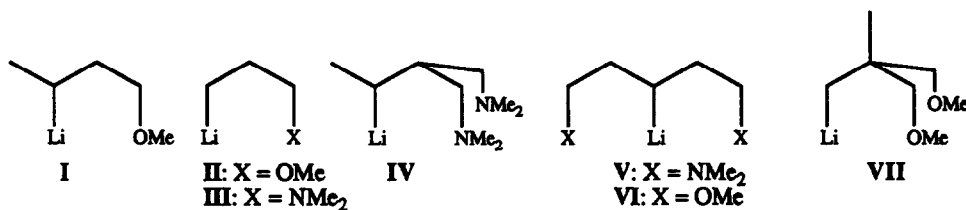


X-RAY CRYSTAL STRUCTURE AND HYDROCARBON SOLUTION BEHAVIOUR OF TETRAMERIC 2,2-BIS(METHOXYMETHYL)-1-PROPYLLITHIUM

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Abstract: The title compound is a tetramer in the solid state and in hydrocarbon solution.

At ambient temperatures alkyllithiums exist prevalently as tetramers or even higher aggregates in the solvents commonly used. Their reactions are accelerated by the presence of Lewis base (B) such as ethers or tertiary amines. Either an increase in the concentration of more reactive lower aggregates $\text{Li}_2\text{R}_2\text{B}_4$ ¹ or the formation of complexes $\text{Li}_4\text{R}_4\text{B}_n$ ($n = 1-4$)² is responsible. These species can be studied by cryoscopy³ and NMR spectroscopy⁴, but more detailed structural investigation by X-ray analysis is impeded by the ease with which both, $\text{Li}_4\text{R}_4\text{B}_n$ and $\text{Li}_2\text{R}_2\text{B}_4$ loose B, the latter thereby reverting to tetramer⁵. *Intramolecularly* coordinated alkyllithiums lack the ephemerality of their intermolecular congeners. When the ratio *internal*-B:Li is one, stable tetramers are obtained and X-ray crystal structures and NMR properties of (I)₄ - (III)₄⁶ have been reported. When this ratio is two, dimers are expected and in line with this (IV)₂ and (V)₂ have been proven by X-ray analysis and NMR, while the structure of (VI)₂ is assigned on the basis of molecular weight determination and NMR⁷.



We now report the X-ray crystal structure and NMR properties of VII, which we expected to form a dimer similar to that of IV. Crystals of VII were obtained by our usual procedure^{6,7} from bis-(2,2-bis(methoxymethyl)-1-propyl)mercury and two equivalents of *t*-Bu⁶Li in *n*-pentane at -20°C. To our surprise X-ray analysis indicated the crystals to consist of tetrameric subunits located at S₄ symmetry sites as shown in Figure 1. The four α -carbon atoms and the four lithium atoms form a distorted cube, also found in the structures of (I)₄-(III)₄ and (EtLi)₄. One of the methoxy groups is coordinated as a fourth ligand to lithium, with the chelate rings arranged as in (I)₄, whereas the other is free. The interatomic distances between Li, α -C and O, respectively, in (VII)₄ are very similar to those in (EtLi)₄ and (II)₄. Probably, non-bonded interactions that would arise in the tetrameric state, are responsible for secondary alkyllithiums IV-VI to prevail as dimers. In the tetramer of the primary alkyllithium VII such interactions apparently are less important. Extensive calculations on methylolithium have shown that tetramer is intrinsically more stable than dimer⁸. 2,6-Dimethoxyphenyllithium represents another case of an organolithium compound, which, the ratio *internal*-B:Li = 2 notwithstanding, is tetrameric in an apolar solvent (toluene)⁹. It should also be noted that, in accordance with a vast body of data¹⁰, lithium in (VII)₄ is tetracoordinated despite the potential for intramolecular pentacoordination^{9,11}.

The ^{13}C NMR spectra of VII reveal the presence of one aggregate in hydrocarbon solution, independent both of concentration and temperature. The proton decoupled ^{13}C resonance of the α -carbon atom at 220K consists of a 1:3:6:7:6:3:1 septet, $J(^{13}\text{C}\text{-}^6\text{Li}) = 4.0$ Hz, caused by the coupling with three equivalent ^6Li nuclei and indicating a tetrameric aggregate⁴ in which intramolecular exchange is slow on the ^{13}C NMR time scale. Only one ^6Li NMR resonance is observed, at $\delta 1.29$ (294K); $\delta 1.36$ at 194K). Although two different types of methoxymethyl groups are present in the X-ray crystal structure of (VII)₄ only one signal is detected by ^{13}C and 250.13 MHz ^1H NMR spectroscopy. However, in the 400 MHz ^1H NMR spectrum at 155K decoalescence is observed to give discernable resonances for the two different methoxymethyl groups. At higher temperatures their nonequivalence is lifted by rapid MeO---Li coordination/decoordination, with $\Delta G^\ddagger = 30.66$ kJ·mol⁻¹. In hydrocarbon solutions at temperatures above -10°C, (VII)₄ readily decomposes to give LiOCH₃ and 1-methoxymethyl-1-methylcyclopropane.

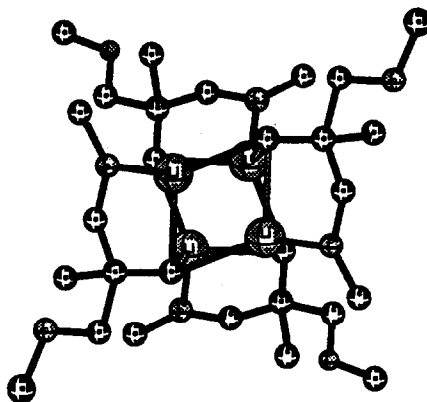


Fig 1: Selected bond lengths (Å): Li-Li': 2.53(3); Li-C(2): 2.26(3); Li'-C(2): 2.29(3); Li"-C(2): 2.30(3); Li-O: 1.87(3).

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