BONDING IN BORON HYDRIDES

W. N. LIPSCOMB

Department of Chemistry, Harvard University
Cambridge, Massachusetts, USA

ABSTRACT

Unique preferred localized valence structures for B_2H_6, B_4H_{10}, B_5H_{11} and B_6H_{10} have been found from accurate self-consistent field wavefunctions by maximizing Coulomb repulsions of electron pairs within orbitals. Objective evidence has thus been obtained for two-centre BH, three-centre bridge BHB, two-centre BB and central three-centre BBB bonds, but not, as yet, for open three-centre BBB bonds. Localization in B_5H_9 is ambiguous, as it is in organic molecules such as benzene. More thermodynamical stable isomers or plausible reaction pathways appear to have more resonance structures, and less reactive (or more plausible) structures or intermediates appear to have more nearly uniform charge distributions.

INTRODUCTION

Given the same number of valence orbitals as carbon but one less electron, boron is said to form electron-deficient compounds. However, in another sense these compounds are not deficient because the extended topologies of carbon chemistry are not found in boron compounds. Instead, a contracted topology occurs, mainly exemplified geometrically by bridge hydrogens and by boron triangles.

The simplest valence-theoretical description of this contracted topology is the three-centre two-electron bond, which has gradually developed into a general theory[1-5] of bonding in boron hydrides, their derivatives and their plausible reaction intermediates. Only among the simplest structures are unique, or preferred, valence descriptions possible. More complex structures require resonance descriptions when three-centre and two-centre bonds are used as a basis[6]. Nevertheless, in the sense that the most stable orbitals are filled, and that a substantial energy gap exists towards the unfilled (excited) state, these 'electron-deficient' molecules are indeed closed-shell species.

Molecular orbital theory in the form of the extended Hückel theory was originated and first applied to these larger boron hydrides[6,7] in order to provide an alternative to these resonance descriptions. Subsequently, both the logical basis and the source of parameters for these molecular orbital studies were greatly improved, and relationships were thereby established[8,9] to the rigorous molecular self-consistent field (SCF) method[10]. By the averaging of Coulomb repulsions, but the inclusion of exchange interactions and use of

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accurate values for all integrals, the SCF method has recently been applied to a variety of complex molecules including B_2H_6[11], B_4H_{10}, B_5H_9, B_5H_{11}[12,13], and B_6H_{10}[14]. Because of the self-consistency condition required to obtain the electron distributions which minimize the total molecular energy, each molecule tends to become an individual, as indeed it is. However, the boron hydrides must be very closely related to one another, as is clearly evident from their chemical behaviour. Hence, one would like more than individual descriptions and more than delocalized descriptions. Can these molecular orbital descriptions be related to localized orbitals, and to resonance pictures?

It turns out that this can be done on a completely objective basis[15-19]. The self-consistent procedure yields delocalized molecular orbitals which correspond to the symmetry properties of the molecule. Mixing of these orbitals is permitted in such a way that no change occurs in the molecular electron density (or total energies) by a process which an organic chemist might call rehybridization, or which a chemical physicist would call more precisely a unitary transformation. A simple example is the sum and difference of the σ bond and the π bond of the double bond in ethylene. The result is one 'banana' bond above the molecular plane (*Figure 1*), and another such bond
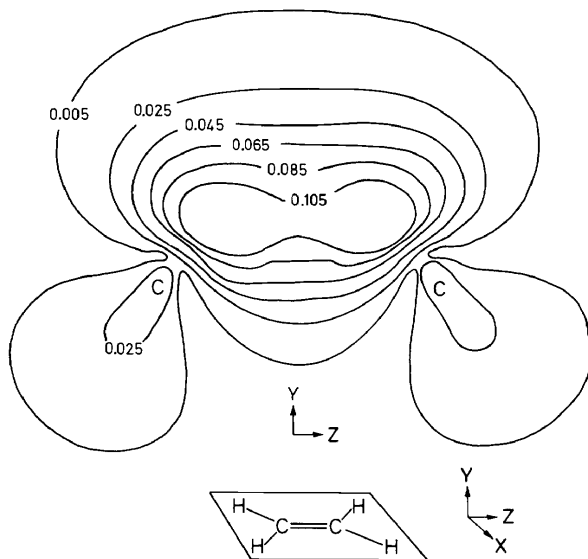

Figure 1. Localized C—C bond in ethylene. Contours are shown for the total density of one electron in electrons/a.u.^{3}, where 1 a.u. = 0.529 Å.

below this plane. Whereas the σ (or π) molecular orbital is related in a simple way to the point group symmetry of the molecule, one of these localized 'banana' bonds is not. Nevertheless, both descriptions give the same total electron density for the double bond, if either pair of wavefunctions is squared

and added together. The two different localized orbitals are more nearly in different spatial regions than are the delocalized (σ, π) orbitals. Moreover, the two electrons within one localized orbital are confined almost entirely to one side of the ethylene molecule, and would tend to show more mutual repulsion than a pair in one of the delocalized (σ or π) orbitals. A more precise description is given below.

An important result in the boron hydrides is the strong unambiguous support for the three-centre hydrogen bridge and for the central three-centre BBB bond. However, in no boron hydride, so far, has the open three-centre BBB bond appeared as a preferred localized bond. Hence, we shall examine the resonance theory of boron hydrides without including this open three-centre BBB bond. It is important to stress that a preferred localization is sometimes not preferred by much; almost invariably valence structures involving an open three-centre BBB bond are very close indeed to a linear combination of structures involving central three-centre BBB bonds together with single BB bonds. For that reason, boron chemists may find it convenient to retain simple valence descriptions in terms of open three-centre bonds, especially since it is often quite impractical to write all resonance structures for a given geometrical formula. For example, one does not misunderstand the organic chemist who writes only one of the many possible resonance structures for a polynuclear aromatic hydrocarbon.

