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THE STRUCTURE AND FORMATION OF METHYLLITHIUM IONIC FRAGMENTS

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Summary

Properties of the methyllithium species $Li_4(CH_3)_3^+$, $Li_4(CH_3)_2^+$, $Li_4CH_3^+$, $Li_2CH_3^+$, $LiCH_3^+$, and $Li_2(CH_3)_2$ have been probed by the application of an ab initio computational procedure. These lithium cluster species are the methyl analogs of the products observed experimentally to result from the fragmentation of ethyllithium and t-butyllithium. The procedure was used to determine the optimum geometry for each species. The total energy calculated for favored conformations of the subject fragments was used to estimate that ΔE's for possible paths through which the optically excited parent, $Li_4(CH_3)_4$, could dissociate. The stable ions found and their modes of formation were compared to photofragments formed by dissociative ionization of $Li_4[C(CH_3)_3]_4$ reported recently.

I. Introduction

The geometric and electronic structures of the polymeric alkyllithiums are subjects of continuing interest, particularly with respect to gaining insights into the relationship between small clusters of metal atoms with bonded alkyl groups and catalysis. Traditional chemical studies on this class of organometallic molecules have convincingly demonstrated that the alkyllithiums occur as stable tetramers and hexamers in hydrocarbon solutions, and, in some cases, in the solid and gas phases. However, purely experimental probes of the physical properties of these cluster molecules have yielded few molecular parameters such as bond lengths and ionization potentials. For this reason we have elected to explore these properties through the application of established computa-

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tional procedures. An understanding of the geometric and electronic changes that occur within the Li_4 unit, and its stability in various charge states as a function of the number of bound alkyl ligands is expected to offer information about the binding of hydrocarbons to extended lithium surfaces, and promises to contribute to decisions for or against a highly localized nature of hydrocarbon-metal interactions.

The present series of calculations was undertaken to determine the geometries of the methyl analogs to the fragmentation products experimentally observed in the ionization of ethyl- and t-butyl-lithium tetramers [1,2]. Results for the methyllithium molecules were helpful in establishing trends and patterns of behavior for the larger homologous alkyllithiums.

II. Calculations

Calculations to determine geometries of minimum energy were done with an SCF-LCAO-MO treatment utilizing the STO-3G basis set [3].

The first set of fragments investigated were Li_4Me_4, $Li_4Me_3^+$, $Li_4Me_2^+$, and Li_4Me^+. These fragments are illustrated in Fig. 1. Also shown are several distances that were systematically varied during energy minimizations. *A* is the longest lithium—lithium distance on tetramer faces from which a methyl group has been dissociated. *B* is the lithium—lithium distance encountered most frequently on occupied tetramer faces (i.e., two out of three times on $Li_4R_3^+$ and $Li_4R_2^+$, and three out of three times on Li_4R^+). *D* is described below. In these calculations the carbon—hydrogen distances were held to a constant 1.095 Å and the H—C—H angle was held to the tetrahedral value. All hydrogens on the same methyl group were fixed at equal distances from the nearest triangular

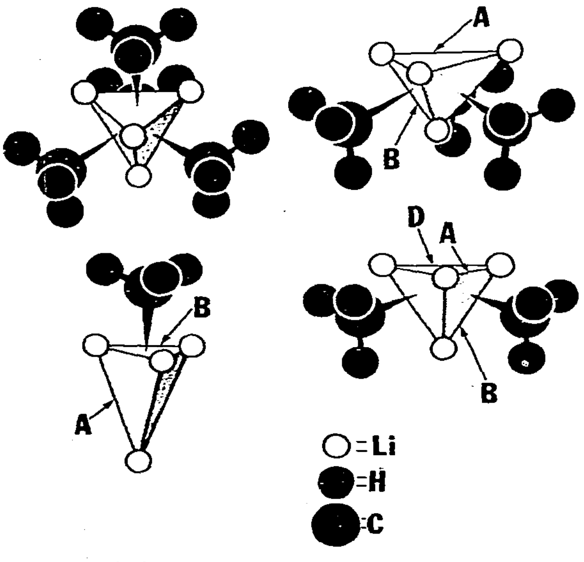


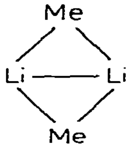
Fig. 1. Methyllithium and its fragmentation products. Clockwise from upper left Li_4Me_4, $Li_4Me_3^+$, $Li_4Me_2^+$, Li_4Me^+. A, B, D are lithium—lithium distances optimized.

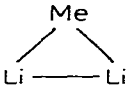
lithium face; i.e., the threefold axis of each methyl group was maintained normal to the microface on which it was bound.

