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## Molecular Orbital Studies of Azaboranes Which Have Nitrogen in a Framework Position

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Molecular orbital studies are presented at the minimum basis set level for the known azaboranes *arachno*-4-$NB_8H_{13}$, *arachno*-$B_9H_{12}NH^-$, and *nido*-10-N-7,8-$C_2B_8H_{11}$ and for the hypothetical closo azaborane 1,12-$NCB_{10}H_{11}$. In all of these compounds, the nitrogen atom occupies a framework position, i.e., a vertex of a polyhedron or a polyhedral fragment. The method of computation, nearly at the minimum basis set SCF level, employs the PRDDO (partial retention of diatomic differential overlap) program. The bonding is analyzed in terms of charge stability, static reactivity indices, degrees of bonding, overlap populations, and localized molecular orbitals obtained by using the criterion of Boys. The most characteristic feature of the bonding in these compounds is the tendency of nitrogen to form polar and whenever possible two-center bonds.

### Introduction

Only a few azaboranes[1] are known in which a nitrogen atom occupies a "framework" position where it has three or more near neighbors in a framework that can be visualized as a polyhedral fragment. We report here the results of theoretical studies on three such compounds, 4-$NB_8H_{13}$,[2] $B_9H_{12}NH$,[3] and 10-N-7,8-$C_2B_8H_{11}$,[4] and on the hypothetical closo 1,12-$NCB_{10}H_{11}$, which is an isoelectronic analogue of the well-known 1,12-$PCH_{10}H_{11}$.[5] Surprisingly few azaboranes of these framework types are known. Our interest is in the tendency for nitrogen to form highly localized, polarized bonds which, when possible, are two-center in character. Associated with this tendency, we expected that other parts of the framework bonding would show abnormally high delocalization.

### Results and Discussion

The molecules are shown in Figure 1, where the numbering systems and final results of bonding are also presented. Calculations were carried out by the PRDDO (partial retention of diatomic differential overlap) method,[6] which closely approximates the minimum basis SCF level.

For 4-$NB_8H_{13}$, the X-ray coordinates[2b] were symmetrized to $C_s$. In general, the X-ray method underestimates the B–$H_t$ and C–$H_t$ distances by about 0.1 Å.[7] However, this systematic shortening of heavy atom to terminal hydrogen bonds normally has a very small effect on the overall bonding pattern (see below). Nevertheless, the experimental N–$H_t$ distance of 0.812 Å seemed too unrealistic and was optimized, although no readjustment was made for the B–$H_t$ distances in this molecule.

For $B_9H_{12}NH^-$, the coordinates were chosen as follows: The symmetrized X-ray coordinates for the isoelectronic $B_{10}H_{14}^{2-}$ [8] with the B–$H_t$ bond lengths readjusted for the lengthening described above were taken. A $BH_2$ unit was replaced by an $NH^+$, orienting the N(6)–H(6) internuclear axis of $B_9H_{12}NH^-$ to be parallel to the B(6)–H(6) internuclear axis of $B_{10}H_{14}^{2-}$. Then, the coordinates of N(6) and B(2) and the N(6)–H(6) distance were subjected to one cycle of optimization.

A nido structure for 10-N-7,8-$C_2B_8H_{11}$ has been verified by an X-ray study[4c,d] of its *N*-benzyl derivative. The coordinates used for 10-N-7,8-$C_2B_8H_{11}$ were chosen as follows: the X-ray coordinates for the 10-C-10-N-7,8-$C_2B_8H_{10}$ fragment of the *N*-benzyl derivative were symmetrized. The $H_t$ attached to N(10) was oriented in the same direction as the carbon in this symmetrized 10-C-10-N-7,8-$C_2B_8H_{10}$ fragment. The N–$H_t$ distance was taken to be 0.04 Å shorter than the C(7)–H(7) distance, where 0.04 Å is the difference between the covalent radii of N and C.[9] On the assumption that all the X–$H_t$ bonds, where X = B, C, or N, were consistently shorter than their ideal lengths by comparable amounts, the overall X–$H_t$ bond lengthening was optimized by increasing all X–$H_t$ bond distances by the same amount. Although this optimization lowered the energy by about 45 kcal/mol, and lengthened the X-$H_t$ bonds by about 0.08 Å, the differences in bonding patterns between the optimized and unoptimized geometries were negligible.

