Organometallics **1994**, *13*, 5141–5148

Intriguing Structures and Stabilities of C_2Li_x Species (x = 6, 8, 10, 12)

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Received July 7, 1994[⊗]

A high-level *ab initio* quantum chemical study of lithiocarbons with the formulae C_2Li_x (x = 6, 8, 10 and 12) has yielded provocative results. The structures predicted for these systems are intriguing and do not follow normal chemical rules. Each compound is predicted to contain a triply bonded C_2^{2-} unit and various cationic Li clusters which act as polydentate ligands. Little direct C - Li covalent bonding is present. Calculated vibrational frequencies show that the lowest-energy isomer for each compound is a true minimum. All species have substantial thermodynamic stability towards loss of Li_2. Binding energies have been evaluated at levels of theory up to QCISD(T)/DZ(2)P and range from 102 kJ/mol for C_2Li_{10} to 170 kJ/mol for C_2Li_6. Predicted vibrational frequencies and their IR intensities are reported.

Introduction

There have been significant recent developments in the exploration of polylithium structural chemistry. The results frequently challenge traditional patterns of thinking about "simple" AB_x compounds. Using the techniques of computational quantum chemistry, structures, stoichiometries and thermodynamic stabilities have been predicted for CLi_6 (O_h[1]), $SiLi_4$ (C_{2v}, not T_d[2]), OLi_4 (T_d[3]), and very recently for XLi_3, XLi_5 (X = F, Cl),[4] YLi_6 (Y = O, S),[4] C_2Li_4[5] and CLi_x (x = 8, 10, 12)[6] which apparently violate such standard chemical principles as the octet and VSEPR rules.[7] Experimental mass-spectral results have confirmed the gas-phase existence of CLi_6,[8] OLi_4[9] and SLi_4,[10] and provided thermodynamic stability data which generally agree well with *ab initio* predictions, but no experimental structural data are yet available.

The first three compounds listed above all contain Li atoms directly bound to the central atom, though not necessarily by a traditional two-electron bond. The remaining species are particularly interesting, as they form new classes of poly-lithium clusters which have novel structures and remarkable thermodynamic stabilities. They contain small Li clusters which behave as polydentate ligands. These clusters consist of Li_3 and Li_4 units, which can themselves act as monovalent or divalent ligands, respectively, as in FLi_3[4] or CLi_8;[6] alternatively, these Li_3 and Li_4 units can condense by vertex- and/or edge-sharing to produce larger polydentate Li_x clusters, as seen in FLi_5,[4] CLi_{10} and CLi_{12}.[6] From the variety and number of novel molecules which have been demonstrated computationally to be thermodynamically stable it is clear that we have only begun to scratch the surface of a rich new area in cluster chemistry. We now extend our previous work on lithiocarbon species[6] to dicarbon systems of the form C_2Li_x (x = 6, 8, 10 and 12).

Only one previous theoretical study has been published on C_2Li_6, in 1980 by Schleyer and co-workers.[11] Although severely limited by the hardware and software restrictions of its time, that pioneering work showed clearly that an ethane-like structure is not favourable for C_2Li_6. The lowest-energy isomer located in that work (at the SCF level of theory with a minimal STO-3G basis) possesses C_{2h} symmetry. It contains a very short C-C distance, comparable to those of traditional triple bonds, and two triangular Li_3 units. The authors suggested that the best way to represent electronically their structure was as an acetylide dianion, C_2^{2-}, sandwiched between two Li_3^+ triangular cations. However, as it was not feasible to calculate vibrational frequencies for molecules of the size of C_2Li_6 at that time, the characterisation of the various isomers studied was necessarily incomplete, and further work was clearly needed. During the course of our study of C_2Li_x systems, a thorough computational analysis of C_2Li_4 was reported by Schleyer and co-workers.[5] They found that the global minimum contains a C_2^{2-} unit which receives its charge by ionic bonding with an Li atom and an Li_3 unit (C_{2v}) similar to that seen in FLi_3.[4] We confirm that C_2Li_6 contains a C_2^{2-} unit, isoelectronic with N_2, coordinated to two triangular Li_3 cationic units; however, the lowest-energy isomer previously located[11] is not in

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[⊗] Abstract published in *Advance ACS Abstracts*, November 1, 1994.

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0276-7333/94/2313-5141$04.50/0

fact the most stable structure of C_2Li_6. We further find that C_2Li_x (x = 8, 10 and 12) systems have remarkable thermodynamic stability towards loss of Li_2. They also contain C_2^{2-} units, bonded to various types (mostly new) of poly-lithium clusters, to give unusual structures which we believe are unprecedented. The bonding patterns in these compounds are analysed, and their calculated vibrational spectra are reported, with the aim of assisting their identification in future experiments.

Computational Details

The Gaussian 92 program[12] was used for all calculations reported in this work, which were performed in Melbourne. Geometries of C_2Li_6 and C_2Li_8 were optimised at the SCF and MP2 (all-electron, or FU[13]) levels of theory from analytic first derivatives using five basis sets of increasing size, denoted 3-21G,[14] DZP, DZ(2)P, DZ(+)(2)P and TZ2P. Structural parameters are converged to better than 0.001 Å or 0.1°. 3-21G is a compact basis which is computationally very efficient; its use allows the study of many possible isomers and it gives geometrical predictions which generally differ only slightly from those obtained with more complete bases at the SCF level. However, it is less suitable for the calculation of binding energies, and it is not appropriate for correlated calculations. "DZP" is a standard notation, meaning a double-zeta basis augmented with a single set of polarisation functions on all atoms. Our DZP basis was obtained from the Huzinaga/Dunning (9s5p)/[4s2p] DZ set for C[15] and the Huzinaga/Dunning (9s)/[4s] DZ set for Li.[15] Since these compounds are rather unusual electronically, we wanted to make sure that our choice of polarisation exponents was close to optimal. Rather than adopt standard values, we varied the exponents of two Li *p* functions, and found the optimum values to be 0.12 and 0.48, subject to the constraint of a factor of four between the larger and smaller, using CLi_6 as the probe molecule at the SCF level of theory. In an analogous manner, the optimum *d*-type polarisation exponents were found to be 0.20 for Li and 0.24 for C. The five spherical-harmonic components of *d*-type functions were used throughout this work.

