# A Theoretical Model of Bonding in Hyperlithiated Carbon Compounds[†]

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**Abstract:** Analysis of SCF wave functions for a series of hyperlithiated carbon species $CLi_n{}^q$ ($n = 4, 5, 6$; $q = 0, \pm 1, \pm 2$) by the method of "natural population analysis" suggests a significantly higher degree of ionic character than does the Mulliken analysis. In all these species, the carbon atom appears to achieve nearly a complete octet, which is stabilized by back-transfer into the enveloping cage of empty Li orbitals. Consideration of the octet rule and the energy level pattern for the enveloping cage suggests that complexes $XLi_n{}^q$ with $Z + n - q = 12$ ($Z$ is the atomic number of the central atom) should evince special stability.

Recent computational studies[1-3] have suggested that $CLi_5$, $CLi_6$, and other "hyperlithiated" carbon species are remarkably stable and adopt symmetric structures quite unlike those of covalent carbon compounds. These species have led to the suggestion that carbon and other first-row atoms may sometimes "violate the octet rule"[4,5] and provoked discussion as to whether or how such species might be reconciled with conventional valence principles.

Theoretical analyses of ab initio wave functions of hyperlithiated compounds have generally been based on the Mulliken population analysis.[6] This method has been criticized for giving an unrealistic picture of charge distribution, particularly in organolithium compounds.[7] In addition, Mulliken populations often exhibit a disturbing sensitivity to basis set changes which renders their interpretive value problematic.[8]

We have recently proposed an alternative method,[9] the "natural population analysis", which obviates a number of these difficulties and seems to give stable, realistic measures of electron distributions even in extreme ionic compounds. The natural populations are simply the occupancies of "natural atomic orbitals" (NAOs),[9] chosen (by analogy with conventional "natural orbitals",[10] which are the delocalized molecular orbitals of maximum occupancy) to be the orthonormal 1-center orbitals of maximum occupancy. The NAOs and their populations, as defined by this optimal characteristic, are therefore intrinsic to the wave function. They are found to converge to unique limits as the basis set is expanded and are expected to give an intrinsic picture of atomic charge distributions. We have applied the method of natural population analysis to wave functions for a number of hyperlithiated compounds $CLi_n{}^q$ ($n = 4, 5, 6$; $q = 0, \pm 1, \pm 2$) in order to investigate whether this alternative measure of electron distribution could shed additional light on the bonding in these novel compounds.

We calculated RHF-SCF wave functions for the species $CLi_5{}^+$, $CLi_5$, $CLi_5{}^-$, $CLi_6{}^{2+}$, and $CLi_6$, as well as for the "normal" species $CLi_4$ and $CLi_4{}^{2-}$, using the MELD computer programs[11] as modified by one of the authors for the Harris/7. The geometries used for the neutral species were those that were previously found to be optimal at the 3-21G basis set level by Schleyer and coworkers,[1,2] (see Table I) and the neutral geometries were then employed for the cations and anions. The basis chosen was the split valence double-$\zeta$ contracted Gaussian basis set of Dunning and Hay (DH).[12] Although the DH set is formally of the same size as the Pople 3-21G set, it includes a larger number of Gaussians per orbital (particularly, a highly contracted core orbital) and is not restricted to equal exponents for s and p functions of the same shell. Our calculated total energies (Table I) were generally 0.4–0.5 au (ca. 300 kcal/mol) lower than previous 3-21G results, and this improvement is expected to significantly reduce the superposition error associated with earlier 3-21G studies.

