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C_2Li_6 STRUCTURAL ISOMERS

Alexander Kos, Dieter Poppinger, and Paul von Ragué Schleyer*
Institut für Organische Chemie der Friedrich-Alexander-Universität Erlangen-Nürnberg
8520 Erlangen, Federal Republic of Germany

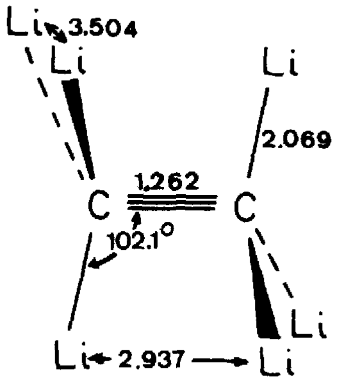
Walter Thiel

Fachbereich Physikalische Chemie, Philipps-Universität Marburg
3550 Marburg, Federal Republic of Germany

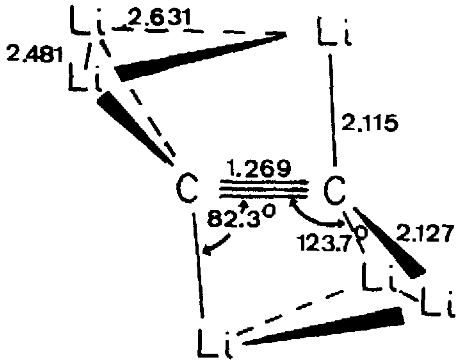
Summary: Three C_2Li_6 isomers characterized by triple (III), double (VII), and single (VI) CC bonds are revealed by minimal basis set ab initio calculations to be favorable minima on the singlet potential energy surface.

A year ago, Shimp and Lagow achieved the synthesis in high yield and purity of a species with the stoichiometry C_2Li_6: gas phase reaction of lithium vapour at 800°C with diethylmercury gave a product which yielded practically pure C_2D_6 when hydrolyzed with D_2O.[1] Because of our interest in the unusual structures of organolithium compounds,[2] we have investigated the complex potential energy surface of C_2Li_6 by means of molecular orbital calculations.[3] Such electron deficient species do not follow conventional structural rules, and a great number of trial geometries must be examined. Our more recent work has been facilitated by the availability of a semi-empirical MNDO program parameterized provisionally for lithium.[4] This program permitted a more extensive geometrical search and an examination of various electronic states without consuming excessive amounts of computer time. The favorable MNDO species then served as starting points for ab initio calculations.[5] This report emphasizes the unusual structures indicated to be potential energy minima at the minimal STO-3G basis set level. We believe these to include the global energy minimum, but this cannot be demonstrated rigorously.

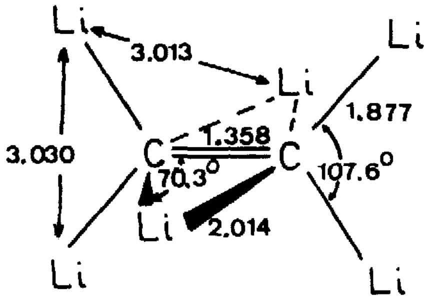
Although lithium compounds almost never exhibit the same basic structures as their hydrogen counterparts,[2] an ethane-like geometry ($\underline{D}_{3d}$, I) is the logical starting point for a study of C_2Li_6. However, I is indicated to possess a carbon-carbon bond essentially triple in length! An acetylide dianion, C_2^{2-}, sandwiched between two Li_3^+ triangular cations,[6] is an interpretive description of the electronic structure of I. However, multicenter covalent and not just ionic bonding determines the structures of lithium compounds;[2] I can equally well be regarded as a combination of neutral Li_3[6,7] and C_2 fragments. I is some 11 kcal/mol (STO-3G) more stable than the eclipsed $\underline{D}_{3h}$ form (II).[8] Neither I nor II are minima on the potential energy surface. Relaxation of the $\underline{D}_{3d}$ symmetry constraint of I and further optimization results in the movement of lithiums attached to different carbons much closer together (compare I and III). The resulting structure, III ($\underline{C}_{2h}$), makes much more efficient use of the lithium and carbon orbitals. III, the lowest energy C_2Li_6 species (STO-3G, Table), still has roughly parallel



