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Abstract - The structures of boron hydrides, B_2H_6 , B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} , and $B_{10}H_{14}$, are interpreted as resonance hybrids of valence bond structures that only contain two-center two electron bonds. Graph-theoretical techniques are used to count the large number of structures incorporated in the hybrids. Calculated bond orders and charges are compared with the results of LCAO-MO-SCF calculations and with three-center valence bond models. The heats of atomization can be correlated with a 4 term linear equation based on the numbers of neighboring boron atom pairs, terminal BH bonds, bridging BH bonds, and estimates of resonance energies. Resonance energies comprise 11 to 29% of the atomization energies for these boron hydrides.

INTRODUCTION

The concept of the three-center (two electron) bond has proven to be highly useful in systematizing structural information regarding electron deficient species like the boron hydrides (Ref. 1-8). Bond-counting rules and topological principles have been developed by Lipscomb and his coworkers that even allow the prediction of the structures of new compounds and reactive non-isolable intermediates (Ref. 3, 5-7, 9-13). The original theory described three-center bonds, open and closed BBB bonds, and BHB bridges. Later, the results of SCF-MO calculations suggested that the open BBB three-center bond should be omitted, and that fractional closed BBB bonds should be introduced as part of the formulism (Ref. 14-17). More recent modifications allow the incorporation of vacancy structures containing trivalent boron atoms with a single formally vacant orbital (Ref. 11, 12), and fractional bridging BHB bonds (Ref. 18). These latter modifications provide links to the types of structures that will be described in this paper.

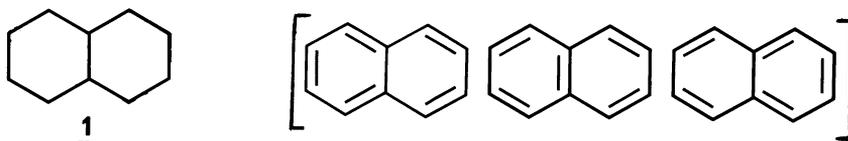
The problem that we address is: can the structures of boron hydrides be usefully depicted solely in terms of normal two-electron covalent bonds? The specific points to be discussed will be some of those also treated by the three-center bond theory: bond orders in the boron framework, bond asymmetries of the bridging BHB moieties, charge distributions, and stabilities. It is well understood that any three-center bond structure can be described in terms of two-center bond structures (Ref. 19), but it is also easy to demonstrate that no three-center bond structure corresponds to the usual first-order assumption that the hybrid structure is an equally weighted summation of two-center bond structures. The use of hybrids of this type has been shown to have quantitative significance in previous studies of aromatic hydrocarbons, radicals, and ions (Ref. 20), and in applications to π -hydrocarbon iron tricarbonyl complexes (Ref. 21). A preliminary investigation of heats of atomization of boron hydrides (Ref. 22) also gave satisfactory results, and led us to attempt a more extensive study.

In this paper we choose the uncharged covalent two-center bond structures and a selection of charged two-center bond structures as a first approximation to the description of a boron hydride. The results for several boron hydrides, B_2H_6 , B_4H_{10} , B_5H_9 , B_5H_{11} , B_6H_{10} , and $B_{10}H_{14}$, are summarized below. We will compare our results with those obtained from MO calculations or the three-center bonding models, but we will not attempt to assess relative merits of two-center or three-center bond viewpoints. However, we do believe that the two procedures can be considered to give complementary valence representations, and we emphatically do not subscribe to the opinion of Muetterties who states (Ref. 23) that "No contemporary two-electron bond approaches can satisfactorily account for this situation" in discussing the bonding in diborane B_2H_6 .

RATIONALE

The boron hydrides are "electron deficient" compounds in the sense that there are more neighboring covalently bound pairs of atoms than there are valence electron pairs (Ref. 24). The π systems of aromatic hydrocarbons are also electron deficient according to this

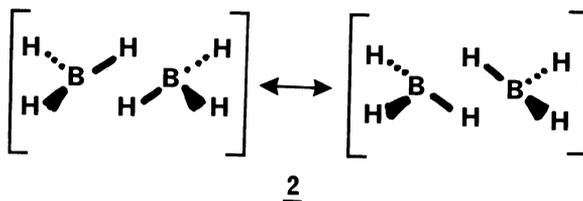
definition. For example, the π system of naphthalene, has eleven nearest-neighbor π bonding regions, 1, and only five bonding electron pairs. It is obvious that a resonance hybrid of



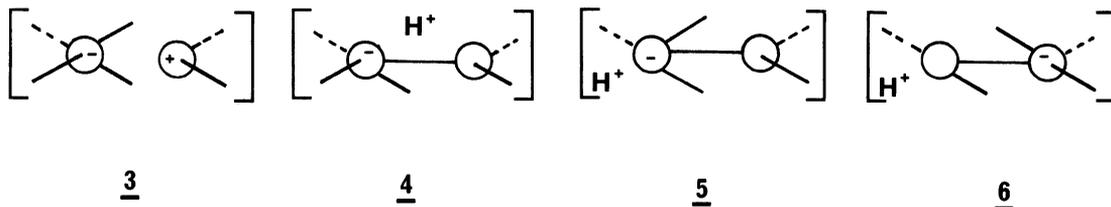
valence bonding structures is required to represent any particular aromatic hydrocarbon. Alternatively and less explored, localized molecular orbitals or the corresponding structures with multicenter (three-center) bonds can be used to describe aromatic hydrocarbon bonding (Ref. 25-29). One may assume that boron hydride structures can also be depicted either in terms of multicenter bonds, or as resonance hybrids of classical covalent structures.