The *d* exponent optimised in this way for the C atoms is much smaller than values typically recommended,[16] implying that the polarisation functions are unusually diffuse. There are two reasons for this anomalous behaviour; firstly the C-Li distances are longer than the bonds normally formed by C atoms, as Li is a very large atom, and secondly the C atoms bear substantial negative net charges (see below). We were concerned that these relatively diffuse functions on C might not be suitable for a good description of the C_2^{2-} units which are a dominant structural feature of the present species (see below), especially when correlation effects are considered. We therefore developed a DZ(2)P basis which contains two sets of polarisation functions on C. It is also based on the Huzinaga/Dunning *s, p* sets described above, but polarisation exponents were chosen from MP2(FU)[13] calculations on the C_2Li_4 molecule, which contains a C_2^{2-} unit.[5] Optimum values were found to be 0.15 and 0.60 for two Li *p* functions, maintaining the factor of four constraint as before, and 0.20 for the single Li *d* function. These values are only slightly different from those earlier optimised at the SCF level for CLi_6. However, the optimum *d* exponent for C was found to be 0.65, which is much larger than the value obtained for CLi_6. For the DZ(2)P basis on C, we adopted *d* exponents of 0.3 and 1.0, to give both diffuse and compact polarisation functions. C_2Li_6 was also studied at the SCF level with two further basis sets, to check for possible inadequacies in the three bases already described. Our TZ2P basis employs the same *d* functions for Li and C as those already described for the DZ(2)P set, but contains larger triple-zeta (10)/[5] *s* and (10,6)/[5,3] *s,p* bases for Li and C, respectively, as contracted by Dunning.[17] We also employed a DZ(+)(2)P basis, (the DZ(2)P basis augmented with diffuse *s* and *p* functions on the C atoms only, whose exponents were chosen by downward extrapolation), in view of the substantial net negative charges on the C atoms (see below). Our results for C_2Li_6 indicate that these two basis enhancements were insignificant, and so the larger bases were not used for the remaining molecules in our series of lithiocarbons.

Table 1. Electronic Energies[a] of C_2Li_x Species

species, symmetry	C_2Li_6, $C_{2h}(b)$[e]	C_2Li_8, C_s	C_2Li_{10}, C_{2v}[f]	C_2Li_{12}, C_{2v}
SCF/3-21G	−119.710 29	−134.512 31	−149.315 80	−164.110 28
SCF/DZP	−120.415 81	−135.312 40	−150.211 69	−165.105 37
SCF/DZ(2)P	−120.431 43	−135.326 59	−150.225 05	−165.117 95
MP2/DZP	−120.792 88	−135.751 26	−150.696 65[d]	−165.654 79[d]
MP2/DZP[b]	−120.696 81	−135.638 87		
MP3/DZP[b]	−120.710 30	−135.655 18		
QCISD/DZP[b]	−120.724 94	−135.669 08		
QCISD(T)/DZP[b]	−120.740 82	−135.690 96		
MP2/DZ(2)P	−120.857 72	−135.815 31		
MP2/DZ(2)P[c]	−120.758 51	−135.691 23		
MP3/DZ(2)P[c]	−120.773 92	−135.710 36		
QCISD/DZ(2)P[c]	−120.785 09	−135.720 86		
QCISD(T)/DZ(2)P[c]	−120.803 27	−135.744 68		

[a] In hartrees. [b] At DZP/MP2 geometry, adopting a frozen-core approximation. [c] At DZ(2)P/MP2 geometry, adopting a frozen core-approximation. [d] At DZP/SCF geometry. [e] Has only C_2 symmetry with 3-21G and DZP basis sets. [f] Has only C_2 symmetry with 3-21G basis set.

For C_2Li_6 and C_2Li_8, final energies were obtained at the QCISD(T) (FC)[13] level with the DZ(2)P basis, adopting geometries optimised with MP2 theory and this basis. Vibrational frequency calculations using analytic second derivatives were performed for C_2Li_6 at both SCF and MP2 levels of theory, but for C_2Li_8 were practicable only at the SCF level. Geometry optimisations for C_2Li_{10} and C_2Li_{12} were performed at the SCF level using the 3-21G, DZP and DZ(2)P basis sets, and vibrational frequencies were calculated from analytical SCF second derivatives in all cases. For C_2Li_{10} and C_2Li_{12}, final calculations were performed at the [MP2(FU)/DZP//SCF/DZP] level of theory. Natural atomic orbital and natural bond orbital analyses were performed with the Gaussian 92 version of the NBO 3.1 program.[18] We do not consider that Mulliken-style population analyses[19] are very informative for compounds of the type considered in this work; the numerical values are particularly sensitive to details of the basis sets used when atoms with rather diffuse orbitals, such as Li, are involved. Absolute electronic energies are reported in Table 1, binding energies are presented in Table 2 and optimised structural parameters are displayed in Tables 3−6 for C_2Li_6, C_2Li_8, C_2Li_{10} and C_2Li_{12}, respectively.

Results and Discussion

(a) Location and Description of Energy Minima. The most stable isomer located in the previous theoretical study on C_2Li_6, which was necessarily restricted to the SCF/STO-3G level of theory,[11] has C_{2h} symmetry. It is illustrated in Figure 1 as C_{2h} *(a)*. It contains two

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Table 2. Binding Energies with Respect to Loss of Li_2^{a}

species, symmetry	C_2Li_6, $C_{2h}(b)$^{e}	C_2Li_8, C_s	C_2Li_{10}, C_{2v}^{f}	C_2Li_{12}, C_{2v}
SCF/3-21G	157.6	86.0	89.9	66.2
SCF/DZP	150.4	71.8	78.8	64.1
SCF/DZ(2)P	144.8	68.0	76.7	62.1
MP2/DZP	172.3	135.6	101.5^d	135.0^d
MP2/DZP^b	154.8	137.9		
MP3/DZP^b	155.8	135.7		
QCISD/DZP^b	152.8	122.6		
QCISD(T)/DZP^b	156.0	138.4		
MP2/DZ(2)P	170.7	133.5		
MP2/DZ(2)P^c	160.8	118.3		
MP3/DZ(2)P^c	161.9	113.9		
QCISD/DZ(2)P^e	159.6	100.7		
QCISD(T)/DZ(2)P^c	161.7	115.5		

[a] In kJ/mol. [b] At DZP/MP2 geometry, adopting a frozen-core approximation. [c] At DZ(2)P/MP2 geometry, adopting a frozen-core approximation. [d] At DZP/SCF geometry. [e] Has only C_2 symmetry with 3-21G and DZP basis sets. [f] Has only C_2 symmetry with 3-21G basis set.

Table 3. Structural Parameters for C_2Li_6^{a}

	$C_2/C_{2h}(b)$				
parameter	SCF/3-21G	SCF/DZP	SCF/DZ(2)P	MP2/DZP	MP2/DZ(2)P
C-C′	1.247	1.255	1.240	1.312	1.279
C-Li^1	4.489	4.445	4.425	4.309	4.281
C-Li^2	2.037	2.019	2.022	2.017	2.007
C-Li^3	2.314	2.222	2.132	2.168	2.130
C′-C-Li^1	120.3	118.1	117.7	114.0	114.3
C′-C-Li^2	157.2	155.7	156.3	152.3	153.0
C-C′-Li^3	68.3	69.9	76.2	71.9	73.2
Li^1-C-C′-Li$^{1'}$	140.9	152.8	180.0	160.6	180.0
Li^2-C-C′-Li$^{2'}$	183.9	182.3	180.0	176.7	180.0
Li^3-C-C′-Li$^{3'}$	129.0	147.8	180.0	154.3	180.0

[a] Distances in Å, angles in degrees. Refer to Figure 1 for atomic numbering scheme.