The coordinates for 1,12-$NCB_{10}H_{11}$ were chosen as follows. By use of a reasonable set of initial bond lengths and a pre-

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[1] For a general review of boron–nitrogen compounds see: Nöth, H. *Prog. Boron Chem.* **1970**, *3*, 211.

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[7] Halgren, T. A.; Anderson, R. J.; Jones, D. S.; Lipscomb, W. N. *Chem. Phys. Lett.* **1971**, *8*, 547.

[8] (a) The crystal structure of $(N(CH_3)_4)_2B_{10}H_{14}$ has been reported by: Kendall, D. S.; Lipscomb, W. N. *Inorg. Chem.* **1973**, *12*, 546. (b) The symmetrized and readjusted $B_{10}H_{14}^{2-}$ coordinates referred to in the text are taken from: Hall, J. H., Jr.; Marynick, D. S.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1974**, *96*, 770. We have interchanged the *y* and *z* axes so that the *xy* plane will become the mirror plane in $B_9H_{12}NH^-$. (c) For PRDDO calculations on $B_{10}H_{14}^{2-}$ and several other open boron hydrides and carboranes, see: Hall, J. H., Jr.; Dixon, D. A.; Kleier, D. A.; Halgren, T. A.; Brown, L. D.; Lipscomb, W. N. *ibid.* **1975**, *97*, 4202.

[9] Coulson, C. A. "Valence", 2nd ed.; Oxford University Press: New York, 1961; Table 13, p 189.

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**Table I.** Coordinates in au[a]

| atom | *x* | *y* | *z* | atom | *x* | *y* | *z* |
|---|---|---|---|---|---|---|---|
| | | | $4\text{-}NB_8H_{13}$ $(C_s)^b$ | | | | |
| B(1) | 3.6764 | 2.7394 | −1.7072 | H(2) | 4.0653 | −1.7435 | 0.0 |
| B(2) | 2.9924 | 0.0 | 0.0 | H(4) | −0.8668 | −1.7172 | 0.0 |
| N(4) | 0.0 | 0.0 | 0.0 | H(5) | 0.6166 | −0.1821 | 4.2281 |
| B(5) | 0.8065 | 1.0571 | 2.5418 | H(6) | 1.6241 | 5.2588 | 4.9465 |
| B(6) | 1.1956 | 4.4468 | 3.0537 | H(7) | 3.6335 | 7.3445 | 0.0 |
| B(7) | 2.5598 | 5.5289 | 0.0 | H(56) | −0.5999 | 3.2525 | 3.0684 |
| H(1) | 5.4849 | 2.7788 | −2.6767 | H(67) | 0.3868 | 6.0173 | 1.6965 |
| | | | $B_9H_{12}NH^-$ $(C_s)^b$ | | | | |
| B(1) | 0.0 | 1.1025 | 1.7007 | H(2) | 4.5626 | 1.4813 | 0.0 |
| B(2) | 2.6817 | 0.3024 | 0.0 | H(4) | −4.5626 | 1.1789 | 0.0 |
| B(4) | −2.6817 | 0.0 | 0.0 | H(5) | 2.6852 | −1.4574 | 4.7973 |
| B(5) | 1.7830 | −1.5538 | 2.7721 | H(6) | 4.6818 | −3.2072 | 0.0 |
| N(6) | 2.7893 | −2.7027 | 0.0 | H(8) | −2.6852 | −1.4574 | −4.7973 |
| B(8) | −1.7830 | −1.5538 | −2.7721 | H(9) | −2.0323 | −5.1579 | 0.0 |
| B(9) | −3.2088 | −3.2611 | 0.0 | H(9)′ | −2.0323 | −5.1579 | 0.0 |
| H(1) | 0.0 | 3.0681 | 2.8095 | H(78) | 0.0 | −3.3097 | −3.3088 |
| | | | $10\text{-}N\text{-}7,8\text{-}C_2B_8H_{11}$ $(C_s)^b$ | | | | |
| B(1) | 0.0 | 0.0 | 0.0 | H(1) | −1.9734 | −1.0436 | 0.0 |
| B(2) | 1.1810 | 1.6340 | −2.6889 | H(2) | 0.1540 | 1.8530 | −4.6257 |
| B(3) | 0.2165 | 3.3885 | 0.0 | H(3) | −1.4015 | 4.9251 | 0.0 |
| B(5) | 2.6601 | −1.1182 | 1.7111 | H(5) | 2.9049 | −3.0605 | 2.7004 |
| C(7) | 3.0187 | 3.9953 | −1.4601 | H(7) | 3.0291 | 5.6877 | −2.3650 |
| B(9) | 4.5521 | 1.6243 | 2.4586 | H(9) | 5.9424 | 1.5404 | 4.1042 |
| N(10) | 5.1642 | 0.0 | 0.0 | H(10) | 6.6718 | −1.0612 | 0.0 |
| | | | $1,12\text{-}NCB_{10}H_{11}$ $(C_{5v})$ | | | | |
| N(1) | 0.1122 | 0.2924 | 0.1935 | C(12) | 1.8698 | 4.8956 | 3.2388 |
| B(2) | 0.0485 | 0.1254 | 3.3353 | H(2) | −0.5980 | −1.5679 | 4.5343 |
| B(3) | 2.8650 | 0.1258 | 1.7092 | H(3) | 4.2270 | −1.5672 | 1.7486 |
| B(4) | 2.5061 | 2.0035 | −0.9219 | H(4) | 3.6122 | 1.6495 | −2.7588 |
| B(5) | −0.5322 | 3.1636 | −0.9219 | H(5) | −1.5928 | 3.6368 | −2.7587 |
| B(6) | −2.0511 | 2.0029 | 1.7092 | H(6) | −4.1949 | 1.6483 | 1.7487 |
| B(7) | 2.5062 | 2.0035 | 4.3403 | H(7) | 3.5806 | 1.6778 | 6.2012 |
| B(8) | 4.0251 | 3.1642 | 1.7092 | H(8) | 6.1455 | 3.6379 | 1.7581 |
| B(9) | 1.9255 | 5.0416 | 0.0831 | H(9) | 2.6000 | 6.8082 | −0.9878 |
| B(10) | −0.8911 | 5.0412 | 1.7093 | H(10) | −2.1562 | 6.8075 | 1.7582 |
| B(11) | −0.5322 | 3.1635 | 4.3404 | H(11) | −1.5501 | 3.6368 | 6.2012 |
| | | | | H(12) | 2.4432 | 6.3974 | 4.2324 |