This resonance hybrid approach is not new in application to boron hydrides. Early suggested valence structures are reviewed by Bauer (Ref. 30) and Shore (Ref. 31). The most detailed treatment of diborane was due to Pauling (Ref. 32), who also developed a statistical theory of resonating valence bond structures for the higher boron hydrides (Ref. 33) which assumed that the bonding electron pairs are distributed randomly among the bond positions, and that the occupancy of the positions is unsynchronized. The bond lengths in several boron hydrides were discussed on this basis but no further developments have been carried out.

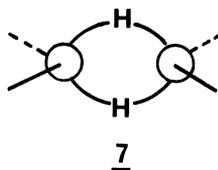
The essential difference between two-center and three-center bond approaches can be illustrated by reference to diborane, where twenty two-center bond structures can be drawn, two covalent structures shown in 2, and eighteen structures with formal charges, given in 3-6.



It should be noted that the entire group of atoms within a set of brackets is considered to



be a single contributing structure to the resonance hybrid, and in general all twenty structures could be required. The contrast with the single three-center bond structure with bridging BHB bonds, 7, shows that the representation of a boron hydride with two-center bond



structures requires more labor than using three-center structures. We surmise that the reason for the lack of further development of this method lies in the extremely large number of structures to be enumerated for all but the most simple molecules.

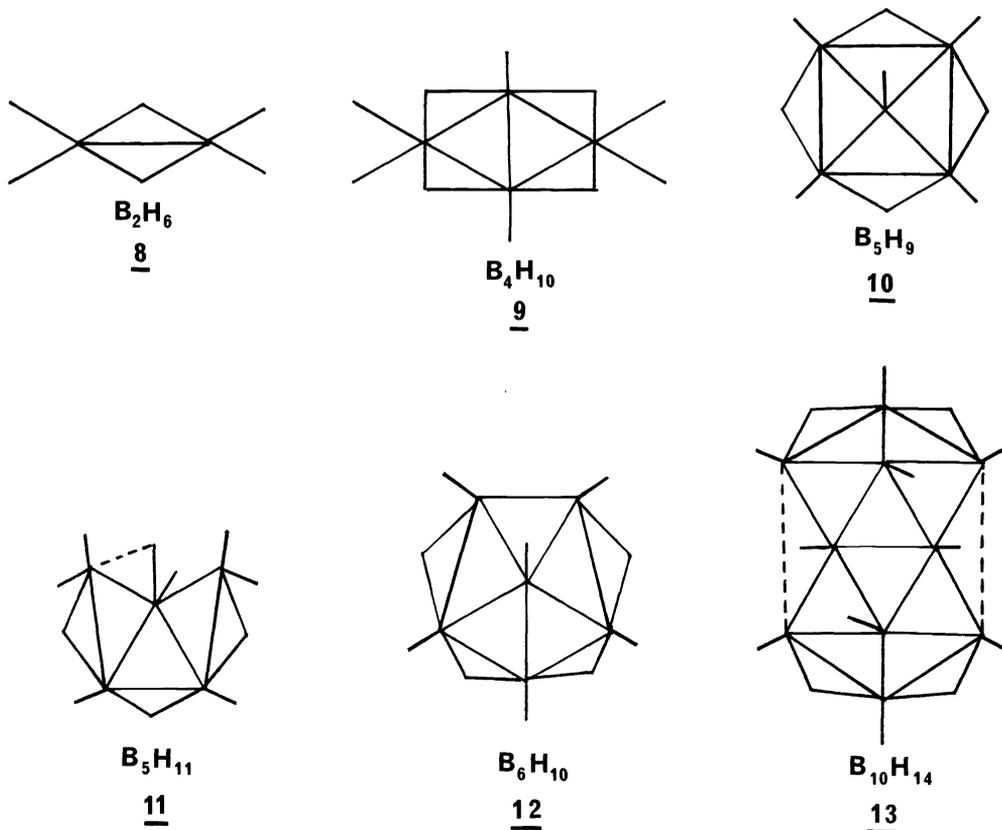
Limiting the basis structures to a particular selection reduces the magnitude of the problem. A similar situation arises when a structure-resonance theory of unsaturated hydrocarbons is limited exclusively to Kekulé structures. Empirically, it has been shown that the quantitative results of such a theory correlate precisely with experimental properties, and with the results of LCAO-MO-SCF calculations (Ref. 20). In this paper, acceptable structures will contain the maximum possible number of covalent bonds (6 for diborane). This eliminates structures with a negative formal charge on hydrogen, not shown in 3-6, which also were not

included in Pauling's original treatment (Ref. 32). Any acceptable ionic structure will therefore have one closed-shell negatively charged tetra-coordinated boron atom as in 3-6.

We also require that the basis ionic structures have formal charges on nearest neighbor atoms in order to maintain a minimum charge separation. This eliminates the eight structures of type 6 which would be of much higher energy, and leads to much larger decreases in the number of allowable structures for the higher boron hydrides. However, even in diborane there are still five times as many ionic structures as covalent neutral structures. Any desired formal charge distribution could be obtained by arbitrary weighting of selected structures in the resonance hybrid. In order to avoid this aspect of resonance theory we made this pre-selection of the kinds of ionic structures to be incorporated into the hybrid, and we preassigned 50% weights to each of the composite ionic and covalent structures. This weight assignment is arbitrary, but is similar to that chosen by Jolly and Perry (Ref. 34) in developing a procedure for estimation of atomic charges by electronegativity equalization. In any case, the weighting and selection of resonance structures is always a matter of concern, and we believe this point will bear further investigation. This same concern has been stated in many of the previous discussions on three-center bond structures for boron hydrides (Ref. 7, 14, 15)

GRAPH THEORY FOR TWO-CENTER BOND STRUCTURES

Covalent Structures. The structures of molecules and ions can be represented by graphs in which the vertices correspond to nuclei (and inner shell electrons), and in which a connecting line indicates nearest-neighbor coordination in the molecular framework or a locus of a covalent bond. For our purposes, the most convenient graphs for the boron hydrides include all terminal and bridging hydrogen atoms. The molecular graphs for the compounds to be discussed are given in 8-13. Monovalent and divalent vertices stand for terminal and



bridging hydrogens respectively, and the other vertices represent boron atoms. Anticipating later discussion, an unusual C_1 structure is depicted for B_5H_{11} , and peripheral BB bonding is indicated for $B_{10}H_{14}$. These graphs are more complicated than those used by Leibowitz, *et al.* in work on the enumeration of three-center bond structures (Ref. 35). A concomitant increase in structural information will be generated, i.e., the asymmetries of bridge and terminal bond orders to hydrogen.