Table 4. Structural Parameters for C_2Li_8^{a}

	C_s				
parameter	SCF/3-21G	SCF/DZP	SCF/DZ(2)P	MP2/DZP	MP2/DZ(2)P
C^1-C^2	1.250	1.258	1.242	1.319	1.287
C^1-Li^1	2.102	2.070	2.068	2.053	2.044
C^1-Li^2	4.529	4.460	4.436	4.301	4.284
C^1-Li^3	2.103	2.080	2.074	2.066	2.054
C^1-Li^4	4.243	4.178	4.151	3.965	3.953
C^1-Li^5	2.279	2.227	2.208	2.190	2.166
C^2-Li^6	4.219	4.204	4.191	4.008	3.989
C^2-Li^7	2.030	2.010	2.012	2.008	1.998
C^2-C^1-Li^1	113.9	108.0	106.1	111.6	112.7
C^2-C^1-Li^2	148.8	143.8	142.3	149.2	150.1
C^2-C^1-Li^3	166.9	170.5	171.8	167.7	167.1
C^2-C^1-Li^4	116.6	118.2	119.4	113.2	113.1
C^2-C^1-Li^5	80.1	80.0	80.7	78.2	78.4
C^1-C^2-Li^6	110.7	111.6	111.1	102.3	102.9
C^1-C^2-Li^7	154.9	154.2	153.5	150.4	150.5
Li^5-C^1-Li^4-Li^3	132.4	133.3	133.1	131.8	131.4

[a] Distances in Å, angles in degrees. Refer to Figure 1 for atomic numbering scheme.

Table 5. Structural Parameters for C_2Li_{10}^{a}

parameter	SCF/3-21G	SCF/DZP	SCF/DZ(2)P
C^1-C^2	1.247	1.255	1.240
C^1-Li^1	2.113	2.097	2.100
C^1-Li^2	4.662	4.640	4.627
C^2-Li^3	2.252	2.217	2.207
C^2-Li^4	4.221	4.190	4.182
C^2-Li^5	2.138	2.122	2.124
C^2-C^1-Li^1	128.1	130.1	130.2
C^2-C^1-Li^2	100.7	101.8	101.8
C^1-C^2-Li^3	93.5	92.5	92.7
C^1-C^2-Li^4	143.4	142.8	142.5
C^1-C^2-Li^5	145.5	145.6	145.7

[a] Distances in Å, angles in degrees. Refer to Figure 1 for atomic numbering scheme.

Table 6. Structural Parameters for C_2Li_{12}^{a}

parameter	SCF/3-21G	SCF/DZP	SCF/DZ(2)P
C^1-C^2	1.256	1.264	1.248
C^1-Li^1	4.602	4.600	4.587
C^1-Li^2	2.205	2.220	2.220
C^1-Li^3	4.364	4.347	4.327
C^2-Li^4	2.292	2.256	2.247
C^2-Li^5	4.169	4.113	4.099
C^2-Li^6	2.057	2.044	2.042
C^2-C^1-Li^2	142.0	142.8	142.7
C^2-C^1-Li^3	95.5	96.4	96.6
C^1-C^2-Li^4	89.5	87.1	87.3
C^1-C^2-Li^5	131.8	131.0	131.5
Li^4-C^2-C^1-Li^3	32.6	32.7	32.8

[a] Distances in Å, angles in degrees. Refer to Figure 1 for atomic numbering scheme.

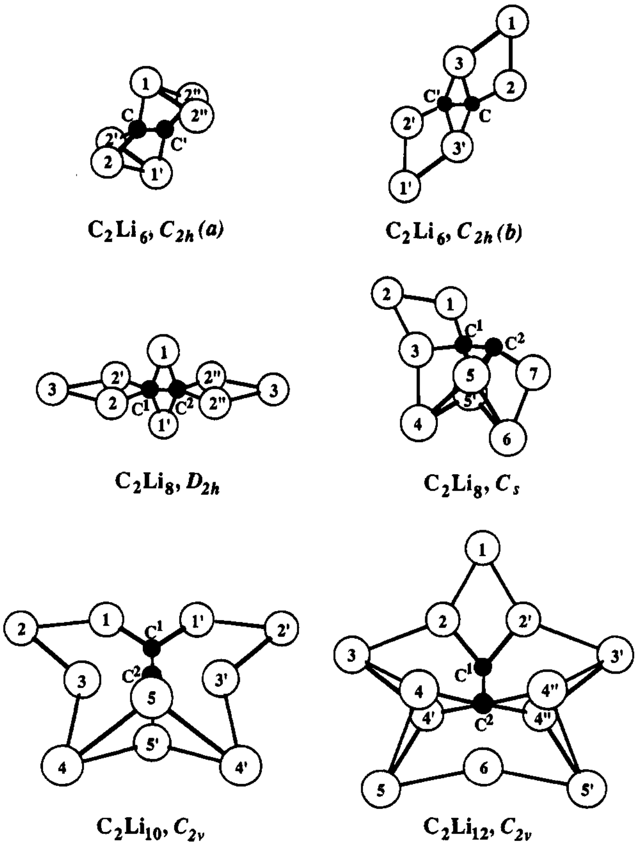


Figure 1. Scaled diagrams of C_2Li_6 (two isomers), C_2Li_8 (two isomers), C_2Li_{10} and C_2Li_{12}. Solid lines indicate the main bonding interactions (electrostatic and covalent) but do not necessarily imply a traditional two-electron bond.

Li_3 triangular units, which are perpendicular to the plane defined by the two C atoms, Li^1 and Li$^{1'}$. While this structure is a true minimum at the SCF/3-21G level, it is a transition state, with a single imaginary vibrational frequency of b_g symmetry (ω = 107i cm^{-1}), at the more complete SCF/DZP level of theory. This vibration corresponds to a rotation of the planes of the two Li_3 triangles, and leads eventually to another C_{2h} isomer, shown in Figure 1 as C_{2h} *(b)*. These are the only two stationary points that we have been able to locate for C_2Li_6 for which all vibrational frequencies are real. This second structure is planar, and the C-C distance is even shorter than in the C_{2h} *(a)* isomer considered by Schleyer and co-workers,[11] by an appreciable margin of some 0.06 Å. The triangular Li_3 units are maintained, but they coordinate to the central C_2 unit in a somewhat unexpected manner, as the Li^1-C-C′ angle is neither 90°

