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Valence bond studies of CLi_5 and CLi_6

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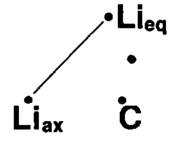
Abstract

Ab initio valence bond calculations with an STO-6G basis set are used to study aspects of the electronic structure of trigonal bipyramidal CLi_5. With lithium $2p$ orbitals initially omitted, a valence bond demonstration is provided for the molecular orbital description of the origin of the hypercoordination, namely Li_{eq}–Li_{ax} as well as C–Li_{ax} bonding. The axial Li_{ax}–C–Li_{ax} bonding involves primarily a three-electron three-centre bonding unit, for which there are eight canonical Lewis-type VB structures in a minimal basis set treatment. Resonance between these structures is equivalent to resonance between the "increased-valence" structures (A) and (B),

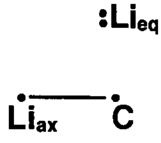
$\mathrm{Li}\ \cdot\ \mathrm{CLi_3}\ :\ \mathrm{Li}$ $\mathrm{Li}\ :\ \mathrm{CLi_3}\ \cdot\ \mathrm{Li}$

(A)   (B)

in which the three axial electrons occupy C–Li_{ax} bonding molecular orbitals. The Li_{ax}–Li_{eq} bonding arises when Li_{ax}-$\rightarrow \sigma^*(CLi_{eq})$ electron delocalizations occur from relevant Lewis structures, to generate four-electron three-centre bonding units, and "increased-valence" structures of the type (C)



(C)



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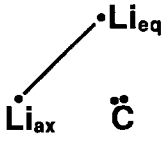

(E)

for the three atoms that are involved in the bonding unit. Structure (C) is equivalent to resonance between the Lewis structures (D) and (E), with Li_{eq}–Li_{ax} bonding occurring in (E). Inclusion of lithium $2p$ orbitals in exploratory calculations leads to a substantial shortening of the axial bonds.

Some consideration is given to three-electron three-centre bonding for CLi_6, and to an elementary increased-valence bonding index for this type of bonding unit.

Key words: Hypercoordination; Lithium; Valence bond calculations; Increased-valence

1. Introduction

The renaissance that has occurred in the valence bond (VB) approach to the study of the electronic structures of molecules [1–4] has led to the development of both new types of qualitative representations [5–13] and ab initio techniques [14–18]. Only technical problems have led to a decline in recent decades in the use of VB theory at the ab initio level [18], and it seems that these problems have now been largely overcome. The new types of VB structures that are associated with the qualitative representations in refs. 7–13 in particular provide a conceptual reformulation of aspects of descriptive valence theory for a large class of molecular systems. Some of this reformulation will be presented in this paper, through consideration of the bonding for the hypercoordinate molecule CLi_5, for which the results of molecular orbital (MO) studies indicate that its D_{3h} isomer is stable towards the dissociation process $CLi_5 \rightarrow CLi_4 + Li$ [19,20]. Consideration will also be given to a VB description of the bonding for octahedral CLi_6.

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2. Hypercoordinate CLi_n compounds

The study of lithium derivatives of Main Group elements provides an exciting application of computational quantum chemistry, with extraordinary structures and stoichiometries predicted for a variety of ALi_n compounds, such as CLi_6, CLi_8, CLi_{10} and CLi_{12} [21,22]. CLi_6, whose gas-phase existence has been identified via mass spectrometry [23,24], has been calculated to have an octahedral shape [19,20,22,25,26]. The most stable geometries of the other three molecules have D_{3d}, C_2 and C_{4v} symmetries, respectively [22], and the main building blocks for these systems are considered to be triangular Li_3 and pyramidal Li_4 units, which can condense by vertex sharing to give Li_7 and Li_{12} clusters [22]. Here we consider the nature of the bonding in trigonal bipyramidal CLi_5 and CLi_6, through minimal basis set VB calculations. The purpose is not to duplicate the numerical values of molecular properties that have been obtained from high quality MO calculations, but rather to focus attention on certain elementary bonding patterns that manifest themselves in these and numerous other molecular systems. We shall provide a VB description of aspects of the origin of the hypercoordination for CLi_5, in particular its stability relative to the axial Li_{ax} + (planar)CLi_3 + Li_{ax} dissociation, via a consideration of Li_{ax}–Li_{eq} bonding as well as C–Li_{ax} bonding. These two forms of bonding manifest themselves as components of four-electron three-centre and three-electron three-centre bonding units, for both of which the VB theory has received considerable attention recently via the construction of "increased-valence" structures [7,8,13]. The three-electron three-centre theory developed for CLi_5 will be adapted to show how both Li–Li and C–Li bonding for CLi_6 may be accommodated.

3. Method of calculation

For a given geometry, resonance between a set of VB structures is equivalent to the construction of a linear combination of their structural wavefunctions (Φ_i), according to

$$\Psi = \Sigma C_i \Phi_i \tag{1}$$

Roso's program [27–30] was used to perform the ab initio VB calculations for eqn. (1), with a minimal STO-6G basis set [31] and best-atom exponents [32].

For trigonal bipyramidal CLi_5, the carbon atom is sp^2 hybridized. To simplify the electron spin theory for the Φ_i of eqn. (1), the six electrons of the equatorial C–Li bonds are located in three bonding MOs of the type

$$\sigma(\mathrm{CLi_{eq}}) = (sp^2_{\mathrm{C}}) + \kappa h_{\mathrm{eq}} \tag{2}$$

in which $h_{\mathrm{eq}} = (2s_{\mathrm{Li}} + \lambda_{\mathrm{eq}} 2p\sigma_{\mathrm{Li}})_{\mathrm{eq}}/(\lambda^2_{\mathrm{eq}} + 1)^{1/2}$ and κ is a variational, bond polarity parameter. These MOs and six doubly-occupied $1s$ AOs form the core ($R = (1s)^{12}(\sigma(\mathrm{CLi_{eq}}))^6$) for the axial three-electron three-centre bonding unit. The axial bonding, with overlapping $h_{\mathrm{ax}} = (2s_{\mathrm{Li}} + \lambda_{\mathrm{ax}} 2p\sigma_{\mathrm{Li}})_{\mathrm{ax}}/(\lambda^2_{\mathrm{ax}} + 1)^{1/2}$ and $2p\sigma_{\mathrm{C}}$ AOs, was studied initially using the Lewis VB structures (1)–(8) of Fig. 1. The electron-pair bond wavefunctions for the axial bonds in the canonical structures (1) and (4) use Heitler–London type wavefunctions. For example, the wavefunction for the C–Li_{ax} bond of structure (1) is $|\ldots b\bar{c}| - |\ldots \bar{b}c|$ in which b and c are $2p\sigma_{\mathrm{C}}$ and h_{ax} AOs.

