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An *ab Initio* Molecular Orbital Study of Iminoborane

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The ground-state electronic and geometric structure of the as yet unisolated molecule iminoborane, HBNH, has been investigated by *ab initio* SCF–LCAO–MO calculations. The molecule is predicted to be linear with a boron–nitrogen bond distance of 1.23 Å and with a dipole moment of 0.86 D. Analysis of the calculated energy and of the localized and delocalized wave functions indicates that the boron–nitrogen bonds, while polar in the sense B^+N^-, are of comparable strength to those in the isoelectronic hydrocarbon acetylene and that the linkage is best represented as a truly triple bond.

Introduction

Boron–nitrogen compounds have attracted considerable experimental[1] and theoretical[2–6] interest, since the hydrides of this system are comparable in many ways to their isoelectronic hydrocarbon analogs. Although most investigations reported to date have been concerned with analogs of the carbon–carbon double-bond and single-bond systems, a few derivatives of the triple-bond analog iminoborane, HBNH, have been isolated.[7] The iminoboranes form a fascinating series of compounds from the theoretical point of view, since one cannot really deduce from qualitative considerations which of the three valence-bond structures—the "ionic" single-bond representation **1**, the double-bond representation **2**, or the triple-bond representation **3**—best represents the boron–nitrogen bond. The iminoboranes are also interesting in that dimerization of HBNH leads to the BN analog of the antiaromatic cyclobutadiene, whereas trimerization yields the analog of the aromatic hydrocarbon benzene.

$$\underset{\mathbf{1}}{H—\overset{+}{B}—\overset{-}{N}—H} \qquad \underset{\mathbf{2}}{H—B{=}N—H} \qquad \underset{\mathbf{3}}{H—\overset{-}{B}{\equiv}\overset{+}{N}—H}$$

For these reasons we have undertaken a series of *ab initio* molecular orbital calculations to study the bonding, energetics, and equilibrium geometry of "inorganic acetylene," HBNH.

Details of Calculations

All wave functions have been determined by the closed-shell SCF–LCAO–MO method of Roothaan.[8] A minimal basis set of Slater-type atomic orbitals, STO's—1s on H; 1s, 2s, and 2p on B and N—was used to expand the molecular orbitals. All the integrals required were evaluated by simulating each AO by a least-squares linear combination of three Gaussian-type orbitals (GTO's) according to the STO-3G expansions of Pople and coworkers.[9] The energy and dipole moment integrals over GTO's were calculated using subroutines from the POLYATOM system.[10] The STO exponents used for the σ orbitals (Table I) were those found optimum for the BH_3 and NH_3 molecules,[9,11] whereas those for the π orbitals were optimized by a "brute force" method (*vide infra*). A set of localized molecular orbitals was generated from the final wave function by the method suggested by Pople and Lennard-Jones[12] and implemented by Edmiston and Ruedenberg.[13] That is, unitary transformations were carried out to maximize the sum D of the MO self-repulsion energies of all the seven doubly occupied orbitals ψ_i

Table I
Atomic Orbital Numbering and Exponents

			Orbital exponent	
STO no.	Atom and orbital type		Isotropic basis set	Anisotropic basis set[a]
1	$H_{(B)}$	1s	1.14	1.14
2	B	1s	4.68	4.68
3	B	2s	1.45	1.45
4	B	$2p_\pi$	1.45	1.29
5	B	$2p_{\pi'}$	1.45	1.29
6	B	$2p_\sigma$	1.45	1.45
7	N	1s	6.67	6.67
8	N	2s	1.95	1.95
9	N	$2p_\pi$	1.95	1.90
10	N	$2p_{\pi'}$	1.95	1.90
11	N	$2p_\sigma$	1.95	1.95
12	$H_{(N)}$	1s	1.21	1.21

[a] Partially optimized with respect to AO's no. 4, 5, 9, and 10. See text for details.

$$D = \sum_{i=1}^{7}(ii|ii)$$

where

$$(ii|ii) = \iint \psi_i(1)\psi_i(1)\left[\frac{e^2}{r_{12}}\right]\psi_i(2)\psi_i(2)\mathrm{d}\tau(1)\mathrm{d}\tau(2)$$

These calculations were executed using a program written in this laboratory and based upon considering successive sequences of pair transformations.[13,14]

Results and Discussion

Although the boron–nitrogen linkage in iminoborane is formally a triple bond, this system differs from acetylene in that all three bonds should be polar in the direction $B^{\delta+}N^{\delta-}$ rather than completely covalent. In the limit of 100% ionic character for the two π bonds, the effective valence-state electron configuration about boron becomes $(sp_\sigma)_a{}^1(sp_\sigma)_b{}^1p_\pi{}^0p_{\pi'}{}^0$ in the linear struc-

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[1] See for example the articles in *Advan. Chem. Ser.*, **No. 42** (1967).