(symmetrical bridging), nor 180° (linear coordination), but intermediate, at close to 115°. We are reasonably confident that this isomer is the global miminum for C_2Li_6, as we have carried out very extensive searches of the potential energy surface. When using the SCF/3-21G, SCF/DZP and MP2/DZP levels of theory, this C_{2h} *(b)* structure in fact lowers its symmetry to C_2. The two Li_3 triangles twist out of the plane, as shown by the last three dihedral angles in Table 3; these differ from 180° for the geometries optimised with the 3-21G and DZP bases. As the quality of the basis is improved from 3-21G through DZP to DZ(2)P at the SCF level, the deviation from planarity decreases; similarly, as the level of theory is improved from SCF to MP2 with the DZP basis, the molecule becomes more nearly planar. We are therefore confident that the true equilibrium geometry is planar C_{2h}. At the SCF level of theory, the C_{2h} *(b)* isomer lies 164 (3-21G basis) or 189 (DZP basis) kJ/mol lower than the previously reported C_{2h} *(a)* structure. More rigorous calculations were not carried out on the C_{2h} *(a)* isomer due to its imaginary vibrational frequency at the SCF/DZP level of theory and its unfavourable energy. The "Z-matrix" which defines the geometry of the C_{2h} *(b)* isomer of C_2Li_6 is presented as part of the Supplementary Material which accompanies this issue, together with the corresponding matrices for the most stable isomers of the other polylithiated molecules studied here and the DZP basis set that we used.

For the most part, the bond lengths and angles optimised for C_2Li_6 are not sensitive to the details of the theoretical method used, as shown by the results presented in Table 3. In particular, we found that insignificant geometrical changes were produced by the addition of diffuse *s* and *p* functions to the C atom DZ2P basis; similarly, the differences between SCF/DZ(2)P and SCF/TZ2P structural parameters are so slight that it is not felt necessary to report the latter, as they are available only for C_2Li_6 and as the DZ(2)P-to-TZ2P changes are trivial compared to those induced by correlation. It is, however, worth commenting on two points which emerge from Table 3. The extra polarisation functions in the DZ(2)P basis lead to a perceptible shortening of the C-C distance, particularly when correlation effects are considered. Our suspicions that the exponent chosen for C in the DZP basis would be inadequate for the C-C interaction, which we shall show below is best regarded as a triple bond, are thus confirmed. It is also noticeable that correlation effects decrease the "long" C-Li^1 distance significantly (by about 0.14 Å at the MP2 level).

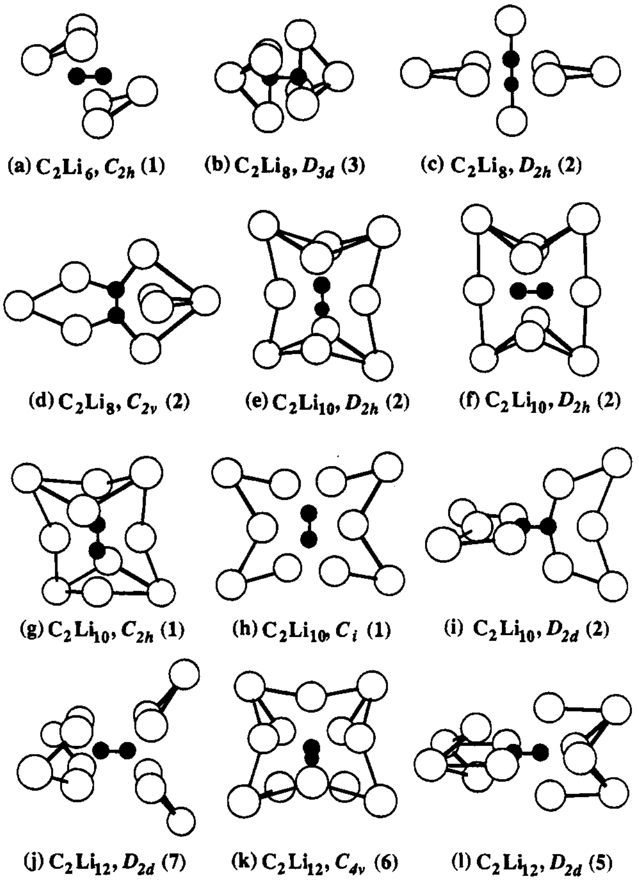
C_2Li_6 is stable relative to (C_2Li_4 + Li_2) at all levels of theory, as shown by the results in Table 2. At the SCF level, the variation in the binding energy with the size of basis is scarcely significant, though the 3-21G value is slightly larger than those obtained with larger bases. The TZ2P binding energy is just 1.6 kJ/mol greater than the DZ(2)P value, and the addition of diffuse functions to the DZ2P carbon basis changes the binding energy even less. The influence of correlation increases the binding energy considerably, by some 25–30 kJ/mol. It is noticeable that the MP2, MP3 and QCISD results obtained with the DZP basis (at MP2 geometries) differ among themselves by no more than 3 kJ/mol, and the more sophisticated QCISD(T) level of theory also changes the binding energy by only a few kJ/mol. However, the "frozen-core" approximation[13] rather surprisingly reduces the binding energy by 10–20 kJ/mol, depending on the basis used. As these variations in the binding energy with level of theory are relatively minor, we feel able to extrapolate to a "best estimate" of the electronic binding energy for C_2Li_6, relative to (C_2Li_4 + Li_2), which is 170 kJ/mol; our estimate of the uncertainty in this value, to encompass the residual limitations in our theoretical methods, is 20 kJ/mol, and we feel that this admittedly subjective estimate is reasonably conservative. Although this binding energy estimate does not include any contribution from changes in zero-point vibrational energy, such terms are not expected to be significant in this case, particularly by comparison with an uncertainty of some 20 kJ/mol. We are therefore quite confident that C_2Li_6 is a thermodynamically stable compound compared to (C_2Li_4 + Li_2), though we have not yet established its stability relative to (graphite + solid lithium), for example. C_2Li_4 has recently been predicted to have a lowest-energy structure of C_s symmetry,[5] which can be described as similar to C_{2h} *(b)* but with atoms Li^1 and Li^2 removed.

After an extensive search of many possible geometrical configurations, two isomers of C_2Li_8 were found which are true minima. Both are illustrated in Figure 1. The D_{2h} species can be described as containing a C_2 unit which is bridged by two Li atoms (Li^1 and $Li^{1'}$) and to which two Li_3 triangles are terminally coordinated. The planes of the two Li_3 triangles are both perpendicular to the C-C-Li^1-$Li^{1'}$ plane. Additional structural units can be distinguished in the more complicated, more highly condensed C_s structure: an Li_3 triangle (atoms Li^1, Li^2 and Li^3) and two linked Li_4 pyramids or distorted tetrahedra (Li^3, Li^4, Li^5 and $Li^{5'}$ form one pyramid and Li^6, Li^7, Li^5 and $Li^{5'}$ form the other). Atom Li^3 links the triangle to one of the pyramids. This C_s isomer is much more stable than the D_{2h} species (117 kJ/mol at the SCF/3-21G level of theory), so no further calculations were considered for the latter geometry. Optimised geometrical parameters for the C_2Li_8 isomers are reported in Table 4 and binding energies relative to (C_2Li_6 + Li_2) are listed in Table 2. As noted earlier for C_2Li_6, most geometrical parameters change only marginally with the level of theory, but analogous comments can be made about the importance of the contracted polarisation functions on C in the DZ(2)P basis and about the effect of correlation on the "long" C-Li distances (C^1-Li^2, C^1-Li^4 and C^2-Li^6) in the C_s isomer).