Finally, we examine below the possibility that three-centre resonance structures can give some indications of relative stabilities of isomers, of isomerization pathways, of plausible intermediates in more complex reactions, and of possible new molecular species.
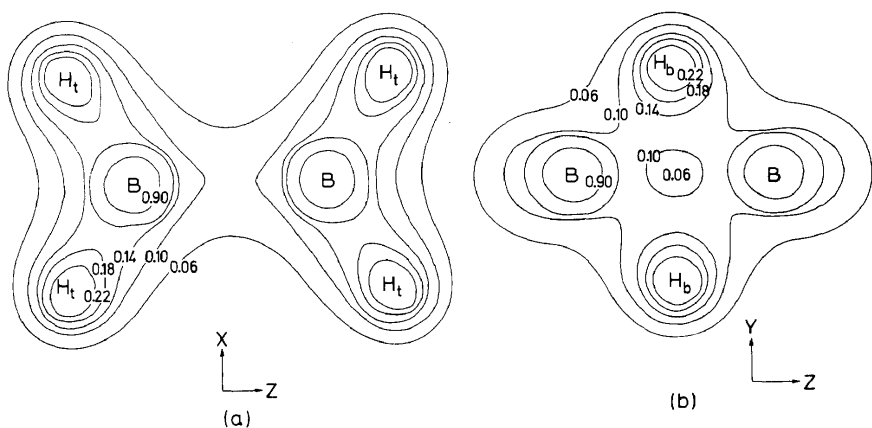
ACCURATE SELF-CONSISTENT FIELD MOLECULAR ORBITALS

Having sketched the historical line, we now proceed to recent studies which are sufficiently accurate to serve as a basis for reference to approximate theories and to experimental studies. In the self-consistent field method for molecules[10] the molecular orbitals are expressed as linear combinations of atomic orbitals, all molecular integrals including those over 1s orbitals are evaluated accurately, and the total energy of the system is minimized with respect to variation of the constants of the linear combinations, and sometimes with respect to variation of orbital exponents. The wavefunction for a given electron is obtained in the space-averaged potential of all other electrons and nuclei, and then the process is repeated iteratively through all electrons as many times as required until the wavefunctions no longer change. In actual practice these variations can largely be made simultaneously. It is this iterative process which makes the procedure self-consistent, and gives it its name. The resulting molecular orbitals are thereby separated into different symmetry classes, and are significantly delocalized over much of the molecule. However, by use of a standard partitioning procedure[20] the square of the wavefunction can be divided into localized charges which are summarized in *Table 1*, and bonding densities exemplified for the two major planes through B_2H_6 in *Figure 2* can be plotted and examined.

The atomic charges (*Table 1*) are all within the range of ± 0.12 electrons.

Table 1. Self-consistent field charge distribution in small boron hydrides

B_2H_6		B_4H_{10}		B_5H_9		B_5H_{11}		B_6H_{10}	
B	0.12	B1	-0.02	B1	0.00	B1	-0.08	B1	-0.02
H_t	-0.07	B3	0.08	B2	0.06	B2	0.05	B2	0.07
H_b	0.01	H_t1	-0.05	H_t1	-0.09	B4	0.09	B3	0.06
		H_t3	-0.07	H_t2	-0.04	H_t1	-0.07	B4	0.04
		H_t5	-0.07	H_b2	0.01	H_t2	0.06	H1	-0.07
		H_b1	0.06			H_t3	-0.03	H2	-0.04
						H_t5	-0.06	H3	-0.04
						H_t7	-0.07	H4	-0.09
						H_b1	0.03	H23	0.03
						H_b2	0.06	H34	0.02

Figure 2. Total electron density ($e/a.u.^3$) in the plane of the four terminal atoms (left), and in the plane of the bridge hydrogen and boron atoms (right).
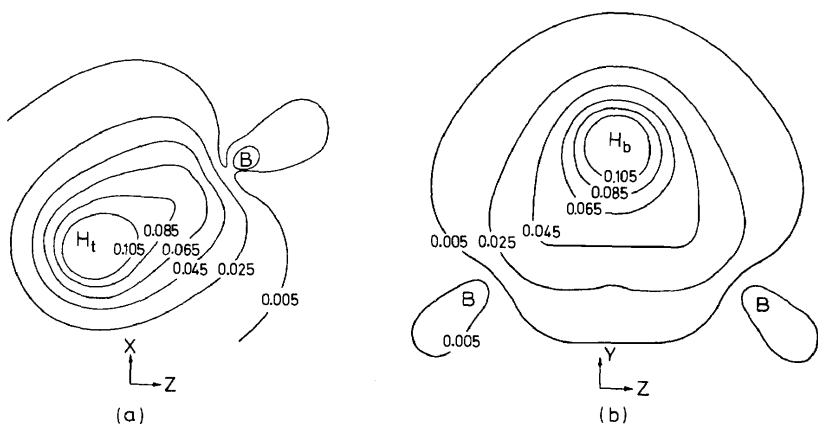
Figure 3. Density for one electron in $e/a.u.^3$ for (a) the B—H_t bond and (b) the BHB bond in B_2H_6.

Also, apex B atoms are more negative than are other B atoms, and those in BH_2 groups are more positive than those in BH groups. Negative H_ts relative to positive H_bs are an artifice of partitioning. The unique hydrogen H_t2 in B_5H_{11}, which we shall discuss later, has charge and other properties more like a bridge hydrogen than a terminal hydrogen, but is intermediate in some and extreme in other properties (*Tables 2* and *3*). Specific comments

Table 2. B—H_t bonds

	Population		sp^x	Angle, degrees	$d\%$†
	B	H_t			
B_2H_6§	0.94	1.08	2.0	3	*
B_4H_{10}					
B1—H_t1	0.94	1.07	1.5	1.0	7
B3—H_t3	0.92	1.09	1.8	0.9	8
B3—H_t5	0.94	1.09	1.8	1.4	7
B_5H_9					
B1—H_t1	0.91	1.10	1.3	0.0	6
B2—H_t2	0.95	1.05	1.5	3.4	6
B_5H_{11}					
B1—H_t1	0.93	1.09	1.7	0.2	6
B1—H_t2	0.76	0.98	3.4	5.1	14‡
B2—H_t3	0.97	1.05	1.4	5.8	6
B5—H_t6	0.94	1.08	1.6	5.6	6
B5—H_t8	0.89	1.10	2.1	1.6	10
B_6H_{10}					
B1—H1	0.93	1.09	1.5	*	7
B2—H2	0.97	1.05	1.4	*	6
B3—H3	0.96	1.05	1.4	*	6
B4—H4	0.92	1.10	1.6	*	7

* Not calculated. † For the definition of the delocalization percentage see text. Values of d for the inner shell vary only from 3.4 to 3.9 per cent.
‡ The unique H_t2 in B_5H_{11} is partially bonded also to B4 and B5. In some ways it resembles a bridge rather than a terminal hydrogen.
§ See *Figure 3*.