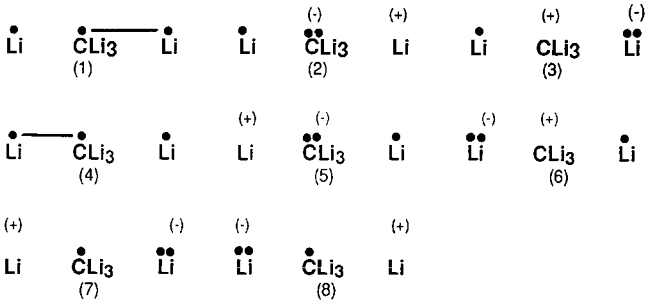


Fig. 1. Canonical Lewis VB structures. $\Phi_1 = |Rab\bar{c}| - |Ra\bar{b}c|$, $\Phi_2 = |Rab\bar{b}|$, $\Phi_3 = |Rac\bar{c}|$, $\Phi_4 = |Rcb\bar{a}| - |Rc\bar{b}a|$, $\Phi_5 = |Rcb\bar{b}|$, $\Phi_6 = |Rca\bar{a}|$, $\Phi_7 = |Rbc\bar{c}|$ and $\Phi_8 = |Rba\bar{a}|$, in which the presence or absence of a bar over an AO in the Slater determinant indicates a β or α spin wavefunction, and $R = (1s)^{12}(\sigma(\mathrm{CLi_{eq}}))^6$.

The equatorial C–Li bond lengths (2.056 Å) reported in ref. 19 have been assumed in the VB calculations, but the lengths of the axial C–Li bonds ($r(\mathrm{CLi_{ax}})$) were varied, in order to examine the origin of the hypercoordination. With lithium $2p$ AOs omitted, some calculations were also performed for (pseudo) CLi_4, with sp^3 hybridization, and bond lengths of 2.056 Å for three of the bonds. The length of the remaining bond, which becomes one of the axial bonds when trigonal bipyramidal CLi_5 is formed, was varied to obtain an energy-optimized length. A covalent and two ionic structures were used to represent this bond.

Although the calculations utilize only a single zeta basis set, the results obtained do portray features of bonding that arise in MO calculations, and illustrate aspects of general valence theory. They will initially be illustrated in Sections 4–7 with $\lambda_{\mathrm{ax}} = \lambda_{\mathrm{eq}} = 0$, in order that the basic models may be established with a minimum number of variational parameters.

4. Axial three-electron three-centre bonding

Attention is now given to the axial three-electron three-centre bonding unit, via the inclusion of the canonical Lewis structures (1)–(8) of Fig. 1 in the resonance scheme.

For the reaction $Li_{ax} + Li_3C–Li_{ax} \rightarrow Li_{ax}–CLi_3 + Li_{ax}$, structures (1)–(3) and (4)–(6) of Fig. 1 are sets of reactant-like and product-like Lewis structures respectively, whereas structures (7) and (8) only contribute to the bonding scheme at intermediate stages along the reaction coordinate. It is the contribution from structures (7) and (8) which is responsible for an apparent hypervalence for the carbon atom in VB structures (I) and (II) (see Appendix) [33].

$\mathrm{Li} \; \bullet \; \mathrm{CLi_3} \; : \; \mathrm{Li}$ (I)

$\mathrm{Li} \; : \; \mathrm{CLi_3} \; \bullet \; \mathrm{Li}$ (II)

These latter structures, which are discussed in Section 5, provide examples of the "increased-valence" representation for a three-electron three-centre bonding unit [8(a),13].

The wavefunctions for structures (1)–(8) of Fig. 1 are reported in the caption for this Figure, in which a and c are $2s$ and $-2s$ AOs located on the axial lithium atoms, and b is the colinear carbon $2p\sigma$ AO that overlaps with them. (With $a = 2s$ and $c = -2s$, the overlap integrals $\langle a | b \rangle$ and $\langle b | c \rangle$ have the same signs.) The odd electron is assumed to have a value of $+1/2$ for its m_s spin quantum number in the structural wavefunctions. Energies and κ values for the ground-state resonance are reported in Table 1. In Table 2, the C_i coefficients for eqn. (1) and the (Chirgwin–Coulson [34]) structural weights are reported for $r(CLi_{ax}) = 4.4$ a.u.

With the set of eight VB structures of Fig. 1, CLi_5 is calculated to be bound with respect to both Li_{ax} + pseudo $CLi_3–Li_{ax}$ and the Li_{ax} + (planar)CLi_3 + Li_{ax} dissociations respectively. However, the equilibrium $C–Li_{ax}$ bond lengths of 4.7_6 a.u. (2.52 Å) for CLi_5 are substantially longer than the 2.089 Å reported in ref. 19. Between $r(CLi_{ax}) = 5.0$ a.u. and 4.1 a.u., the value of κ for eqn. (2) shows little variation, and values of 0.53–0.57 for this parameter indicate that the equatorial C–Li bonds are strongly polarized towards the carbon atom. As a consequence, the dominant Lewis VB structures for the axial bonding are calculated (cf. Table 2) to be (3) and (6) of Fig. 1. These structures do not involve occupancy of the carbon $2p\sigma$ AO, and presumably the source of the hypercoordination is primarily the electrostatic attraction between the negatively charged axial Li^- and the positively charged CLi_3^+.

TABLE 1. Energies (a.u.) for (a) resonance between structures (1)–(8) of Fig. 1, (b) resonance between structures (1)–(8) + six structures of type (V), with κ obtained from the calculations of (a), and (c) pseudo CLi_4 + Li with one energy-optimized C–Li bond length of 3.75 a.u. (see text)

$r(CLi_{ax})$	κ	$-E^{(a)}$	$-E^{(b)}$
4.3	0.57	74.5128	74.5440
4.4	0.56	74.5139	74.5446
4.5	0.56	74.5146	74.5455 [a]
4.6	0.55	74.5150	74.5454 [a]
4.7	0.55	74.5152	74.5459 [a]
4.8	0.54	74.5153	74.5452 [a]
4.9	0.54	74.5151	74.5454 [a]
5.0	0.53	74.5148	74.5443
99	0.39	74.3886	74.3886
(c)	0.71		74.3635

[a] The lack of consistency arises because the optimum κ values for the calculations of (a) require more significant figures when they are used in the calculations for (b).