In order to avoid an abstract presentation, the procedures to be employed will be illustrated with the graph of B_4H_{10} . A contributing structure to the resonance hybrid is a subgraph of

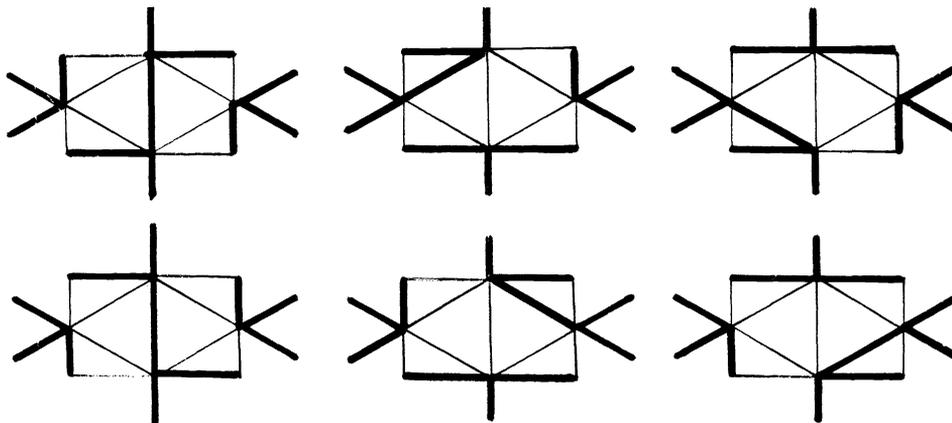
9 in which three lines or edges are incident on each boron atom, and in which one line is attached to each hydrogen atom (Ref. 36). Each subgraph contains disconnected branched tree graphs that are subtrees of the original topological molecular graph. The total number of subgraph lines is given by

$$(3N_B + N_H) \div 2 = \text{Subgraph lines} \quad (1)$$

and the number of subtrees in each structure is

$$(N_H - N_B) \div 2 = \text{Number of Subtrees} \quad (2)$$

where N_B and N_H are the number of boron and hydrogen atoms respectively. For B_4H_{10} there are eleven lines in each structure and each structure is composed of three subtrees. All subtrees must have length of at least three lines, so the only possible subgraphs combine subtrees of lengths three (twice) and five lines. Each subtree terminates at hydrogen vertices. The six allowed structures for B_4H_{10} are listed below in 14, where the light lines outline the underlying molecular graph. The results for each compound will be discussed

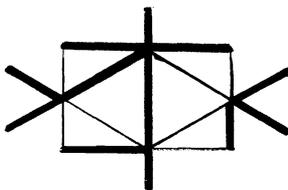


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individually later, but one can see that B-H bridge asymmetries will arise from this approach, that different B-B bond orders will be manifest in the boron framework, and that all terminal BH bonds will have bond orders of unity in the neutral covalent composite structure graph.

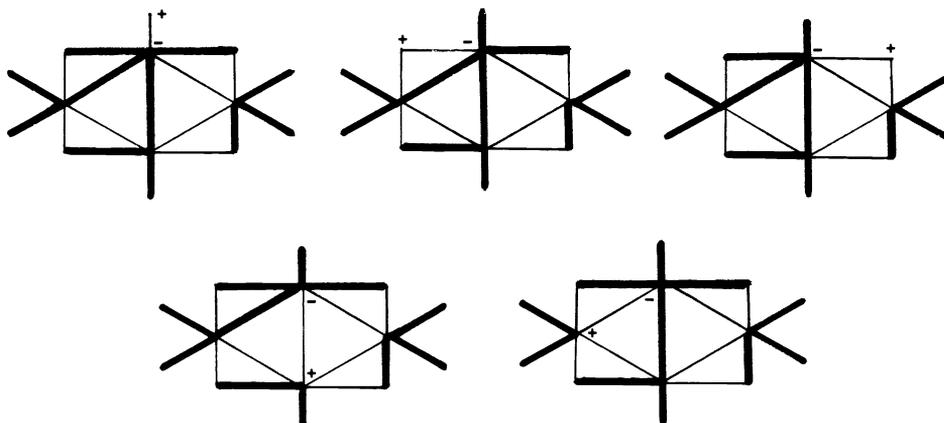
The enumeration of allowed structures is therefore the graph theoretical problem of counting covering subgraphs with specified properties. There is no known general solution to this problem in the literature of graph theory, where the difficulty of obtaining a general solution increases with increasing specification of properties (Ref. 37). However, for efficient hand calculation, the structural properties of the graphs are useful, and they can be calculated using eq. 1 and 2. We only carried out hand calculations for the boron hydrides through B_5H_{11} . Our main graph-theoretical tool was the so-called "back-tracking" technique for finding all Hamiltonian paths and circuits in a graph (Ref. 38). This method ensures that all structures will be found, and that duplicates will be eliminated. We will not describe the method further, except to say that its use requires about an hour for molecules as large as B_5H_{11} .

