

Theoretical Investigations on Boron-Nitrogen Molecules

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A method previously applied to the study of hydrocarbon conformations is here used to investigate a variety of conformational problems in boron-nitrogen chemistry. Barriers and isomerization energies as well as charge distributions are presented for many simple boron-nitrogen molecules of the borazane, amino-borane, and borazarobenzene types. The usual resonance picture of the B-N bond is highly misleading, and the nitrogen always carries a larger negative net charge.

Recently we have developed an extended Hückel LCAO-MO (linear combination of atomic orbitals - molecular orbital) method which allows one to make a surprisingly good guess at the wave functions of medium sized molecules (11). The procedure makes no initial distinction between aromatics and aliphatics, or between organic and inorganic molecules. In the first application of the theory we performed calculations on nearly all simple hydrocarbons and were able to describe semiquantitatively a wide variety of phenomena such as barriers to internal rotation, cis-trans isomerism, and the relative roles of σ and π frameworks in aromatics. In this contribution we have extended our calculations to a wide variety of compounds involving boron and nitrogen, a field where theoretical work has been nearly absent and which because of its rapidly developing nature offers an unsurpassed opportunity for a theorist to stick out his neck and make some predictions. In what follows we present some of the results of these calculations, the details of which will be published elsewhere.

One important point should be made initially: The line between molecules that do in fact exist and those that do not is rather thin for the theorist today. Stability of molecules is a thermodynamic property and one could never on the basis of a theoretical calculation make the positive statement that a particular molecule should be stable, without having performed a calculation on all molecules which could be possible decomposition or reaction products. With the present state of the art any calculation would have to be approximate; one is then faced with the possibility of erroneous conclusions due to a different degree of goodness of calculations for the molecule and its components.

Let us illustrate this with an example. We can calculate that HBNH is stable with respect to $B+N+2H$. This does not imply that it exists for any reasonable length of time, for it may be unstable with respect to $BN+H_2$ or $B_3N_3H_6$. Moreover, it is conceivable that a calculation on $BN+H_2$ or $B_3N_3H_6$ could be "worse" than one on HBNH, and we would be led to predict stability where none exists. I dwell on this point so that when a statement is made below, attributing stability to such and such a molecule, it will be understood that the claim should be augmented with a disclaimer expressing the above ideas. I would also like to apologize for my unfamiliarity with what molecules have or have not been synthesized.

Method of Calculation

Details of the automated program are given in previous papers (11). A molecular orbital is computed as a linear combination of atomic orbitals, with a basis set consisting of 2s and 2p Slater orbitals on B, N, and C and 1s on H. (The program is equipped to handle all first-row elements, but calculations have been carried out only with B, N, C, and H so far.) The set of Hückel equations

$$\sum_i (H_{ij} - ES_{ij})C_{ij} = 0 \quad j = 1, 2, 3, \dots$$

is solved with all interactions and overlaps retained. The H_{ij} are chosen as valence state ionization potentials, the values used being essentially those of Skinner and Pritchard (18, 20).

	$H_{ii}(2s)$, E. V.	$H_{ii}(2p)$, E. V.	$H_{ii}(H 1s)$, E. V.
B	-15.2	-8.5	-13.6
C	-21.4	-11.4	
N	-26.0	-13.4	

The parameters for nitrogen are an average of the two common N valence states (sp^4 , s^2p^3). The H_{ij} are approximated by the relation

$$H_{ij} = 0.5K(H_{ii} + H_{jj})S_{ij}$$

with $K = 1.75$. Energies and wave functions are calculated and the latter subjected to a Mulliken population analysis (16), yielding gross atomic populations or net charges, and overlap populations. The latter are analogs of bond orders in the simple Hückel theory. From some previous work on hydrocarbons the coordinates of a large number of saturated and unsaturated molecules were available, constructed with C—C 1.54 Å., C=C 1.34 Å., C—C aromatic 1.40 Å., and C—H 1.10 Å., tetrahedral angles at unstrained aliphatic carbons, and 120° HCH angles in olefins. Convenience dictated the use of these geometries in our calculations on boron-nitrogen compounds, though we are well aware that a B—N single bond distance is about 0.05 Å. longer than the value used. Borazane and aminoborane were processed with more realistic B—N, B—H, N—H distances as well as with some different

assumptions regarding the N valence state. It was found that energetic relationships and qualitative charge distributions were fairly insensitive to these changes.

