(4) The other interference terms also appear in Table VIII. The OH and NH orbital contributions are larger than $\Delta I_{\mathrm{Me}}(\mathrm{av})$ in ethane by about the same amount that $\Delta I_{\mathrm{Me}}(\mathrm{av})$ in methanol and methylamine are smaller. Thus, *the decrease in the barriers in the order ethane > methylamine > methanol is largely due to the loss of vicinal bonds* (three in ethane, two in methylamine, one in methanol). This is slightly distorted, however, by the smaller contributions from the lone pairs. *In propene, the lower barrier (relative to ethane) is mostly due to the smaller contribution from the vinyl CH orbital, while in acetaldehyde this contribution and the reduced contributions from the methyl CH orbitals are responsible for the lower barrier.*

Except for H_2O_2, the molecules studied within the localized charge distribution analysis contain at least one methyl rotor. Work is presently underway to investigate the two-rotor analogs of the molecules discussed in this paper. Of particular interest will be the so-called steric hindrance in the all-eclipsed rotamers. Also being investigated is the applicability of the method to geometric isomerization, keto–enol tautomerism, ring strain, pseudorotation, and hydrogen bonding. The results will appear in future publications.

Acknowledgments. The authors gratefully acknowledge the computer time made available to them by the North Dakota State University Computer Center and the support of Professor Klaus Ruedenberg. One of us (M. S. G.) was supported in part by a National Science Foundation Institutional Grant to North Dakota State University.

Localized Molecular Orbitals for 1,2- and 1,6-Dicarbahexaborane(6). The Open Three-Center Bond and Implications for Carborane Topology

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Received August 28, 1972

Abstract: Localized molecular orbitals (LMO's) have been calculated for the 1,2 and 1,6 isomers of $C_2B_4H_6$ by the Edmiston–Ruedenberg procedure. The 1,2 isomer is the first example found in LMO calculations of the existence of the open three-center bond, and it occurs here only for the BCB nuclear configuration. The LMO structure for the 1,6 isomer is best interpreted in terms of fractional three-center bonding. We discuss the implications of these results for the general application of topological methods to boranes and carboranes.

The carboranes constitute a fascinating series of molecules for experimental and theoretical chemists alike. The polyhedral geometries and the peculiar bonding properties of these compounds give rise to such recently discovered phenomena as carborane analogs of ferrocene,[2] commercially significant high-temperature carborane–siloxane polymers,[3] and the fractional three-center bond.[4,5]

Although self-consistent-field (SCF) and localized molecular orbital (LMO) studies have been of enormous utility in elucidating the nature of chemical bonding in the boron hydrides,[6] only two carboranes, 2,4-$C_2B_5H_7$[4b] and 4,5-$C_2B_4H_8$,[5] have been studied by SCF and LMO methods. In these studies, special attention was paid both to the applicability of the topological theory of the boron hydrides[7,8] to carboranes and also to the relationship between the topological theory and the LMO approach. Briefly, it was found that neither the LMO's of $C_2B_5H_7$ nor those of $C_2B_4H_8$ closely correspond to a valence structure which satisfies the set of rules proposed by Epstein and Lipscomb (E–L) in their simplified topological treatment of the boron hydrides.[8] However, with a modification suggested earlier[9] for the bonding rules in $C_2B_4H_8$, we have found simple linear combinations of E–L allowed structures which correctly describe the relative bond strengths and atomic charges obtained from the SCF calculations in both of these molecules. By recognizing that complex molecules may require a linear combination of a few or several valence structures for their description, one can thus preserve the important simplification that conservation of orbitals, electrons, and topology[8] may be achieved with only two-center and three-center bonds in the boron or boron–carbon framework. In view of the potential usefulness of the topo-

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(1) (a) Brandeis University. (b) Harvard University.

(2) M. F. Hawthorne, L. F. Warren, Jr., K. P. Callahan, and N. F. Travers, *J. Amer. Chem. Soc.*, **93**, 2407 (1971), and references therein; the σ,π potential of bonding to the open face of a polyhedral fragment was recognized by E. B. Moore, Jr., L. L. Lohr, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **35**, 1329 (1961).

(3) K. O. Knollmueller, R. N. Scott, H. Kwasnik, and J. F. Sieckhaus, *J. Polym. Sci., Part A*, **9**, 1071 (1971).

(4) (a) D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 1748 (1972); (b) *ibid.*, **94**, 8692 (1972).

(5) D. S. Marynick and W. N. Lipscomb, *J. Amer. Chem. Soc.*, **94**, 8699 (1972).

(6) See W. N. Lipscomb, *Pure Appl. Chem.*, **29**, 493 (1972), for a recent review.

(7) R. E. Dickerson and W. N. Lipscomb, *J. Chem. Phys.*, **27**, 212 (1957).

(8) I. R. Epstein and W. N. Lipscomb, *Inorg. Chem.*, **10**, 1921 (1971).

