# AN ELECTROSTATIC MODEL OF METHYLLITHIUM TETRAMER, A NON-NONCLASSICAL SYSTEM *

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## Summary

A collection of 4 positive and 4 negative point charges arranged as two interpenetrating tetrahedra subject only to Coulombic forces has a minimum electrostatic energy at a ratio of the two tetrahedra sides of 0.783, a value consistent with the observed Li—Li to C—C distance ratio of 0.73 in the structure of methyllithium tetramer.

The crystal structure of methyllithium is that of tetrameric units consisting of two interpenetrating tetrahedra of four lithiums and four methyls [1]. This type of structure has been considered in terms of carbon—lithium covalent bonding, consistent with the general description of organolithium compounds in terms of comparable contributions of CLi covalent and ionic bonding. The NMR spectrum of methyllithium in various solvents has been interpreted in terms of aggregates with substantial C—Li covalency and only ~0.1 e charge transfer from Li to $CH_3$ [2], a value which T.L. brown [3] has considered to be too small, even on a partial covalent/partial ionic model. Alkyllithium aggregates have often been considered as electron-deficient bridge-bonded organometallic compounds [4,5]. Some recent MO [6—10] calculations of methyllithium monomer and aggregates and other organolithium compounds [11] have been interpreted in a comparable manner with use especially of Mulliken atom and overlap population analyses. We [12] have previously cautioned that such analyses are especially unreliable for lithium. Electron density functions show but little shared electron density between carbon and lithium [10,12] and, hence, that covalent Li—C bonding is small. Moreover, integrated electron populations around Li and $CH_3$ show extensive charge transfer and a high degree of lithium cation methyl anion ion pair character [12]; the ionic character by this criterion is comparable to that of lithium fluoride [13]. This picture of organolithium

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* This paper is dedicated to Professor H.C. Brown on occasion of his 66th birthday.

compounds as essentially ionic with little C—Li covalency is consistent with the absence of Li—Li coupling in the NMR [14] and with Raman intensities [15] of alkyllithium aggregates. In this paper we show how another aspect of the methyllithium tetramer structure is consistent with an ionic model.

We consider a tetrahedron of four point charges with a distance $a$ and an interpenetrating tetrahedron of the opposite charges having a distance $b$ along each side. If $a = b$, the result is a cube with alternating charges at the corners. The Coulombic energy of such an assembly of point charges is readily shown to be that given in eqn. 1.

$$E_{Coul.} = \frac{3}{\sqrt{2}a} + \frac{3}{\sqrt{2}b} - \frac{12}{(3b^2 + 3a^2 - 2ab)^{1/2}} - \frac{4}{\sqrt{3}(a + b)} \tag{1}$$

We let the ratio of distances $b/a = \lambda$ and find the value of $\lambda$ for which $E_{Coul}$ is a minimum:

$$a\frac{d\,E_{Coul.}}{d\,\lambda} = 0 = -\frac{3}{\sqrt{2}\lambda^2} + \frac{12(3\lambda - 1)}{(3\lambda^2 - 2\lambda + 3)^{3/2}} + \frac{4}{\sqrt{3}(\lambda + 1)} \tag{2}$$

This equation has a solution at $\lambda = 0.7830$; that is, the minimum electrostatic energy does not occur for a cubic structure for which $\lambda = 1$! In the structure of methyllithium tetramer reported by Weiss and Hencken [1] the two edges of the interpenetrating tetrahedra are given as Li—Li = $2.6_8$ Å and C—C = $3.6_8$ Å, a ratio of 0.73. Actually, in a methyl anion we expect the center of negative charge to be somewhat in front of the pyramidal methyl carbon; the electrostatic value of $\lambda$ of 0.783 corresponds to a point negative charge 0.26 Å from carbon, a not unreasonable figure. Thus, the observed Li—Li and C—C bond ratio in methyllithium tetramer is completely consistent with a wholly ionic model for the compound. No unusual multicenter bonding is required to explain the structure; that is, methyllithium tetramer can be interpreted as an aggregate of ion pairs without involvement of nonclassical character. The present example is limited, of course, by considering only the electrostatic interactions within a single tetramer unit of what is in fact an extended solid structure in which adjacent tetramer units are rather close to one another [1]. Spectra of t-butyllithium have been interpreted in terms of a similar tetrameric structure. In such a structure the tetramer units must be farther apart because of the methyl groups; unfortunately, the crystal structure of t-butyllithium has not yet been reported. Within these limitations the present example points up the growing generality that much, if not all, of organolithium chemistry can be interpreted as ion pair chemistry and involves at most only weak covalency.

Acknowledgement

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