The binding energy of C_2Li_8, relative to (C_2Li_6 + Li_2), is substantial. It is affected only slightly by the size of the basis at the SCF level, though as for C_2Li_6 the 3-21G value is higher than those obtained with larger bases. However, correlation effects are much more important for C_2Li_8 than for C_2Li_6, as the binding energy is almost *doubled* when correlation is taken into account. With the benefit of hindsight (!), this correlation influence on the binding energy should not be unexpected; the most stable C_s isomer of C_2Li_8 contains additional structural features which are not found in C_2Li_6, such as the condensing of small Li units into an extended cluster and the presence of Li_4 pyramids, whereas there are no structural features in C_2Li_6 which are not also present in C_2Li_4. It is unrealistic to expect that the SCF method could describe different types of Li_x units with equal accuracy. Improving the treatment of correlation from MP2 to QCISD with the DZP basis causes the binding energy of C_2Li_8 to decrease modestly, but the inclusion of triple excitations just balances this decrease. The effect of the frozen-core approximation is irregular, being negligible with the DZP basis but as large as 15 kJ/mol with the DZ(2)P basis. C_2Li_8 is, without a doubt, a stable species compared to (C_2Li_6 + Li_2), with our best estimate of the thermodynamic stability being 130 kJ/mol (an uncertainty of 20 kJ/mol once again seems reasonable). This stability is perhaps surprising for what would initially seem an unfavourable stoichiometry, in view of the general applicability of the octet rule for first-row elements such as carbon.

For each of C_2Li_{10} and C_2Li_{12}, just one true minimum was located, despite extensive searches of the potential surface. Both structures have C_{2v} symmetry. They are sketched in Figure 1, while optimised structural parameters are given in Tables 5 and 6 for C_2Li_{10} and C_2Li_{12}, respectively. It is striking to notice the constancy of the C-C distance in these various lithiocarbons; the variation is only 0.008 from the shortest (C_2Li_6) to the longest (C_2Li_{12}) at the SCF/DZ(2)P level of theory. The structure of C_2Li_{10} is closely related to the C_s isomer of C_2Li_8; the two additional lithium atoms form a new triangle, linked to one Li_4 pyramid by vertex-sharing. The C_{2v} geometry is a true minimum when using the DZP and DZ(2)P basis sets at the SCF level, with only Li^5 and $Li^{5'}$ lying out of the molecular plane, but at the SCF/3-21G level of theory, the C_{2v} structure has one imaginary vibrational frequency which prompts the molecule to buckle slightly, producing a minimum with C_2 symmetry. Other geometrical parameters are not significantly affected by this change in symmetry. The Li_{12} unit which encapsulates C_2 in C_2Li_{12} is built up from one triangle and four pyramidal units. It was not feasible to optimise the structure of either C_2Li_{10} or C_2Li_{12} at the MP2 level of theory due to computer limitations; by analogy with the results obtained for C_2Li_6 and C_2Li_8, we may anticipate that the SCF values for the "long" C-Li distances in C_2Li_{10} (C^1-Li^2 and C^2-Li^4) are too large by about 0.15 Å.

All vibrational frequencies are real for the C_{2v} structure of C_2Li_{12} at all levels of theory used in this work. The variations in structural parameters noted as the basis is enlarged are very minor. Absolute energies are shown in Table 1, and binding energies with respect to (C_2Li_{10} + Li_2) are reported in Table 2. Correlation effects increase the binding energy of both C_2Li_{10} and C_2Li_{12}, particularly for the latter. Both species are unquestionably bound; in view of their substantial size, it was not feasible to exceed the MP2/DZP level of theory when calculating final energies for these compounds, though the results obtained for C_2Li_6 suggest that MP2/DZP results should also be reasonably reliable for the larger systems. Their binding energies are therefore determined with lower reliability than for the smaller systems discussed above, and uncertainties of perhaps at least 30 kJ/mol should be attached to the MP2/DZP values of 102 and 135 kJ/mol for C_2Li_{10} and C_2Li_{12}, respectively. These stabilities are indeed unexpected for such stoichiometries and surprisingly, C_2Li_{12} has greater resistance to dissociation than does C_2Li_{10}. There is no suggestion from these binding energies that the C_2 unit is coordinatively saturated in C_2Li_{12}, but it was beyond the scope of this work to study even higher lithiocarbons such as C_2Li_{14}.


(a) C_2Li_6, C_{2h} (1) (b) C_2Li_8, D_{3d} (3) (c) C_2Li_8, D_{2h} (2)

(d) C_2Li_8, C_{2v} (2) (e) C_2Li_{10}, D_{2h} (2) (f) C_2Li_{10}, D_{2h} (2)

(g) C_2Li_{10}, C_{2h} (1) (h) C_2Li_{10}, C_i (1) (i) C_2Li_{10}, D_{2d} (2)

(j) C_2Li_{12}, D_{2d} (7) (k) C_2Li_{12}, C_{4v} (6) (l) C_2Li_{12}, D_{2d} (5)

Figure 2. Scaled diagrams of additional stationary points, located for C_2Li_6 (one isomer), C_2Li_8 (three isomers), C_2Li_{10} (five isomers) and C_2Li_{10} (three isomers). All have at least one imaginary vibrational frequency; the number for each species is presented in parentheses. See text for details.

(b) Description of Additional Stationary Points. For all the molecules described above, further stationary points were found in addition to those described above, but all contained one or several imaginary vibrational frequencies (up to seven in one case!). We present here a brief description of these additional isomers. Only systems containing a central C_2 unit were considered, in view of the high bond energy of this species and its demonstrated importance in C_2Li_4.[5] The imaginary modes of vibration were analysed, and it was possible in most cases to show from these modes that the additional isomers would collapse to one of the minima described above. These additional isomers were studied only at the SCF/3-21G level of theory, in view of their high energy and imaginary vibrational frequencies. Although an extensive study has been undertaken on the potential energy surface of these systems, we cannot be absolutely certain that we have located the global minima for the larger molecules, due to the very large number of possible isomers and the nonapplicability of normal structural rules in these compounds.