(9) F. P. Boer, W. E. Streib, and W. N. Lipscomb, *ibid.*, **3**, 1666 (1964).

logical approach to electron-deficient molecules, the question of its applicability to carboranes is an extremely important one.

In this paper we present the results of LMO calculations on the two isomers of $C_2B_4H_6$, the first carboranes for which SCF wave functions were calculated.[10] These results constitute another example of the utility of the fractional three-center bond concept for describing highly symmetric electron-deficient molecules. Perhaps more significantly, the LMO calculations provide the first clear evidence for the necessity of employing open three-center bonding in the description of carborane frameworks.

We discuss the relationship of our LMO's and the results of the SCF calculations to the topological theory of the carboranes, with particular reference to the role of the open three-center bond. Finally, we present a preliminary consideration of the modifications required to extend the E–L topological theory to carboranes in general.

Localization Procedure and Results

The original SCF calculations[10] employed an idealized geometry for the 1,6 isomer, obtained by averaging the B–B and B–C distances in the 1,2 isomer. After completion of that work, a microwave study of the molecule resulted in the determination of accurate molecular parameters.[11] For the present LMO calculations, the SCF wave function for the 1,6 isomer has been recalculated using the experimental geometry. The change in the energy on going from the idealized to the experimental geometry is only about 3 kcal/mol. Surprisingly, the idealized geometry gives the lower energy. Changes in the various population parameters are also quite small, and hence we feel that no significant error was introduced into the SCF calculation by employing the idealized geometry for the 1,6 isomer. However, for the sake of consistency the LMO's have been calculated using the experimental geometries for both molecules.

Localized orbitals were calculated for both isomers by maximizing the self-repulsion energy according to the Edmiston–Ruedenberg procedure.[12] The localization and the second derivative test[13] were performed with programs which have previously been described.[13,14] Each calculation required about 2 hr of IBM 360/65 computing time. The localized orbital populations and analyses of the two-electron energies are given in Tables I and II, respectively.

Starting from several different random unitary matrices, the $1,2\text{-}C_2B_4H_6$ calculation consistently yielded the set of LMO's given in Table I and illustrated in Figure 1. Application of the second derivative test showed that these orbitals represent a local maximum on the self-energy surface, and our previous experience with LMO calculations on molecules of similar symmetry (*i.e.*, no three- or higher fold symmetry elements) strongly suggests that this maximum is unique.

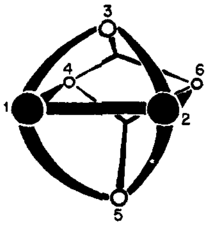

Figure 1. The LMO valence structure of $1,2\text{-}C_2B_4H_6$. Large shaded circles represent carbon atoms 1 and 2. Open three-center bonds are $B_3C_1B_5$ and $B_3C_2B_5$, central three-center bonds are $B_3B_4B_6$ and $B_4B_5B_6$, and two-center bonds are C_1C_2, C_1B_4, and C_2B_6. Terminal BH and CH bonds have been omitted from the diagram.

Table I. Electron Populations in Localized Orbitals[a]

$1,2\text{-}C_2B_4H_6$				$1,6\text{-}C_2B_4H_6$			
			Inner Shells				
C_1	2.00			C_1	2.00		
B_3	2.00			B_2	2.00		
B_4	2.00			C_6	1.98		
			B–H and C–H Orbitals				
C_1–H_1	1.07	0.95		C–H	1.06	0.96	
B_3–H_3	0.92	1.08		B–H	0.93	1.07	
B_4–H_4	0.92	1.09					
			Framework Orbitals				
B_3–B_4–B_6	0.78	0.63	0.63	C_1–B_2–B_3	0.83	0.63	0.54
C_1–B_3–B_5[b]	1.02	0.40	0.43	C_1–B_3–B_4	0.85	0.56	0.58
C_1–B_4	1.12	0.62		C_1–B_4–B_5	0.79	0.56	0.64
C_1–B_2	0.91	0.91		C_1–B_2–B_5	0.59	0.65	0.67
				C_6–B_2–B_3	1.04	0.63	0.32
				C_6–B_3–B_4	1.02	0.54	0.46
				C_6–B_4–B_5	1.05	0.21	0.66

[a] Populations are given only for symmetry-unique orbitals. Numbering conventions as in Figures 1 and 4. Populations are given in the order that the atoms are listed; *e.g.*, in the B_3–B_4–B_6 orbital of $1,2\text{-}C_2B_4H_6$, the populations are B_3, 0.78, B_4, 0.63, B_6, 0.63. [b] Open three-center bond.

Table II. Components of the Two-Electron Energy[a]

	$1,2\text{-}C_2B_4H_6$		$1,6\text{-}C_2B_4H_6$	
	Canonical	Localized	Canonical	Localized
Total two-electron	232.1771	232.1771	236.0384	236.0384
Interorbital Coulomb[b]	230.8930	206.9746	237.3931	217.1869
Exchange[c]	−13.4807	−1.5216	−14.8506	−4.7475
Self-repulsion[d]	14.7649	26.7241	13.4960	23.5991

[a] Atomic units. [b] $\Sigma_{i>j}4\langle ii|jj\rangle$. [c] $-\Sigma_{i>j}2\langle ij|ij\rangle$. [d] $\Sigma_i\langle ii|ii\rangle$.

