C_3Li_4 Revisited: A Theoretical Study

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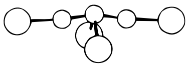
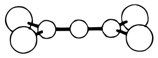
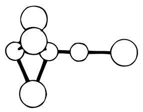
Summary: Extensive searches of the C_3Li_4 potential surface culminated in the location of eight stationary points at the MP2/6-311G level. Reevaluation of the energetics at the MP4/6-311G(df) level leads to the following conclusions. First, the closed-shell singlet ground state of C_3Li_4 is of C_{2v} symmetry, as predicted earlier. Second, two other remarkable structures, with triple lithium bridges and naked carbon atoms, lie very close (2−4 kcal/mol) to the ground state. Third, all stable structures have one of two structural features: either multiple bridging lithiums or clusters of lithium atoms bound to the carbon moiety.*

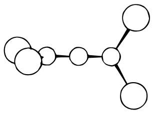
It is well-known[1] that the geometries of many lithium compounds do not follow classical bonding patterns. One of the best examples of this phenomenon is the structure of C_3Li_4, for which early theoretical work[2] indicated an unusual ground-state structure of C_{2v} symmetry.



In this early work, several other structures were found to be energetically competitive at the Hartree−Fock level with a 4-31G basis set. For instance, the following structures were all calculated to lie within 19 kcal/mol of the C_{2v} minimum:







Given the renewed theoretical interest in polylithiated species,[3−10] it seems appropriate to reinvestigate[11] the structure of C_3Li_4. We describe here the location of eight minima on the closed-shell C_3Li_4 potential surface, and we conclude that the minimum energy structure is indeed of C_{2v} symmetry. Two other remarkable structures (Figure 1), with triple lithium bridges and naked carbon atoms, lie very close (2−4 kcal/mol) to the ground state. All stable structures have one of two structural features: either multiple bridging lithiums or clusters of lithium atoms bound to the carbon moiety.

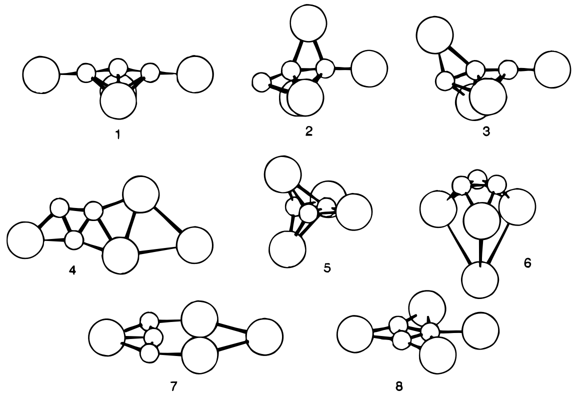


Figure 1. The eight local minima on the C_3Li_4 potential energy surface at the MP2/6-311G* level.

Table 1. Energetics

	energy[a]		rel energy[b]		
isomer	MP2[d]	MP4[e]	MP2[d]	MP4[e]	ZPE[c]
1	−143.7739	−143.8632	0.0	0.0	11.0
2	−143.7706	−143.8604	2.1	1.8	10.8
3	−143.7681	−143.8572	3.6	3.8	10.8
4	−143.7501	−143.8448	14.9	11.5	10.4
5	−143.7395	−143.8302	21.6	20.7	11.1
6	−143.7327	−143.8282	25.9	21.9	10.2
7	−143.7166	−143.8178	36.0	28.4	9.8
8	−143.7096	−143.8164	40.3	29.4	10.3

[a] au. [b] kcal/mol. [c] Zero-point energy, MP2/6-311G*. [d] MP2/6-311G*//MP2/6-311G*. [e] MP4/6-311G(df)//MP2/6-311G*.

Computational Details

All calculations were done with the Gaussian 92 suite of programs.[12] Initially, we searched for minima on the potential surface at the STO-3G level. This proved to be an efficient strategy, since the STO-3G surface seems to exhibit more minima than are present at higher correlated levels. Initial starting geometries included the following: (1) the classical structures (analogous to methylacetylene, allene, and cyclopropene); (2) nonclassical structures considered previously;[2] (3) a wide variety of polyhedral structures based on pentagonal bipyramids, hexagonal pyramids, and body- or face-centered octahedrons. Eleven minima were located. These structures were subsequently reoptimized at the HF/6-311G* level and ultimately at the MP2/6-311G* level. Analytic frequency

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Table 2. Optimized Geometries[a]