Table 3. BH_bB bonds

		Population			Angle, degrees		
		B—H_b—B′			sp^x	B—H_b—B′	$d\%$
B_2H_6							
B—H_b—B′§	0.51	1.02	0.51		2.5,2.5	2	2	*
B_4H_{10}							
B1—H_b1—B3	0.63	0.95	0.43		3.5,4.3	4	19	10
B_5H_9							
B—H_b—B′	0.50	1.01	0.50		3.4,3.4	3	3	10
B_5H_{11}							
B2—H_b1—B3	0.53	0.97	0.53		3.4,3.4	12	12	10
B2—H_b2—B4	0.59	0.96	0.44		4.2,4.8	9	15	10
B_6H_{10}							
B2—H_b—B3	0.55	0.99	0.48		3.7,3.4	*	*	10
B3—H_b—B4	0.58	1.01	0.42		3.6,7.2	*	*	10

* Not calculated. § See *Figure 3*.

will be made about the total density for individual molecules below, but at least two observations appear to be general. First, bridge hydrogens between BH and BH_2 groups are more strongly bonded towards the BH group, and, secondly, the electron density is very low directly between two boron atoms which are connected by a bridge hydrogen[12].

Localization of these symmetry orbitals produces new linear combinations of atomic orbitals in such a way that the molecular density and total energy are unaltered. Another quantity which also remains invariant is the total two-electron energy: that part which depends upon integrals over the electron repulsion term, e^2/r_{ij}, i.e. $1/r_{ij}$ in atomic units (a.u.) of -27.2 eV. The quantities changed by this rehybridization procedure are the three terms which make up this total two-electron energy. The simplest of these conceptually is the self-repulsion energy for two electrons within the same orbital, summed over all such orbitals,

$$D = \sum_k (kk|kk) = \sum_k \int \phi_k(i)\, \phi_k(j)\, \frac{1}{r_{ij}}\, \phi_k(i)\, \phi_k(j)\, \mathrm{d}V_i \mathrm{d}V_j$$

which is maximized if the electrons are as localized as possible. The other two terms are the exchange energy,

$$-2 \sum_{k>l} 2(kl|kl)$$

which is minimized, and the interorbital Coulomb energy,

$$\sum_{k>l} 4(kk|ll)$$

which is minimized. For example, in B_6H_{10} in which the total two electron energy is 225 a.u., the self-repulsion energy changes from 16 to 26 a.u., the exchange energy changes strikingly from -11 to -1 a.u., and the interorbital Coulomb energy changes from 219 to 200 a.u. as one transforms from delocalized symmetry orbitals to localized orbitals.

We now turn to a discussion of these localized orbitals and other aspects of electron density in the smaller boron hydrides, as summarized in *Tables 2, 3* and *4*. The striking consistency of populations in BH_t and BH_bB bonds among these several molecules is a reminder of their common chemical and spectroscopic properties. Also, the angles between the localized hybrids and bond directions vary up to about 6 degrees in BH_t bonds and to 19 degrees in BH_bB bonds, so that perhaps 'orbital steering' is not an important effect in boron hydrides. A quantitative evaluation of localization is given by the delocalization index

$$d\% = 100[\tfrac{1}{2} \textstyle\int (\phi_k^L - \phi_k^T)^2 \,\mathrm{d}V]^{\frac{1}{2}}$$

expressed as a root mean square. Here ϕ_k^L is the localized orbital, concentrated, for example, on a particular B and H_t for a BH_t bond, or on a particular H_b and its two bonded B atoms in a bridge bond. However, the localization is not complete so that there are some smaller tails of the localized wavefunctions associated with all other atoms of the molecule. If these tails are truncated, i.e. if contributions from these other atoms are omitted, and if the

wavefunction is then renormalized the truncated (localized) orbital ϕ_k^T is obtained. We note that if ϕ_k^L and ϕ_k^T are identical the delocalization index is zero and that if they are orthogonal the index is 100 per cent. These indices are summarized in *Tables 2, 3* and *4* for BH_t, BH_bB and single bonds or central three-centre bonds among boron atoms. For the inner shell ls orbital of boron, values of d range from 3.4 to 3.9 per cent in B_4H_{10}, B_5H_{11}, B_5H_{10} and B_5H_9

Table 4. Boron—boron bonds

Population				sp^x			$d\%$
B_4H_{10}							
B1—B2	0.81	0.81		3	3		14
B_5H_9							
A* { B1—B2—B3	0.71	0.63	0.65	5	3	3	15
B1—B5—B2	0.71	0.85	0.33	5	3	5	15
B1—B3—B4	0.71	0.31	0.86	5	5	3	16
B* { B1—B2—B3	0.71	0.55	0.72	5	4	3	15
B1—B5—B2	0.71	0.81	0.42	5	3	4	15
B1—B3—B4	0.72	0.23	0.88	5	6	3	16
B_5H_{11}							
B1—B2—B4	0.72	0.77	0.44	4	3	2	14
B_6H_{10}							
B1—B2	0.69	0.83		7	3		17
B4—B5	1.00	1.00		2	2		11
B1—B3—B4	0.72	0.67	0.57	3	3	5	14

* Two distinct localized bond sets are obtainable for B_5H_9: A is close to a central three-centre bond and two single bonds, while B is less close to this simplified description.

In B_4H_{10} (*Figure 4*), the localized B—B orbital (*Figure 5*) is very well concentrated between B_1 and B_2. The hybridization of sp$^{3.0}$ is similar to that in many C—C bonds[21]. Most of the 14 per cent of delocalization is associated with the B atoms of the two BH_2 groups, in which each of these borons accounts for 0.19e in the total orbital population. This aspect of delocalization is noticeable in *Figure 5*.

In B_5H_{11} (*Figure 6*) the objective localization procedure has produced a clear choice for the localized bonds of I rather than II of *Figure 7*. If the result becomes general, one may conclude that central three-centre BBB bonds are to be preferred over open three-centre BBB bonds. The orbital itself (*Figure 8*) is rather strongly displaced away from B_4 of the outer BH_2 group, towards the apical B_1 and the inner basal B_2 atoms. This displacement is also supported by the directions of hybridization for the three atomic hybrid orbitals which make this three-centre bond (*Figure 9*). Further brief comments on plausible displacements of bonding density in central three-centre bonds will be made below in relation to $B_{10}H_{14}$.

