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# Novel, Remarkably Stable Polylithiated Carbon Species: CLi$_8$, CLi$_{10}$, and CLi$_{12}$

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Lithium derivatives of main-group elements do not follow normal chemical rules. Remarkable structures, stoichiometries, and stabilities have been predicted for CLi$_6$ ($O_h$[1]), SiLi$_4$ ($C_{2v}$ rather than tetrahedral[2]), OLi$_4$ ($T_d$[3]), PLi$_5$ ($C_{4v}$ rather than trigonal-bipyramidal[4]), and very recently for XLi$_3$, XLi$_5$ (X = F, Cl; all four molecules planar with $C_{2v}$ symmetry),[5] YLi$_6$ (Y = O, S; both $D_{2d}$), SLi$_8$, and SLi$_{10}$,[5] using the methods of theoretical chemistry. Mass spectrometry confirms the gas-phase existence of CLi$_6$,[6] OLi$_4$,[7] and SLi$_4$[8] and has provided thermodynamic stability data which generally agree quite well with computational predictions, but no experimental structural data are available yet. Here we report calculations on a new class of polylithiated carbon compounds which possess fascinating structures. They contain small Li clusters which act as polydentate ligands. The main building blocks are triangular Li$_3$ and pyramidal Li$_4$ units, which can condense by vertex-sharing to give Li$_7$ and Li$_{12}$ clusters. While the thermodynamic stability of the known "hyperlithiated" molecule CLi$_6$ is intriguing,[1,6] the predicted thermodynamic stabilities of polylithiated CLi$_8$, CLi$_{10}$, and CLi$_{12}$ are truly astonishing. We are unaware of any binary AB$_n$ molecular system in which $n$ is as large as 12; the largest value known to us is 10 in SLi$_{10}$.[5] Li$_3$ units have already been identified in FLi$_3$, ClLi$_3$, OLi$_6$, SLi$_6$,[5] and C$_2$Li$_4$,[9] but we know of no previous examples of pyramidal Li$_4$ moieties.

Geometries of CLi$_8$, CLi$_{10}$, and CLi$_{12}$ were optimized at the SCF level of theory from analytic first derivatives and frequencies evaluated from analytic SCF second derivatives. 3-21G, DZ(P), DZP, and TZ2P basis sets were used. The DZP basis was derived from the Huzinaga/Dunning (9s5p)/[4s2p] DZ set for C[10] and the (9s)/[4s] DZ set for Li.[10] Exponents were optimized at the SCF level for two Li p functions (0.12 and 0.48, subject to the constraint of a factor of four between the larger and smaller values) and for the spherical-harmonic components of d-type polarization functions (0.2 for Li and 0.24 for C) in CLi$_6$. The DZ(P) basis contains d-type functions only on C. The TZ2P basis used the Huzinaga/Dunning (10s)/[5s] Li set,[11] and the (10s6p)/[5s3p] set for C,[11] augmented with three sets of p functions (exponents 0.72, 0.24 and 0.08) and one d set (exponent 0.2) for Li and two sets of d functions (exponents 0.48 and 0.12) for C. SCF/DZP-optimized geometries were used for final calculations. The QCISD(T)/DZP level of theory, with one core orbital frozen on each atom, was feasible for CLi$_6$ and CLi$_8$, but only MP2/DZP or MP4SDQ/DZ(P) calculations were practicable for CLi$_{10}$ and CLi$_{12}$. The Gaussian 90 program was used throughout.[12]