Mulliken populations for the DH basis are generally in line with corresponding 3-21G values reported previously (see Table I),

though tending to suggest somewhat higher ionic character (as is generally observed when the basis set is improved). The Mulliken populations suggest a net charge of −0.8 to −1.3 on carbon in all these compounds, except $CLi_6{}^{2+}$, where carbon is made to be 0.25 e more negative than in $CLi_6$. These values are in turn about 1 e more negative than STO-3G Mulliken charges, which seem to make the carbon atom nearly electroneutral.[2]

Natural populations for these species give a strikingly different picture of the charge distribution (see Table I). The net natural charge on carbon is about −3.4, −3.1, and −3.1 for the hexa-, penta, and tetralithiated species, respectively. Each C–Li bond is therefore of high ionic character, in agreement with the results of Streitwieser et al.[7] concerning $CH_3Li$ and related organolithium compounds.[13] From the large values of the natural charges, it

(1) (a) Schleyer, P. v. R.; Würthwein, E. U.; Kaufmann, E.; Clark, T.; Pople, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 5930–5932. (b) Schleyer, P. v. R. In "New Horizons of Quantum Chemistry"; Löwdin, P.-O., Pullman, B., Eds.; D. Reidel Publishing Co.; New York, 1983; pp 95–109. (c) Würthwein, E.-U.; Schleyer, P. v. R.; Pople, J. A. *J. Am. Chem. Soc.* **1984**, *106*, 6973–6978.

(2) Jemmis, E. D.; Chandrasekhar, J.; Würthwein, E.-U.; Schleyer, P. v. R.; Chinn, J. W., Jr.; Landro, J. J.; Lagow, R. J.; Luke, B.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 4275–4276.

(3) Schleyer, P. v. R.; Tidor, B.; Jemmis, E. D.; Chandrasekhar, J.; Würthwein, E.-U.; Kos, A. J.; Luke, B. T.; Pople, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 484–488.

(4) Schleyer, P. v. R.; Würthwein, E.-U.; Pople, J. A. *J. Am. Chem. Soc.* **1982**, *104*, 5839–5841.

(5) Maugh, T. H. *Science* **1983**, *221*, 403. See also letters by Arduengo, Schleyer, and Martin [Arduengo, A. J.; Schleyer, P. v. R.; Martin, J. C. *Chem. Eng. News* **1984**, Nov. 28, 3; May 28, 4].

(6) (a) Mulliken, R. B. *J. Chem. Phys.* **1955**, *23*, 1833–1840, 1841–1846, 2338–2342, 2343–2346. (b) Mention may also be made of a previous analysis of $CLi_6$ [Gopinathan, M. S.; Jug, K. *Theor. Chim. Acta* **1983**, *63*, 511–527]. We consider the semiempirical wave functions employed in that study to be inadequate for organolithium compounds. Their finding that a valency index for carbon in $CLi_6$ is "only 3.88" is of no significance, since the value could not exceed 4.00 by the method they employed. We have computed the Gopinathan-Jug valency index for carbon for the $CLi_6$ wave function of the present paper in the NAO basis, finding it to be only 1.06, which reflects the ionic character of $CLi_6$.

(7) Streitwieser, A., Jr.; Williams, J. E., Jr.; Alexandratos, S.; McKelvey, J. M. *J. Am. Chem. Soc.* **1976**, *98*, 4778–4783. Collins, J. B.; Streitwieser, A., Jr. *J. Comput. Chem.* **1980**, *1*, 81–87.

(8) See, e.g.: Lüthi, H. P.; Ammeter, J. H.; Almlöf, J.; Faegri, K., Jr. *J. Chem. Phys.* **1982**, *77*, 2002–2009.

(9) (a) Reed, A. E.; Weinhold, F. *J. Chem. Phys.* **1983**, *78*, 4066–4073. (b) Reed, A. E.; Weinstock, R. B.; Weinhold, F. *J. Chem. Phys.*, to be published.

(10) Löwdin, P.-O. *Phys. Rev.* **1955**, *97*, 1474–1489.

(11) The MELD system of programs, developed by E. R. Davidson and co-workers at the University of Washington, Seattle, was kindly made available to us by Professor Davidson.

(12) Dunning, T. H.; Hay, P. J. In "Methods of Electronic Structure Theory"; Schaefer, H. F.; Ed.; Plenum Press: New York, 1977; pp 1–27.

