obtain crystalline materials from their solutions. We now report the crystal structure of the *intramolecularly* etherated title compound (**1**) obtained from the corresponding mercury derivative by reaction with lithium in pentane (2 days, 25 °C).

Crystal data: Crystals of compound (**1**) grown from solution in pentane were block shaped, transparent, and colourless. $C_{20}H_{44}O_4Li_4$, $M = 376.33$, tetragonal, space group $P\bar{4}b2$, $a = b = 12.389(3)$, $c = 8.218(1)$ Å, $U = 1261.4(5)$ Å^3, $Z = 2$, $D_c = 0.991$ g/cm^3, Ni-filtered Cu-K_α radiation, $\lambda = 1.5418$ Å. The specimen, *in vacuo*, was mounted in a Lindemann glass capillary; 868 reflections ($\theta \leqslant 70°$; $\omega/2\theta$ scan mode) were measured on an ENRAF NONIUS CAD4F-diffractometer. The structure was solved by direct methods (MULTAN 80) and refined by full matrix least squares (SHELX 76) including hydrogen atom positions and anisotropic thermal parameters for the non-hydrogen atoms. Final $R = 0.046$ [$w = 1$, 664 reflections with $I > 2.5\sigma(I)$].†

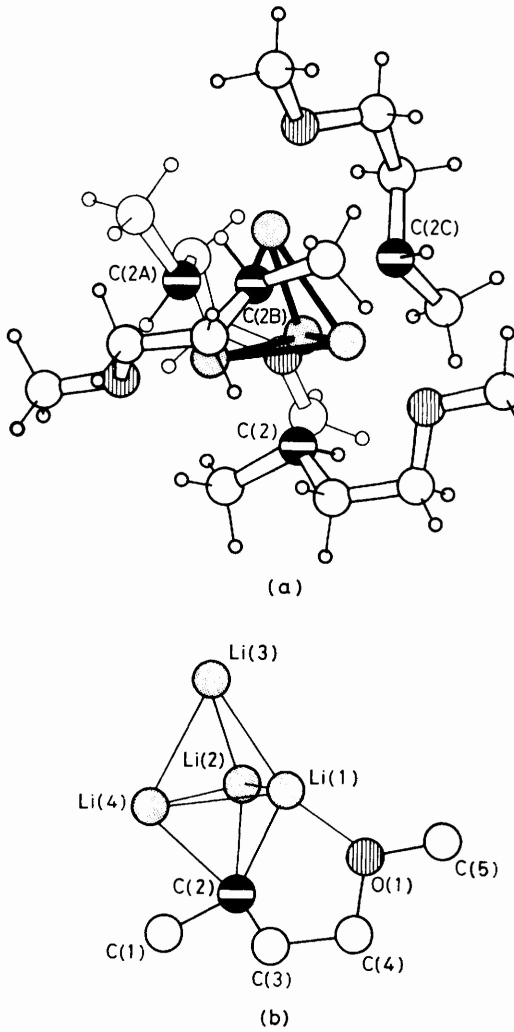

Figure 1. (a) Overall structure of the tetramer of (**1**). (b) Li_4 tetrahedron and bonding of one of the 4-methoxy-2-butyl groups to it. Some important distances (Å) and angles (°) are (e.s.d.'s in parentheses): Li(1)–Li(2), 2.506(7); Li(2)–Li(4), 2.506(7); Li(1)–Li(4), 2.474(7); Li(1)–C(2), 2.362(6); Li(2)–C(2), 2.288(6); Li(4)–C(2), 2.291(6); O(1)–Li(1), 1.923(5); Li(1)C(2)Li(2), 65.2(2); Li(1)C(2)Li(4), 64.2(2); O(1)Li(1)Li(2), 124.4(3); O(1)Li(1)Li(3), 164.6(3); O(1)Li(1)Li(4), 135.0(3); O(1)Li(1)C(2), 88.0(2); Li(1)C(2)C(3), 86.7(2); Li(1)O(1)C(4), 111.5(2); C(1)C(2)C(3), 106.7(3); C(4)O(1)C(5), 112.6(2).

In the crystalline state compound (**1**) is composed of the tetrameric units shown in Figure 1 and located at $\bar{4}$ symmetry sites in the unit cell. The four lithium atoms form a distorted tetrahedron to each face of which a 4-methoxy-2-butyl group is attached by four-centre bonding. Of the four chiral carbon atoms present in the crystalline tetramer $(\mathbf{1})_4$ two have the (*R*) configuration (C-2 and C-2B) and the two others have the (*S*) configuration. Each oxygen atom is co-ordinated as a fourth ligand to one of the lithium atoms. Increased accessibility in the intramolecular situation permits the lithium–oxygen distance in the tetramer *meso*-$(\mathbf{1})_4$ to be 1.923(5) Å, the shortest distance observed so far between an ether oxygen and a lithium atom incorporated into a cluster.‡ In benzene solutions (0.005—0.035 M, 28.6 °C) compound (**1**) was also tetrameric.§ At 0 °C the ^{7}Li n.m.r. spectrum of (**1**) in benzene showed one main signal at 0.73 p.p.m. and two smaller ones at 0.55 and 0.66 p.p.m., downfield from 7% LiBr in water (external standard). Upon warming the signal at 0.66 p.p.m. increased in intensity, coalescence of all signals taking place at *ca.* 40 °C. (All temperature dependent changes were reversible.) Obviously, in benzene the tetramer *meso*-$(\mathbf{1})_4$ is in rapid equilibrium with its diastereoisomers and/or diastereoisomers of the tetramer $(\mathbf{1})_4$ in which one or more chelate rings are opened. The *meso*-tetramer of compound (**1**) is the first ether adduct of an alkyl-lithium tetramer whose structure has been established by unequivocal means. It is also the first tetrameric secondary alkyl-lithium[6] for which structure data have become available. In Table 1 average distances within the Li_4C_4 skeleton of the tetramer *meso*-$(\mathbf{1})_4$ are given together with those of the other organolithium compounds for which tetrahedral structures have been established by single crystal *X*-ray analysis.