Ionic Structures. Two-center bond ionic structures are more difficult to count by hand than are the neutral covalent structures. However, one can define a graph counting method which leads to an efficient enumeration of the ionic structures as follows. Since charges are restricted to nearest-neighbor atoms, an equivalent ionic structure graph can be defined to contain one pentavalent boron vertex if the ionic bond is interpreted as a normal covalent bond. The graph for this species contains one more subgraph line, and the number of subtrees is one less than in the neutral structure graph. One of the ionic structure equivalent graphs for B_4H_{10} is shown in 15.



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Each pentavalent vertex structure corresponds to five ionic structures where each one of the five bonds is ionic in turn as depicted in 16. The graph containing the pentavalent vertex



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consequently represents one (terminal BH bond ionic), two (bridging BH bonds ionic), or two (BB bonds ionic) structural graphs. This equivalent graph approach therefore allows one to count either a subset of allowed ionic structures or the full set. The symmetry of the system can of course be utilized to reduce bookkeeping problems.

The pentavalent graph "bond orders" are obtained as usual as the ratio of structures (graphs) containing a bond to the total number of structures. Composite ionic structure bond orders are found by subtracting 1/5 of each of the partial pentavalent graph bond orders. The partial pentavalent bond order is defined to be the ratio of structures containing a bond

$$p(\text{ionic structure}) = p(\text{pentavalent graph}) = p(\text{partial}) \div 5$$

attached to a pentavalent vertex divided by the total number of structures. Formal charges for each atom in the composite ionic structure are determined by subtracting the sum of the bond orders of the attached bonds from the normal valence of the atom. The resulting ionic structure graph has small fractional charges on all boron and hydrogen atoms.

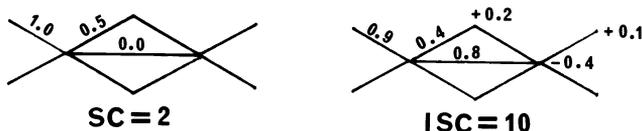
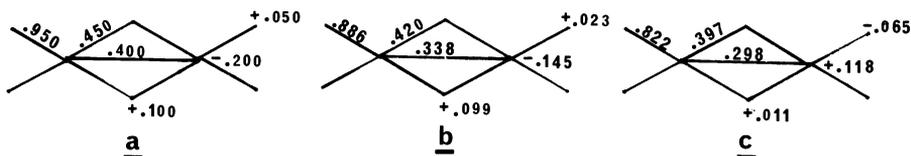
Computer Program for Two-Center Bond Structures. The design of a computer program to carry out these calculations is essentially based on the procedures outlined in the previous sections. The program was verified and tested by carrying out hand calculations for the smaller boron hydrides. The input consists of the numbers of boron and hydrogen atoms, the adjacency matrix, and the number of electron pairs in the molecular graph. Essentially the computer permutes the bonds (electron pairs) among the topological connections, and tests the structure for validity. Our test for validity is very simple, and may not have been used previously. It involves comparison of the sum of the indices for the chosen bonds to a required number, unique for each molecule. A bond is indexed a_{ij} where i and j are the numbers of the atoms connected by the bond. The required number is the sum of the hydrogen atom designations plus three times the sum of the boron atom designations. A second part of the validity test ensures that the correct valence of each atom is preserved by checking all bond indices in each retained structure. The required validity number is varied in accordance with the altered valence of the boron vertices in the pentavalent ionic structure graphs.

The computer program output consists of a list of structures and bond orders. Neutral covalent structure and pentavalent ionic structure calculations are carried out in separate batches. The final resonance hybrid bond orders are obtained by averaging the bond orders from the two calculations. The formal charges are obtained by hand.

Storage requirements for the program are minimal. A structure is generated canonically, tested, printed if valid, and discarded if invalid. The time required for generation of a permutation is about 10^{-4} seconds (IBM-360-50). The permutations are generated in groups of bonds to hydrogen atoms and then bonds to boron atoms. A comparison with the number of bond permutations to be tested using three-center structures for $B_{10}H_{14}$ shows that there are actually fewer using a two-center bond approach (10^8 , three-center bonds (Ref. 15); 10^7 , two-center bonds).

RESULTS

Diborane(6). The composite neutral covalent and the ionic structure graphs are shown in 17, along with the number of contributing structures (ISC = ionic structure count). The bond

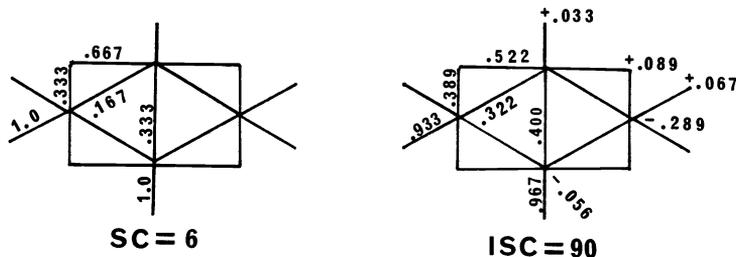
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order and charge diagram obtained for diborane by averaging the composite structure graphs is shown in 18a. The bond orders and charges are in qualitative agreement with overlap populations and charges derived from an LCAO-MO-SCF calculation with an extended basis set of Slater-type orbitals (Ref. 39) given in 18b. The results of a minimal basis set calculation, shown in 18c, give terminal hydrogen and boron atom charges that differ in sign from the other two calculations. One notes that BB bond order only arises in the simplified valence bond treatment through inclusion of ionic structures.