The lithium—lithium and lithium—carbon distances were initialized to values found previously for the neutral methyllithium tetramer [4]. The fragment energies were first minimized with respect to A and were then minimized with respect to B. The energy was reminimized with respect to each parameter when distances changed by more than 0.05 Å. This reiterative optimization was continued until the "best" arrangements for the four lithium atoms were located for each fragment. At this stage in the calculation the energy was minimized with respect to the lithium—carbon distance. As before, whenever large changes in the initial lithium—carbon geometry were encountered, the parameters A, B, and then the lithium—carbon distances were reoptimized.

Several additional distortions were carried out on some of the fragment ions once the "best" lithium—lithium and lithium—carbon distances were obtained. For example, the methyl groups on the $Li_4Me_3^+$ ion were translated away from the centers of their triangular microfaces in order to determine whether the energy would be lowered when the groups resided more directly over a "subsurface" lithium. It was concluded that a geometry based on equal lithium—carbon distances from all three surface lithiums was the most stable, although only small energy increases were associated with methyl displacements near the center of the lithium microface. The equivalence of the three C—Li distances clearly shows a preference for a four center bond to the microsurface. For the $Li_4Me_2^+$ ion the angle between the planes containing the methyl groups was slightly increased and found to give the lithium—lithium distance marked D in Fig. 1.

The determination of the spatial arrangement of atoms in the neutral Li_2Me_n fragments (n = 1, 2) followed an analogous cyclic interplay between the lithium—lithium and lithium—carbon distances and resulted in planar geometries of the type illustrated below:





A similar geometry for Li_2Me_2 has been determined previously by Baird, Barr, and Datta [5].

III. Results

The geometric and electronic structure of neutral Li_4Me_4, which is the molecular parent for the fragment ions, has been determined previously by the procedure used in this study of the fragment ions [4]. Selected results are included in Tables 1 and 5 for completeness and later use. The calculated geometry was close to that extracted from X-ray powder patterns observed from Li_4Me_4 (s) [6]. The calculated lithium—lithium distance was not in as close agreement with the observed Li—Li distances as is ususally obtained when employing a STO-3G basis for species containing only C—C, C—H, C—O, etc. dis-

TABLE 1

ALKYLLITHIUM FRAGMENT ENERGIES AND GEOMETRIES [a] (See Fig. 1)

Fragment	STO-3G energy (a.u.)	Geometry			
		A (Å)	B (Å)	D (Å) [b]	C—Li (Å)
Li_4Me_4 [c]	−185.86114	—	2.37	—	2.25
$Li_4Me_3^+$	−146.60419	2.92	2.32	—	2.21
$Li_4Me_2^+$	−107.46042	2.76	2.35	2.98 [d]	2.24
Li_4Me^+	−68.32615	3.17	2.50	—	2.25
Li_4t-Bu^+ [e]	−184.06517	3.17 [f]	2.50 [f]	1.54 [g]	2.21
$Li_4Me_3H^+$	−147.08159	2.92 [h]	2.32 [h]	2.29 [i]	2.21
Li_2Me_2	−92.89693	—	2.08	—	2.18
Li_2Me	−53.75669	—	2.29	—	2.25 [j]
Li_2Me^+	−53.63424	—	2.88	—	2.07
LiMe	−46.42028	—	—	—	2.03
$LiMe^+$	−46.24381	—	—	—	2.26

[a] The energies listed in column 2 are calculated precise to ±0.00001 a.u. but are subject to inaccuracies inherent to the theory used and to geometric restrictions indicated in Section II of the text. In similar manner the distances are calculated precise to ±0.01 Å. b The definition of this quantity varies. See notes following and text. [c] See ref. 4. [d] See Fig. 1. [e] See text for carbon and hydrogen orientations. [f] Constrained to values in Li_4Me^+. [g] C—C distance in the group. [h] Constrained to values in $Li_4Me_3^+$. [i] Li—H distance on Li_3 triad face. [j] Not optimized.

tances. This deviation from the average behavior was attributed in part to the fact that the isolated molecule modeled in the calculation lacked the packing interactions of the solid. In Li_4Me_4 the ionization potentials obtained with Koopmans theorem [7] for the valence level molecular orbitals were 6.9, 9.2, 12.9, 13.2, and 13.3 eV.

The atom—atom distances and the minimum energies found for the $Li_4Me_n^+$ fragment ions are listed in Table 1. The rotational orientation of the methyl groups with respect to each triangular lithium facet is shown in Fig. 1. From the total energy for the fragments listed in Tables 1 and 3, one finds each ion of the type $Li_4Me_n^+$ to be energetically favored with respect to dissociation into $LiMe_{n-1}^+$ + Me. For example $Li_4Me_3^+ \rightarrow Li_4Me_2^+ + Me$ has a ΔE of 1.9 eV.