Polarity of the B—N Bond

In Figure 1 we show the results of the population analysis for borazane, aminoborane, and borazine, and for comparison give similar diagrams for the analogous carbon compounds. It is apparent that in each case the nitrogen is much more negative than the boron. For borazane there is a net transfer of 0.43 electron from the ammonia moiety to the borane, but the nitrogen still remains negative at the expense of its hydrogens. In aminoborane, in the π system 0.23 electron is transferred from N to B, but the effect in the σ system is reversed and the total charge transfer is 0.28 electron from B to N. In borazine the calculations show 0.27 π electron transferred from N to B, but again the greater electronegativity of the nitrogen overrides this, so that in the total charge distribution the nitrogen is negative. The top-filled orbitals in aminoborane and borazine are σ type.

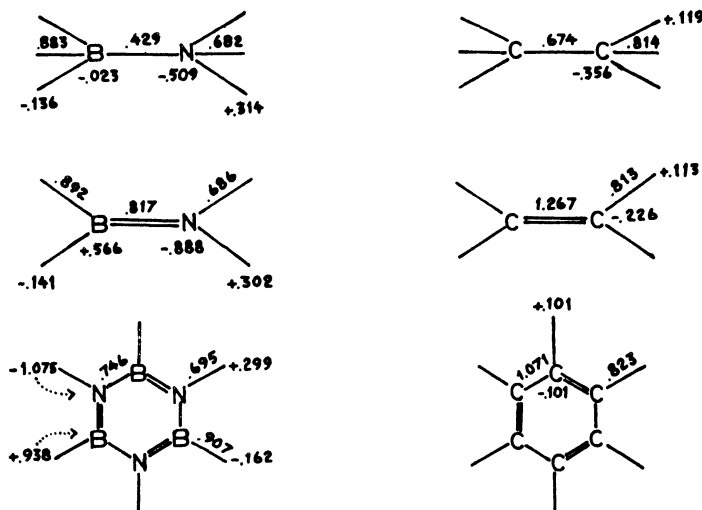


Figure 1. Population analysis of wave functions for borazane, aminoborane, and borazine compared to ethane, ethylene, benzene. Signed quantities are net charges, unsigned numbers Mulliken overlap populations.

Now for some 30 years people have been writing resonance structures for B—N compounds which imply charge transfer from N to B. While this is certainly true in the π system, the total charge distribution in fact certainly shows the opposite effect in aminoboranes and borazine, but not in borazane. To my knowledge the only workers who fully recognize the possibility of this have been Becher (2), Goubeau (10), and Coates and Livingstone (8). Becher measured the dipole moments of some methyl-substituted borazanes and aminoboranes and concluded that the aminoborane B—N bond moment was close to zero. While our calculation actually indicates that this moment has the direc-

tion B→N, Becher's conclusions and ours agree that in all B-N compounds the nitrogen bears a larger negative net charge than the boron. I would like therefore to enter an earnest plea for the abandonment of the misleading formulation of $B^- - N^+$ and a re-examination of the reactions of B-N compounds in view of the fact that a better picture of the charge distribution is $B^+ - N^-$.

Borazanes and Aminoboranes

In Figure 2 we show the calculated charge distributions in some simple borazanes and aminoboranes. As usual with simple LCAO-MO calculations, these no doubt exaggerate somewhat the distribution of electrons. The qualitative conclusions of an examination of various stereochemical problems for these molecules are given below.