Aside from the open B–C–B bonds, the only unusual feature in the $1,2\text{-}C_2B_4H_6$ LMO's is the rather high degree of delocalization of the B–C single bonds. The sizable nonlocal population (0.26 electron) resembles that found in the B–B single bond LMO of B_4H_{10}.[4a,12] Hybridizations[14] in the other framework orbitals are comparable to those found in other carboranes,[4b,5] ranging from $sp^{1.45}$ at carbon in the B–C single bonds to $sp^{3.54}$ at B_4 and B_6 in the central three-center bonds.

The open B–C–B bond LMO has properties remarkably similar to those postulated earlier[15] for the open B–B–B bond. For example, the populations (Table I) are quite close to the idealized pattern of ($^1/_2$, 1, $^1/_2$). Also, hybridization at the central carbon atom

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(10) I. R. Epstein, T. F. Koetzle, R. M. Stevens, and W. N. Lipscomb, *Inorg. Chem.*, **9**, 7019 (1970).

(11) G. L. McKown and R. A. Beaudet, *ibid.*, **10**, 1350 (1971).

(12) C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 467 (1967).

(13) E. Switkes, W. N. Lipscomb, and M. D. Newton, *J. Amer. Chem. Soc.*, **92**, 3847 (1970).

(14) E. Switkes, R. M. Stevens, W. N. Lipscomb, and M. D. Newton, *J. Chem. Phys.*, **51**, 2085 (1969).

(15) (a) W. N. Lipscomb, "Boron Hydrides," W. A. Benjamin, New York, N. Y., 1963, pp 27–79; (b) W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

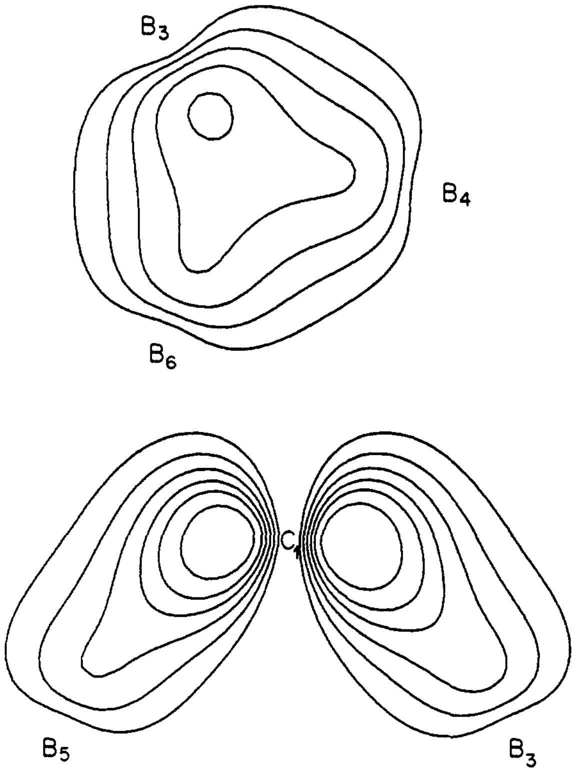

Figure 2. Electron density map of three-center bonds in 1,2-$C_2B_4H_6$. The upper half of the figure is the central three-center $B_3B_4B_6$ bond, while the lower half is the open three-center $B_3C_1B_5$ bond. Contours correspond to electron densities of 0.25, 0.17, 0.14, 0.11, 0.09, and 0.07 electron/au^3.

is sp^{1587}, *i.e.*, essentially pure p. Figures 2 and 3 contrast the open and central three-center bonds in terms of electron density and directional character of the orbitals, respectively. Finally, the B–C–B orbitals are the best localized (in terms of either population or delocalization index[14]) of all of the framework orbitals in the molecule.

The LMO's for 1,6-$C_2B_4H_6$, shown in Figure 4, have been reported in a preliminary discussion of the fractional three-center bond.[4a] The considerably lower self-repulsion energy and lower degree of localization obtained for this isomer may be attributed to its higher symmetry.[4b,16] The computational difficulties associated with this localization have been discussed elsewhere.[17] Application of the second derivative test gives a greatest eigenvalue of $+1.22 \times 10^{-3}$ for the self-repulsion energy matrix. While we feel that this structure is at a relative maximum of the self-repulsion energy, the nearly zero eigenvalue, to the precision of the calculation, indicates that the self-repulsion energy surface is nearly flat in the region of the maximum. This situation is exactly analogous to that found for B_5H_9.