[a] Although the coordinates are listed to four decimal places, they were taken to five or six decimal places in most of the calculations.
[b] Only unique atoms are listed. The other atomic positions may be obtained by reflection through the *xy* plane.

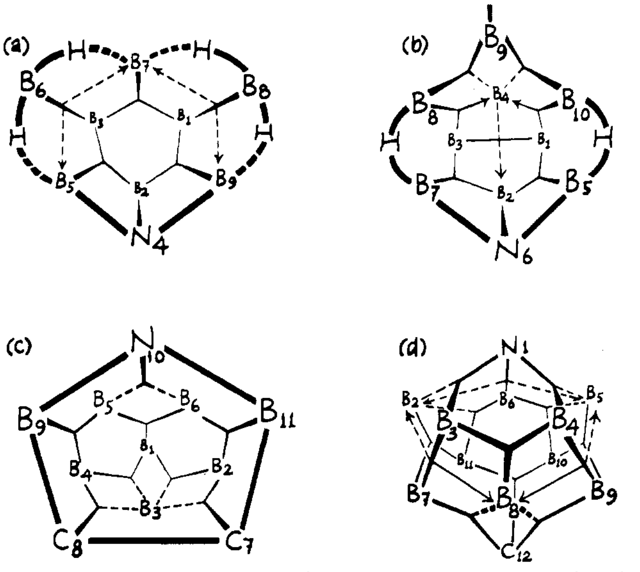

**Figure 1.** The molecules examined, the numbering systems used, and the LMO structures: (a) $4\text{-}NB_8H_{13}$; (b) $B_9H_{12}NH^-$; (c) $10\text{-}N\text{-}7,8\text{-}C_2B_8H_{11}$; (d) $1,12\text{-}NCB_{10}H_{11}$. Planar projections are shown for the open molecules in (a)–(c), while the LMO's of $1,12\text{-}NCB_{10}H_{11}$ are depicted in three dimensions. The bond notation is as follows: —, >0.50 e; - - -, 0.35–0.50 e; —>, 0.25–0.35 e; - - ->, 0.15–0.25 e. One $H_t$ has been omitted at each framework atom except the N in $1,12\text{-}NCB_{10}H_{11}$ which has no $H_t$'s.