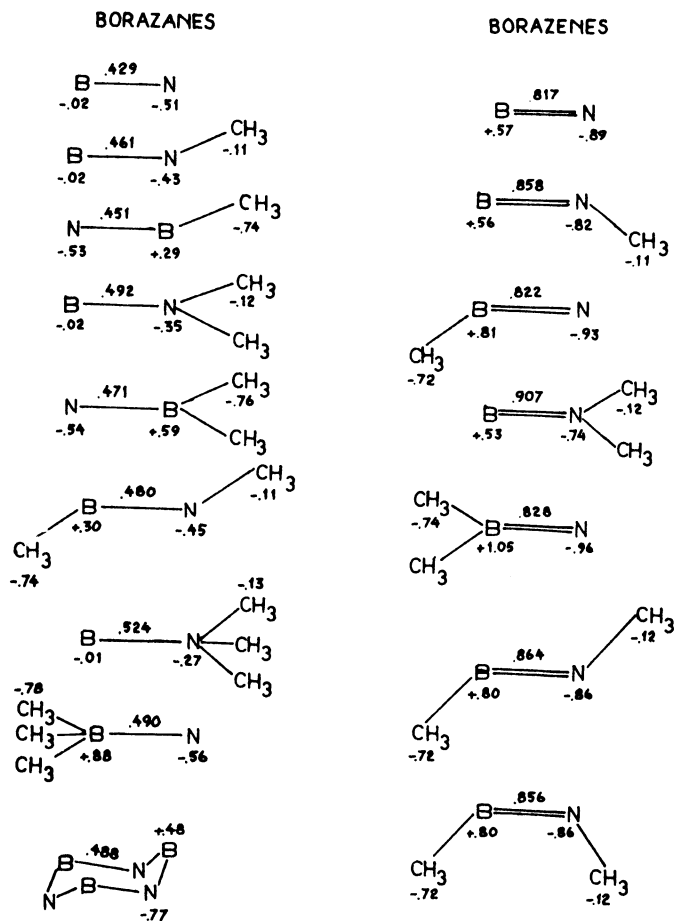


Figure 2. Charge distributions in some borazanes and borazenes

Only B-N overlap populations are shown. Charge next to CH₃ refers to C charge only; charges on H are not shown

1. The barrier to internal rotation in borazane is predicted to be in the region of 1.5 kcal. per mole in favor of the staggered form.

2. It would be interesting to look in the vacuum ultraviolet spectra of the borazanes for the internal charge transfer transition corresponding to an electron being excited from the B-N bonding orbital (charge mainly on N) to the B-N antibonding orbital (charge mainly on B). Our calculations show that this transition should most conveniently be observed in *N*-trimethylborazanes, though there may be some difficulty in obtaining a spectrum, since a nearby transition involves excitation of B-H bonding electrons with probable ensuing bond fracture. Several charge transfer transitions might be observable in the aminoboranes.

3. The barrier to rotation in aminoborane is estimated to be near 10 kcal. per mole, very much less than the corresponding ethylene barrier. For (dimethylamino)borane this torsional barrier is somewhat greater, for (amino)dimethylborane about the same as in aminoborane. Tentatively we find that in the excited charge transfer state corresponding to a $\pi-\pi^*$ excitation, the molecule still prefers a planar disposition in contrast to ethylene, which favors a D_{2d} geometry for the related state (17). The first $\sigma-\pi^*$ excited state prefers a twisted molecule. The order of magnitude of the calculated aminoborane barrier appears to be correct (4).

4. In *N*-methyl-*B*-methylborazane, the energy difference between the *gauche* and *trans* arrangements is calculated to be very similar to that in the hydrocarbon analog, *n*-butane, but the potential maximum corresponding to a methyl group on B eclipsing a hydrogen on N is expected to be of much higher energy in the B-N compound.

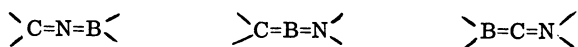
5. The isomerization energy of *cis*- to *trans*-(methylamino)methylborane is expected to be similar to that of *cis*- to *trans*-2-butene. A lesser certain result is that the heat of formation of (amino)dimethylborane should be very close to that of *cis*-(methylamino)methylborane, while the (dimethylamino)borane - *trans*-(methylamino)methylborane isomerization energy should be greater than that of the isobutylene-*trans*-2-butene pair.

6. Buttler, Gaines, and Schaeffer's (7) hypothesis that the boat-chair equilibrium in cyclotriborazane might not be as unfavorable to the boat form as it is in cyclohexane has been confirmed. The boat-chair difference in the former compound has been calculated at about one half of the corresponding cyclohexane energy difference. Moreover, ΔE between axial and equatorial methyl cyclotriborazane is predicted to be less than the corresponding energy in cyclohexane for *N*-methyl, more for *B*-methyl. This is in agreement with the evidence quoted by the above authors. Incidentally, the N hydrogen in piperidine is predicted to favor the axial location, the B hydrogen even more so in the as yet unsynthesized cyclic $(CH_2)_5BH$ (planar configurations at B and N have not yet been examined). Cyclodiborazane is expected to be much more resistant to distortions from planarity than cyclobutane.

7. Calculations were performed for *cis* and *trans* conformations of isomeric analogs of butadiene, with the atom arrangements



These are arranged in order of calculated decreasing stability, left to right. In each case the trans conformation is favored, and as expected from a simple charge model, the cis-trans energy difference is less than that in butadiene for 1 and 4, and more for 2. Surprisingly, the calculation shows a very small difference between the cis and trans forms of 3. Derivatives of 1, 2, and 3 are known. The following allene analogs are arranged in order of decreasing stability.