TABLE 2. Unnormalized coefficients (C_i) and (Chirgwin-Coulson) structural weights (W_i) for resonance between (a) structures (1)–(8) of Fig. 1, and (b) structures (1)–(8) + six structures of type (V), with $r(CLi_{ax}) = 4.4$ a.u. N.B. $C_1 = -C_4$, $C_2 = -C_5$, $C_3 = C_6$, $C_7 = -C_8$

Structure	$C_i^{(a)}$	$C_i^{(b)}$	$W_i^{(a)}$	$W_i^{(b)}$
(1)	0.3342	0.2169	0.172	0.083
(2)	0.0011	0.0128	0.0001	−0.001
(3)	0.9565	0.3930	0.313	0.109
(7)	0.1472	0.1049	0.016	0.009
(V)		0.4660		0.100

Values of 0.53–0.57 for the $C–Li_{eq}$ polarity parameter κ of eqn. (2) reflect the greater electronegativity of the carbon atom and the consequent development of formal positive charges on the equatorial lithium atoms. The opposite effect is obtained for the axial lithium atoms. Resonance between structures (2) and (5) generates +0.5 formal positive charges on these atoms, whereas resonance between structures (3) and (6) generates −0.5 formal charges on the same atoms. Because the latter pair of structures have higher weights (Table 2) than the former pair, the net formal charges are negative. The results of MO calculations [19] indicate the presence of positive formal charges on all lithium atoms, and positive charges may be obtained via the procedures that are described below in Section 6.

5. Increased-valence structures for three-electron three-centre bonding

In refs. 8a and 13 it is shown that for a three-electron three-centre bonding unit, a wavefunction may be formulated so that resonance between increased-valence structures (I) and (II) is equivalent to the "variational best" resonance between the Lewis structures (1)–(8) of Fig. 1. For a symmetrical three-centre bonding unit, the electrons occupy the localized MOs (LMOs) of eqns. (3) and (4):

$$\varphi_{ab} = a + lb, \quad \varphi'_{bc} = b + k'c, \quad \varphi''_{bc} = c + k''b \tag{3}$$

$$\varphi_{bc} = c + lb, \quad \varphi'_{ab} = b + k'a, \quad \varphi''_{ab} = a + k''b \tag{4}$$

in which l, k' and k'' are (variational) polarity parameters. Using these MOs, the $S = M_s = 1/2$ spin wavefunctions of eqns. (5)–(8) for VB structures (**I**) and (**II**) may be constructed:

$$\begin{aligned}\Phi'_{\mathrm{I}} &= |\varphi_{ab}\varphi'_{bc}\overline{\varphi''_{bc}}| - |\varphi_{ab}\overline{\varphi'_{bc}}\varphi''_{bc}| \\ &\equiv (1 + k'k'')\Phi_1 + 2k''\Phi_2 + 2k'\Phi_3 \\ &\quad - l(1 + k'k'')\Phi_5 + 2lk'\Phi_7 \end{aligned} \tag{5}$$

$$\begin{aligned}\Phi''_{\mathrm{I}} &= 2|\overline{\varphi_{ab}}\varphi'_{bc}\varphi''_{bc}| - |\varphi_{ab}\overline{\varphi'_{bc}}\varphi''_{bc}| - |\varphi_{ab}\varphi'_{bc}\varphi''_{bc}| \\ &\equiv (1 - k'k'')(2\Phi_4 - \Phi_1 - 3l\Phi_5) \end{aligned} \tag{6}$$

$$\begin{aligned}\Phi'_{\mathrm{II}} &= |\varphi_{bc}\varphi'_{ab}\overline{\varphi''_{ab}}| - |\varphi_{bc}\overline{\varphi'_{q}a_{b}}\varphi''_{ab}| \\ &\equiv (1 + k'k'')\Phi_4 + 2k''\Phi_5 + 2k'\Phi_6 \\ &\quad - l(1 + k'k'')\Phi_2 + 2lk'\Phi_8 \end{aligned} \tag{7}$$

$$\begin{aligned}\Phi''_{\mathrm{II}} &= 2|\overline{\varphi_{bc}}\varphi'_{ab}\varphi''_{ab}| - |\varphi_{bc}\overline{\varphi'_{ab}}\varphi''_{ab}| - |\varphi_{bc}\varphi'_{ab}\overline{\varphi''_{ab}}| \\ &\equiv (1 - k'k'')(2\Phi_1 - \Phi_4 - 3l\Phi_2) \end{aligned} \tag{8}$$

We may then write

$$\Psi_{\mathrm{I}} = \Phi'_{\mathrm{I}} + \mu\Phi''_{\mathrm{I}} \tag{9}$$

$$\Psi_{\mathrm{II}} = \Phi'_{\mathrm{II}} + \mu\Phi''_{\mathrm{II}} \tag{10}$$

and

$$\Psi = \Psi_{\mathrm{I}} - \Psi_{\mathrm{II}} \tag{11}$$

for which four variational parameters (l, k', k'' and μ) arise in eqn. (11). For a given value of the hybridization parameter κ in eqn. (1), only three linearly independent variational parameters are associated with eqn. (1), and this number may be achieved in eqn. (11) by several methods. In each case, the ground-state values for the three parameters may be determined from the C_j of eqn. (1) by equating coefficients of the Φ_i in eqns. (1) and (11). Equations (12)–(14)

$$l = C_7/C_3 \tag{12}$$

$$1 + k'k'' - 3\mu(1 - k'k'') = 2k'C_1/C_3 \tag{13}$$

$$2k'' + l(k'k'' + 1) + 3\mu l(1 - k'k'') = 2k'C_2/C_3 \tag{14}$$

are thereby obtained with one disposable parameter. Four choices of this parameter, namely either $\mu = 0$, or $\mu = \pm l$ or $k' = k''$, lead to a negative value for one of k' and k'' when $r(\mathrm{CLi_{ax}}) = 4.4$ a.u. If either k' or k'' is negative, the associated electron occupies an antibonding MO rather than a bonding MO. In VB structures (**I**) and (**II**), each of the electrons is C–$\mathrm{Li_{ax}}$ bonding. To obtain positive values for each of k' and k'', the following procedure has been adopted. It is illustrated for $r(\mathrm{CLi_{ax}}) = 4.4$ a.u.