Several isomers of C_2Li_6 have already been investigated in the earlier study by Schleyer and co-workers.[11] We have located one further stationary point, of C_{2h} symmetry, sketched in Figure 2 (a). It may be derived from the structure preferred by Schleyer and co-workers

(*C_{2h} (a)* in Figure 1) by a rotation of one Li_3 triangle about its approximate three-fold axis. This additional stationary point has one imaginary frequency (b_g symmetry, 85i cm^{-1}) and lies 167 kJ/mol above the C_{2h} (b) isomer in Figure 1 which we believe to be the global minimum for C_2Li_6.

Three further isomers of C_2Li_8 are sketched in Figure 2 as (b), (c) and (d). Isomer (b) has D_{3d} symmetry, and contains two Li_4 pyramids which are coordinated to the central C_2 unit in a staggered fashion. This species has three imaginary vibrational frequencies and lies 427 kJ/mol above the C_s global minimum shown in Figure 1. Stationary point (c) has D_{2h} symmetry. It is closely related to the D_{2h} minimum shown in Figure 1, but the central C_2 unit has been rotated by 90°, so that Li^1 and $Li^{1'}$ which were bridging atoms have become terminally coordinated. It has two imaginary vibrational frequencies (b_{3u} 111i, b_{1g} 25i cm^{-1}) and lies 138 kJ/mol above the C_s minimum, or 21 kJ/mol above the D_{2h} minimum in Figure 1. The final stationary point (d) located for C_2Li_8 has C_{2v} symmetry; it contains a familiar Li_3 triangle and a five-membered roughly square-pyramidal Li_5 moiety, a unit which has not yet been characterized in any polylithium cluster, so far as we are aware. This isomer lies 88 kJ/mol above the global minimum and has two imaginary vibrational frequencies.

Five additional isomers of C_2Li_{10} are shown in Figure 2 as (e), (f), (g) (h) and (i). Both (e) and (f) have D_{2h} symmetry, and contain four Li_4 pyramids which are linked to their neighbours by vertex- or edge-sharing to form a highly condensed Li_{10} group. In (e), the central C_2 unit lies in the plane which contains the four approximate three-fold axes of the pyramids, whereas in (f) the C_2 group is perpendicular to that plane. Isomers (e) and (f) lie 59 or 35 kJ/mol, respectively, above the true minimum structure for C_2Li_{10} which is shown in Figure 1; both have two imaginary vibrational frequencies. Isomer (g) also contains four condensed Li_4 pyramids; it is related to (e) by a cooperative motion of those groups, so that their local three-fold axes no longer lie in a plane, lowering the symmetry to C_{2h}. It lies 35 kJ/mol above the minimum-energy isomer, and has just one imaginary vibrational frequency. Isomer (h) is built on two Li_5 units, which themselves can be regarded as two condensed Li_3 triangles; similar structural units have already been reported in FLi_5, $ClLi_5$ and SLi_{10}.[4] In this case, the Li_5 groups are puckered rather than planar; to give C_i symmetry. This isomer lies 29 kJ/mol above the most stable form of C_2Li_{10}, and has a single imaginary vibrational frequency. The final isomer of C_2Li_{10}, (i), is related to (h) in that it also contains two Li_5 units, but these are now arranged in perpendicular planes, giving D_{2d} symmetry overall. This is effectively the same structure as that predicted recently for SLi_{10}.[4] Isomer (i) lies just 17 kJ/mol above the C_{2v} minimum-energy structure, but has two imaginary vibrational frequencies.

Three unstable isomers of C_2Li_{12} are shown in Figure 2 as (j), (k) and (l). Isomer (j), with D_{2d} symmetry, lies 283 kJ/mol above the most stable structure. It is remarkable in that it has no fewer than seven imaginary vibrational frequencies! Isomer (k) has C_{4v} symmetry, and, with its four Li_4 pyramids linked by vertex-or edge-sharing, closely resembles the structure recently predicted for CLi_{12};[6] the central C_2 unit lies along the four-fold symmetry axis. Despite its pleasing high symmetry, isomer (k) has six imaginary vibrational frequencies, and is 138 kJ/mol less stable than the minimum-energy structure. Finally, isomer (l) contains four Li_4 pyramids linked in two groups by edge-sharing; these two groups are arranged in perpendicular planes, rather than all in the same plane as for (k), to give D_{2d} symmetry overall. Five imaginary vibrational frequencies remain for (l), which is 114 kJ/mol above the global minimum for C_2Li_{12}.

(c) Electronic Structures. Analysis of the bonding in these molecules reveals features which are similar to those found in other recent studies of poly-lithiated species.[4-6] From the structural point of view, the short C-C distances in all of the C_2Li_x compounds imply the presence of triple bonds. The C-C distances optimised for the polylithium cluster compounds discussed in this work are remarkably similar to those predicted for free C_2^{2-} (1.273/1.250 Å at the SCF level with the DZP/DZ2P bases, or 1.300/1.273 Å at the MP2 level of theory); these values vary by no more than 0.018 Å from their analogues in C_2Li_6 (see Table 3). These distances are appreciably longer than those found for "normal" C-C triple bonds, as in C_2H_2 (1.2024 Å),[21] presumably due to the considerable Coulombic repulsion between the negatively charged C atoms. Similar effects have been noted for the linear isomer of C_2Li_2.[20]

Some of the C - Li distances in our C_2Li_x compounds are so large (over 4.0 Å) that significant direct C - Li orbital overlap seems impossible; Li - Li bonded interactions must therefore be present. Very many clusters are of course already known containing only lithium atoms; the bonding interactions found in such systems have recently been reviewed.[22] Atom Li^3 in C_2Li_6 is roughly equidistant from atoms C and C′ (MP2/DZ(2)P distances are 2.13 and 2.29 Å, respectively), and is thus in a similar position to the lithium atoms in dilithioacetylene, which has a dibridged D_{2h} structure.[20] However, from the structural point of view the Li_3 triangles are in fact the dominant units in C_2Li_6. The Li-Li distances predicted here for C_2Li_6 (MP2/DZ(2)P values are Li^1-Li^2 2.99 Å, Li^1-Li^3 2.96 Å and Li^2-Li^3 2.78 Å) are similar to those recently reported at the MP2/DZP level for FLi_3 (Li^1-Li^2 3.05 Å) or OLi_6 (Li^1-Li^2 3.18 Å),[4] and in triangular Li_3^+ (D_{3h} symmetry, bond length 2.99 Å at the MP2 level with our DZP basis). The importance of the triangular unit in polylithium chemistry has also been emphasized by work from Schleyer's group.[5,11]

Geometrical considerations therefore imply that C_2Li_6 can be described, to a reasonable approximation, as containing C_2^{2-} and Li_3^+ units, with relatively little covalent C-Li bonding, as already suggested by Schleyer and co-workers.[11] These initial ideas are verified by examination of the molecular orbitals (MO's) in C_2Li_6 (*C_{2h} (b)*), of which fifteen are occupied. The lowest eight are, unsurprisingly, all 1*s*-like core orbitals, while the next five are essentially made up only of carbon contributions. MO's fourteen and fifteen are primarily ($2s_{Li}1$ + $2s_{Li}1'$) and ($2s_{Li}1$ - $2s_{Li}1'$), respectively; they are almost degenerate, since the large separation of over 9 Å between Li^1 and $Li^{1'}$ leads to very poor overlap. A contour diagram of MO 14, presented in Figure 3,