On going from $(MeLi)_4(TMEDA)_2$ to the tetramer *meso*-$(\mathbf{1})_4$ one observes a gradual lengthening of the average carbon–lithium distance accompanied by a contraction of the Li_4 cores of the clusters. The differences between the four compounds are visualized most clearly by comparing the distances by which the respective α-carbon atoms are separated from their Li_3 face. The changes parallel the increase in steric bulk of the

Table 1. Average distances (Å) in tetrameric organolithium clusters.

	$(MeLi)_4$-$(TMEDA)_2$[a]	$(EtLi)_4$[b]	$[2\text{-}(CH_2NMe_2)\text{-}C_6H_4Li]_4$[c]	*meso*-$(\mathbf{1})_4$
C–Li	2.262	2.271[d]	2.283	2.313
Li–Li	2.564	2.553[d]	2.512	2.495
C–{Li}$_3$[e]	1.709	1.748[f]	1.747[f]	1.809

[a] TMEDA = tetramethylethylenediamine: ref. 7. [b] Ref. 8. [c] Ref. 9. [d] Low temperature data. [e] Distance between α-carbon atom and Li_3 plane calculated from atomic co-ordinates. [f] Average of two crystallographically independent values.

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† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. Full details of the crystallographic work will be published in *Acta Crystallogr., Sect. C.*

‡ Li–O(Et_2O) in $[Li(OC_6H_2Me\text{-}4\text{-}Bu^t{}_2\text{-}2,6)OEt_2]_3$ and related molecules: 1.961 Å (ref. 4). Li–O(THF) in lithium 3,3-dimethylbut-1-en-2-olate–THF: 1.97 Å (ref. 5) (THF = tetrahydrofuran).

§ Determined by isothermal distillation (A. van Vulpen and J. Coops, *Recl. Trav. Chim. Pays-Bas*, 1966, **85**, 203).

α-carbon atoms,[¶] seemingly irrespective of the type of these carbon atoms as well as the presence (or absence) of different Lewis bases co-ordinated to lithium. This suggests that bond lengths of tetrahedral organolithium clusters are *not* affected to a significant degree by co-ordination of Lewis bases and that the accelerations of reactions of alkyl-lithium tetramers by ethers and tertiary amines may originate mainly from strong effects of these additives upon transition states.[10]

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References

1 Wurtz-coupling: J. F. Eastham and G. W. Gibson, *J. Am. Chem. Soc.*, 1963, **85**, 2171; iodine–lithium exchange: D. E. Applequist and D. F. O'Brien, *ibid.*, 1963, **85**, 743; bromine–lithium exchange: H. R. Rogers and J. Houk, *ibid.*, 1982, **104**, 522; ethylenation: P. D. Bartlett, C. V. Goebel, and W. P. Weber, *ibid.*, 1969, **91**, 7425.

2 T. L. Brown, *Pure Appl. Chem.*, 1970, **23**, 447; L. D. McKeever, 'Ions and Ion Pairs in Organic Reactions,' vol. 1, ed. M. Szwarc, Wiley–Interscience, 1972, p. 263 and references given in these papers.

3 H. L. Lewis and T. L. Brown, *J. Am. Chem. Soc.*, 1970, **92**, 4664; I. Kminek, M. Kaspar, and J. Trekoval, *Collect. Czech. Chem. Commun.*, 1981, **46**, 1132.

4 B. Cetinkaya, I. Gümrükcü, M. F. Lappert, J. L. Atwood, and R. Shakir, *J. Am. Chem. Soc.*, 1980, **102**, 2086.

5 R. Amstutz, W. B. Schweizer, D. Seebach, and J. D. Dunitz, *Helv. Chim. Acta*, 1981, **64**, 2617.

6 For a hexameric secondary alkyl-lithium see: G. R. Zerger, W. Rhine, and G. Stucky, *J. Am. Chem. Soc.*, 1974, **96**, 6048.

7 H. Köster, D. Thoennes, and E. Weiss, *J. Organomet. Chem.*, 1978, **160**, 1.

8 H. Dietrich, *J. Organomet. Chem.*, 1981, **205**, 291.

9 J. T. B. H. Jastrzebski, G. van Koten, M. Konijn, and C. H. Stam, *J. Am. Chem. Soc.*, 1982, **104**, 5490.

10 *Cf.* E. Y. Darensbourg, B. Y. Kimura, G. E. Hartwell, and T. L. Brown, *J. Am. Chem. Soc.*, 1970, **92**, 1236.

[¶] Values of $E'_{s,\mathrm{CH_2-R}}$ for R = Me, Et, Ph, Bu^s are: −0.08, −0.31, −0.38, −0.93 (J. A. MacPhee, A. Panaye, and J.-E. Dubois, *Tetrahedron*, 1978, **34**, 3553).