A VB calculation with structures (7) and (8) of Fig. 1 omitted, i.e. $l = 0$, gives $k' = 1.474$ and $k'' = 0.000771$ when $\mu = 0$. (Resonance between the reactant-like and product-like canonical structures (1)–(6) of Fig. 1 is then equivalent to resonance between the LMO Lewis structures (**III**) and (**IV**)

$$\dot{\mathrm{Li}} \quad \underset{\text{(III)}}{\mathrm{CLi_3}} : \mathrm{Li} \qquad \mathrm{Li} : \underset{\text{(IV)}}{\mathrm{CLi_3}} \quad \dot{\mathrm{Li}}$$

in which the bonding electrons occupy the relevant LMOs of eqns. (3) and (4).) With $k'' = 0.000771$, the eight structure calculation then gives $l = 0.121$, $k' = 3.445$ and $\mu = -0.455$. These values of k', k'' and l indicate that the one-electron and (fractional) two-electron axial bonds of structures (**I**) and (**II**) are strongly polarized towards the axial lithium atoms, thereby reflecting the importance of structures (3) and (6) to the Lewis structure resonance scheme.

6. Four-electron three-centre bonding and VB structures that arise from $\mathrm{Li_{ax}} \dashrightarrow \sigma^*(\mathrm{CLi_{eq}})$ electron delocalizations

For trigonal bipyramidal $\mathrm{SiH_5^-}$, Hiberty and coworkers [6,35–37] have shown how appreciable delocalization of axial $\mathrm{H^-}$ electrons into the equatorial σ^*_{SiH} MOs helps to account for the existence of this anion as a stable hypercoordinated species. An analagous type of delocalization is invoked here to illustrate one technique that may be used to introduce $\mathrm{Li_{ax}}$–$\mathrm{Li_{eq}}$ bonding into the VB treatment for $\mathrm{CLi_5}$. One consequence of antibonding $\sigma^*(\mathrm{CLi_{eq}})$ occupancy is to lengthen the equatorial C–Li bonds relative to those of $\mathrm{CLi_4}$, and this effect has been calculated to occur (cf. lengths of 2.056 Å and 1.929 Å for $\mathrm{CLi_5}$ and $\mathrm{CLi_4}$ [19]).

To develop additional formal positive charge on the axial lithium atoms, it is necessary to back-donate a $2s$ electron from either of the negatively charged axial lithium atoms of structures (3), (6), (7) and (8) of Fig. 1 into each of the three antibonding $\sigma^*(\mathrm{CLi_{eq}})$ MOs of the general type indicated in eqn. (15).

$$\sigma^*(\mathrm{CLi_{eq}}) = (sp^2_{\mathrm{C}}) - \kappa^*(2s_{\mathrm{Li}})_{\mathrm{eq}} \tag{15}$$

This MO is orthogonal to the $\sigma(\mathrm{CLi_{eq}})$ of eqn. (2) when κ^* is given by

$$\begin{aligned}\kappa^* = {}&\left(1 + \kappa\langle(sp^2_{\mathrm{C}})|(2s_{\mathrm{Li}})_{\mathrm{eq}}\rangle\right) \\ &/\left(\kappa + \langle(sp^2_{\mathrm{C}})|(2s_{\mathrm{Li}})_{\mathrm{eq}}\rangle\right)\end{aligned} \tag{16}$$

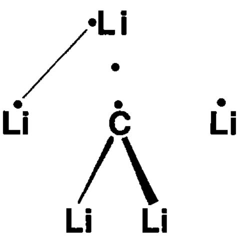
When the delocalization occurs for VB structures (3) and (6), six ($S = 0$ spin) wavefunctions of the type

$$\Psi(\sigma_{eq}^{\star} - 2s_{ax}) = |(\sigma_{eq})(\overline{\sigma_{eq}})(\sigma_{eq}^{\star})(\overline{2s_{ax}})| - |(\sigma_{eq})(\overline{\sigma_{eq}})(\overline{\sigma_{eq}^{\star}})(2s_{ax})| \quad (17)$$

are obtained for the four associated electrons, in which the $\sigma_{eq}^{\star}$ electron is spin-paired with the lithium $2s_{ax}$ electron. With $y = (2s)_{ax}$, $a = (sp_C^2)$, and $b = (2s_{Li})_{eq}$, this wavefunction may be transformed (cf. refs. 38–40) to give:

$$\Psi(\sigma_{eq}^{\star} - 2s_{ax}) = \Phi_V \equiv -(1 + \kappa\kappa^{\star})\left(|a(\overline{a + \kappa b})b\bar{y}| + |\bar{a}(a + \kappa b)\bar{b}y|\right) \quad (18)$$

for which the associated VB structure is (**V**) [cf. refs. 38–40):



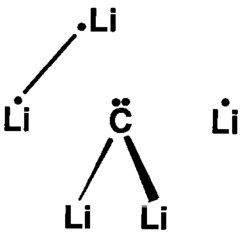
(V)

VB structure (**V**) is an example of an increased-valence structure for a four-electron three-centre bonding unit [8,9,11,12a,27,38–40], and its wavefunction is also equivalent to those of eqns. (19) and (20):

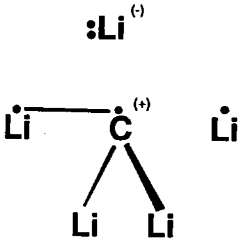
$$\Psi(\sigma_{eq}^{\star} - 2s_{ax}) = \Phi_V \equiv -(1 + \kappa\kappa^{\star})\left(|a\bar{a}b\bar{y}| + |\bar{a}a\bar{b}y| + \kappa\left(|a\bar{b}b\bar{y}| + |\bar{a}b\bar{b}y|\right)\right) \quad (19)$$

$$= -(1 + \kappa\kappa^{\star})(\Phi_{VI} + \kappa\Phi_{VII}) \quad (20)$$

This identity shows that increased-valence structure (**V**) is equivalent * to resonance between the Lewis structures (**VI**) and (**VII**):



(VI)



(VII)

Inclusion of the Lewis structure (**VI**) permits some (fractional) Li_{eq}–Li_{ax} covalent bonding to occur. Such an effect is associated with the development of a metal cage around the carbon atom, to which reference has been made in several MO studies of the origin of the hypercoordination of either CLi_5 or CLi_6 [19,20,26]. When the six structures of type (**V**) participate in resonance with structures (1)–(8) of Fig. 1 (Table 3), and the κ values obtained in Section 3 are used in the calculations, the C–Li_{ax} bond lengths are shortened from 4.7_6 a.u. to 4.5_4 a.u. (2.38 Å), and the total energy is lowered from −74.5153 a.u. to −75.5455 a.u.