Localization in B_6H_{10} (*Figure 10*) has clearly indicated only one preferred valence structure, that of *Figure 11a*. Of the 12 valence structures listed
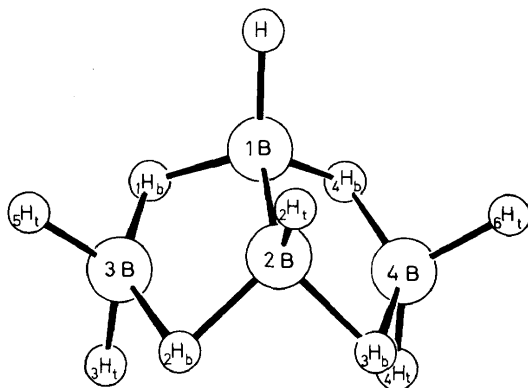
Figure 4. B_4H_{10}.
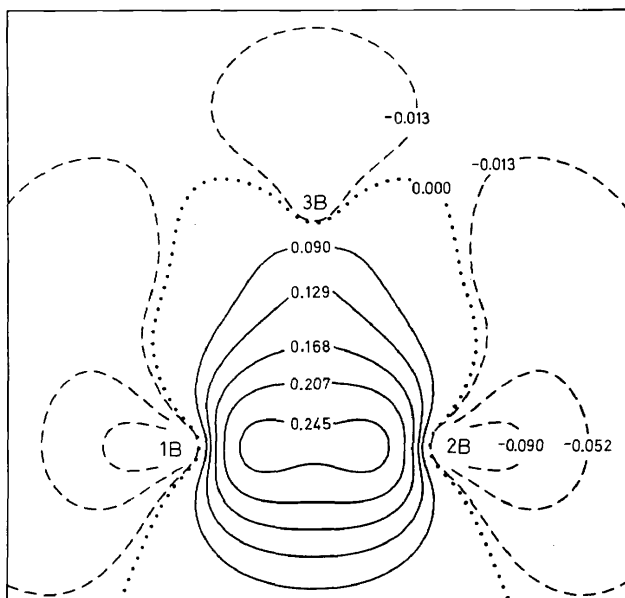
Figure 5. The B—B bond in B_4H_{10}. This is the orbital, not the electron density. Units are $(e/a.u.^3)^{\frac{1}{2}}$ and are normalized for one electron.
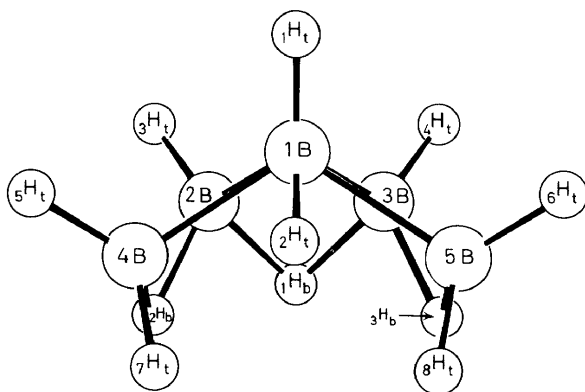
Figure 6. B_5H_{11}.

(I)

(II)

Figure 7. Nearly equivalent valence bond structures for B_5H_{11}. (I) has two central three-centre BBB bonds, while (II) has one central and one open three-centre BBB bond.
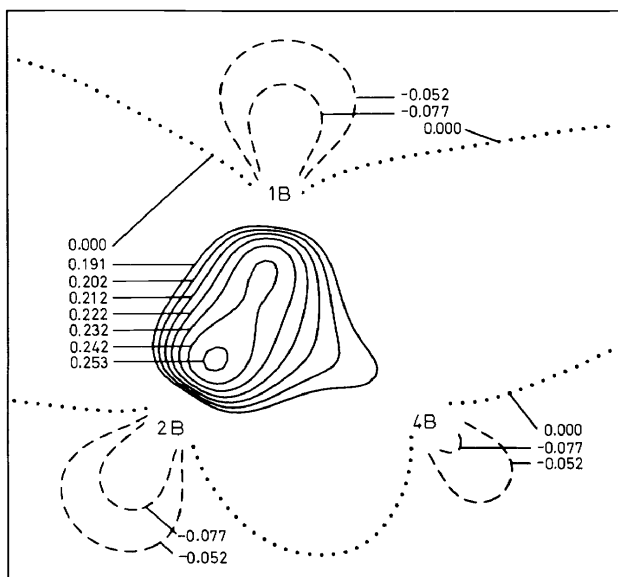

Figure 8. Localized central three-centre BBB bond in B_5H_{11}. This is the orbital in $(e/a.u.^3)^{\frac{1}{2}}$, not the electron density, normalized to an occupancy of one electron.

501
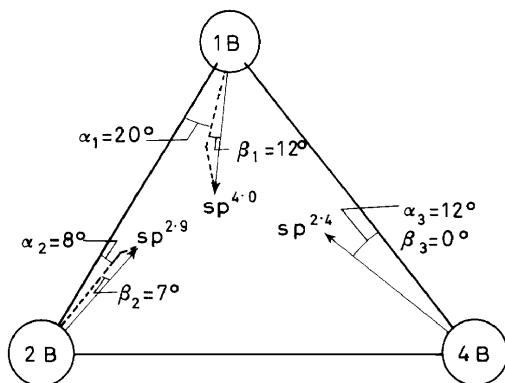
Figure 9. Direction of hybridization in the central three-centre 1B—2B—4B bond in B_5H_{11}.
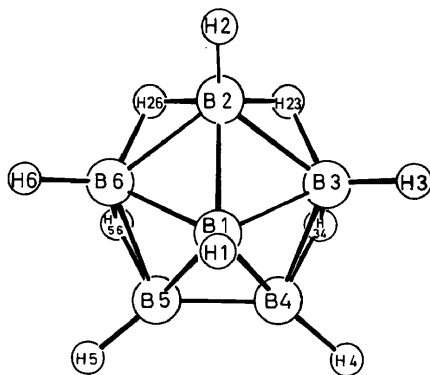
Figure 10. B_6H_{10}.

previously[1], the 3 which contain central three-centre bonds are shown in *Figure 11*, together with π donation models made plausible by the very short B_4—B_5 distance of 1.60 Å (*Figure 12*) and a comparison with the structure of $C_2B_4H_8$[22]. An extensive series of tests starting with different initial hybridizations, either randomly generated or like known valence structures including the π donation model, all yielded only the structure of *Figure 11a*. Again, no open three-centre BBB bond is found. Even though B_4—B_5 localizes as a single bond, not a double bond, it is very different from the other, not so localized, B_1—B_2 single bond (*Table 4*). Nor does the preferred structure eliminate substantial double bond character of the short B_4—B_5 bond. Nevertheless, the preferred three-centre description of bonding in B_6H_{10} has been very greatly simplified by this criterion which most localizes electron pairs.