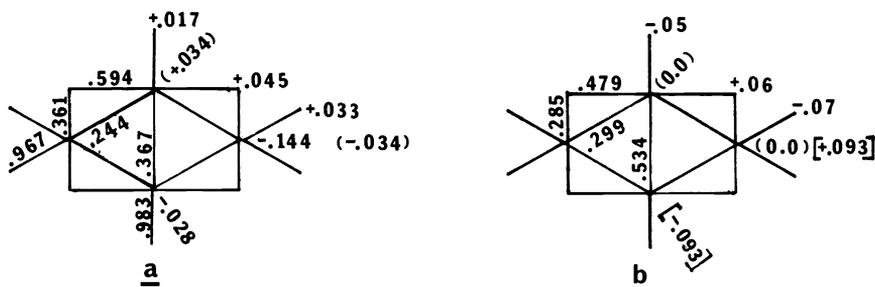
We would like to ascribe some significance to the numerical agreement of diagrams 18a and 18b in the hope that this resonance theory could mimic the results of more elaborate MO calculations. The three bond orders and the charges do exhibit high correlation coefficients of 0.998 and 0.988 respectively. However, extended basis set results are not available for the higher boron hydrides, so one cannot test further for the desired congruency.

The results in 18 indicate that one should probably not compare minimal basis set charges with the resonance theory formal charges except as an indicator of relative charge densities. A similar decision has been reached by Lipscomb and coworkers in using their SCF calculated Mulliken populations as static reactivity indices in a series of boron hydrides, ions, and carboranes (Ref. 9-11, 40). Instead they use group charges for boron atoms, defined as the Mulliken atomic charge for each boron plus the atomic charge of attached terminal hydrogens plus one-half that of attached bridge hydrogens. The results of the bond overlap population analysis are more consistent, so these will be compared with the resonance theory bond orders where appropriate.

Tetraborane(10). X-ray (Ref. 41) and electron diffraction studies (Ref. 42, 43) show that the bridging hydrogens in B_4H_{10} are not equidistant from boron atoms (1.315 and 1.484 Å), and that the two types of BB bonds have different bond lengths (1.705 and 1.856 Å). Both of these structural features are correctly reflected in either of the composite structural graphs, 19, and in the resonance hybrid diagram 20a. The results of minimal basis set

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LCAO-MO-SCF calculations (referred to hereafter as SCF calculations)(Ref. 44) are given in

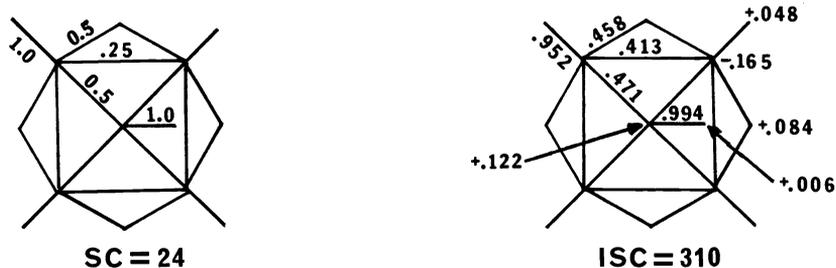


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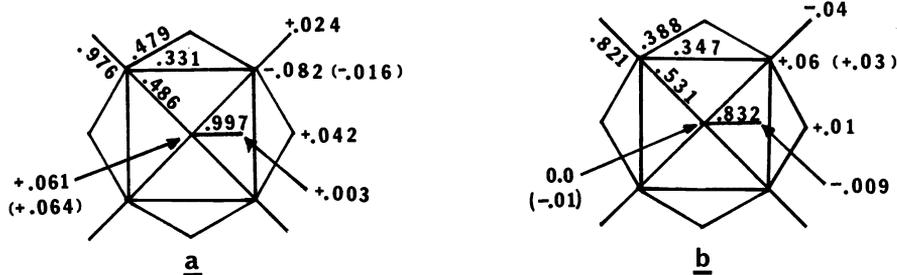
20b, and are also in qualitative agreement with the experimental data. As usual, the SCF calculations give terminal hydrogens with negative charges, but the group charges in parentheses exhibit minor differences for the two different calculations that are probably not significant. Possibly more important, the relative order of hydrogen charges are not the same in 20a and 20b. Also, calculations using the approximate PRDDO ab initio method (Ref. 45) give boron group charges shown in brackets (Ref. 11, 12) that are opposite in sign from those in 20a and are somewhat larger.

The original three-center valence bond representation of B_4H_{10} used a single 4102 (styx) structure (Ref. 46) containing the central BB bond as the only boron framework bond. The recent reformulation using a resonance hybrid of several vacancy structures (see Introduction) introduces the peripheral type of BB bonding in the predicted structure. The BHB bridge bond asymmetry is also correctly predicted only after incorporating the vacancy structures.

Pentaborane(9). B_5H_9 cannot be represented by a single three-center bond structure (Ref. 46), and localization procedures applied to the SCF wave function for B_5H_9 do not give convergence to a single unique structure (Ref. 14). This is the same kind of result obtained when one tries to carry out a localization of wave functions for certain polycyclic aromatic hydrocarbons (Ref. 25-28). This delocalized nature of B_5H_9 is well characterized by the large number of two-center bond structures that are obtained for the two structural graphs, 21, and by the final resonance hybrid structure 22a.