For $r(CLi_{ax}) = 4.4$ a.u., the sum of the weights for the six structures of type (**V**) exceeds the sum of the weights for the canonical Lewis structures (1)–(8) (cf. Table 2). The importance of structures of type (**V**) is associated with the existence of a large value for the Li_{ax}–Li_{eq} overlap integral $\langle 2s_{ax}|2s_{eq}\rangle$, namely 0.499 when $r(CLi_{ax}) = 4.4$ Å, as well as with the reduction of formal negative charge on the axial lithium atoms. It may be noted that the axial C–Li bonds in the Lewis structures (1) or (4) of Fig. 1, and in structure (**VII**), involve $2s_{ax} - 2p\sigma$ and $2s_{ax} - sp^2$ overlap respectively, for which their associated overlap integrals, ($\langle 2s_{ax}|2p\sigma\rangle$ and $\langle 2s_{ax}|sp^2\rangle \equiv \langle 2s_{ax}|2s_C\rangle/\sqrt{3}$), have similar values, namely 0.152 and 0.173 when $r(CLi_{ax}) = 4.4$ a.u.

7. Polarization of the equatorial C–Li bonds, and the axial C–Li bond lengths

The calculations of the previous section were repeated (Table 3) with the optimized κ value for eqn. (2) determined from resonance between the six increased-valence structures of type (**V**). When these structures participate in resonance with the eight Lewis structures of Fig. 1, rather lower energies are obtained compared with those reported in Table 1. However, the optimized axial bond lengths (6.1 a.u.) are now much longer than the 4.5_4 a.u. obtained from Table 1. The origin of this lengthening is associated with the larger values that are calculated for the C–Li_{eq} polar-

TABLE 3. Energies (a.u.) for resonance between (a) six structures of types (V), (b) six structures of type (V) + structures (1)–(8), with κ obtained from the calculations of (a)

$r(CLi_{ax})$	κ	$-E^{(a)}$	$-E^{(b)}$
4.4	0.64	74.5378	74.5462
4.6	0.65	74.5423	74.5495
5.0	0.66	74.5493	74.5556
6.0	0.66	74.5572	74.5620
7.0	0.65	74.5559	74.5599
8.0	0.64	74.5511	74.5545

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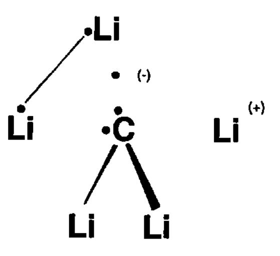
* Because of this equivalence, fractional Li_{ax}–C as well as fractional Li_{ax}–Li_{eq} bonding occurs in the increased-valence structure (V). However, in accord with previous practice [7–12,38–40], the fractional electron-pair bonding in (V) is indicated only between the pairs of atoms whose AOs overlap best, and, for CLi_5, it is the Li_{ax} and Li_{eq} pair. When $r(CLi_{ax}) = 4.4$ a.u., $\langle 2s_{ax}|2p\sigma\rangle = 0.152$ and $\langle 2s_{ax}|2s_{eq}\rangle = 0.499$.

TABLE 4. Energies (a.u.) for resonance between VB structures of type (V) with selected values of κ

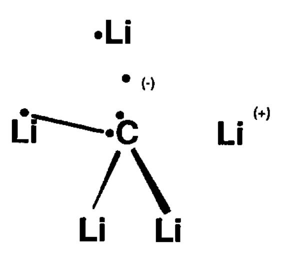
$r(CLi_{ax})$	$\kappa = 0.4$	$\kappa = 0.2$	$r(CLi_{ax})$	$\kappa = 0.4$
3.885		−74.4011	4.7	−74.49561
4.1		−74.3994	4.8	−74.49560
4.3		−74.3969	4.9	−74.4955
4.5	−74.4954	−74.3943		

ity parameter κ, (0.64–0.66), thereby reducing the importance of Lewis structures of type (VI) to the resonance scheme (cf. eqns. (19) and (20)). To demonstrate how an increase in the contribution of these structures leads to a shortening of the C–Li_{eq} bonds, further calculations have been performed for resonance between the six increased-valence structures of type (V), with κ set at values of 0.4 and 0.2. The results of these calculations (Table 4) show that as the polarity of the C–Li_{eq} bonds increases in the sense $Li_{eq} \rightarrow C$, the C–Li_{ax} bond lengths are dramatically decreased. No such shortening occurs when $\kappa = 0.2$ is used in calculations with the eight Lewis structures of Fig. 1 (Table 5).

Li_{ax}–Li_{eq} bonding may also be obtained when an axial Li^- electron of structure (7) or (8) is delocalized into an antibonding $\sigma^*(CLi_{eq})$ MO. VB structures of types (VIII) and (IX)



(VIII)



(IX)

are thereby obtained in which the remaining axial lithium 2s electron is spin-paired with either the $\sigma^*(CLi_{eq})$ electron or the carbon 2$p\sigma$ electron. The wavefunctions for the relevant five electrons of these structures are those of eqns. (21) and (22):

$$\Psi(\sigma^*_{eq} - 2s_{Li}) = |(2p\sigma)(\sigma_{eq})(\overline{\sigma_{eq}})(\sigma^*_{eq})(\overline{2s_{ax}})| + |(2p\sigma)(\overline{\sigma_{eq}})(\sigma_{eq})(\overline{\sigma^*_{eq}})(2s_{ax})| \quad (21)$$

TABLE 5. Energies (a.u.) for resonance between VB structures (1)–(8) of Fig. 1, with selected values of κ

$r(CLi_{ax})$	$\kappa = 0.2$	$\kappa = 2.0$
4.8	−74.4135	−74.1050
5.0	−74.4144	−74.1066
6.0	−74.4180	−74.0995
7.0	−74.4184	
8.0	−74.4159	