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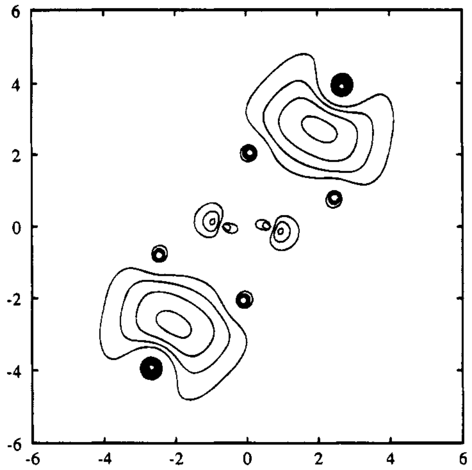

Figure 3. Contour plot, from an SCF/DZ2(P) calculation, showing the electron density corresponding to the 14th occupied MO of C_2Li_6, isomer C_{2h} *(b)*. Orientation of atoms is the same as seen in Figure 1 with the section taken through the plane in which all nuclei lie. Lengths are in angstroms and contours extend from 0.0015 to 0.06 $Å^{-3}$ with intervals of 0.0015 $Å^{-3}$.

clearly shows the delocalized nature of the bonding. As there are thirty nine separate contours in Figure 3, it is clear that atoms Li^1 and $Li^{1'}$ make much greater contributions to that MO than do Li^2 and Li^3. MO 15 is very similar to 14, apart from the change in phase already noted.

Natural charges at the SCF/DZ(2)P level for atoms C, Li^1, Li^2, and Li^3 are −0.92, −0.33, 0.63, and 0.62*e*, respectively. A natural bond orbital (NBO) analysis[18] reveals that each carbon atom can be described as *sp* hybridized, to give a C-C triple bond and a lone pair pointing away from the other C atom. The only other occupied bonding orbitals are two equivalent 3-centre bonds, one involving atoms Li^1, Li^2, and Li^3, and the other their primed counterparts. Both are primarily made up of 2*s* atomic orbitals, with atoms Li^1 and $Li^{1'}$ being the major contributors, as shown in Figure 3. This electronic analysis has therefore confirmed that C_2Li_6 is best described as a C_2^{2-} unit interacting with two Li_3^+ clusters. Little covalent C - Li bonding is present, and it is now generally agreed that C - Li bonding interactions are predominantly ionic in nature.[23-25]

Similar principles can be used to understand the bonding in C_2Li_8. Small Li_x moieties have the ability to condense by vertex and edge-sharing to produce larger polydentate Li_x clusters.[4,6] The C_2Li_8 species also contains a triply bonded C_2^{2-} ion which receives its charge from an Li_8 cluster, itself built up from smaller Li_x units. Natural atomic charges for C^1 and C^2 are −1.15 and −0.80*e*, respectively. Natural charges for the "outer" atoms Li^2, Li^4 and Li^6 are −0.26, −0.23, and −0.24*e*, respectively, while the remaining "inner" Li atoms all have charges of between 0.4 and 0.6. The Li_8 ligand consists of an Li_3 unit joined by vertex-sharing to an Li_4 pyramid (also seen in CLi_8 [6]) which is itself connected by a common edge to another Li_4 unit. Li-Li distances in C_2Li_8 at the MP2/DZ(2)P level are Li^1-Li^2 2.95 Å, Li^2-Li^3 3.13 Å, Li^3-Li^4 3.24 Å, Li^4-Li^5 3.39 Å and Li^5-Li^6 3.20 Å. These are similar to those already noted above for the triangular units in C_2Li_6 or to the distance of 3.39 Å reported for CLi_8 (D_{3d} symmetry),[6] confirming the identification of individual triangular and pyramidal Li subclusters in C_2Li_8. NBO analysis again suggests each carbon in C_2Li_8 to be *sp* hybridized with a lone pair, and provides 3-centre bonding orbitals to explain the substantial Li - Li interactions, of which some are partially occupied. Partial occupancies arise because the NBO analysis as implemented in Gaussian 92[18] does not consider the possibility that more than three centres might be involved in any bonding orbital, whereas the highly delocalized nature of the bonding within a lithium cluster may have electrons spread over more than this number of atoms.

Table 7. Vibrational Wavenumbers[a] and Infrared Intensities[b] (in Parentheses) for C_2Li_6 ($C_{2h}(b)$)

symmetry	SCF/DZ(2)P	MP2/DZ(2)P	symmetry	SCF/DZ(2)P	MP2/DZ(2)P
a_g	2106 (0)	1819 (0)	b_u	223 (91)	242 (86)
b_u	587 (578)	585 (493)	b_g	257 (0)	242 (0)
a_g	509 (0)	504 (0)	a_g	197 (0)	208 (0)
b_u	488 (136)	488 (119)	a_u	186 (78)	179 (67)
a_g	414 (0)	422 (0)	a_g	163 (0)	175 (0)
a_g	375 (0)	364 (0)	b_g	122 (0)	122 (0)
b_u	305 (270)	329 (155)	b_u	70 (8)	76 (3)
a_g	301 (0)	320 (0)	a_u	57 (1)	62 (0)
b_u	245 (1)	256 (13)	a_u	8 (0)	16 (0)

[a] In cm^{-1}. [b] In km/mol.

Table 8. Vibrational Wavenumbers[a] and Infrared Intensities[b] (in Parentheses) for C_2Li_8 (C_s)

symmetry	SCF/DZ(2)P	symmetry	SCF/DZ(2)P	symmetry	SCF/DZ(2)P
a′	2086 (52)	a′	280 (122)	a″	155 (6)
a′	556 (238)	a′	269 (5)	a′	136 (23)
a′	508 (150)	a″	259 (4)	a″	135 (13)
a′	461 (1)	a′	241 (90)	a″	109 (6)
a′	403 (8)	a′	225 (49)	a′	92 (4)
a″	348 (7)	a″	211 (23)	a′	63 (0)
a′	321 (54)	a′	209 (87)	a″	63 (2)
a′	297 (149)	a′	161 (96)	a″	29 (0)

[a] In cm^{-1}. [b] In km/mol.