**Table I.** SCF Total Energies and Carbon Populations for Some Lithiated Carbon Species $CLi_n^q$, as Calculated with 3-21G and Dunning–Hay (DH) Split Valence Basis Sets (See Text)[h]

| species | symmetry | C–Li bond length (Å) | calcd total energy (au) 3-21G[a,b] | DH[c] | Mulliken population on C 3-21G[a,b] | DH[c] | natural population on C DH[c] |
|---|---|---|---|---|---|---|---|
| $CLi_4$ | $T_d$ | 1.929 | −67.13154 | −67.520562 | 6.81 | 7.09 | 9.13 |
| $CLi_4^{2-}$ | $T_d$ | 1.929 | | −67.396262 | | 7.05 | 8.97 |
| $CLi_5$ | $D_{3h}$ | $2.087_a$ $2.056_e$ | −74.59934 | −75.001260 | 6.81 | 7.18 | 9.08 |
| $CLi_5^-$ | $D_{3h}$ | $2.087_a$ $2.056_e$ | | −75.000853 | | 7.14 | 9.19 |
| $CLi_5^+$ | $D_{3h}$ | $2.087_a$ $2.056_e$ | −74.45440[d] | −74.885704 | $(6.02)^e$ | 7.26 | 9.19 |
| $CLi_6$ | $O_h$ | 2.058 | −82.00344 | −82.483723 | 6.93 | 7.28 | 9.44 |
| $CLi_6^{2+}$ | $O_h$ | 2.094 | −81.63028[f] | −82.104959 | $(6.05)^g$ | 7.53 | 9.34 |

[a] See ref 2. [b] See ref 1. [c] Present work. [d] 3-21G optimized geometry $(2.022_a, 1.999_e)$. [e] STO-3G basis set and geometry $(1.979_a, 1.953_e)$. [f] 3-21G optimized geometry (2.094). [g] STO-3G basis set and geometry (2.063). [h] Note that the charge on carbon is assessed as being much more negative in the natural population analysis than in the Mulliken population analysis.

**Table II.** Analytic Expressions for Ground-State Eigenvalues of Hückel-Type Matrices for Some $n$-Orbital Cages of High Symmetry[a]

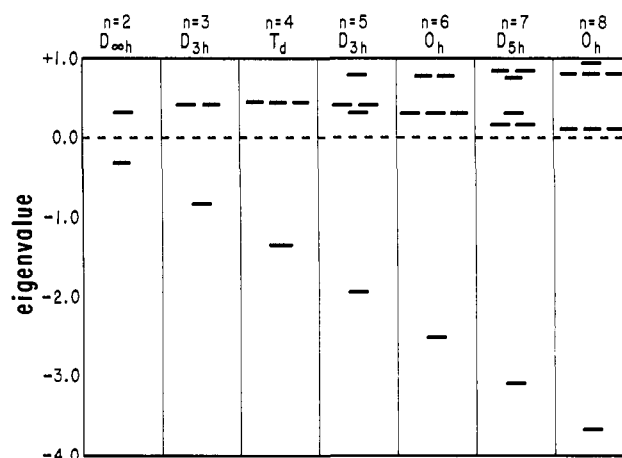| $n$ | symmetry | lowest eigenvalue |
|---|---|---|
| 2 | $D_{\infty h}$ | $-S_{180}$ |
| 3 | $D_{3h}$ | $-2S_{120}$ |
| 4 | $T_d$ | $-3S_{109.47}$ |
| 5 | $D_{3h}$ | $-^1/_2(S_{180} + 2S_{120})\ [1 + \{1 - 8(S_{180}S_{120} - 3S_{90}^2)/(S_{180} + 2S_{120})^2\}^{1/2}]$ |
| 6 | $O_h$ | $-(S_{180} + 4S_{90})$ |
| 8 | $O_h$ | $-(3S_{70.53} + 3S_{109.47} + S_{180})$ |

[a] Cf. ref 14, Figure 1. Each eigenvalue is expressed in terms of overlap integrals $S_\theta$ between orbitals separated by angle $\theta$ (as measured from the cage center). For Li 2s STOs at 2.0 Å from the cage center, the overlap integrals used to construct Hückel matrices for various $n$ were $S_{60} = 0.7368$, $S_{63.43} = 0.7141$, $S_{70.53} = 0.6676$, $S_{72} = 0.6581$, $S_{90} = 0.5496$, $S_{109.47} = 0.4543$, $S_{116.57} = 0.4261$, $S_{120} = 0.4136$, $S_{144} = 0.3487$, $S_{180} = 0.3143$.

is difficult to avoid the inference that the carbon atom is in the (−IV) oxidation state in these hyperlithiated compounds.