TABLE 2

COMPARISON OF ORBITAL PARENTAGES [a] FOR Li_4Me^+ AND Li_4-t-Bu^+

Symmetry	Energy (eV)	%Li(2s)	%Li(2p)	%C(2p)	%α-C(2p)
Li_4Me^+					
(LUMO) e	−2.1	46.6	48.0	—	
(HOMO) a_1	−8.9	47.4	30.9	12.5	
(HOMO) a_1	−13.2	8.6	7.6	64.8	
(HOMO) e	−18.2			41.9	
Li_4-t-Bu^+					
(LUMO) e	−1.8	43.1	49.6		—
(HOMO) a_1	−8.5	47.2	26.6		14.9
(HOMO) a_1	−11.8	6.7	12.3		43.4
(HOMO) e	−15.7				26.4

[a] The orbital parentages are based on the sum of squares of the coefficients of the contributing atomic orbitals.

TABLE 3

METHYL FRAGMENT ENERGIES [10]

Fragment	STO-3G energy (a.u.)
CH_4	—39.72686
CH_3	—39.07701
CH_3^+	—38.77948
CH_3^-	—38.83385 [a]
CH_2 ($^1A_1$)	—38.37230
CH_2 ($^3B_1$)	—38.43623
H	—0.46658

[a] Ref. 1.

Hence each of the ions containing a Li_4 unit is itself a relatively stable unit. The lithium—carbon distance is very nearly the same in all of the Li_4 species whether neutral or ionic. B, the Li—Li distance in the occupied microface, remains fairly constant until all but one of the methyls have been removed to form Li_4Me^+. Significant changes occur in A, the longest Li—Li distance in vacant tetrad faces, as alkyl groups are removed from the Li_4 cluster. The final geometry obtained for $Li_4Me_2^+$ contained an additional parameter, D, the lithium—lithium distance at the junction of two unoccupied tetramer faces.

Also listed in Table 1 are the geometric parameters found for the Li_2Me_n fragments. As for the tetrameric species, dramatic geometry changes accompany the removal of methyl groups and electrons from the neutral dimer Li_2Me_2. The rotational orientations of the methyl groups were not found to affect the total energies of the $Li_2R_n^+$ and Li_2R_n fragments, but it was found that the Li_4R_n ions and neutrals were more stable when the methyls were oriented in such a way as to minimize the lithium—hydrogen distances. This orientation is referred to as the eclipsed orientation, and has been found to be the more stable orientation for CH_3 on 4, 7, 10, and 13 atom clusters of lithium used to model surface behavior on bulk lithium [4]. This orientation is consistent with the locations of hydrogens reported in an X-ray diffraction study of the ethyllithium tetramer [8] but is not in agreement with the methyl orientation found in the X-ray powder diffraction study on the methyllithium tetramer [6]. The calculated and observed stability of the Li_4 unit is notable. It persists through multiple dissociations of alkyl groups from the faces of the lithium tetrad and in complexation with ethylenediamine to form $Li_4(Me)_4(NH_2CH_2CH_2NH_2)_2(s)$. The calculated values for the Li—C(methyl) distances agree well with those observed in both $Li_4(Me)_4(s)$ [6] as well as in the ethylenediamine complex where each lithium is also coordinated to the lone pair of a nitrogen [9]. Observed values of atom—atom distances in the $Li_4R_n^+$ ($n = 1$, 2, 3) fragment ions are not available for comparison but the calculated values provide both the approximate values and the appropriate changes with fragmentation.

In order to test the expectation that methyllithium fragmentation can be used to model the behavior of similar alkyllithiums, especially $Li_4[C(CH_3)_3]_4$, a detailed comparison was carried out for the ions Li_4Me^+ and Li_4-t-Bu^+. These ions were small enough to be computationally tractable but large enough to offer some qualitative insight. The geometry for Li_4-t-Bu^+ was built around the "best" Li_4 arrangement found for Li_4Me^+ (see Table 1) and a rigid $C(CH_3)_3$ unit based on tetrahedral bond angles, C—C distances of 1.538 Å, and C—H distances of 1.095 Å. The energy of Li_4-t-Bu^+ was optimized with respect to the lithium to α-carbon distance, the rotational orientation of the CH_3 units about their C—C axes, and the rotational orientation of the t-butyl group with respect to the Li_4 group. The most stable conformation placed the three methyl carbons in positions analogous to the eclipsed hydrogen locations found for the methyllithium fragments; i.e., with each of the C—C axes projecting onto a bisector of angle LiLiLi in the microface. The methyl subgroups were oriented such that one hydrogen on each was vertical with respect to the plane defined by the three lithiums on the bonding surface; i.e., one CH direction of each methyl was parallel to the three-fold axis of CH_3. It was found that the ordering of the molecular orbital levels in the two systems was the same and that the major atomic orbitals contributing to the top filled and lowest empty molecular orbitals were the three lithiums in the bonding microface and nearest neighbor carbon (or α-carbon). It was further determined that the contribution of lithium atoms to these orbitals was nearly identical in the two cases as shown in Table 2.