As for the smaller C_2Li_x systems, C_2Li_{10} and C_2Li_{12} also contain C_2^{2-} units, but now with relatively large Li_x clusters assembled from smaller subunits. Charges for the "outer" Li atoms are again negative, and the "inner" ones positive. The Li_{10} unit in C_2Li_{10} is built up from consecutively connected Li_3, Li_4, Li_4, and Li_3 units. In C_2Li_{12}, the Li_{12} ligand is formed from an Li_3 unit and four Li_4 pyramids which are joined in a cyclical fashion. The identification of these subunits is confirmed by representative Li-Li distances in C_2Li_{12}, which are similar to those noted above for other lithiocarbons; Li^1-Li^2 3.13 Å, Li^2-Li^3 3.21 Å, Li^3-Li^4 3.16 Å, Li^4-Li^5 3.29 Å and Li^5-Li^6 3.14 Å. Comparable distances are also found in C_2Li_{10}.

(d) Comments on Experimental Detection. Calculated vibrational wavenumbers and IR intensities for C_2Li_6, C_2Li_8, C_2Li_{10} and C_2Li_{12} are presented in Tables 7−10, respectively. For each molecule there is a single high-frequency mode at slightly over 2000 cm^{-1} (SCF results), with a progressively larger number of bands predicted below 600 cm^{-1} as the number of lithium atoms increases. For most of the molecules the high-frequency band is expected to have rather low IR intensity, but several quite intense bands are predicted in the 400−600 cm^{-1} region. There is a rule-of-thumb

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Table 9. Vibrational Wavenumbers[a] and Infrared Intensities[b] (in Parentheses) for C_2Li_{10}

symmetry	SCF/DZ(2)P	symmetry	SCF/DZ(2)P	symmetry	SCF/DZ(2)P
a_1	2089 (9)	b_2	285 (107)	b_1	140 (21)
b_2	462 (285)	b_2	262 (21)	a_2	138 (0)
a_1	460 (34)	b_2	243 (52)	a_1	104 (4)
b_2	432 (158)	a_1	243 (63)	b_2	99 (4)
a_1	431 (43)	a_1	233 (1)	a_1	86 (0)
b_1	366 (3)	b_1	220 (11)	a_2	85 (0)
a_1	350 (20)	a_2	209 (0)	b_1	60 (1)
a_1	337 (10)	b_1	202 (0)	a_2	28 (0)
b_2	322 (21)	a_1	181 (21)	b_1	24 (0)
a_1	302 (173)	b_2	172 (5)	b_2	23 (12)

[a] In cm^{-1}. [b] In km/mol.

Table 10. Vibrational Wavenumbers[a] and Infrared Intensities[b] (in Parentheses) for C_2Li_{12}

symmetry	SCF/DZ(2)P	symmetry	SCF/DZ(2)P	symmetry	SCF/DZ(2)P
a_1	2019 (19)	a_2	261 (0)	a_2	159 (0)
a_1	482 (13)	b_1	261 (3)	b_2	139 (7)
b_2	469 (359)	b_2	244 (12)	b_1	137 (0)
a_1	403 (7)	a_1	243 (6)	a_1	113 (2)
a_1	378 (10)	b_1	237 (0)	a_2	109 (0)
b_2	362 (197)	a_1	232 (152)	b_2	107 (0)
a_1	332 (200)	b_2	209 (64)	a_1	100 (1)
b_1	312 (2)	a_1	200 (2)	b_1	98 (3)
a_1	304 (0)	a_1	190 (38)	b_2	85 (4)
b_2	299 (57)	b_2	183 (8)	a_2	55 (0)
b_2	292 (0)	b_1	181 (41)	b_1	46 (0)
b_2	273 (23)	a_2	175 (0)	b_1	41 (6)

[a] In cm^{-1}. [b] In km/mol.

that frequencies obtained at the SCF level of theory are likely to be about 10% too high,[26] with smaller systematic errors of about 5% expected for MP2 results, but the present compounds are sufficiently different electronically from those for which the rules were established that those estimates should not be adopted without thought. For C_2Li_6 we have both SCF and MP2 vibrational data; the highest-frequency mode, which corresponds essentially to the stretching of the central C-C triple bond, is decreased by nearly 15% by MP2-level correlation effects, but the other modes are much less affected, and some of them are actually higher at the MP2 than SCF level of theory. Given the similarity in C-C distances in the isolated C_2^{2-} ion and C_2Li_6, to which we have already drawn attention, it is not surprising that the vibrational frequency calculated for isolated C_2^{2-} (1857 cm^{-1} at the MP2/DZ2P level of theory) is close to the highest-frequency mode for C_2Li_6. In view of the small SCF/MP2 differences noted for most of the vibrational frequencies of C_2Li_6, the SCF results for the larger C_2Li_x systems in Tables 8–10 are likely to be relatively reliable, with the single exception of the highest-frequency mode, which is probably overestimated by rather more than 12% in each case. Unsurprisingly, these species are quite floppy (several very low-frequency modes, such as only 16 cm^{-1} for C_2Li_6) and it is quite possible that there are transition states which are not much higher in energy. If so, then these systems may be considered non-rigid, as constant structural reorganization is almost certain to occur at higher temperatures.

Experimental detection of the C_2Li_x compounds described here should be possible in view of their high thermodynamic stabilities. Mass spectrometry seems the most promising technique and it has already been used to confirm the gas-phase existence of other hyperlithiated species such as CLi_6[8] and OLi_4.[9] CLi_6 can be detected in the vapour above heated C_2Li_2,[8] despite the unfavourable stoichiometry, so investigation of the vapour above a heated mixture of C_2Li_2 and Li should yield worthwhile data. Characterisation by matrix-isolation IR spectroscopy seems possible for C_2Li_6 but definitive identification would naturally be difficult in view of the relatively large number of bands expected, and the possibility of simultaneous formation of several different C_2Li_x species, whose spectra will overlap considerably. Positive identification by IR spectroscopy of the higher lithiocarbon systems considered in this work would be difficult.

Summary

We have reported a high-level theoretical study which indicates intriguing structures and stabilities for a series of novel polylithiated molecules of general formula C_2Li_x, where x can be 6, 8, 10 or 12. Our computational methods are sufficiently sophisticated to give quantitatively reliable results for molecular structures and reasonably reliable binding energies. These compounds contain C_2^{2-} units coordinated by a variety of cationic lithium clusters. The unprecedented structures and stabilities of the species described here illustrate the limits of our current understanding of lithium chemistry, as it would not have been possible to predict the most stable structure for individual species, nor indeed which C_2Li_x molecules might be thermodynamically stable relative to elimination of Li_2, in the absence of our calculated data. The discovery of many new compounds seems possible once the principles suggested in this report are fully developed.

Acknowledgment. We thank the University of Melbourne and Cray Research (Australia) for generous access to supercomputing facilities, and the Australian Research Council for support. Joseph Ivanic thanks Saint Hilda's College, University of Melbourne for the award of a Pam Todd Research Scholarship which has provided financial assistance.

Supplementary Material Available: Listings of the Z matrices for the polylithiated molecules and of the DZP basis set (3 pages). Ordering information is given on any current masthead page.

OM940528A

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