A simple model of the bonding in $CLi_n^q$ species is thereby suggested. Consider a central carbon atom surrounded by $n$ electropositive lithium atoms in some near-spherical arrangement. The carbon atom requires four electrons to complete its valence octet, thereby achieving the Ne-like configuration of the (−IV) oxidation state. Such a large formal charge can be stabilized by strong donor-acceptor interactions from the filled Ne-like C(−IV) core to the enveloping "cage" of unfilled Li 2s orbitals. It is significant that donor–acceptor orbital interactions are in general not limited by the Pauli principle as to the number of interactions in which a given donor (filled) or acceptor (unfilled) orbital may participate. For example, a single donor 2s orbital on carbon could "back-donate" to as many empty Li 2s orbitals as could favorably overlap the spherically symmetric charge distribution. The preferred geometries for such donor–acceptor stabilized species will therefore be the highly symmetric arrangements characteristic of close packing about a central spherical ionic core, and the number of "bonds" is limited only by the geometrical constraints of core and ligand radii.

A second stabilization mechanism is available to an electron-rich core surrounded by a cage of empty (or partially filled) 2s orbitals. In highly packed spherical cages of $n$ ligands, the empty 2s orbitals of different ligands will overlap significantly. A simple Hückel



**Figure 1.** Eigenvalues of Hückel-type matrices $H = 1 - S$ for a cage of lithium 2s orbitals surrounding a central core, $n = 2-8$. Each Li is 2.0 Å from the cage center, with symmetries as indicated.

treatment (Figure 1) indicates[14] that any such near-spherical array of 2–8 Li 2s orbitals will have exactly *one* low-lying "cage orbital" of net bonding type, the all-in-phase linear combination of ligand 2s orbitals.[15] All other cage orbitals are antibonding.[16] The spherical cage of $n$ Li^{+} ligands will therefore be most stabilized if exactly *two* electrons remain (after the core octet has been formed) to fill this deep bonding cage MO. Some stabilization remains if only one electron is available to occupy this orbital, but other numbers of electrons would result in progressive destabilization of the cage through occupation of antibonding cage orbitals.

According to this picture, unusual stability of the donor-acceptor cage complex is associated with 10 valence electrons, viz.,

(13) Regarding the ionicity of $CH_3Li$, we note from ref 9b that, with the 4-31G basis set, the natural charge on Li and the charge computed in ref 7 by a density integration method are nearly identical at +0.79. By contrast, the Mulliken analysis gives a charge of +0.45 on Li, making $CH_3Li$ only as ionic as $CH_3F$, in which (in the same basis set) the Mulliken charge on F is −0.46. For further discussion of C–Li bond ionicity and of the role of lithium p orbitals, see: Clark, T.; Rohde, C.; Schleyer, P. v. R. *Organometallics* **1983**, 2, 1344–1351.

(14) for an n-orbital Li cage, the n × n Hückel-type Hamiltonian $\tilde{H}$ with elements

$$(\tilde{H})_{ij} = \begin{cases} \alpha, & i=j \\ -\beta S_{ij}, & i \neq j \end{cases}$$