For B_5H_9 (*Figure 13*), the aromatic-like (benzene-like) member of the smaller hydrides, the localization is ambiguous, depending upon the starting set of linear combinations. The two localized descriptions which were found upon maximizing the intraorbital Coulomb repulsion energy are shown in *Table 4*. In Set A, one may reasonably interpret the B1—B2—B3 bond as being central three-centre, and the other two being approximately single bonds B1—B5 and B1—B4. However, atoms B4 and B5 are adjacent, not opposite, in the basal plane of B_5H_9, so that Set A (*Table 4*) corresponds closely to one of the four equivalent resonance structures of *Figure 14 II*. Yet again, this localization has yielded a preference for a central three-centre BBB bond, rather than for an open three-centre BBB bond. The alternative Set B does not have a simple interpretation in terms of two-centre and three-centre BBB bonds. Perhaps this is intermediate between the hybrids I and hybrids II of *Figure 14*, but if so this set does not come close to preference for the open three-centre BBB bond, even for the B1—B2—B3
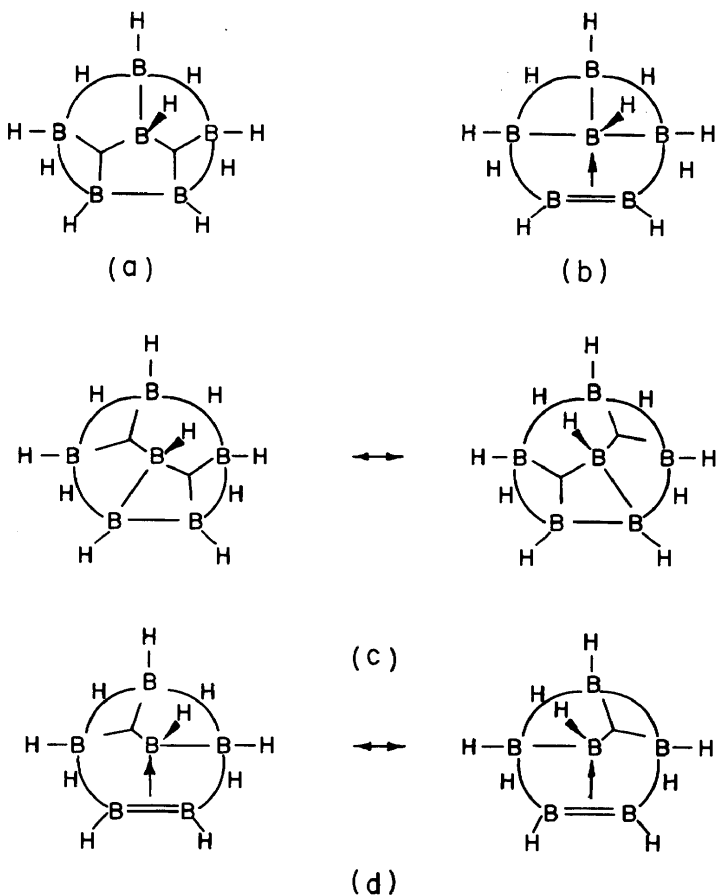

(a)   (b)

(c)

(d)

Figure 11. Central three-centre and π donation bond models for B_6H_{10}. Model (b) has an open three-centre $B_3B_1B_6$ bond.

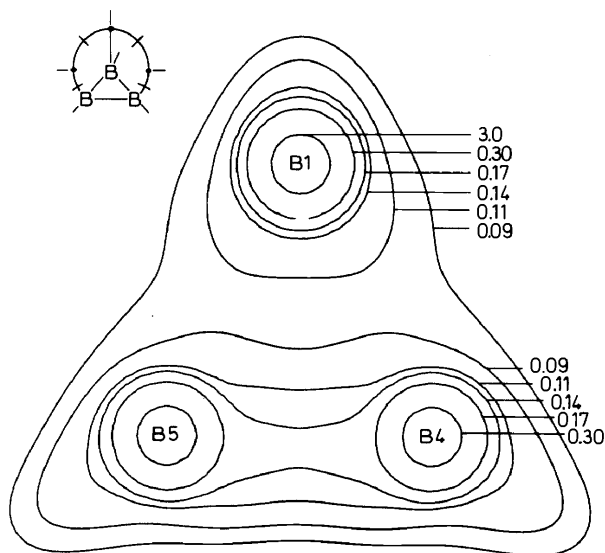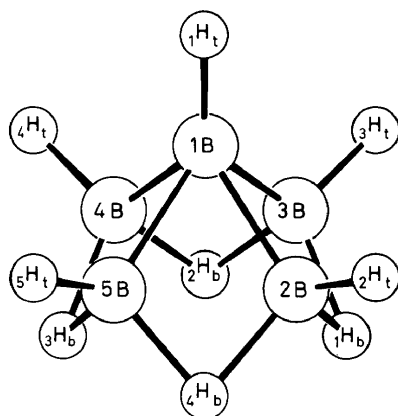*Figure 12.* Total electron density (e/a.u.^{3}) in the B1—B4—B5 plane of B_6H_{10}.

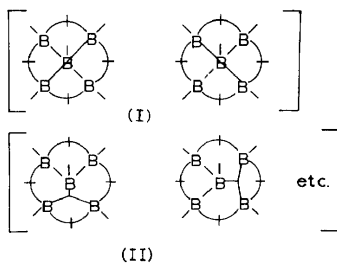*Figure 13.* B_5H_9.

(I)

(II)

Figure 14. Resonance structures corresponding to 4120 (styx) bond arrangement in B_5H_9.

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bond. More generally, one may expect ambiguities in the localization when the resonance hybrids are strictly equivalent by molecular symmetry.

Summarizing thus far, we find that reduction of delocalized SCF orbitals to single preferred valence structures for B_2H_6, B_4H_{10}, B_5H_{11} and B_6H_{10} yields a striking correlation with three-centre bond theory. The resonance description required for a description of B_5H_9 when three-centre bonds are used is perhaps indicative of the relative stability of this member of the series of small boron hydrides. Perhaps these simple descriptions will persist for the more open boron hydrides as large as B_9H_{15}, but the more compact and larger species will ordinarily require resonance descriptions if three-centre bonds are employed. Even so, one can expect simple localized bond descriptions for the simplest polyhedral species, such as B_4H_4 and $1,2\text{-}C_2B_4H_6$, but not in general for the higher members of polyhedral molecules and ions.

RESONANCE, CHARGE DISTRIBUTION AND REACTIVITY

Chronologically, three-centre bond theory gave way to extended Hückel theory, parametrized molecular orbital theory and self-consistent field (SCF) theory. We now note the influence of this development on the original three-centre theory itself. Assume for the present that the evidence from a very limited number of examples is general: that open three-centre BBB bonds do not occur as preferred valence structures when nearly equivalent valence structures can be drawn in terms of central three-centre bonds together with two-centre bonds. Results are first examined for $B_{10}Cl_4$, $B_9H_{14}^-$, $B_{10}H_{14}^{2-}$ and $B_{10}H_{13}^-$, and then some general speculations are made on a few reaction pathways and intermediates.