TABLE 6. (Chirgwin-Coulson) structural weights (W_i) for resonance between 26 VB structures, with $r(CLi_{ax}) = 4.4$ a.u. and $\kappa = 0.61$. For each of (V), (VIII) and (IX), there are six equivalent structures

(1), (3)	0.043	(V)	0.109
(2), (5)	−0.001	(VIII)	0.019
(3), (6)	0.058	(IX)	0.006
(7), (8)	−0.003		

$$\Psi(2p\sigma - 2s_{Li}) = |(\sigma^*_{eq})(\sigma_{eq})(\overline{\sigma_{eq}})(2p\sigma)(\overline{2s_{ax}})| + |(\sigma^*_{eq})(\overline{\sigma_{eq}})(\sigma_{eq})(\overline{2p\sigma})(2s_{ax})| \quad (22)$$

Because structures (VIII) and (IX) are derived from VB structures (7) and (8) of Fig. 1, they should make a smaller contribution to the resonance scheme than do the six structures of type (V). This has been confirmed by the structural weights that have been calculated for resonance between 26 VB structures (Table 6).

As well as by the use of better AO basis sets—for example (but not only) via the inclusion of lithium 2p AOs—the above sets of calculations may be improved in a variety of ways, in particular through the introduction of some electron correlation into the equatorial C–Li bonds. From the $(\sigma(CLi_{eq}))^6)$ configuration of each structure, three $(\sigma(CLi_{eq}))^4(\sigma^*(CLi_{eq}))^2$ configurations may be constructed, and these would be included in the calculations. It has yet to be examined how the inclusion of these configurations affects the value of the polarity parameter κ for the equatorial C–Li bonds.

8. Inclusion of lithium 2p orbitals

The inclusion of lithium 2p AOs, via the use of axial and equatorial hybrid AOs $h_{ax} = (2s_{Li} + \lambda_{ax}2p_{Li})_{ax}$ and $h_{eq} = (2s_{Li} + \lambda_{eq}2p_{Li})_{eq}$, complicates considerably the VB calculations for the following reasons.

(a) The number of hybridization and bond polarity variational parameters increases, and

(b) the optimum orientations of the 2p components of h_{ax} and h_{eq} for structures of type (V), and in particular their type (VI) Lewis components, are not along the Li_{ax}–C and Li_{eq}–C bond axes.

For each of the calculations described in this Section, the 2s and 2p AO exponents have been assigned the same values (cf. ref. 41), and it has been assumed that $\kappa = 0.56$ in eqn. (2). Variational estimates for the hybridization parameters λ_{ax} and λ_{eq} were determined for $r(CLi_{ax}) = 4.1$ a.u. It has been assumed for simplicity that the axes of the lithium h_{ax} and h_{eq} orbitals are orientated along the Li_{ax}–C and Li_{eq}–C bond axes respectively, thereby reducing the importance of h_{ax}–h_{eq} type overlap for Lewis structures of type (VI).

TABLE 7. Energies (a.u.) with lithium $2p$ AOs included (see text)

$r(CLi_{ax})$	(a)	(b)	(c)
3.9	−74.5192	−74.6148	−74.6148
4.1	−74.5224	−74.6157	−74.6158
4.3	−74.5236	−74.6149	−74.6150
4.4	−74.5237	−74.6140	−74.6142
4.6	−74.5231	−74.6117	−74.6120

In structures (2), (3), and (5)–(8), no C–Li_{ax} electron-pair bonds occur, and therefore the hybridization parameter λ_{ax} has been assigned a value of zero in the lithium AOs of these structures. Pilot calculations indicate that the resulting energies are substantially lower than those that are obtained when the same value of λ_{ax} is assigned to each of the eight structures.

Because the variational treatment is incomplete, the following sets of calculations are primarily exploratory in nature, and the conclusion that is obtained from the calculations of (c) in particular, must be considered as provisional only. Results are reported in Tables 7 and 8.

(a) Resonance between structures (1)–(8), with $\lambda_{eq} = 0$, and variation of λ_{ax}. An optimum value of −0.3 is calculated for λ_{ax}, to give $r_e(CLi_{ax}) = 4.4$ a.u.

(b) The structures of (a), with $\lambda_{ax} = -0.3$ and λ_{eq} energy optimized at a value of 0.7. The value of $r_e(CLi_{ax})$ shortens to 4.0_9 a.u., and the resulting energy of −74.6157 a.u. now lies below the MO 3-21G estimate of −74.5993 a.u. [19].

(c) The calculations of (b) together with the six structures of type (V). With $\kappa = 0.56$, $\kappa^* = 1.198$ and $\lambda_{eq} = 0.7$. A minimum energy of −74.6158 a.u. is obtained when $r_e(CLi_{ax}) = 4.1_0$ a.u. However, in contrast to what has been calculated when the lithium $2p$ AOs are omitted (Table 2), the six structures of type (V) make very minor contributions to the ground-state resonance scheme.

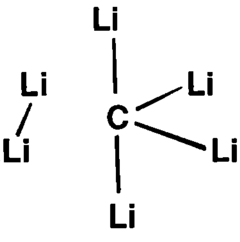
The importance of lithium $2p$ orbitals for helping to shorten the axial bonds is reflected in the results of the (b) and (c) calculations. With them, the origin of the hypercoordination is calculated to be associated largely with resonance between structures (1)–(8) of Fig. 1, with little contribution from Li_{ax}–Li_{eq} bonding. However, the latter effect should be more significant when more complete variational procedures are invoked to estimate optimized values of the bond parameters and the orientations of the lithium AOs. (It may be noted that for the 14 structure calculations, the optimized values of these quantities for structures (1)–(8) should differ from those for structures of type (v).) In contrast with what should be the case with either a MOCI (MO configuration interaction), or a generalized VB, or a spin-coupled VB calculation, a "classical" type VB treatment for CLi_5 no longer becomes easy to manage.