**Table II.** Exponents

| orbital | exponent | orbital | exponent |
|---|---|---|---|
| $B_{1s}$ | 4.68 | $N_{1s}$ | 6.67 |
| $B_{2s=2p}$ | 1.45 | $N_{2s=2p}$ | 1.95 |
| $C_{1s}$ | 5.67 | H | 1.24 |
| $C_{2s=2p}$ | 1.72 | | |

viously described procedure for deriving a set of coordinates for a closo compound from a given set of bond lengths,[10] the initial coordinates were obtained. The N–B, C–B, and B–B bond lengths were subjected to one cycle of optimization. To minimize computational expenses, we assumed all B–B bond lengths to be equal, although there are three symmetry-distinct types of B–B bond lengths in this molecule. The B–$H_t$ and C–$H_t$ bond distances were not optimized, but a calculation carried out at distances of 1.15 and 1.00 Å, respectively, gave an energy of about 9.4 kcal/mol lower than a calculation performed at distances of 1.19 and 1.09 Å, respectively. However, this abnormal shortening is characteristic of the PRDDO method and not indicative of short distances to $H_t$ in the molecule.

The coordinates (Table I), the Pople exponents[11] (Table II) used in all of the calculations, and the energetics (Table III)

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(11) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657.

Table III. Energetics[a]

| structure | NRE[b] | KE[c] | NAE[d] | ERE[e] | E[f] | VR[g] | $\Delta E$[h] |
|---|---|---|---|---|---|---|---|
| 4-$NB_8H_{13}$ ($C_s$) | 379.797 | 259.843 | −1357.867 | 459.000 | −259.226 | 0.998 | 0.578 |
| $B_9H_{12}NH^-$ ($C_s$) | 429.974 | 284.813 | −1530.202 | 531.491 | −283.924 | 0.997 | 0.515 |
| 10-N-7,8-$C_2B_8H_{11}$ ($C_s$) | 522.034 | 333.877 | −1816.320 | 626.471 | −333.937 | 1.000 | 0.547 |
| 1,12-$NCB_{10}H_{11}$ ($C_{5v}$) | 586.046 | 346.131 | −1968.423 | 690.811 | −345.435 | 0.998 | 0.583 |

[a] All energies are in au. [b] Nuclear repulsion energy. [c] Kinetic energy. [d] Nuclear attraction energy. [e] Electron repulsion energy. [f] Total energy. [g] Virial ratio ($-E/T$). [h] Magnitude of the energy difference between the highest occupied and lowest unoccupied molecular orbitals.

of the final calculation for each molecule lead to energies which are reasonable and virial ratios which are very close to unity. The gap between the highest occupied and lowest unoccupied molecular orbitals is quite large for each molecule, indicative of some resistance to oxidation or reduction.

Valencies, atomic charges, and inner-shell eigenvalues (Table IV[12]) are sometimes useful as static reactivity indices, in addition to providing valuable information about the nature of the electron distribution. The valency[13] of an atom in a molecule is defined as the sum of the degrees of bonding[13] of that atom to all other atoms. This index of covalent bonding, and the atomic charges and inner-shell eigenvalues are frequently correlated: the more negative the atomic charge, the less negative is the inner-shell eigenvalue because of repulsion between these valence and inner-shell electrons.[14] If correlation corrections (not included here) are made, the inner-shell eigenvalues become observables.[15]

The results in Table IV[12] show that N is always negatively charged. The valency of N is smallest in 1,12-$NCB_{10}H_{11}$ where N has a lone pair. Most of the borons are negatively charged, although positive charges are often encountered. In general, the borons attached to nitrogen are less negative than most of the other borons in the same molecule. The less negative boron inner-shell eigenvalues are well correlated with the more negatively charged borons for a given molecule, although exceptions may be found. The charges on the $H_t$'s fall into the ranges $-0.08 \leq q(H_t,B) \leq 0.02$, $0.07 \leq q(H_t,C) \leq 0.10$, and $0.12 \leq q(H_t,N) \leq 0.20$. Thus, the less electronegative the atom to which $H_t$ is attached, the more negative is the $H_t$ itself as the electrons shift toward this $H_t$. The BHB bridge hydrogens are slightly acidic, and their atomic charges are about 0.1 e. The valencies of all the hydrogens are close to unity, being generally lowest for $H_t$'s attached to nitrogen.