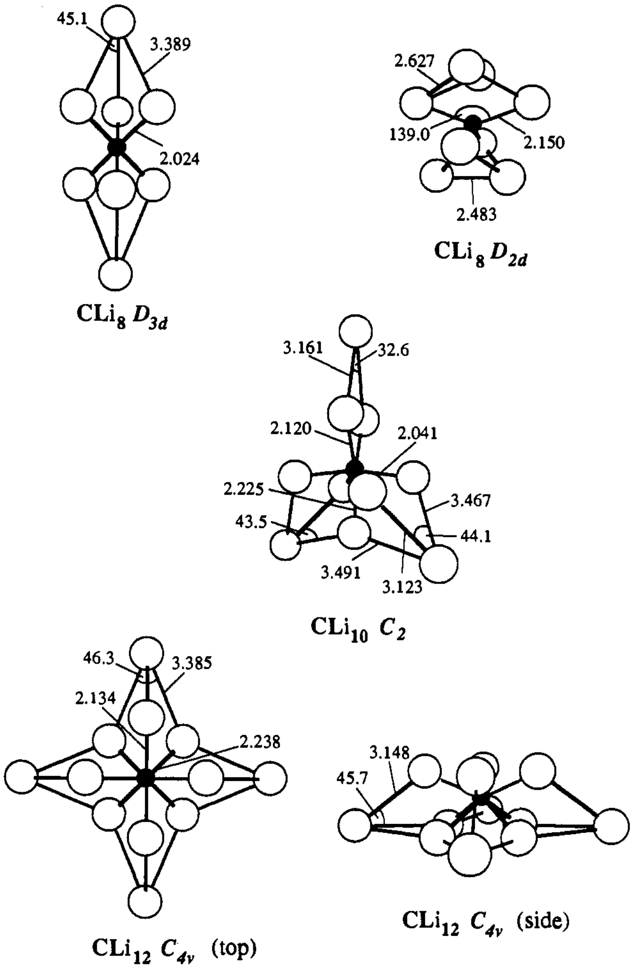

**Figure 1.** Scaled diagrams of CLi$_8$ (two isomers), CLi$_{10}$, and CLi$_{12}$ (two views). Principal geometrical parameters, optimized at the SCF/DZP level, are given; units are Å for bond lengths and degrees for angles. Solid lines indicate the main bonding interactions but do not necessarily imply the existence of a traditional two-electron bond.

Three stationary points, each possessing no imaginary vibrational frequencies at both the 3-21G*/SCF and DZP/SCF levels of theory, were located for CLi$_8$. Only modest changes in structure were found as the basis was improved from 3-21G through DZP to TZ2P. The two lowest energy isomers are shown in Figure 1, which presents the principal geometrical parameters. Their energies are reported in Table I, and binding energies for CLi$_8$ relative to loss of Li$_2$ are displayed in Table II. We believe that the $D_{3d}$ structure is the global minimum for CLi$_8$ as very extensive geometry searches were performed. CLi$_8$ is stable relative to (CLi$_6$ + Li$_2$) at all levels of theory, with a binding energy of 72 kJ/mol predicted by the most sophisticated calculation (QCISD(T)/DZP). Since the predicted binding energy is scarcely affected either by the size of the basis at the SCF level or by the influence of correlation (if we disregard the low-level MP2 results), we are quite confident that CLi$_8$ is a thermodynamically stable compound.

After a prolongued geometry search, a thermodynamically stable $C_2$ structure was found for CLi$_{10}$ which is a true minimum at both SCF/3-21G and SCF/DZP levels of theory. It is illustrated in Figure 1. Absolute energies are shown in Table I,

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**Table I.** Absolute Energies in hartrees

| species, symmetry | $Li_2$, $D_{\infty h}$ | $CLi_6$, $O_h$ | $CLi_8$, $D_{2d}$ | $CLi_8$, $D_{3d}$ | $CLi_{10}$, $C_2$ | $CLi_{12}$, $C_{4v}$ |
|---|---|---|---|---|---|---|
| SCF/3-21G | −14.769 25 | −82.003 45 | −96.744 44 | −96.802 04 | −111.602 26 | −126.400 97 |
| SCF/DZ(P) | −14.869 23 | −82.500 01 | −97.338 38 | −97.396 48 | −112.292 52 | −127.188 46 |
| SCF/DZP | −14.869 26 | −82.501 17 | −97.340 65 | −97.398 98 | −112.295 63 | −127.192 21 |
| SCF/TZ2P | −14.871 04 | −82.509 94 | | −97.410 52 | | |
| MP2/DZ(P) | −14.884 48 | −82.739 33 | −97.599 76 | −97.638 91 | −112.556 45 | −127.481 63 |
| MP3/DZ(P) | −14.890 10 | −82.726 23 | −97.599 87 | −97.641 44 | −112.567 22 | −127.498 72 |
| MP4DQ/DZ(P) | −14.892 29 | −82.728 90 | −97.601 58 | −97.647 20 | −112.574 29 | −127.506 11 |
| MP4SDQ/DZ(P) | −14.892 41 | −82.733 49 | −97.606 33 | −97.652 25 | −112.579 36 | −127.511 41 |
| MP2/DZP | −14.887 68 | −82.758 70 | −97.626 14 | −97.664 39 | −112.582 67 | −127.512 87 |
| MP3/DZP | −14.893 05 | −82.744 72 | −97.624 48 | −97.666 16 | | |
| MP4DQ/DZP | −14.895 23 | −82.746 04 | −97.624 41 | −97.670 33 | | |
| MP4SDQ/DZP | −14.895 38 | −82.750 69 | −97.629 51 | −97.675 45 | | |
| QCISD/DZP | −14.897 43 | −82.749 63 | | −97.676 80 | | |
| QCISD(T)/DZP | −14.897 43 | −82.773 90 | | −97.698 57 | | |