IV. Discussion

It is always tempting and often instructional to apply the results of a series of model calculations to predictions of actual behavior. In order to do this honestly one must make consistent use of the same basis set and same level of computation throughout, even when these lead in some instances to answers that are known a priori to be wrong. One generally hopes that in following a set of molecular fragments from reactants to products the errors introduced by any computational scheme, e.g. correlation errors, will cancel in the energy differences. The power of such theoretical procedures from the experimentalist's point of view lies not so much in the exactness of the calculated result, but in their ability to stimulate experiments and correlate experimental results.

The volatile alkyllithiums have been shown by both electron impact [2] and photoionization studies [1] to follow a dissociative ionization pattern as shown below:

$$Li_4R_4 \rightarrow Li_4R_3^+ + R' + e^- \qquad \text{(a)}$$

$$\Delta E_1 \sim 6\text{ eV}$$

$$Li_4R_4 \rightarrow Li_4R_3^+ + Li_4R_2^+ + Li_4R^+ + Li_2R^+ + LiR^+ + R' + e^- \qquad \text{(b)}$$

$$\Delta E_2 \sim \Delta E_1 + 2\text{ eV}$$

(R' = alkyl or alkene fragment)

The remarkable feature of this dissociation is the appearance of only one type of lithium-bearing fragment in the 2 eV range between energies ΔE_1 and ΔE_2, and the onset of formation of all combinations of $Li_nR_m^+$ ($m < n$) at exactly ΔE_2. The observation suggest that reaction b takes place when electrons are ejected from a molecular orbital having a different energy, orbital parentage, and directional character than is accessed by energy ΔE_1.

The calculated ground state energy of methyllithium fragments listed in Table 1 can be combined with the calculated energy of methyl fragments, calculated at the same level of theoretical approximation [10] and listed in Table 3, to estimate the internal energy change necessary to form fragmentation products similar to those observed on photolysis and electron impact excitation of the ethyllithium and the t-butyllithium molecules. The calculation of ΔE's permits a number of fragmentation processes to be eliminated as likely transformations. For example, the absorption by Li_4Me_4 of light whose photon energy equals the first ionization potential (calculated as 6.9 eV) cannot in theory yield $Li_4Me_3^+ + Me^-$ because the ΔE for reactants and products in their calculated geometric arrangements is 11.5 eV; i.e., the energy requirement is 4.6 eV larger than is available from 6.9 eV photons (see eq. 1, Table 4). Although optical absorption below the first ionization potential is generally possible, the evidence for alkyllithiums suggests that the first observed absorption at 6.2 eV in Li_4-t-Bu_4(g) [1] is associated with dissociative ionization, and that no anionic fragments are produced. The first ionization potential is always an upper bound to the lowest absorption edge and in the Li_4R_4 class of molecules the first excited state levels are evidently very close to the first ionization level.

Equations 2 through 8 of Table 4 represent reactions that were calculated to require less energy than that available to the system following absorption of light tuned to the first or second ionization potentials. These transformations represent thermodynamically reasonable paths for formation of the types of ions and neutrals observed experimentally. Eq. 6 shows two paths for the formation of methylene, which may be taken as an analog for the production of isobutylene, known to be formed on photolysis of t-butyllithium above 6.2 eV [1]. Eqs. 9 and 10 are alternate paths for producing methylene. One of these paths leaves a hydrogen resident on the lithium moiety while the other does not. The calculated 0.30 eV difference in energy between these paths is not