Isocyanate boranes can be considered derivatives of the first of these.

8. Lappert and Majumdar report the synthesis of the first $(\text{BHNH})_2$ derivative (14). Since the carbon analog, cyclobutadiene, is of considerable interest, we have looked at the conformations of the BN compound in some detail. However, because of the presence of amino substituents on the borons of the actual molecule prepared by Lappert, no conclusions can be reached as to its conformation from our calculations on $(\text{BHNH})_2$. We find that $(\text{BHNH})_2$ prefers a planar arrangement of atoms, and with little deviation, if any at all, from a square arrangement. The study is not yet complete, since we have examined so far only distortions of the B-N ring. If we consider the π -electron system of this molecule, we find that the two states which would be degenerate in cyclobutadiene are split considerably. Here the charge transfer transition (corresponding to an excitation from one of the above-mentioned levels to the other) is forbidden, but two allowed $\pi \rightarrow \pi^*$ transitions, close in energy, should be found in the molecular ultraviolet spectrum.

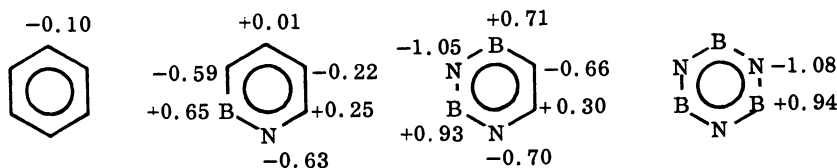
9. In connection with the question of the conformation of the recently synthesized derivatives of the B-N analog of cyclo-octatetraene (22, 23) we have examined a number of geometrical arrangements for C_8H_8 and $(\text{BHNH})_4$. We find the tub configuration favored for both, and relative to this conformation the cubane arrangement is more favorable for $(\text{BHNH})_4$ than for C_8H_8 . The anion and dianion of cyclo-octatetraene are found to prefer the planar geometry, in agreement with NMR and ESR evidence (12, 13, 21); it is an interesting conclusion of the calculation that it predicts retention of tub geometry for the hypothetical $(\text{BHNH})_4^-$ and approximately equal energies for tub and planar $(\text{BHNH})_4^{-2}$.

10. In the equilibrium conformation of propylene one of the methyl hydrogens eclipses the double bond. A calculation shows that this is also likely to be the equilibrium geometry in (amino)methylborane, but that in (methylamino)borane the methyl hydrogens will be staggered with respect to the B-N bond.

11. A general observation independent of our calculations can be made on steric problems where a BH_2 or BH_3 group is involved. These groups will generally cause greater steric problems than a corresponding methylene or methyl group, since not only are the B-H bonds longer, but, because of the ordering of electronegativities, hydrogens bonded to B acquire considerable negative charge. The converse statement is applicable to NH_2 and NH_3 groups.

Heteroaromatic B-N Compounds

We have performed LCAO-MO calculations for both the σ and π electron systems of benzene, the three borazarobenzenes, 11 diboradiazarobenzenes, and the three triboratriazarobenzenes. In general the energy of the σ electrons emerged as a function only of the number of various bonds involved, while the π energy varied considerably. Dewar's conjecture regarding the relative stabilities of the borazarobenzenes (9) is confirmed - i. e., in order of decreasing thermochemical stability we have 2,1-, 4,1-, 3,1-borazarobenzene. The most stable of the diboradiazarobenzenes is the isomer 2,4-dibora-1,3-diazarobenzene, followed by 4,6-dibora-1,3-diazarobenzene. In general, isomers with B-B or N-N bonds are unfavored. Of the triboratriazarobenzenes, borazine is easily the most stable. Total charge distributions are shown for the most stable isomer of each class:



The calculation shows also that borazarene and 2,4-dibora-1,3-diazarobenzene are much less stable than either borazine or benzene. One general principle emerges: B and N "like" to come adjacent into a molecule, and if a molecule already has positions of alternating negative and positive charge density, a very stable B-N compound would be one with a nitrogen in what was originally the most negative site in the molecule, and a boron in an adjacent most positive location.

We have also calculated wave functions for 2,1-borazaronaphthalene, 10,9-borazarophenanthrene, and some of the other compounds synthesized by Dewar and coworkers. The qualitative features of the charge distributions are in agreement with those calculated by Dewar (9). We show only for comparison in Figure 3 the results of our population analysis for the π and $\sigma + \pi$ systems of 2,1-borazaronaphthalene.