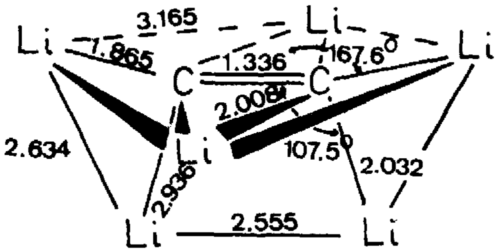
I, D_{3d}



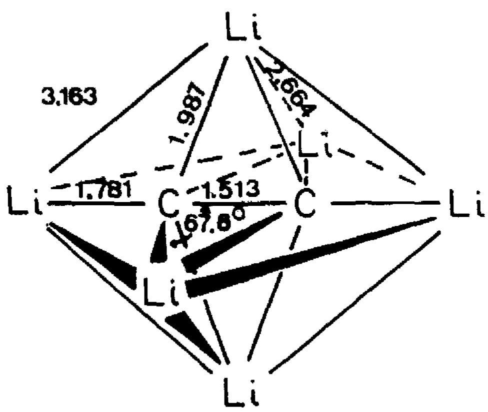
III, C_{2h}



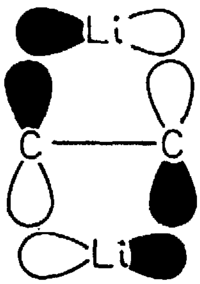
V, D_{2h}



VII, C_{2v}



VI, D_{4h}



VIII

placement of C_2 between two Li_3 triangles. Similarly, if the symmetry restraint is reduced from D_{3h} to C_{2v}, II gives IV on further optimization. However, the energy lowering is much less; IV is not an energy minimum either.

I and III can formally be derived by appropriate placement of the C_2 unit within an Li_6 antiprism; a trigonal prism functions analogously for II.[8] Two additional trial geometries can be derived similarly from octahedral Li_6 clusters: the doubly bridged diborane-like D_{2h} form V (C_2 pointing at opposite edges of the octahedron) and the quadruply bridged D_{4h} form VI (C_2 pointing at opposite corners). VI, but not V, is an energy minimum. When the D_{2h} symmetry constraint is removed, V distorts to VII (C_{2v}) by disrotatory in-plane movement of the CLi_2 groups. Interestingly, the carbon-carbon bonds in V and VII are double and in VI single in length. The lithium bridging exhibited in V-VII requires occupancy of orbitals of type VIII which are CC antibonding and result in CC bond lengthening. Two such degenerate orbitals are occupied in VI, one in V and VII, but none in I-IV. This accounts for the CC bond lengths: single in VI (like F_2), double in V and VII (like O_2), and triple in I-IV (like N_2). Li-Li partial bonding is prevalent, but is not indicated in any consistent way in the drawings which are intended to show the atom locations.

Structures in which lithiums bridge two carbon atoms have been examined frequently in our work.[2] For example, four bridging lithiums are found in the dimers of CH_2Li_2[2c] and CLi_4.[9] The preferred form of C_2Li_2 has two bridging lithiums, but, unlike V-VII, orbitals of type VIII are not occupied and the CC bond is triple in length.[2b]

As suggested by Streitwieser for methyl lithium tetramer,[10] point charge calculations have been carried out on I-VII and many other geometries. VI is indicated to be quite stable, but the energy ordering of the other forms can only be described as "random" when compared with the ab initio results. We do not believe that ion pair clustering models based on electrostatic bonding provide adequate descriptions of these species.

The low energy isomers, III, VI, and VII, are candidates for the global energy minimum. In addition, the triplet state of V may be competitive with these in energy. Although interconversion among III, VI, and VII is formally orbital symmetry forbidden, energy barriers in such electron deficient species tend to be small and only one form might be observable in the gas phase,[11] to which these calculations refer. We have not yet calculated these interconversion barriers, however. In the solid state,[1] C_2Li_6 should aggregate and exhibit consequent structural modification.[2c,9]

The remarkable structures exhibited by carbon-lithium compounds extend the limits of our present understanding of chemical bonding.[1,2] The full report of this work will describe these C_2Li_6 species in greater detail and will include additional geometries and electronic states as well as results of higher level calculations.

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Table. STO-3G Energies of I-VII

Species	I	II	III	IV	V	VI	VII
Point Group	D_{3d}	D_{3h}	C_{2h} [a]	C_{2v}	D_{2h}	D_{4h} [a]	C_{2v} [a]
Total Energy (a.u.)	-118.68328	-118.66975	-118.75285	-118.6873[b]	-118.71611	-118.74174	-118.73703
Rel. Energy (kcal/mol)	43.7	52.1	0.0	41[b]	23.1	7.0	9.9

[a] Minima on the potential energy surface. [b] Optimization nearly complete.

References and Notes

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9. E.-U. Würthwein, unpublished calculations on $(CLi_4)_2$, $(CH_2Li_2)_n$, etc.
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