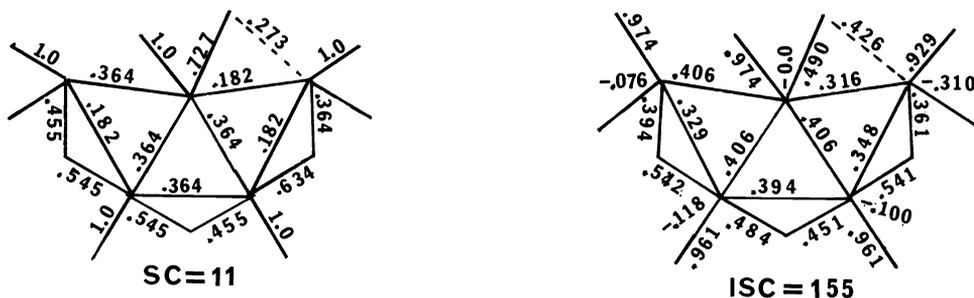
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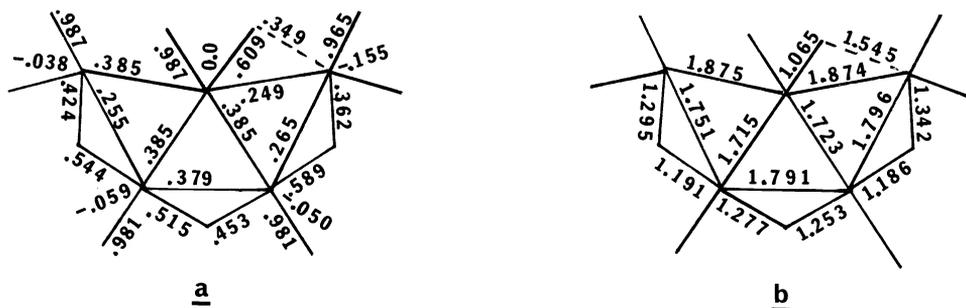
In comparing the results to SCF calculations, 22b (Ref. 44), the salient points are a general parallelism of bond orders and relative hydrogen charges, and a distinct difference in relative charges on the two types of boron atoms. The relative BB bond orders agree with the relative BB bond lengths (Ref. 47), and the orders of hydrogen atom charges agree with recent measurements of aromatic solvent induced NMR chemical shifts (Ref. 48). The resonance theory calculated positive charge on the apical boron atom is due to incorporation of structures with ionic BB bonds as in the B_2H_6 structure in 3. If these structures were eliminated from the resonance hybrid or given lower weights, the apical boron would be calculated to have a negative formal charge. At the present time we prefer not to make adjustments of this type.

Pentaborane (11). This molecule contains a unique structural feature not found in any other of the known boron hydrides. The apical BH_2 group is the only example in which the BH_2 boron atom is coordinated to more than two other boron atoms, and one of its bonded terminal hydrogen atoms is the only instance of a non-bridging hydrogen calculated (SCF) to have a positive charge (Ref. 44, 49). Localization procedures indicate that this hydrogen atom participates in multicenter bonding (Ref. 14), and a recently obtained crystal structure (Ref. 50) places this hydrogen ca. 0.3A closer to one adjoining BH group than to the other. This structural feature is built into the structural graph calculations summarized in 23.

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For clarity of presentation the easily calculated (all positive) hydrogen formal charges are not shown in these figures.

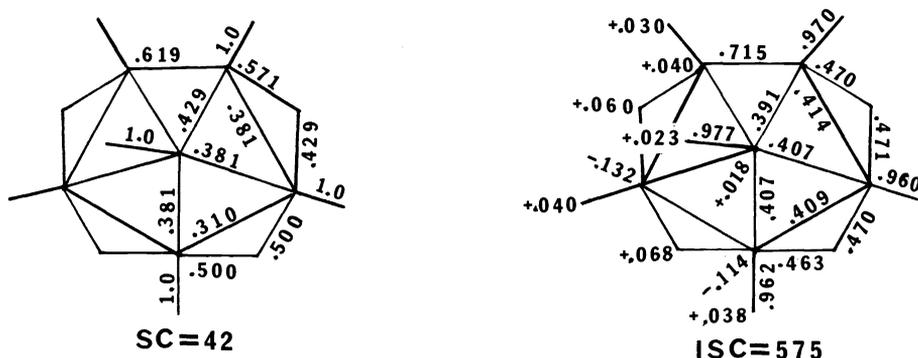
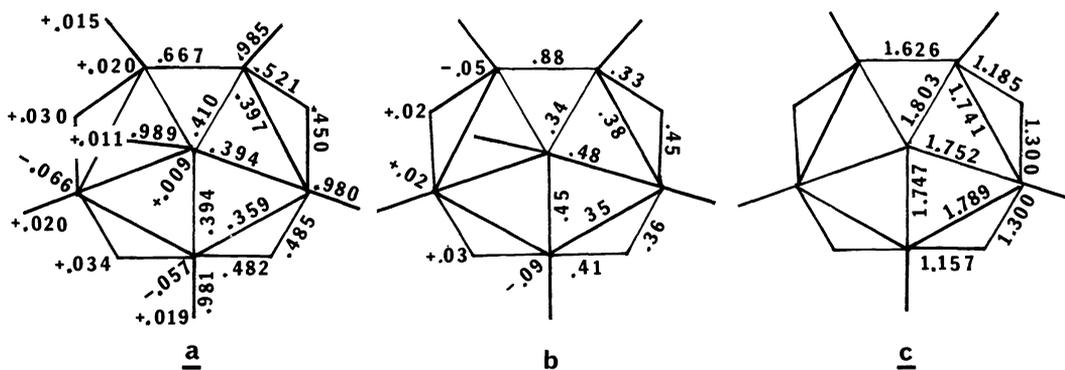
The resulting charge-bond order diagram 24a is compared with the X-ray structure (Ref. 50) in 24b, since an SCF calculation for the chosen bonding geometry is not available. Points

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of excellent agreement are the correctly correlated orders of asymmetries in the positions of the bridging hydrogen atoms. However the BB bond distances are in no more than roughly qualitative correspondence to the bond orders, and two of the bond orders are in definite disagreement. We find that the disagreement is substantially increased if both hydrogens of the apical BH_2 group are considered to be terminal hydrogen atoms, and we feel that this circumstance supports the existence of a C_1 structure for B_5H_{11} .