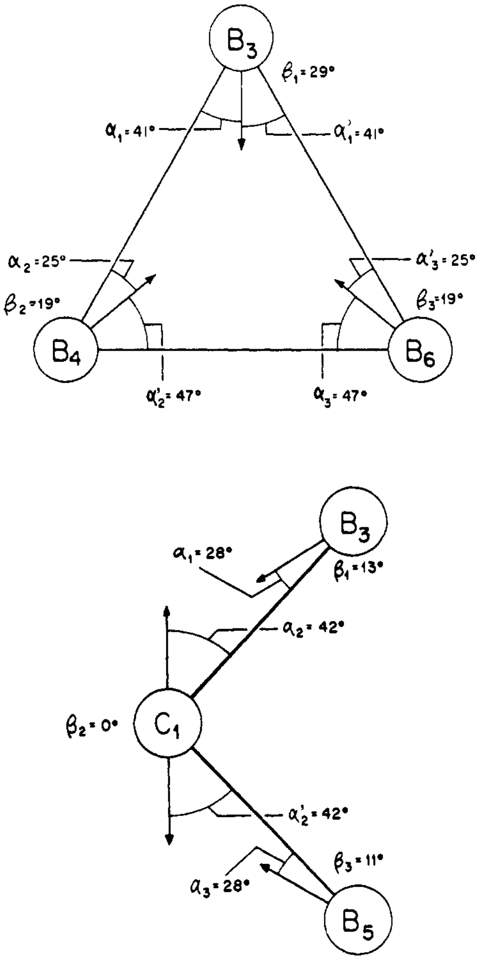

Figure 3. Directional character of three-center bond orbitals in 1,2-$B_2C_4H_6$. (a) Open three-center bond LMO. (b) Central three-center bond LMO. The angles α are in the plane of the drawing while the angles β are in a plane perpendicular to that of the drawing.

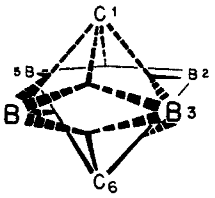

Figure 4. The LMO valence structure of 1,6-$C_2B_4H_6$. Dotted lines represent fractional three-center bonds.

We also point out that the notion of fractional three-center bonding contains a certain amount of arbitrariness, which results from the fact that *all* LMO's contain finite nonlocal contributions. Thus, one might prefer to think of the B2–B3–C6 and B4–B5–C6 "bonds" of 1,6-$C_2B_4H_6$ as very poorly localized two-center bonds. However, it is difficult to envision any way to label the LMO's so that there are only four LMO's, involving C1. Since the fractional bond or some similar concept *must* be invoked for this atom, there seems little point in avoiding it in these other cases. Hence, we have chosen a chemically reasonable, though admittedly arbitrary, minimum atomic population of 0.20 electron for an atom to be deemed to participate in a bond.

Extension of the Topological Approach to Include Carboranes

The calculations presented here should be of great utility in extending the topological theory of the boron hydrides[7,8] to carboranes and other electron-deficient molecules. Before we discuss the implications of the

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(16) I. R. Epstein, J. A. Tossell, E. Switkes, R. M. Stevens, and W. N. Lipscomb, *Inorg. Chem.*, 10, 171 (1971).

(17) D. S. Marynick and E. Switkes, *Chem. Phys. Lett.*, 15, 133 (1972).

LMO calculations for the topological approach to the carboranes, we comment briefly on the relationship between the topological approach (TA) and localized molecular orbital approach (LMO) to molecular electronic structure.

Unlike traditional molecular orbital theory, which describes molecules in terms of charge distributions spread over the entire system, both the LMO and the TA descriptions are "valence-bondlike" in seeking to characterize molecules in terms of one-, two-, and three-center charge distributions confined to a relatively small region of space. In spite of this common feature, key differences between these two approaches make it quite remarkable (and highly satisfying) that the LMO and TA descriptions offer nearly identical pictures of most molecules and compatible views of almost all. It is this convergence to the same end point from such basically different starting points that suggests the fundamental chemical significance of the results obtained.

In the LMO approach,[12] one starts from a wave function which has been calculated objectively by a relatively accurate method such as the self-consistent field procedure.[18] One then employs some criterion (such as maximal self-repulsion energy) in order to obtain, from the starting set of molecular orbitals, a new set of orbitals which are more localized in space and which may be identified with the bonds, lone pairs, etc., which constitute the valence structure of the molecule. In other words, one obtains the best *single* valence structure description of the molecule, subject to the restriction that the orbitals yield the same wave function as the starting set of orbitals. The only other constraint in the LMO method is that the orbitals are required to be orthogonal to one another. The localization criterion of maximal self-repulsion energy *does not require* that the LMO's be interpretable as two and three-center bond orbitals, and in fact the LMO's always possess some nonlocal character, in some cases enough to justify speaking of fractional bonds.[4a]