	1				**2**		
	x	*y*	*z*		*x*	*y*	*z*
C	0.000 000	0.000 000	0.365 984	C	0.000 000	0.537 678	0.000 000
C	0.000 000	1.320 321	0.171 280	C	−0.351 649	−0.839 317	0.000 000
C	0.000 000	−1.320 321	0.171 280	C	0.707 543	1.625 468	0.000 000
Li	−1.502 897	0.000 000	−0.801 531	Li	−0.696 705	−2.638 993	0.000 000
Li	1.502 897	0.000 000	−0.801 531	Li	1.007 744	−0.107 638	1.497 965
Li	0.000 000	3.170 565	0.092 987	Li	1.007 744	−0.107 638	−1.497 965
Li	0.000 000	−3.170 565	0.092 987	Li	−2.030 570	0.206 610	0.000 000
	3				**4**		
	x	*y*	*z*		*x*	*y*	*z*
C	0.000 000	0.278 637	0.000 000	C	−0.770 987	−0.653 543	−0.000 000
C	−1.165 110	0.954 135	0.000 000	C	−1.445 050	0.637 251	−0.000 000
C	0.891 137	−0.741 247	0.000 000	C	−0.036 030	0.590 275	−0.000 000
Li	−0.773 781	−0.662 920	1.462 500	Li	−2.763 927	−0.767 882	0.000 000
Li	0.006 093	2.482 909	0.000 000	Li	1.181 257	−1.179 875	−0.000 000
Li	−0.773 781	−0.662 920	−1.462 500	Li	4.213 043	−0.577 419	−0.000 000
Li	2.089 415	−2.140 119	0.000 000	Li	1.873 763	1.377 209	−0.000 000
	5				**6**		
	x	*y*	*z*		*x*	*y*	*z*
C	0.000 000	0.000 000	0.658 562	C	−0.718 195	0.414 650	−0.773 266
C	0.000 000	−0.967 910	−0.413 878	C	0.718 195	0.414 650	−0.773 266
C	0.000 000	0.967 910	−0.413 878	C	0.000 000	−0.829 300	−0.773 266
Li	1.559 900	0.000 000	−1.120 903	Li	0.000 000	0.000 000	3.286 424
Li	−1.559 900	0.000 000	−1.120 903	Li	0.000 000	1.863 341	0.451 057
Li	0.000 000	1.828 940	1.290 097	Li	−1.613 701	−0.931 670	0.451 057
Li	0.000 000	−1.828 940	1.290 097	Li	1.613 701	−0.931 670	0.451 057
	7				**8**		
	x	*y*	*z*		*x*	*y*	*z*
C	0.000 000	0.000 000	0.577 058	C	0.000 000	0.000 000	0.578 749
C	0.000 000	1.316 340	0.745 877	C	0.000 000	0.721 548	−0.658 758
C	0.000 000	−1.316 340	0.745 877	C	0.000 000	−0.721 548	−0.658 758
Li	0.000 000	0.000 000	−3.978 267	Li	0.000 000	0.000 000	2.650 349
Li	0.000 000	1.505 400	−1.330 123	Li	0.000 000	0.000 000	−2.520 951
Li	0.000 000	0.000 000	2.500 890	Li	0.000 000	2.293 584	0.674 067
Li	0.000 000	−1.505 400	−1.330 123	Li	0.000 000	−2.293 584	0.674 067

[a] Å.

calculations were performed in all cases, and structures which were not true minima were distorted along the imaginary frequency until a true minimum was found. Eight structures resulted (Figure 1), and the lowest frequencies at the MP2/6-311G* level for each isomer were as follows (in cm^{-1}): 89 (**1**), 115 (**2**), 73 (**3**), 67 (**4**), 97 (**5**), 147 (**6**), 66 (**7**), and 106 (**8**). Energetics were then reevaluated at the MP4/6-311G(df)//MP2/6-311G* level. The energetics, including MP2/6-311G* zero-point energies, are presented in Table 1, while the optimized geometries are presented in Table 2.

Discussion

With one exception (**5**) the stable structures can be described as having a near-linear arrangement of the carbons (**1**−**3** and **7**) or as having a C_3 ring (**4**, **6**, and **8**). Structure **5** represents an intermediate case with one long C−C distance (1.94 Å, C−C−C = 84°). The most stable structure is **1**, as originally proposed many years ago.[2] The next two most stable structures are closely related to **1** by the conversion of one terminal lithium to a bridging lithium. Structure **2** is best described as acetylenic, with a short C−C distance between the naked carbon and the central carbon (1.298 Å). This structure lies only 1.8 kcal/mol higher than **1** at the MP4/6-311G(df)//MP2/6-311G* level and possesses a remarkably stabilized "lone pair" orbital, which corresponds to the *third* highest occupied molecular orbital in spite of being fairly well-localized on the naked carbon atom (1.41e$^-$ at the 6-31G level). Structure **3**, which is 3.8 kcal/mol higher in energy than **1**, is best described as possessing an allyl-like backbone, with C−C distances of 1.347 and 1.354 Å. The ability of lithium to stabilize π systems has been noted previously, and similar effects are clearly operative in structures **2** and **3**.

These structures can conceptually be divided in another way. In most (**1**−**3**, **5**, and **8**) bonding is primarily between carbon and lithium, while in some (**4**, **6**, and **7**) there is direct lithium−lithium bonding. These same trends were recently noted[8] for C_2Li_x systems and may represent a general trend for these systems.[6,13] Some of the structures of the latter type can be surprisingly stable. For instance, structure **4**, which can be considered an adduct of Li_3 and C_3Li, is only 11.5 kcal/mol less stable than **1**.

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