The degrees of bonding and the overlap populations listed in Table V[12] are useful as qualitative indices of bond strength, and their values clearly reflect such features of the bonding as the bridge bond asymmetries in 4-$NB_8H_{13}$. The trends in these two indices for bonds of the same type within a given molecule parallel each other quite closely.

In Table VI[12] we list the localized molecular orbitals (LMO's) obtained by the criterion of Boys.[16] The LMO structures of 4-$NB_8H_{13}$, $B_9H_{12}NH^-$, and 10-N-7,8-$C_2B_8H_{11}$ are unique and have the $C_s$ symmetry of these molecules. The LMO's of 1,12-$NCB_{10}H_{11}$ also have $C_s$ symmetry, giving a total of five symmetry-related maxima on the LMO hypersurface, as this molecule has $C_{5v}$ symmetry. While the localizations for the nido structures always converged in less than 20 iterations, it took 65 iterations for the localization of 1,12-$NCB_{10}H_{11}$ to converge. Each LMO structure was shown by the second-derivative test[17] to be a maximum, not a saddle point on the LMO hypersurface.

The LMO's listed in Table VI are depicted in Figure 1. Some striking results are the tendency of N to form two-center bonds whenever possible, the substantial polarity of all the LMO's involving N, the manifestation of the bridge-bond asymmetries in 4-$NB_8H_{13}$ in the form of fractional BHB LMO's,[18] and the similarities of the LMO's of 4-$NB_8H_{13}$ to the 6330 valence structure of iso-$B_9H_{15}$[19] and of the LMO's of $B_9H_{12}NH^-$ and 10-N-7,8-$C_2B_8H_{11}$ to the LMO's of $B_{10}H_{14}^{2-}$[8c] and $B_{11}H_{13}^{2-}$,[8c] respectively. The LMO structure of 1,12-$NCB_{10}H_{11}$ very closely resembles the LMO structures of 1,12-$C_2B_{10}H_{12}$[20] and of $B_{12}H_{12}^{2-}$.[20]

Table VI[12] also lists the percent s characters at the major contributing centers for each LMO, whenever available. The hybridization ($sp^h$) at a given atom is related to the percent s character by $h = (100 - \%\ s)/\%\ s$.

It seems surprising that the number of known azaboranes with nitrogen occupying a framework position is so small, in view of the results reported here and of the fact that many other equally reasonable structures can be conceived. We hope that our study will encourage further work in this field.

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**Registry No.** 4-$NB_8H_{13}$, 58920-21-1; $B_9H_{12}NH^-$, 66272-83-1; 10-N-7,8-$C_2B_8H_{11}$, 54452-77-6; 1,12-$NCB_{10}H_{11}$, 73622-40-9.

**Supplementary Material Available:** Table IV (atomic charges, valencies, and inner-shell eigenvalues), Table V (unique bonds), and Table VI (Boys localized molecular orbitals) (9 pages). Ordering information is given on any current masthead page.

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(12) Supplementary material.

(13) Armstrong, D. R.; Perkins, P. G.; Stewart, J. P. *J. Chem. Soc., Dalton Trans.* **1973**, 838.

(14) See ref 8c for linear regression analyses of the inner-shell eigenvalue–atomic charge correlations in several open boron hydrides and carboranes.

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(17) Switkes, E.; Lipscomb, W. N.; Newton, M. D. *J. Am. Chem. Soc.* **1970**, *92*, 3847.

(18) The concept of fractional bonding has been extended to BHB bridge bonds by J. Bicerano, I. M. Pepperberg and W. N. Lipscomb (to be submitted for publication).

(19) (a) Lipscomb, W. N. "Boron Hydrides"; W. A. Benjamin: New York, 1963; p 60. (b) Moody, D. C.; Schaeffer, R. *Inorg. Chem.* **1976**, *15*, 233.

(20) Dixon, D. A.; Kleier, D. A.; Halgren, T. A.; Hall, J. H., Jr.; Lipscomb, W. N. *J. Am. Chem. Soc.* **1977**, *99*, 6226; Figure 9d,e. (Note that the polyhedra are oriented and numbered in a different way in this reference.)