The less quantitative topological approach (TA)[7,8] differs in three major ways from the LMO method. First, in the TA there is no constraint on the total wave function. One does not start from a wave function and attempt to derive the "best" partitioning of the electron density as in the LMO method. Instead, one attempts to construct the wave function from the various possible partitions or valence structures. Second, orbitals in the TA are required to be perfectly localized (though not necessarily orthogonal) two- and three-center bonds. The *only* allowed valence structures in the TA are those constructed from these orbitals according to the conservation rules[8] for electrons, orbitals, and topology. Third, and most important, while the LMO approach seeks the single best valence structure description for the molecular wave function, the TA attempts to represent the wave function as a linear combination of all allowable valence structures. While one might wish to compare the orbitals in terms of energies or the degrees of delocalization or orthogonality, carrying out such a comparison is difficult at best. One could, presumably, estimate the total energy of a topological structure by using the appropriate combination of truncated,[13] renormalized LMO's. The individual orbital energies are difficult to estimate, since they do not correspond directly to ionization potentials. Some use has been made of LMO "energies" as a guide to chemical reactivity.[16] In contrast to the perfectly localized TA orbitals, LMO's appear to have nonlocal contributions ranging from about 5 to 20%, measured either by atomic populations or by delocalization indices.[14] Finally, the degree of departure of the TA orbitals from perfect orthogonality is probably small in view of the spatial separation and directional properties of the orbitals.

Since the TA was formulated with the assumption that all framework (*i.e.*, nonhydrogen) atoms are electronically equivalent, it is not unreasonable that certain modifications may be necessary in order to extend the TA from boron hydrides, in which this equivalence assumption is relatively good, to carboranes, in which it is relatively poor. One must then ask what modifications must be made and, equally important, whether these modifications allow us to maintain most, if not all, of the conceptual simplicity and chemical utility of the topological approach[8] to boron hydride structures. In order to answer these questions, we should require that any topological extension to the carboranes give results compatible with those of the SCF–LMO method in the following two senses. (1) There must exist a linear combination of topologically allowed valence structures which gives the same ordering of charges and bond strengths as the SCF–LMO calculation. Recognizing that significant ambiguities arise in partitioning electron density among nonequivalent atoms, we shall limit this requirement to comparisons between atoms or bonds of the same type. Thus, we will require that the modified TA give at least one possible linear combination of structures that reproduces the SCF ordering of boron charges, carbon charges, and B–B, B–C, and C–C bond orders. (2) Since carbon has a higher nuclear charge and a greater electronegativity than boron, we shall require that there exist a linear combination of TA structures which satisfies the conditions in 1 and also has as many or more electrons on the most positive carbon atom than on the most negative boron atom. This requirement is a partial allowance for the fact that boron and carbon atoms are not in fact equivalent. It constrains the TA electron density in the direction of small atomic changes,[19] in accordance with both experimental and theoretical results. Clearly, what is being sought in the TA is a weighting scheme[8] from which to construct the linear combination of valence structures. The two conditions stated above represent a crude first step toward development of such a scheme.

Either a single E–L structure or an appropriate linear combination of E–L structures is regarded as compatible with the E-L TA if it satisfies conditions 1 and 2. The results of Marynick and Lipscomb[4b] on 2,4-$C_2B_5H_7$ provide an example in which no single structure will do, but where a suitable linear combination can be found. However, 4,5-$C_2B_4H_8$ is somewhat different, since there are *no* E–L allowed structures for the molecule. The early proposal[9] that a double

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[18] C. C. J. Roothaan, *Rev. Mod. Phys.*, 23, 69 (1951).

[19] If all boron and carbon atoms in the molecules $C_mB_nH_{m+n}$ have equal numbers of electrons and all C–H and B–H bonds are nonpolar, then each carbon will have a positive charge of n ($m + n$) electrons and each boron will have a charge of $-m$ ($m + n$).

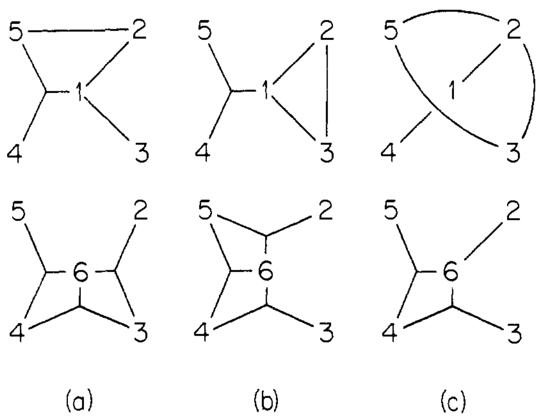

Figure 5. Some topologically allowed valence structures for $C_2B_4H_6$.

bond between the carbon atoms showed π donation toward the apex B atom was a realization of this unusual bonding situation. Here, in order to render the LMO and TA compatible, one must relax the restriction against joining two atoms by both a two-center and a three-center bond. A minimum change would restrict this relaxation to a bonded pair of carbon atoms and for a BC pair. When this modification is made in the E–L TA one can again find[5] a linear combination of topologically allowed structures compatible with the single LMO structure for 4,5-$C_2B_4H_8$.