Hexaborane (10). B_6H_{10} contains a basal BB bond which is much shorter (1.626 Å) than those found in other boranes (Ref. 51, 52), and Lipscomb, *et al.*, have found that this unique basal BB bond is especially strongly localized in comparison to other BB bonds in B_6H_{10} and in other boranes (Ref. 53). The possibility of localized double bond character for this bond has been raised because of its short length and very high Mulliken bond population in MO calculations (Ref. 53). We felt that the observed short bond required the inclusion of structures in the resonance hybrid that contained a double bond at the basal BB position.

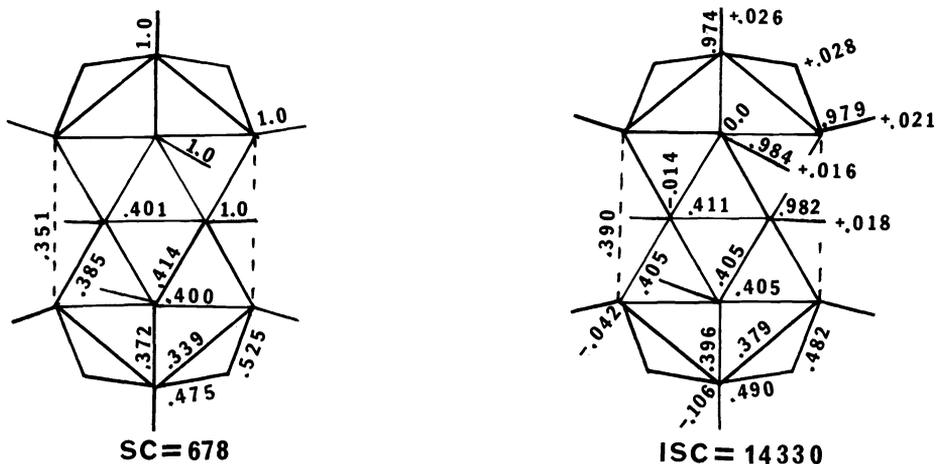
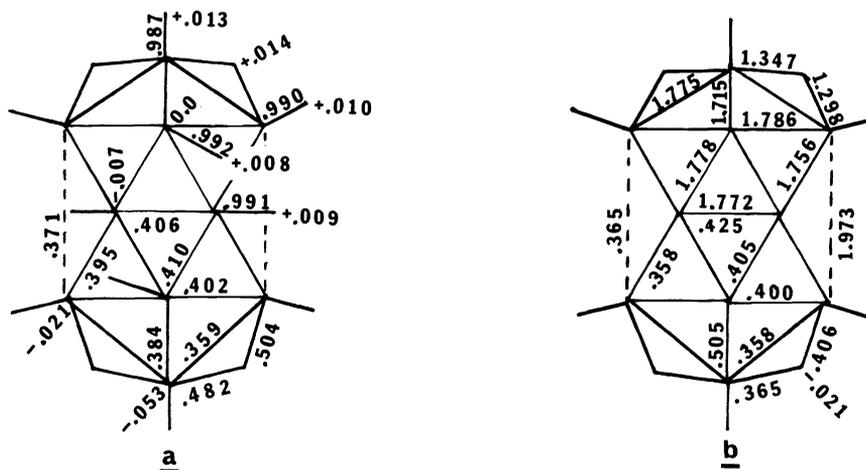
Our computer program finds all possible double bond structures but generally discards them because of our prior restrictions on the allowed structures. After lifting this restriction for the unique basal BB bond we obtained the structure-graphs shown in 25, which lead to the charge and bond order diagram given in 26a.

2526

Discrepancies between the SCF calculations, depicted in 26b, reported by Lipscomb's group (Ref. 53) and our crude valence bond calculations are most evident in this case. The BHB bond asymmetries are not in parallel order, and BB bond orders do not correlate very well with bond overlap populations. The small differences between the calculated charges are probably insignificant, and the short length of the basal BB bond is well correlated by both calculations.

The most recent experimental X-ray structure is shown in 26c (Ref. 51) and this structure reverses the previous asymmetry (Ref. 52) of one of the bridging BHB bonds in agreement with the valence bond diagram 26a. It is also appropriate to mention at this point that the positions of bridging hydrogens from the earliest X-ray determination (Ref. 52) were placed in nearly symmetrical positions in a refinement (Ref. 54) of the earlier data. Considering that the internal framework BB bonds are also not well correlated by our calculation, we conclude that only qualitative agreement of theory with experiment has been reached for B_6H_{10} .

Decaborane(14). Three-center bonding theory applied to $B_{10}H_{14}$ indicates that an extensive component of resonance among several three-center bond structures is needed to interpret its properties (Ref. 12, 46). The number of two-center bonding valence structures given in the composite structure graphs 27 is likewise large which points to the importance of resonance stabilization for the molecule. The final bond order-charge diagram also exhibits the effects of extensive delocalization since there is an almost statistical distribution of bonding electron pairs in the boron framework as shown in 28a.

2728

A neutron diffraction study (Ref. 55) of $B_{10}D_{14}$ provided the bond lengths and coordinates for an SCF population analysis (Ref. 56), both of which are shown in 28b. The small range of bond lengths for the internal BB bonds (1.715-1.786Å) is in good agreement with the small range of resonance hybrid bond orders. The relatively high bond order calculated for the long peripheral BB bond (1.973 Å) could be lowered by adjusting the weights of structures containing that bond, but again we choose not to use variable weights of the chosen allowed valence structures. Bridge BHB bond asymmetry is correctly correlated by the calculations of bond order (bond populations), and the actual bond distances differ by only 0.05 Å in accord with the small differences in bond order.