A typical result is the great reduction in the number of valence structures, as exemplified for $B_{10}H_{14}$. Inclusion of open three-centre BBB bonds in $B_{10}H_{14}$ led to 111 valence structures, but their elimination reduces the number to 24 (*Figure 15*), thereby increasing considerably the probability that someone can discover all of them without the use of a computer program†. If the charge distributions of valence structures of types I-IV or of types I–VI are averaged the results of *Table 5* are found. For comparison we give the charge distribution for the only valence structure having the full C_{2v} molecular symmetry in *Figure 16*. Of course, this C_{2v} valence structure has two open three-centre BBB bonds. However, with due regard for the changes of hybridization of B_2 (and B_4) from sp^2 to sp^3, one may think of this valence structure as almost equivalent to the set IV (*Figure 15*). Hence, for convenience in drawing the structure of $B_{10}H_{14}$ it may be appropriate to suggest the continuance of its already widespread use.

The charge distribution from a structure, such as that in *Figure 16*, is obtained by dividing two-centre bonds equally between bonded atoms, central three-centre bonds equally among three bonded atoms, and open three-centre BH_bB or BBB bonds as $-0.5e$, $-e$ and $-0.5e$ on the three

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† Replacement of a computer by a person is analogous to replacement of SCF theory by three-centre bond theory.
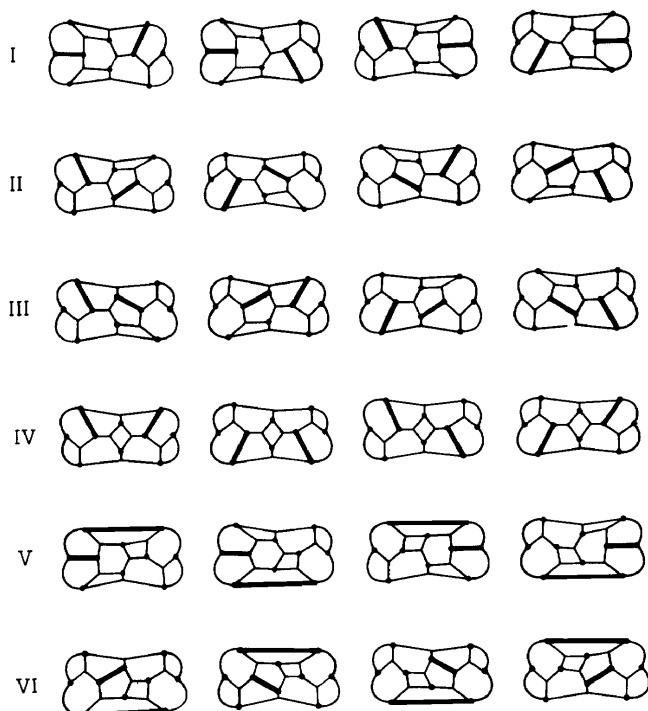
Figure 15. Resonance structures for $B_{10}H_{14}$. No open three-centre BBB bonds are included here. Hybrids of types V and VI may make smaller contributions than do types I–IV in view of the long B_5—B_{10} distance.

Table 5. Charges for resonance forms of $B_{10}H_{14}$

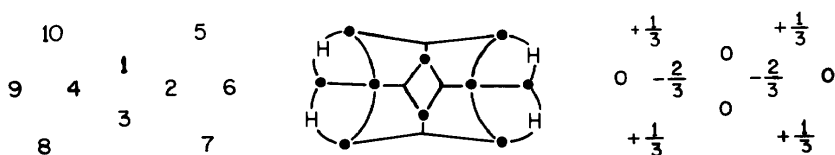|	I	II	III	IV	Av(I–IV)	V	VI	Av (I—VI)
B_1	0	$-\frac{1}{6}$	$-\frac{1}{6}$	0	-0.08	0	$-\frac{1}{6}$	-0.08
B_2	$-\frac{1}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$	$-\frac{1}{3}$	-0.33	$-\frac{1}{6}$	$-\frac{1}{6}$	-0.28
B_5	$\frac{1}{12}$	$\frac{1}{12}$	$\frac{1}{12}$	0	0.06	0	0	0.04
B_6	$\frac{1}{6}$	$\frac{1}{3}$	$\frac{1}{3}$	$\frac{1}{3}$	0.29	$\frac{1}{6}$	$\frac{1}{3}$	0.28

Figure 16. Numbering system, full-symmetry valence structure (with two open three-centre BBB bonds) and exaggerated charge distribution arising from this valence structure for $B_{10}H_{14}$.

bonded atoms. We note that the charge distribution in $B_{10}H_{14}$ is poorly represented by this structure containing open three-centre bonds in at least two respects: the reversal of charges on B_5 and B_6, and the exaggeration of negative charge on B_2 (*Figure 16*). Neither of these problems arises with any set of the six types of valence structures for $B_{10}H_{14}$. Furthermore, either the average of sets I–IV or of sets I–VI places charges on the four B atoms in the order expected from reactions with the wide variety of those nucleophilic and electrophilic reagents which appear to retain some memory of the initial ground state charge distribution in the transition state (e.g. H^+ attack, Friedel–Crafts substitution, ligand attack, halogenation, ethoxide attack, etc.). The way in which this oversimplified view of reactivity correlates boron hydride chemistry has yet to be evaluated on a mechanistic basis, although it appears that the carboranes show some atomic charge versus reactivity correlation[23]. Closer study of the outer charges, and perhaps the phase of the wavefunctions in the highest filled and lowest unfilled molecular orbitals is needed, as are studies which yield information about the pathways and probable structures of reaction intermediates.

No electron density for $B_{10}H_{14}$ is available at present at a level of accuracy comparable with densities in the smaller hydrides. However, a careful x-ray and neutron diffraction study[24] has yielded molecular density from which spherical atoms have been subtracted. This difference function yields, to first order, the electron densities in the BH_t and BH_bB bonds. When a correction has been incorporated for these, smaller difference densities appear in the boron framework: between B_2 and B_6, between B_1 and B_5, and in the $B_1B_2B_3$ triangle (*Figure 17A*). While there is some general correspondence
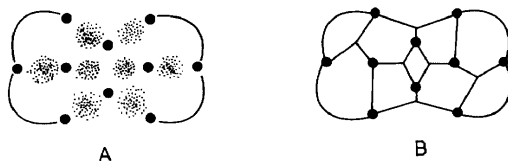

A   B

Figure 17. Difference densities (schematic) in the boron framework summarized from the x-ray study of Brill, Dietrich and Dierks. One of four equivalent (by C_{2v} symmetry) resonance structures showing probable unsymmetrical central three-centre bonds, more open towards hydrogen bridges and towards the long B—B contacts.

of these difference densities with a composite of the three-centre bond descriptions of *Figure 14*, especially for the B_2—B_6 bond and the $B_1B_2B_3$ triangle, the long distance B_5—B_{10}, not explained by three-centre bond theory, may imply a very unsymmetrical central three-centre BBB bond in the B1—B5—B10 triangle, as suggested by four equivalent hybrids of the type shown in *Figure 17B*. This abnormally long distance may result from a poorly directed hybrid orbital on B_5 (and B_{10}). However, $B_{10}H_{14}$ is sufficiently intermediate between the open hydrides and the larger polyhedral hydrides that no simple three-centre bond description, or small number of hybrids, can be adequate.