Our LMO calculations on the two isomers of $C_2B_4H_6$ constitute another case in which modification of the E–L TA rules (for boranes only) appears to be required. In the 1,6 isomer we have another case of fractional three-center bonding, while in the 1,2 isomer we have the first appearance in an LMO structure of an open three-center bond, except B–H–B bridge bonds, of course.

Inspection of the 32 valence structures allowed for 1,6-$C_2B_4H_6$ by the E–L TA shows that a linear combination of all 32 structures with equal weights satisfies our conditions for compatibility with the LMO–SCF results. The two symmetry-unique E–L valence structures for the molecule are shown in Figures 5a and 5b. There exist 24 and 8 symmetry-equivalent structures, respectively, for the two structures shown. We thus conclude that 1,6-$C_2B_4H_6$ does not require any further modifications of the E–L TA, although one might obtain more satisfactory, *i.e.*, smaller, atomic charges by relaxing one or more of the topological rules.

On the other hand, for 1,2-$C_2B_4H_6$ we find that no possible linear combination of structures 5a and 5b, and their symmetry equivalents, produces a structure in which both conditions 1 and 2 are satisfied. For example, suppose that we stay strictly within the E–L TA. Then the assignment of weights to structures which put electrons on the two adjacent carbons in order to satisfy the electronegativity requirements (condition 2) pulls electrons away from B_4 and B_6 and puts them on B_3 and B_5. This result is in contradiction to both the SCF charge distribution (condition 1) and the experimentally observed fact[20] that borons bonded to two carbons tend to be less negative than borons bonded to one or no carbons. In this case, a modification of the E–L TA is clearly called for. The most obvious change would be to allow for the existence of at least some open three-center bonds in the carboranes, perhaps only those centered on one or both carbon atoms. If we make this modification in the topological rules, then the LMO structure is most nearly representable by the allowed topological structure (Figure 5c), which is identical with the LMO valence structure, Figure 1. On carrying out the population analysis, we find that the open B–C–B bond structure of Figure 5c does, in fact, satisfy our two compatibility conditions. Thus, modification of the TA to allow for open B–C–B bonds makes possible a topological treatment of 1,2-$C_2B_4H_6$ compatible with the SCF–LMO results.

Further extension of the TA to other carboranes and to other electron-deficient molecules raises the following questions. What other modifications of the simple TA method are required, if any, beyond the two discussed above, are these modifications required for most or only a very few other molecules, and what chemical insight is revealed by the differences in the TA for boron hydrides, carboranes, and other molecules? Answers will require detailed analyses of LMO results for other molecules not yet studied, but a preliminary study of the TA to three simple polyhedral carboranes, $C_2B_3H_5$ (trigonal bipyramidal), $C_2B_4H_6$ (octahedral), and $C_2B_5H_7$ (pentagonal bipyramidal), is briefly discussed here.

We may define three classes of topological valence structures: type A, those allowed by the E–L TA; type B, those allowed by the E–L TA modified to include open three-center bonds; and type C, those allowed by the TA modified to allow atoms to be simultaneously joined by both two-center and three-center bonds. For simplicity, we shall omit consideration of structures in which the modifications of both types B and C are permitted. Table III gives the number of allowed structures of each type found for each of the three molecules.[21]

Table III. Numbers of Topologically Allowed Valence Structures for Some Polyhedral Carboranes[a]

	Type A	Type B	Type C
$C_2B_3H_5$	2 (1)	51 (6)	12 (1)
$C_2B_4H_6$	32 (2)	196 (6)	40 (2)
$C_2B_5H_7$	20 (1)	270 (15)	30 (2)

[a] Number given is total number of valence structures. Number in parentheses is number of symmetry-unique structures. Note that in this table the open three-center bonds (type B) are not restricted to BCB bonds, nor are the pairs of atoms joined by both a single and a central three-center bond (type C) restricted to adjacent C atoms. However, see the text.

As we have seen, of the two possible isomers of $C_2B_4H_6$, the 1,6 isomer is representable by structures of type A only, while the 1,2 isomer requires structures of type B in order to qualitatively reproduce the SCF charge distribution. There are four possible isomers of $C_2B_5H_7$, corresponding to the carbons at the 1,2, 1,7, 2,3, or 2,4 positions. However, only the 2,4 isomer

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(20) J. A. Potenza and W. N. Lipscomb, *Inorg. Chem.*, 5, 1471, 1478, 1483 (1966).

(21) The number of allowed structures will be the same for a given molecule regardless of the isomer chosen. That is, the placement of the carbon affects the coefficients in the linear combination, but not the structures which are being combined.

is known, and Marynick and Lipscomb's theoretical results for this isomer[4b] are compatible with a linear combination of type A structures. Little can be said about the hitherto unobserved isomers in the absence of further calculations.