was reduced to dimensionless form, $H = (\tilde{H} - \alpha1)/\beta = 1 - S$, and diagonalized for $n = 2, 3, ..., 8$ Li 2s Slater type orbitals in arrangements of high symmetry, with each 2s orbital located 2.0 Å from the cage center. Numerical eigenvalues of this model Hamiltonian for each $n$ are depicted in Figure 1. Calculated elements of the overlap matrix $S$ and analytic expressions for the lowest eigenvalue of high-symmetry cages are given in Table II.
(15) Schleyer and co-workers[1,4] have previously noted the importance of such an orbital (labeled $4a_{1g}$ in their calculations on $CLi_6$).
(16) We also investigated the case for $n = 12$, in both icosahedral and cube-octahedral arrangements. In this case, a weakly bonding set of triply degenerate levels $\epsilon_1$ accompanies the extreme low-lying level $\epsilon_0$ (numerical values: $\epsilon_0 = -6.0151$, $\epsilon_1 = -0.3321$ for $O_h$ symmetry; $\epsilon_0 = -6.0153$, $\epsilon_1 = -0.3297$ for $I_h$ symmetry). This suggests the possibility of coordination number 12.
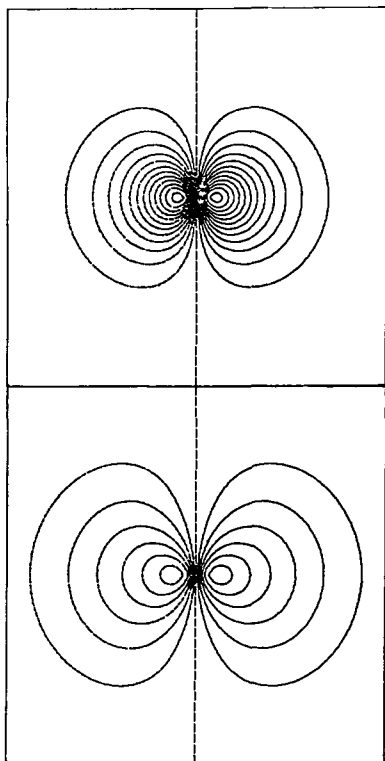
**Figure 2.** Comparison of 2p NAOs in neutral carbon atom (top) and the carbon atom of $CLi_6$ (bottom), showing the much greater diffuseness of the latter compared to "normal" carbon orbitals. (The orbitals shown are the "pre-NAOs", preceding interatomic orthogonalization, whose overlaps allow direct estimates of NAO Fock matrix elements and are more readily visualized.) Contour intervals are 0.02 au with outermost contour at 0.02 au.

the valence octet of the donor core plus two electrons for the acceptor cage. Species of the type $XLi_n{}^q$ involving a first-row central atom of atomic number $Z$ should therefore have special stability when $(Z - 2) + n - q = 10$, or

$$n + Z - q = 12 \qquad (1)$$

The carbon species $CLi_6$, $CLi_5{}^-$ conform to this rule, as do the corresponding nitrogen, oxygen, and fluorine species[17]

anion:　　$NLi_4{}^-$

neutral:　　$NLi_5$, $OLi_4$

cation:　　$NLi_6{}^+$, $OLi_5{}^+$, $FLi_4{}^+$

The special stability of electron configurations conforming to (1) would likely be manifested,[18] e.g., in ionization potential or electron affinity data, similar to those suggesting the stability of atomic filled and half-filled shells.[19]

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(17) Theoretical and experimental evidence pertaining to the stability of a number of these species has been given in ref 1 and 4.

(18) Equation 1 should not be taken to imply the stoichiometries or relative stabilities of non-cage-type structures, since this rule clearly has no relevance when the lithiums are not all bound to the central atom. However, our arguments suggest that $XM_n{}^q$ complexes that do *not* conform to this rule should prefer non-cage-type structures (if they are stable at all). Thus, in comparing $CLi_6$ and $OLi_6$, it is interesting that the first prefers the high-symmetry cage-type structure (and satisfies $n + Z - q = 12$) while the second does not. We thank Professor P. v. R. Schleyer for helping to clarify this point and for information pertaining to $OLi_6$.