The $B_9H_{14}^-$ structure[25], which is like one of two alternatives proposed earlier[26], raises a question about the formal structural analogy exemplified here between $B_9H_{13}L$ (where L is a ligand such as $NCCH_3$) and $B_9H_{14}^-$. These structures were thought to be analogous[26] but with strong tendencies for rearrangements among bridge H and extra H of the BH_2 groups in the negative ions. However, the structures of $B_9H_{13}L$[26] (*Figure 18A*) and of $B_9H_{14}^-$ (*Figure 18B*) are different in a way which, in this case, allows for both a more nearly uniform formal charge distribution among boron atoms and for

A   B
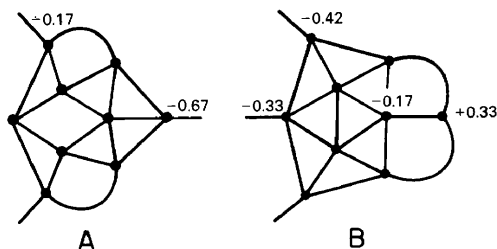
Figure 18. $B_9H_{14}^-$ structures: A (like $B_9H_{13}NCCH_3$) has two bond structures. B (in CsB_9H_{14}) has four bond structures, and a less extreme charge distribution. Unmarked atoms have zero formal charges.

more resonance structures for the $B_9H_{14}^-$ ion. The extra·nuclear charge of the ligand nucleus helps to accommodate the excess of negative charge on the boron to which it is attached in $B_9H_{13}L$. In the following examples, we suggest that one may generally expect different structures for ligand compounds as compared with the boron hydride ions obtained by formal replacement of L by H^-.

Two structures for $B_{10}H_{14}$ are compared in *Figure 19*. Structure A is analogous to the known structures for $B_{10}H_{12}L_2$ compounds, where L is
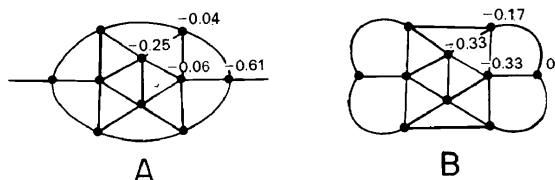

A   B

Figure 15. $B_{10}H_{14}^{2-}$ structures: A (like $B_{10}H_{12}L_2$) has 24 bond structures. B (H arrangement like $B_{10}H_{14}$) has only one bond structure but has a considerably less exaggerated charge distribution. Unmarked atoms have zero formal charges.

$NCCH_3$ or $S(CH_3)_2$, while structure B has a hydrogen arrangement like that of $B_{10}H_{14}$. Here, in contrast to $B_9H_{14}^-$ structures, the uniformity of charge distribution favours B, while a resonance stabilization argument favours A for $B_{10}H_{14}^{2-}$. The structure, still under x-ray investigation, is not yet known; nor is it easy to decide on theoretical grounds between these structures. Even details such as the placement of fairly negative charge on adjacent atoms in B, or non-adjacent atoms in A, may be important.

A similar ambiguity appears in the $B_{10}H_{13}^-$ structures (*Figure 20*) for which charge distribution favours C, but the number of three-centre resonance structures favours A. Again we must await the experiment, but in this example the charge argument is stronger than the resonance argument, as compared with the situation in the $B_{10}H_{14}^{2-}$ structures.
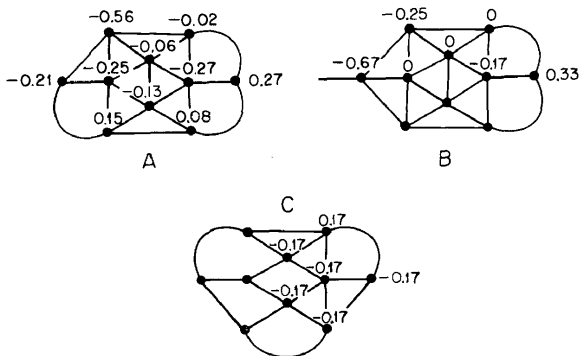

Figure 20. Examples of possible $B_{10}H_{13}^-$ structures. A has 16, B has 8 and C has 8 bond structures. Of these three, C has the least exaggeration of charges.

With respect to reaction pathways and intermediates, we are suggesting the hypothesis that those which can be described in terms of two-centre and three-centre bond structures are to be preferred over those which require other valence structures containing, for example, vacant orbitals or other types of multi-centre orbitals. Moreover, those intermediates which have a more nearly uniform charge distribution are less reactive and those which have more valence structures are probably more thermodynamically stable. These preferences may yield pathways which do not correspond to least motion of the atoms in some cases.

Some immediate examples are of rather a negative type, where intermediates seem unsatisfactory at present but where many possibilities still exist for satisfactory structures. For example, the first suggested product of the reaction of ethanol with $B_{10}H_{12}L_2$ has a reasonable structure[1], but later proposed steps do not. The same comment applies to the rearrangement suggested[1,27] for $B_{10}H_{16}$ to give $B_{10}H_{14} + H_2$. Moreover, loss of a ligand from $B_9H_{13}L$ gives the eminently satisfactory B_9H_{13} structure[28]. This loss of ligand is known to give $B_{18}H_{22}$[29]. One plausible intermediate, B_9H_{11}, has no satisfactory three-centre bond structures based upon the boron arrangement of $B_9H_{13}L$ compounds. However, we hasten to note that intermediates having a vacant orbital do indeed occur. For example, it need not be supposed that B_4H_{10} arises from two B_2H_6 molecules, with loss of hydrogen, since the importance of BH_3 with its vacant orbital is a reminder that exceptions may arise when a reaction may proceed in the presence of a very small concentration of an unstable intermediate. A similar comment may also apply to B_3H_7 as an intermediate, but for larger unstable species more satisfactory alternate pathways and structures probably exist.