For $C_2B_3H_5$, there are three possible isomers: 1,2, 1,5, and 2,3 of which only the second is well known. While there are no SCF–LMO calculations for this molecule, symmetry considerations and a nonempirical approximate molecular orbital (NEMO) calculation[22] on the 1,5 isomer permit us to draw some tentative conclusions. First, a linear combination of the two symmetry-equivalent type A structures does appear to give a satisfactory charge distribution for the 1,5 isomer. Second, the other isomers, if they exist, will have to have type B or C valence structures, type C for the 1,2 isomer and type B for the 2,3 species. Substituted derivatives of the 1,2 isomer of $C_2B_3H_5$ have been reported.[23]

With these results in mind we now ask if there are any common features among the molecules which require modifications of the E–L TA, *i.e.*, type B or C structures, for their topological description. We find that, for our admittedly small sample, modifications of the E–L TA are required *only for species possessing two adjacent carbon atoms*, *i.e.*, 1,2-$C_2B_4H_6$, 4,5-$C_2B_4H_8$, and the hypothetical 1,2- and 2,3-$C_2B_3H_5$. We interpret this result as follows. The simple TA without modifications of types B or C is adequate to deal with the boron hydrides, in which all nonhydrogen atoms are equivalent. Introduction of a single carbon atom or several nonadjacent carbon atoms into the molecular framework perturbs the charge distribution according to our conditions 1 and 2, but this relatively small perturbation may be allowed for by a modification of the weighting scheme for constructing the linear combination of allowed valence structures. Inclusion of two or more adjacent carbon atoms in the molecule produces a significant departure from the basic assumptions of the boron hydride TA, and hence requires modification of the topological rules. In a sense, the adjacent carbons constitute a local "hydrocarbon-like" region in the molecule, in contrast to the assumed global "boron hydride-like" nature of the system.

One can now view the modifications to the TA as arising from the need to accommodate the hydrocarbon-like region into the overall molecular framework. The prohibition against two- and three-center bonds between the same two atoms arises[15] from a consideration of the hybridization about a boron atom in a boron hydride. However, if one admits pure or nearly pure "hydrocarbon-like" p-type hybridization as found in ethylene and more recently in 4,5-$C_2B_4H_8$,[5] then this restriction can be removed, but only for two adjacent carbon atoms and for each BC pair. Relaxation of the prohibition against open three-center bonds is now viewed as a result of a region of high electronegativity in the molecule. The central three-center bond places only $^2/_3$ electron on each participating atom. In order to fulfill our condition 2 then, we must weight most heavily those structures in which carbon participates in a large number of two-center bonds. However, two-center bonds to carbon will also make the carbon atom's neighbors more negatively charged. Thus, we will not be able to produce the desired situation in which the two adjacent carbons have a relatively large number of electrons while the borons bonded to both of them have relatively few electrons. Condition 1 will be violated. However, by allowing open B–C–B bonds, we obtain exactly the desired result. Since the open B–C–B bond places $^1/_2$ electron on each of the borons, and 1 electron on the carbon, we simultaneously make the carbon more and the borons less negative than if we had employed two-center or central three-center bonding. The situation may be likened to that of the open B–H–B bond, in which hydrogen is also more electronegative than boron. We expect then that in the carboranes, carbon will form two-center in preference to central three-center bonds, and that when two or more adjacent carbon atoms are present open B–C–B bonding will be found.

Conclusions

The three-center bond theory[15] provides a useful description of the electron distributions in boranes and carboranes. As a result of SCF, LMO, and topological calculations, as well as experimental data, the following generalizations can be offered in describing the current state of the theory.

(1) No open three-center bonds are required to describe the boranes.[8]

(2) Unique preferred valence structures exist for many boranes and carboranes, including B_2H_6, B_4H_{10}, B_5H_{11}, B_6H_{10}, 1,2-$C_2B_4H_6$, 2,4-$C_2B_5H_7$, and 4,5-$C_2B_4H_8$.

(3) The concept of fractional three-center bonding[4a] facilitates the description of some boranes and carboranes. These systems fall into two categories:[4b] (a) those (such as B_5H_9 and 1,6-$C_2B_4H_6$) which contain a high-order symmetry element and a relatively small number of framework orbitals; and (b) those (such as 4,5-$C_2B_4H_8$ and 2,4-$C_2B_5H_7$) which possess a grouping of four atoms which might be described by an open three-center bond, and a two-center bond from the fourth atom to the central atom of the open bond.

(4) For carboranes only, the description may also include open three-center bonds with carbon as the central atom, and pairs of atoms joined by both a two-center and an open three-center bond ("π-donation structures"[5]). This situation applies especially when both atoms are carbon, and possibly when one is carbon and the other is boron.