TABLE 8. (Chirgwin–Coulson) structural weights with lithium $2p$ AOs included (see text)

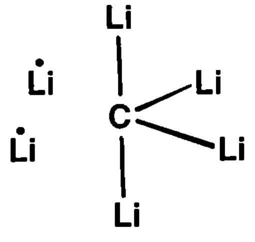
$r(CLi_{ax})$	(a) 4.4	(a) 4.1	(b) 4.1	(c) 4.1
(1)	0.212	0.236	0.142	0.140
(2)	0.002	0.002	0.001	0.0005
(3)	0.275	0.250	0.349	0.344
(7)	0.011	0.011	0.009	0.009
(V)				0.002

9. Aspects of a VB description for CLi_6

Comments on the bonding for octahedral CLi_6 will be restricted primarily to a consideration of three-electron three-centre bonding units. To do this, attention is given initially to the orbital description of the bonding for VB structures of type (X).



(X)



(XI)

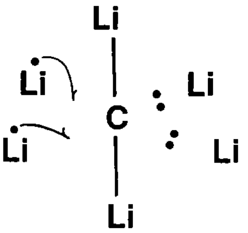
9.1. *Lewis octet structures of type (X)*

The VB theory for CLi_5 may be adapted to describe the bonding for octahedral CLi_6. In the VB description for the Lewis octet structure (X), carbon *sp* hybridization replaces sp^2 hybridization, and two digonal hybrid AOs are involved in the formation of two C–Li electron-pair bonds. The remaining two $2p$ AOs of carbon help form electron-pair bonds to two of the lithium ligands. An electron-pair bond may then be formed between the two lithium atoms that are not bonded to the carbon atom. In the subsequent discussions, it will always be assumed that the two bonds formed from $(sp_C) - h_{Li}$ overlap involve double occupation of two bonding LMOs of the type indicated in eqn. (23):

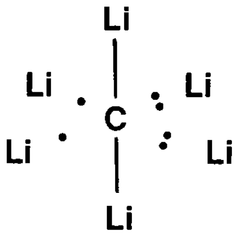
$$\phi(CLi) = (sp_C) + \kappa h_{Li} \qquad (23)$$

in which $h_{Li} = (2s + \lambda 2p)_{Li}/(\lambda^2 + 1)^{1/2}$.

If the Li–Li bond of (X) is omitted, and the relevant Coulson–Fischer type MOs of eqns. (3) and (4) are used to accommodate the electrons of the bonds that are formed from $2p_C - h_{Li}$ overlap, the resulting VB structures of type (XI) correspond to VB structures of types (III) and (IV) for CLi_5. Structures of type (XI) may be stabilized via the one-electron delocalizations that are indicated in **(XI)** [8a,13] to afford increased-valence structures of type **(XII)**.



(XI)



(XII)

The latter types of structure, of which there are twelve, correspond to structures of type (I) and (II) for CLi_5.

Each of the two unhybridized $2p_C$ AOs is involved in the formation of a linear three-electron three-centre bonding unit, via overlap with the lithium hybrid AOs. Therefore $3 \times 8 \times 8$ distinct canonical Lewis structures that involve combinations of the type displayed in Fig. 1 for one three-centre bonding unit are associated with the three pairs of these bonding units for CLi_6. For computational purposes, it is useful to relate the wavefunctions for the VB structures to those for configurations that may be constructed from three-centre MOs.

9.2. Resonance between 12 increased-valence structures with two three-electron three-centre bonding units

It will now be demonstrated how the delocalized MO description for each three-electron three-centre bonding unit corresponds to a restricted form of resonance between either the eight canonical Lewis structures of Fig. 1, or increased-valence structures (I) and (II).

If a, b and c are a linear set of overlapping h_{Li}, $2p_C$ and $-h_{Li}$ AOs, the delocalized MOs are those of eqn. (24):

$$\phi_1 = a + k_1 b + c, \quad \phi_2 = a - c \quad \text{and } \phi_3 = a - k_3 b + c \qquad (24)$$

The lowest-energy MO configuration for the three electrons is $|\phi_1\overline{\phi_1}\phi_2|$, from which eqn. (26) may be derived:

$$|\phi_1\phi_1\phi_2| = -0.5|(\phi_1+\phi_2)\overline{\phi_1}(\phi_1-\phi_2)| \qquad (25)$$

$$= -0.5|(2a+k_1b)(\overline{(a+0.5k_1b)+(0.5k_1b+c)})(k_1b+2c)|$$

$$= -0.25(|\phi_{ab}\overline{\phi_{ab}}\phi_{bc}| + (|\phi_{ab}\overline{\phi_{bc}}\phi_{bc}|) = -0.25(\Phi_{II}+\Phi_I) \qquad (26)$$

with $\phi_{ab} = 2a + k_1 b$ and $\phi_{bc} = k_1 b + 2c$. The latter MOs are special cases of the φ'_{ab}, φ''_{ab}, φ'_{bc} and φ''_{bc} MOs of eqns. (3) and (4), and are obtained from them by setting $k' = 1/k'' = 1/l = 2/k_1$. On substitution of these values for k', k'' and l into eqns. (5)–(11), we obtain:

$$\Psi \approx 2(\Phi_1 - \Phi_4) + 2k_1(\Phi_2 - \Phi_5) + (4/k_1)(\Phi_3 - \Phi_6) + 2(\Phi_7 - \Phi_8) \qquad (27)$$

thereby showing that the three-centre MO configuration $|\phi_1\overline{\phi_1}\phi_2|$ is equivalent to a restricted form of resonance between the canonical Lewis structures of Fig. 1.

Increased-valence structure **(XII)** involves two increased-valence structures of type **(I)** or **(II)**. Each of the latter structures is equivalent to resonance between LMO Lewis structures of type **(III)** or **(IV)** and charge-transfer structures (cf. eqns. (5) and (7) in particular with $l \neq 0$). Therefore the presence of two structures of type **(III)** or **(IV)**, as occurs in the LMO Lewis structure **(XI)**, permits fractional Li–Li bonding to manifest itself in increased-valence structure **(XII)**. In the MO treatment of each of the two three-centre bonding units, the odd-electron occupies a ϕ_2-type MO of eqn. (24). When the two odd electrons are spin-paired in a Heitler–London manner to give an $S = 0$ spin configuration, the resulting configuration is equivalent to resonance between four increased-valence structures of type **(XII)**, in each of which fractional Li–Li bonding occurs as a consequence of the contributions of Lewis structures of type **(XI)**.