**Table II.** Binding Energies with Respect to Loss of $Li_2$ (kJ/mol)

| species, structure | $CLi_8$, $D_{2d}$ | $CLi_8$, $D_{3d}$ | $CLi_{10}$, $C_2$ | $CLi_{12}$, $C_{4v}$ |
|---|---|---|---|---|
| SCF/3-21G | −74.2 | 77.0 | 81.3 | 77.4 |
| SCF/DZ(P) | −81.0 | 71.5 | 70.4 | 70.1 |
| SCF/DZP | −78.2 | 75.0 | 71.9 | 71.7 |
| SCF/TZ2P | | 77.6 | | |
| MP2/DZ(P) | −63.2 | 39.7 | 86.8 | 106.9 |
| MP3/DZ(P) | −43.2 | 65.9 | 93.7 | 108.7 |
| MP4DQ/DZ(P) | −51.5 | 68.3 | 91.4 | 103.8 |
| MP4SDQ/DZ(P) | −51.4 | 69.2 | 91.1 | 104.1 |
| MP2/DZP | −53.1 | 47.3 | 80.3 | 111.6 |
| MP3/DZP | −34.9 | 74.5 | | |
| MP4DQ/DZP | −44.3 | 76.3 | | |
| MP4SDQ/DZP | −43.5 | 77.1 | | |
| QCISD/DZP | | 78.1 | | |
| QCISD(T)/DZP | | 71.5 | | |

and binding energies relative to ($CLi_8$ ($D_{3d}$) + $Li_2$) are reported in Table II. As was found for $CLi_8$, the thermodynamic stability of $CLi_{10}$ is insensitive to the nature of the theory employed, and its binding energy is substantial. A search for a stable $CLi_{12}$ structure was successful. The aesthetically pleasing $C_{4v}$ geometry is illustrated in Figure 1, while absolute and binding energies are presented in Tables I and II, respectively. $CLi_{12}$ lies well below ($CLi_{10}$ + $Li_2$) at all the levels of theory which were feasible for this system, which is relatively large by the standards of quantum chemistry. As the calculations become more rigorous, its binding energy tends to increase. At the MP4SDQ/DZP level, binding energies for $CLi_8$, $CLi_{10}$, and $CLi_{12}$ are 77, about 85, and about 110 kJ/mol, respectively (these are extrapolated values for $CLi_{10}$ and $CLi_{12}$, based on MP2/DZ(P), MP4SDQ/DZ(P), and MP2/DZP data); these results provide no suggestion that carbon is coordinatively saturated by lithium even for a stoichiometry of $CLi_{12}$, but we have not, as yet, probed the possible existence of higher clusters. Although we have investigated many structural possibilities for both $CLi_{10}$ and $CLi_{12}$, we cannot be certain that we have located the global minima for these stoichiometries, in view of the very large number of possible isomers and the nonapplicability of normal structural rules in these compounds.

Mass spectrometry appears the most direct experimental technique to use for the detection of the $CLi_x$ compounds described in this communication. $CLi_6$ can be detected in the vapor above heated $C_2Li_2$,[6] despite the unfavorable stoichiometry, so investigation of the vapor above a heated mixture of ($C_2Li_2$ + Li) should be most worthwhile. Characterization by matrix isolation vibrational spectroscopy also seems possible. The IR spectrum of octahedral $CLi_6$ is very simple; only one intense band is expected, whose calculated frequency of 278 $cm^{-1}$ (SCF/DZP) is likely to be a few percent too high.[13] At the same theoretical level, intense bands are predicted at 217, 375, 590, and 653 $cm^{-1}$ for $CLi_8$, at 256, 357, 380, 388, 414, 448, 545, and 607 $cm^{-1}$ for $CLi_{10}$, and at 362, 405, and 508 $cm^{-1}$ for $CLi_{12}$.

The $CLi_x$ compounds described here share common structural features. $CLi_8$ is probably best described as two tridentate $Li_4$ pyramids bonding to a central carbon. Two of these pyramids may condense by sharing one vertex, to form the $Li_7$ unit seen in $CLi_{10}$, which also contains a well-characterized $Li_3$ unit,[5,9] while the $CLi_{12}$ structure is built on four $Li_4$ pyramids which are linked by vertex sharing. C is six-coordinate in $CLi_8$ but eight-coordinate in both $CLi_{10}$ and $CLi_{12}$. The C–Li bonded distance in $CLi_8$ is very similar to that in $CLi_6$.[1] As the coordination number of C increases, the C–Li bonded distances also increase, by about 0.1 Å from $CLi_4$ to $CLi_6$[1] and by a similar amount from $CLi_6$ or $CLi_8$ to $CLi_{12}$. It does not seem possible to give a simple yet accurate description of the bonding in these cluster compounds. There are extensively delocalized Li–Li bonding interactions in both the triangular $Li_3$ and pyramidal $Li_4$ units, as indicated by the overlap populations,[14] while there is both a covalent and ionic component to the C–Li interactions. The C atoms have a pronounced negative charge of about −0.9 to −1.0*e*; Li atoms farthest from the carbon are also substantially negative (about −0.2 *e*), in both the triangular and pyramidal units, while the "inner" Li atoms are positive (about +0.2*e*). There is little bonding between the inner Li atoms, even though they are closer to each other than to the outer Li atoms. SCF/DZP population data have been quoted; they should not be interpreted literally but are a useful semiquantitative guide.

It seems probable that the systematic exploration of the structural principles suggested by the results in the communication will lead to the discovery of many new compounds.

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