ACKNOWLEDGEMENT

APPENDIX I

Charge distribution in $B_{16}H_{20}$

In *Figure 12* the charge distribution at each atom is averaged over the 218 valence structures for $B_{16}H_{20}$. The decaborane-like part has a charge
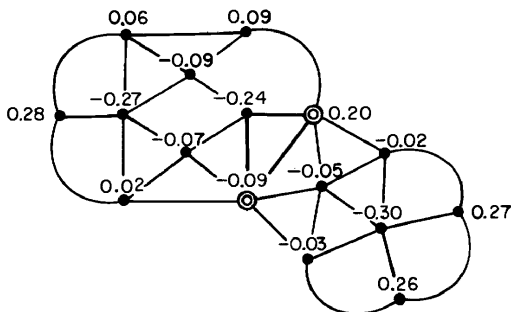

Figure 21. Charge distribution arising from the 218 valence structures for $B_{16}H_{20}$. The charge distributions for each valence structure have been given equal weight in this average distribution.

distribution similar to that for $B_{10}H_{14}$, and thus may undergo similar reactions. As usual, such charge distributions are exaggerated, and take no account of the non-orthogonality of the various valence structures.

APPENDIX II

Localized orbitals in $1,2\text{-}C_2B_4H_6$

A self-consistent field calculation[30] of delocalized molecular orbitals from a minimum basis set of Slater-type atomic orbitals has recently been sub-
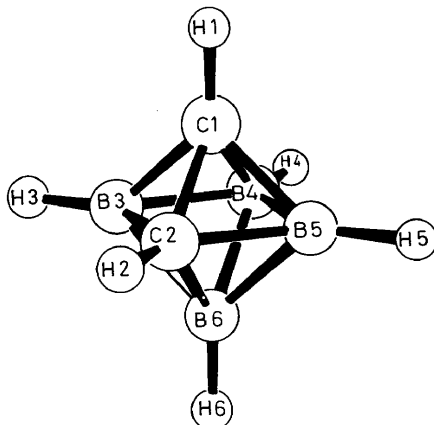

Figure 22. The structure of the $1,2\text{-}C_2B_4H_6$ molecule.

510

jected[31] to the localization procedure described above. The 13 valence pairs of electrons are distributed among 4 B—H bonds, 2 C—H bonds, and then among 4 three-centre bonds and 3 two-centre bonds among the remaining B and C orbitals. The structure localizes uniquely to a single C_1—C_2 bond, single C_1—B_4 and C_2—B_6 bonds, central three-centre $B_3B_4B_6$ and $B_5B_4B_6$ bonds, and open $B_3C_1B_5$ and $B_3C_2B_5$ three-centre bonds (Figure 22). While there are thus no open three-centre BBB bonds, there are two open three-centre BCB bonds! The extra nuclear charge at C, as compared with B, may favour the charge distribution $(-e/2, -e, -e/2)$ characteristic of an idealized open three-centre bond.

REFERENCES

[1] W. N. Lipscomb, Boron Hydrides W. A. Benjamin: New York (1963).
[2] R. E. Dickerson and W. N. Lipscomb. J. Chem. Phys. 27, 212 (1957).
[3] W. H. Eberhardt. B. L. Crawford and W. N. Lipscomb. J. Chem. Phys. 22, 989 (1954).
[4] H. C. Longuet-Higgins, J. Roy. Inst. Chem. 77, 197 (1953).
[5] H. C. Longuet-Higgins. J. Chim. Phys. 46, 275 (1949).
[6] R. Hoffmann and W. N. Lipscomb. J. Chem. Phys. 36, 2872 (1962).
[7] R. Hoffmann and W. N. Lipscomb. J. Chem. Phys. 37, 2179 (1962).
[8] M. D. Newton, F. P. Boer and W. N. Lipscomb. J. Am. Chem. Soc. 88, 2353 (1966).
[9] F. P. Boer, M. D. Newton and W. N. Lipscomb. J. Am. Chem. Soc. 88, 2361 (1966).
[10] C. C. J. Roothaan. Rev. Mod. Phys. 23, 69 (1951).
[11] E. Switkes, R. M. Stevens, W. N. Lipscomb and M. D. Newton, J. Chem. Phys. 51. 2085 (1969).
[12] E. Switkes, I. R. Epstein, J. A. Tossell, R. M. Stevens and W. N. Lipscomb. J. Am. Chem. Soc. 92, 3837 (1970).
[13] E. Switkes, W. N. Lipscomb and M. D. Newton, J. Am. Chem. Soc. 92, 3847 (1970).
[14] I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens and W. N. Lipscomb. Inorg. Chem. 10, 171 (1971).
[15] J. E. Lennard-Jones, Proc. Roy. Soc. (London) A198, 1, 14 (1949).
[16] G. G. Hall and J. E. Lennard-Jones. Proc. Roy. Soc. (London) A202, 155 (1950).
[17] J. E. Lennard-Jones and J. A. Pople. Proc. Roy. Soc. (London) A202, 166 (1950).
[18] J. E. Lennard-Jones and J. A. Pople. Proc. Roy. Soc. (London) A210, 190 (1951).
[19] C. Edmiston and K. Ruedenberg, Rev. Mod. Phys. 35, 467 (1963).
[20] R. S. Mulliken. J. Chem. Phys. 23, 1833 (1955).
[21] M. D. Newton, E. Switkes and W. N. Lipscomb. J. Chem. Phys. 53, 2645 (1970).
[22] F. P. Boer, W. E. Streib and W. N. Lipscomb. Inorg. Chem. 3, 1666 (1964).
[23] T. F. Koetzle and W. N. Lipscomb. Inorg. Chem. 9, 2743 (1970).
[24] R. Brill, H. Dietrich and H. Dierks, Angew. Chem. 82, 524 (1970); Acta Cryst. B27, 2003 (1971).
[25] N. N. Greenwood, H. J. Gysling, J. A. McGinnety and J. D. Owen, Chem. Commun. 505 (1970).
[26] F. E. Wang, P. G. Simpson and W. N. Lipscomb. J. Chem. Phys. 35, 1335 (1961).
[27] R. Grimes and W. N. Lipscomb. Proc. Nat. Acad. Sci. U.S. 48, 496 (1962).
[28] W. N. Lipscomb. Inorg. Chem. 3, 1683 (1964).
[29] J. Plešek, S. Heřmánek, B. Štíbr and F. Hanousek. Collection Czech. Chem. Commun. 32, 1095 (1967).
[30] I. R. Epstein. T. F. Koetzle, R. M. Stevens and W. N. Lipscomb. J. Am. Chem. Soc. 92. 7019 (1970).
[31] I. R. Epstein, D. S. Marynick and W. N. Lipscomb, to be published