(19) For example, the calculated energy differences between $CLi_n$ and $CLi_n{}^+$ (0.1155 a.u. for $n = 5$, 0.1236 a.u. for $n = 6$) suggest the greater stability of $CLi_6$ than of $CLi_5$ toward removal of an electron. Similarly, for anion formation, the corresponding differences between $CLi_n$ and $CLi_n{}^-$ (−0.0004 au for $n = 5$ and −0.0303 au for $n = 6$) suggest that $CLi_5$ would be more likely to add an electron than would $CLi_6$.



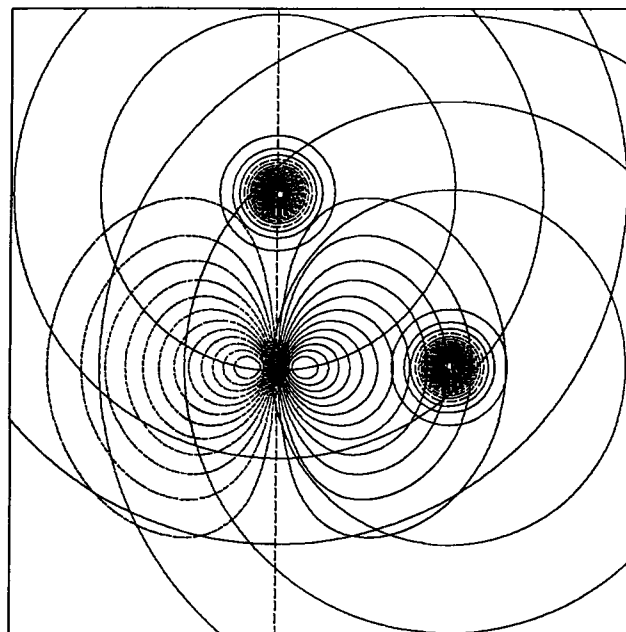**Figure 3.** Overlapping pre-NAOs (see Figure 2) of $CLi_6$ ($R = 2.058$ Å), showing the extreme diffuseness of C 2p and Li 2s orbitals and the high overlap of adjacent Li 2s orbitals leading to "cage" MOs. The plot depicts a C 2p orbital and two of the adjacent Li 2s orbitals in the same plane. Contour intervals are 0.01 au with outermost contour at 0.01 au.

It is to be emphasized that the validity of this simple Hückel model depends on the high ionic character of core–cage bonding, which prevents significant mixing of the donor core 2s orbital with the bonding cage orbital. If the MOs are transformed from the AO to the NAO basis, it is found that the bonding cage MO in $CLi_6$ (the HOMO, labeled $4a_{1g}$) has only 9.5% carbon character. The C–Li antibonding character of this orbital is thus rather small, in agreement with the previous findings of Schleyer.[1b]

In natural population analysis and the forms of the natural atomic orbitals help to add many details to this basic picture but no not alter its basic features. The central ion core appears to donate about 0.1 e back to each lithium of the surrounding cage, thereby greatly stabilizing the complex while retaining its essentially Ne-like character. The valence 2p NAO of the central carbon is found (consistent with its large negative oxidation state) to be much more diffuse than a normal covalent carbon 2p orbital, as shown in Figure 2, thus leading to high overlap with acceptor 2s orbitals of the lithium cage as shown in Figure 3. Relative to the lithium 2s orbital, the lithium 2p orbital set appears to play only a minor role.[20]

According to this simple model, the electronic structure of these highly ionic complexes furnishes a striking *confirmation* of the "octet rule", at least so far as the donor core is concerned. It is interesting that the electronegativity relationships between core and cage ions in hyperlithiated complexes of the form $XM_n$ are inverted with respect to those in "normal" $MX_n$ complexes (e.g., of transition-metal type). However, in other respects the bonding of $XM_n$ and $MX_n$ complexes may show unexpected analogies.

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(20) This is indicated by the natural populations of the 2s orbital and the 2p orbital set, which are respectively 0.41 and 0.02 on each Li in $CLi_6$. This small lithium p orbital occupancy is, however, of quantitative significance, as it supplys about one-third of the total SCF binding energy of 131 kcal/mol in $CLi_6$. (See ref 7 and 13 for further discussion of the role of lithium p orbitals.)