With C–Li bond lengths of 2.024 Å [19], some STO-6G calculations have been performed with $h_{Li} = 2s_{Li}$, and three MO configurations that correspond to the resonance between the 12 increased-valence structures of type **(XII)**. Values of $1/1.8 = 0.5_6$ and $\sqrt{2}/1.6 = 0.8_8$ were obtained for the κ and k_1 polarity parameters, to give an energy of −82.0500 a.u. (cf. −82.0034 a.u. for the SCF/3-21G calculation of ref. 20). With $k_1 = 0.8_8$, each three-centre bonding unit locates (fractional) negative charge on the associated lithium atoms, and therefore as for CLi_5, $Li^- \rightarrow \sigma^*(CLi)$ delocalizations, with $\sigma^*(CLi) = (sp)_C - \kappa^*(2s)_{Li}$, should also have relevance for the introduction of additional Li–Li bonding.

Further development of the delocalized MO approach to three-electron three-centre bonding for CLi_6 involves the introduction of configuration interaction, either via $\phi_1 \rightarrow \phi_3$ excitations within each three-electron three-centre bonding unit or via charge transfer excitations between three-electron three-centre bonding units.

10. Conclusions

When lithium $2p$ orbitals are excluded, the results of the calculations suggest strongly that the origin of the pentacoordination in CLi_5 is associated rather more with the Li_{ax}–Li_{eq} bonding than with the axial three-electron three-centre bonding. When the $2p$ orbitals are included, the converse of this conclusion is obtained from exploratory calculations that are not fully variational. However, regardless of the nature of the primary origin of hypercoordination, the axial three-centre bonding may be associated with resonance between two increased-valence structures, and this resonance is equivalent to resonance between the eight canonical Lewis structures that are associated with three electrons and three overlapping AOs. For CLi_6, the presence of fractional Li–Li bonding is partly a consequence of the presence of two three-electron three-centre bonding units.

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Appendix: Some comments on increased-valence

The simplest reason for designating VB structures (I) and (II) as "increased-valence" structures is that these structures are stabilized energetically relative to the corresponding Lewis structures (III) and (IV). When the one-electron bond parameter l for structures (I) and (II) is set equal to zero in the wavefunctions of eqns. (5) and (7), the wavefunctions Φ_{III} and Φ_{IV} are obtained for the Lewis structures (III) and (IV). A variational choice of the LMO parameters k', k'' and l in eqns. (5) and (7) must generate energies that are lower than when $l = 0$.

Another approach to the "increased-valence" designation for VB structures (I) and (II) is to demonstrate that, with respect to the axial a–b, a–c and b–c bonding, the sum of the atomic valencies for the axial a, b and c AOs in these structures can exceed the maximum value of two that occurs in each of the Lewis structures (III) and (IV). To do this, we shall adopt the simplest approach, which involves setting $k'' = 1/k' = k$, and omitting AO overlap integrals from MO normalization constants and orthogonality relationships. For structure (I), Φ_I of eqn. (9) then reduces to

$$\Phi_I \propto |\varphi_{ab}\varphi_{bc}\bar{\varphi}_{bc}| \tag{A1}$$

in which $\varphi_{ab} = a + lb$ and $\varphi_{bc} = b + kc$.

An orthogonal transformation of the $m_s = +1/2$ molecular spin orbitals gives

$$\Phi_I \propto |\varphi_1\varphi_2\bar{\varphi}_{bc}| \tag{A2}$$

in which φ_1 and φ_2 are the orthogonal three-centre MOs of eqn. (A3):

$$\varphi_1 = a + (l + \mu)b + \mu kc$$
$$\text{and } \varphi_2 = \mu a + (\mu l - 1)b - kc \tag{A3}$$

with μ given by

$$\mu + (l + \mu)(\mu l - 1) - \mu k^2 = 0 \tag{A4}$$

From the normalized MOs of eqn. (A3), the atomic valencies for the four-electron configuration $|\varphi_1\varphi_2\bar{\varphi}_1\bar{\varphi}_2|$ may be calculated from the Armstrong–Perkins–Stewart formulae [42] of eqn. (A5):

$$V_{ab} \equiv V_{ba} = P_{ab}^2,\ V_{ac} \equiv V_{ca} = P_{ac}^2,\ V_{bc} \equiv V_{cb} = P_{bc}^2 \tag{A5}$$

in which P_{ab}, P_{ac} and P_{bc} are the bond orders of eqns. (A6)–(A8):

$$P_{ab} = 2\{N_1^2(l + \mu) + N_2^2\mu(\mu l - 1)\} \tag{A6}$$

$$P_{ac} = 2k\mu(N_1^2 - N_2^2) \tag{A7}$$

$$P_{bc} = 2\{N_1^2\mu k(l + \mu) + N_2^2 k(1 - \mu l)\} \tag{A8}$$

for this configuration. The N_1 and N_2 are the normalizing constants for the MOs. In eqn. (A2), the φ_1 and φ_2 MOs are singly-occupied, and therefore the (α spin) valencies (V_{ab}^{α} etc.) that arise from occupation of these MOs are one-half of those given in eqn. (A5). The normalized φ_{bc}^{β} spin orbital of eqn. (A2) will also contribute to the b and c AO valencies according to

$$V_{bc}^{\beta} \equiv V_{cb}^{\beta} = 2k^2/(k^2 + 1)^2 \tag{A9}$$

which are one-half of the Armstrong–Perkins–Stewart valencies for these AOs when φ_{bc} is doubly occupied. The total a, b and c AO valencies for configuration Φ_I of eqn. (A1) are then given by

$$V_a = V_{ab}^{\alpha} + V_{ac}^{\alpha},\quad V_b = V_{ba}^{\alpha} + V_{bc}^{\alpha} + V_{bc}^{\beta},$$
$$V_c = V_{ca}^{\alpha} + V_{cb}^{\alpha} + V_{cb}^{\beta} \tag{A10}$$

For $k = 1.06$ and $l = 0.59$ in structure (I), $V = V_a + V_b + V_c$ has a maximum value of 2.268. When $l = 0$, as occurs in the Lewis LMO structure (III), the maximum for V is 2, which occurs when $k = 1$. Therefore for appropriate values of the LMO parameters k and l, the sum of the a–b, a–c and b–c valencies for structure (I) is able to exceed the corresponding total for the Lewis structure (III), for which the V_a of eqn. (A10) is equal to zero. However, V_b can never exceed unity, with $V_b = 1$ for $k = 1$ and $l = 0$, i.e. when structure (I) reduces to structure (III) with a homopolar b–c bond. Thus the hypervalence of the carbon atom in structures (I) and (II) is apparent, not real.

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