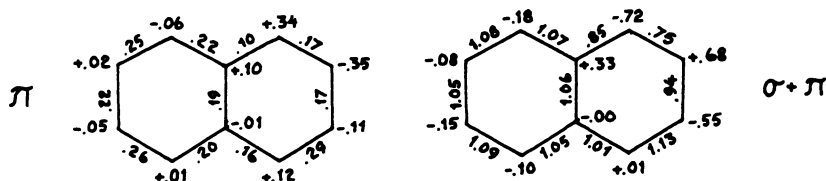
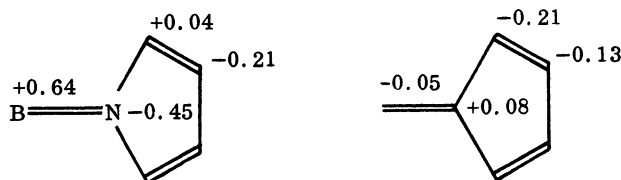
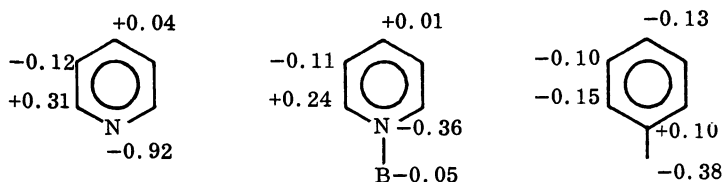


Figure 3. Population analysis for π and $\sigma + \pi$ frameworks in 2,1-borazaronaphthalene

Becher has synthesized a substituted B-N analog of fulvene (3). The calculated $\sigma + \pi$ charge distribution in $C_4H_4NBH_2$ (6,1-borazaro-fulvene ?) is shown below, along with the corresponding fulvene diagram. While fulvene is experimentally and in theory about 30 kcal. per mole less stable than benzene, the borazarofulvene is calculated to be about 25 kcal. per mole more stable than the isomeric borazarene.



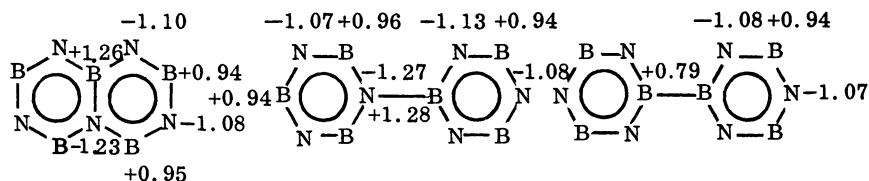
We have also performed a series of calculations on some substituted pyridine boranes. Charge distributions for pyridine, pyridine-borane, and toluene are shown below.



The calculations show that, of the picolines, 2-methylpyridine is most stable, followed by 4-, 3-, while in the adduct the 4-methylpyridine borane is favored, followed by 3-, 2-. On examination of the reaction forming the pyridine boranes, the net result is that the heat of formation of the 2-methylpyridine adduct is substantially greater than that of the 3- or 4-methyl isomer — in agreement with the measured heats of Brown and Domash (6).

In the charge distribution for pyridine borane, the charge on carbons 3, 4, and 5 is changed little from pyridine, while the charge on positions 2 and 6 is increased. In this calculation coordination with BH_3 not only produces charge transfer from N to B but also from N to its neighboring carbons (the N-C overlap population is also greater in PyBH_3). Probably this is an artifact of the calculation which uses the same parameters for N in pyridine and pyridine borane. Though the PyBH_3 NMR anomaly as reported by Brey *et al.* (4) can be explained on the basis of our computation, invoking increased ring currents, the calculation is probably not reliable here and the explanation for the deshielding at select positions in the pyridine borane lies in the removal of N paramagnetic anisotropy. A similar effect is noted in pyridinium cation (1, 19).

We have also examined the per-*B, N*-naphthalene (15) and per-*B, N*-biphenyl linked via a B-N bond (15) and a B-B bond (5). In the naphthalene analog the gap between filled and unfilled orbitals is large and only slightly smaller than in borazine. This situation, very different from the benzene-naphthalene progression, indicates the trend which culminates in a colorless hexagonal boron nitride. The B-N linked biphenyl analog prefers to be slightly twisted, while the B-B linked compound should be planar. (The *N*-hydrogens which are the source of steric difficulties in the planar form are positively charged and thus appear "smaller.") The total charge distributions shown below may be of some interest when NMR spectra of these compounds are examined.



Acknowledgment

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