The SCF calculations of charges give an unusual result in that the bridging hydrogen atoms are calculated to have a small negative Mulliken charge. In all of the previous compounds bridging hydrogens have a positive charge, and the valence bond calculation is of course constrained to give a small positive charge at those positions. The magnitude of the valence bond bridging hydrogen charge does turn out to be the smallest of this type that we calculate. The significance of differences of this type remains to be determined.

RESONANCE ENERGIES AND ΔH (ATOMIZATION)

The interpretation of boranes as resonance hybrids of a large number of classical valence bond structures leads to the inference that these molecules should be stabilized by resonance. An analysis of the heats of atomization based on this postulate (Ref. 22) was reasonably successful. The experimental ΔH_a were correlated with a four term linear equation in which the dependent variables were the numbers of terminal and bridging BH bonds, the number of coordinating boron atom pairs, and an estimate of the resonance energy. The resonance energy estimate was based on the number of covalent resonance structures and used the algorithm, eq. 3.

$$\text{Resonance Energy} = A \ln(SC) \quad (3)$$

(A = constant)

This equation has been shown to be a valid measure of resonance energies in neutral aromatic hydrocarbons (Ref. 57-59), ions and radical ions (Ref. 60, 61), radicals (Ref. 62, 63), and in polyhedral borane dianions (Ref. 64).

In this paper we have used modified basis structure sets for the two molecules B_5H_{11} and B_6H_{10} , so a new analysis of the ΔH_a data is summarized in Table 1. References for the

Table 1. Two-center bond structures, ΔH_a , and resonance energies for boranes

Compound	Covalent Structures	Ionic Structures	ΔH_a , (expt.)	ΔH_a (calc.)	Resonance Energy (%)
BH_3	1	0	267.7	270.2	0.0
B_2H_6	2	10	570.5	567.8	11.1
B_4H_{10}	6	90	1040.6	1040.5	15.7
B_5H_9	24	310	1120.6	1125.1	25.9
B_5H_{11}	11	155	1217.6	1217.9	18.0
B_6H_{10}	42	575	1301.4	1298.2	26.2
$B_{10}H_{14}$	678	14,330	2056.5	2056.4	29.0

thermodynamic data used to obtain the experimental ΔH_a are given in the earlier work (Ref. 22). The ΔH_a (calc.) are obtained from a single multilinear regression analysis which give eq. 4

$$\Delta H_a (\text{calc.}) = 90.05 H_t + 64.15 H_b + 15.99 BB + 91.34 \ln(SC) \quad (4)$$

H_t and H_b are the numbers of terminal and bridging hydrogens respectively, and BB is the number of boron-boron nearest neighbors in the molecular graph. The multiple correlation coefficient for eq. 4 is unity (6 significant figures) and the average deviation of a calculated ΔH_a value is ± 1.9 kcal. The average deviation obtained after regression analysis without the resonance energy term is ± 13.0 kcal.

The results indicate that these boron hydrides are extensively resonance stabilized, e.g., 29% of the ΔH_a for $B_{10}H_{14}$ being attributed to resonance energy. One can compare the similar ΔH_a scheme for aromatic hydrocarbons (Ref. 59, 65) where resonance energies comprise only 1-2% of the total ΔH_a . However, these results are understandable. Only a small fraction of the valence electrons of aromatic hydrocarbons take part in the delocalized π bonding, but all of the bonding electrons of the boranes are involved. We believe that the correlation obtained using eq. 4 justifies the use of resonance theory to describe boron hydrides, at least for calculations of ΔH_a .

A ΔH_a scheme of this type can also be used to calculate the relative stabilities of other postulated structures or intermediates in boron hydride reactions. Studies of this nature are being carried out.

CONCLUSIONS

The two-center bond, structure-resonance interpretation of boron hydrides that we have outlined is a straightforward application of resonance theory, with the usual *ad hoc* characteristics. In particular we have made use of experimental data and available MO calculations to help choose our basis structures, and we have made an arbitrary assumption regarding the relative weights of neutral covalent structures and ionic structures. We note that many of the extensive theoretical investigations of Lipscomb and his coworkers have been carried out to help delineate the weights and types of three-center bond structures for various boranes and carboranes. One essential difference is that many of the simpler molecules have a unique or simple representation in terms of three-center bonds (Ref. 12, 66), whereas many structures are required in the two-center bond resonance theory. Even so, both types of valence bond approaches are relatively inexpensive in terms of human effort or computer time. A particular advantage of the two-center bond structure procedures is the very simple graph-theoretical structure counting method which is easily programable.

Significant results of the two-center bond calculations are the BHB bridging bond order asymmetries, which are in good agreement with the experimental bond lengths, and the excellent correlation of ΔH_a data which includes even the highly "resonance stabilized" $B_{10}H_{14}$ (Ref. 11, 15). Presumably, the ΔH_a of other large boranes can also be accurately calculated using this method. At the other extreme of size, the recently published bond length-based bond-enthalpy scheme of Housecraft and Wade (Ref. 67) gives relatively poor results for ΔH_a of B_2H_6 , B_4H_{10} , and B_5H_9 (The average deviation from the experimental values is ± 16.9 kcal).

The analogy that we have drawn between the π -resonance structures of benzenoid aromatic hydrocarbons and the contributing resonance structures of boranes can be used simply as a heuristic device. However, the results obtained indicate that two-center bond resonance hybrids seem to provide reasonable first-order descriptions of either the boranes or the benzenoid hydrocarbons. We propose that the electron deficient natures of the boron hydrides are consistent with resonance hybrid descriptions even for the smaller compounds. Therefore the terms "aromatic" or "superaromatic" (Ref. 13) are not inappropriate in describing many properties of the three-dimensional boron hydrides.

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