TABLE 4

PARTIAL LISTING OF REACTION PATTERNS LEADING TO VARIOUS REACTION PRODUCTS

				ΔE (eV)	
	$\mathrm{Li_4Me_4}$	$\not\longrightarrow$	$\mathrm{Li_4Me_3^+ + Me^-}$	11.5	(1)
1st *IP* (6.9 eV (calcd.))	$\mathrm{Li_4Me_4}$	$\longrightarrow$	$\mathrm{Li_4Me_3^+ + Me^\bullet + e^-}$	4.89	(2)
		$\longrightarrow$	$\mathrm{Li_4Me_2^+ + 2Me^\bullet + e^-}$	6.7	(3)
		$\longrightarrow$	$\mathrm{Li_4Me^+ + 3Me^\bullet + e^-}$	8.26	(4)
2nd *IP* (9.2 eV (calcd.))	$\mathrm{Li_4Me_4}$	$\longrightarrow$	$\mathrm{Li_2Me_2 + Li_2Me^+ + Me^\bullet + e^-}$	6.88	(5)
		$\longrightarrow$	$\mathrm{Li_4Me_2^+ + CH_4 + CH_2^\bullet\ (^1A_1) + e^-}$	8.23	(6a)
		$\longrightarrow$	$\mathrm{Li4Me_2^+ + CH_4 + CH_2^\bullet\ (^3B_1) + e^-}$	6.49	(6b)
		$\longrightarrow$	$\mathrm{Li_2Me + Li_2Me^+ + 2Me^\bullet + e^-}$	8.61	(7)
		$\longrightarrow$	$\mathrm{Li_2Me_2 + LiMe^+ + LiMe + e^-}$	8.16	(8)
	$\mathrm{Li_4Me_4}$	$\not\longrightarrow$	$\mathrm{Li_4Me_3H^+ + CH_2^\bullet\ (^1A_1) + e^-}$	11.07	(9a)
		$\not\longrightarrow$	$\mathrm{Li_4Me_3H^+ + CH_2.\ (^3B_1) + e^-}$	9.33	(9b)
	$\mathrm{Li_4Me_4}$	$\not\longrightarrow$	$\mathrm{Li_4Me_3^+ + H + CH_2^\bullet\ (^1A_1) + e^-}$	11.37	(10a)
		$\not\longrightarrow$	$\mathrm{Li_4Me_3^+ + H + CH_2^\bullet\ (^3B_1) + e^-}$	9.63	(10b)

TABLE 5

COMPARISON OF CALCULATED VERTICAL IONIZATION POTENTIALS FOR Li_4Me_4 WITH MEASURED VERTICAL IONIZATION POTENTIALS FOR Li_4-t-Bu_4

IP Li_4Me_4 (calcd.)	*IP* Li_4-t-Bu_4 (Found) [1]
6.9	6.7
9.2	10.4
12.9	11.1
13.2	12.7

sufficient evidence for the selection of one transformation over the other. However, both eq. 9 and 10 require 3 eV more energy than eq. 6 and this difference is significant.

The ionization potential calculated for Li_4Me_4 was 6.9 eV. An onset for dissociative ionization in Li_4-t-Bu_4 was found at 6.2 eV and a lowest vertical ionization potential was located about 6.7 eV [1]. The approximate agreement between the calculated vertical *IP* value for Li_4Me_4 and the experimental results for Li_4-t-Bu_4 indicate both the quality obtainable with the STO-3G basis set for this kind of system and the validity in projecting from the calculated results for methyllithium species to the experimental behavior obtained with the t-butyllithium species of corresponding group composition. Examination of the calculated atomic parentages listed in Table 2 shows that the highest occupied molecular orbitals for Li_4Me^+ and Li_4-t-Bu^+ resemble each other in orbital composition and orbital energy more closely than any of the MO's lying lower and illustrates the source of the approximate agreement.

The occupied MO's of progressively lower energy in the model Li_4Me_4 evidently depart further in their parentage and energy from those present in Li_4-t-Bu_4 because the calculated vertical ionization potentials depart further from those observed in t-butyllithium. This trend is shown in Table 5. That the HOMO in the alkyllithiums receive large contributions, about 40%, from the lithium 2*s* AO is also consistent with the relatively low absorption cross-section found over the range extending from the lowest absorption edge near 6.2 eV in t-butyllithium up to the beginning of a second absorption region beginning about 8.0 eV. The smaller absorption can be viewed as associated with the transparency of *s*-band metals above the plasma frequency.

The calculated results in this system of fragments provide a good guide to the geometry realized by known reaction products in a moderately complicate system of metal atoms and hydrocarbon groups where those geometries are no experimentally accessible. The quantitative agreement among calculated reaction energies and thresholds for photolytic behavior are , of course, imperfect but the patterns of calculated orbital energies and fragment binding energies ar consistent with the patterns of observed behavior. Results from models of hydrocarbons bound to microfaces of metal clusters and the results from experimental work on similar systems should eventually provide a clearer picture of the factors guiding the behavior of complexes formed on metallic substrates.

Acknowledgments

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