(5) It seems probable that transition states and reaction intermediates which may be described in terms of topologically allowed structures are peferred to those which are not.[24]

(6) When a question arises as to the preferred structure for a molecule, resonance (topological) arguments appear to outweigh arguments based upon the necessity for an evenly distributed charge distribution.[8,25]

It is hoped that these principles will form the basis of a unified and useful description of the chemical properties of electron-deficient molecules. Confirmation or revision of these ideas must, of course, await

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further SCF–LMO and experimental studies on such systems as $B_3C_2H_5$, $B_7C_2H_9$, $B_8C_2H_{10}$, $B_{10}H_{14}$, and the isomers of $B_{10}C_2H_{12}$. Such investigations are now in progress.

Acknowledgments. We thank J. H. Hall, Jr., for helpful discussion and the Office of Naval Research for financial support. D. S. M. and I. R. E. are grateful to the National Science Foundation for predoctoral fellowships. Portions of this study were supported by a grant from the Research Corporation to I. R. E.

Infrared Studies of Matrix Isolated Species in the Hydrogen–Boron–Nitrogen System

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Abstract: Infrared spectra of the 1216-Å photolysis products of ammonia-borane (H_3NBH_3) in rare gas matrices indicate that the major product is imidoborane (HNBH). Two of the three Σ^+ vibrations for a linear HNBH structure are observed at 3700 cm^{-1} (ν_1) and 1785 cm^{-1} (ν_3) for the ^{11}B, ^{14}N species in an argon matrix. Calculations based on isotope effects predict a frequency of 2800 cm^{-1} for ν_2. One of the bending vibrations of HNBH is observed at 460 cm^{-1}. A second species appearing after prolonged photolysis of ammonia–borane is identified as HNB. Spectra of the photolysis products of borazine are associated with a species formed by ring opening, loss of hydrogen, and multiple BN bond formation.

Matrix isolation is a valuable technique for study of small molecules that are highly reactive under ordinary experimental conditions. In studies involving reactive boron species we have recently isolated the intermediate HBO.[1] We have now extended this investigation to the H–B–N system, and the main purpose of this paper is to report the isolation and infrared spectra of imidoborane, HNBH. This intermediate is frequently discussed in the chemical literature as a precursor to the more stable trimeric species, borazine. Physical evidence for the existence of imidoborane has not been reported. Recently two theoretical molecular orbital calculations[2,3] have indicated that HNBH should exist in a linear configuration analogous to its organic counterpart HCCH.

Experimental Section

In these experiments we have investigated the photodecomposition products of H_3NBH_3 (ammonia–borane) and $H_3N_3B_3H_3$ (borazine). The procedure is similar to that used by Lory and Porter.[1] The matrix-isolation apparatus has been described.[4] Ammonia-borane was prepared by the reaction of isotopically labeled borane etherate and ammonia.[5] The photolysis source was a microwave-powered (Raytheon Model CMD-4) hydrogen discharge in a quartz tube fitted with a LiF window. The window was baked for several hours at 550° after each experiment to restore its transparency.[6] The lamp body was extended through a sealed flange into the vacuum system to place the lamp window within 4 cm of the target window. Infrared absorption spectra (4000–250 cm^{-1}) were recorded on a Perkin-Elmer 521 spectrometer calibrated with HCl and NH_3. The sample was sublimed into a stream of the matrix gas and the mixture deposited on a cooled (5°K) CsI target window. Simultaneous deposition and photolysis produced more products than did sequential deposition and photolysis. Matrix ratios of 300/1 or higher were used based on a vapor pressure of ammonia-borane of 1 μ at room temperature.[4]

Borazine was prepared by treating *B*-trichloroborazine with $NaBH_4$.[7] Two deposition nozzles were used, one dispensing borazine-matrix gas mixture at room temperature and the other pure matrix gas at 77°K. Matrix ratios of 300 to 800 were used. Photolysis conditions were similar to those described above.

Results

Photolysis of ammonia–borane in argon matrices yielded a species with two strong absorption bands at 3700 and 460 cm^{-1} and a medium absorption band at 1785 cm^{-1}. The band at 1785 cm^{-1} in argon was usually quite broad. Spectra obtained in xenon matrices showed the same absorption bands which were narrow but shifted to slightly lower frequencies (Figure 1). After a considerable period of irradiation and deposition, a second series of weak bands appeared at 3675 and 2035 cm^{-1} (see Figure 1). In most experiments with H_3NBH_3 as precursor, a strong broad absorption centered at 1370 cm^{-1} appeared after prolonged irradiation. This feature did not exhibit an obvious isotope effect in experiments with perdeuterioammonia–borane.

A spectrum of the photolysis products of borazine is shown in Figure 2. The spectrum consists of a small number of narrow well defined bands and a broad poorly defined band structure in the region between about 1800 and 2000 cm^{-1}. The conversion of borazine to products was very high when irradiation and matrix deposition were conducted simultaneously. Irradiation following deposition produced no photolysis products. Experiments with matrix ratios of 300, 500, and 800 showed no change in the sharp features in the spectrum of the photolysis products. The major absorption bands appear at 3700 and 3672 cm^{-1}, the region between 2000 and 2100 cm^{-1}, and in a region near 500 cm^{-1}.

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