[2] R. Hoffmann, *J. Chem. Phys.*, **40**, 2474 (1964).

[3] N. C. Baird and M. A. Whitehead, *Can. J. Chem.*, **45**, 2059 (1967).

[4] D. R. Armstrong, B. J. Duke, and P. G. Perkins, *J. Chem. Soc. A*, 2566 (1969).

[5] S. D. Peyerimhoff and R. J. Buenker, *J. Chem. Phys.*, **49**, 312 (1968).

[6] S. D. Peyerimhoff and R. J. Buenker, *Theor. Chim. Acta*, **19**, 1 (1970).

[7] P. Paetzold, *Angew. Chem., Int. Ed. Engl.*, **6**, 572 (1967).

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

[9] W. J. Hehre, R. F. Stewart, and J. A. Pople, *J. Chem. Phys.*, **51**, 2657 (1969).

[10] Available from the Quantum Chemistry Program Exchange, Indiana University, Bloomington, Ind., as QCPE 47A.

[11] E. Switkes, R. M. Stevens, and W. N. Lipscomb, *J. Chem. Phys.*, **51**, 5229 (1969).

[12] J. E. Lennard-Jones and J. A. Pople, *Proc. Roy. Soc., Ser. A*, **201**, 190 (1951).

[13] C. Edmiston and K. Ruedenberg, *Rev. Mod. Phys.*, **35**, 457 (1963).

[14] See also E. Switkes and W. N. Lipscomb, *J. Chem. Phys.*, **53**, 2645 (1970).

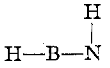
TABLE II

MOLECULAR ORBITALS AND ENERGIES (AU) FOR HBNH[a]

	AO												Orbital
MO	1	2	3	4	5	6	7	8	9	10	11	12	energies
1σ	−0.0011	0.0002	−0.0089	0.0	0.0	−0.0083	0.9935	0.0332	0.0	0.0	−0.0032	−0.0058	−15.4023
2σ	−0.0062	0.9922	0.0304	0.0	0.0	−0.0008	−0.0010	−0.0035	0.0	0.0	−0.0034	0.0009	−7.4819
3σ	0.0367	−0.1120	0.1634	0.0	0.0	0.1437	−0.2311	0.7665	0.0	0.0	−0.0568	0.1736	−1.0888
4σ	−0.1194	0.1542	−0.2859	0.0	0.0	−0.1140	−0.0100	0.0434	0.0	0.0	0.6101	0.4078	−0.7102
5σ	0.5431	−0.1145	0.3300	0.0	0.0	−0.4044	0.0255	−0.0543	0.0	0.0	0.1677	0.1086	−0.5722
$1\pi_u$	0.0	0.0	0.0	0.4448	0.0	0.0	0.0	0.0	0.7650	0.0	0.0	0.0	−0.4037
$2\pi_u$	0.0	0.0	0.0	0.0	0.4448	0.0	0.0	0.0	0.0	0.7650	0.0	0.0	−0.4037
$1\pi_g$	0.0	0.0	0.0	0.9567	0.0	0.0	0.0	0.0	−0.7265	0.0	0.0	0.0	0.3068
$2\pi_g$	0.0	0.0	0.0	0.0	0.9567	0.0	0.0	0.0	0.0	−0.7265	0.0	0.0	0.3068

[a] Electronic energy −103.1009; nuclear energy 23.8145; total energy −79.2864; virial ratio 2.0142.

ture **1**. In such a situation, the optimum B–N–H bond angle may be close to 90° rather than 180°, since the latter would correspond to the more energetically favorable electron configuration $s^2p^2p^1p^1$ for nitrogen (representation **4**). A third possibility for the geometry of



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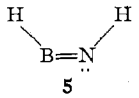
iminoborane results when one considers structures containing nonequivalent π bonds. The most stable of these should correspond to the cis-bent representation **5** in which both B and N are formally trivalent and



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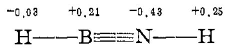
employ sp^2 hybrids to form two σ bonds each. In this "ethylenic" structure, both B and N have a singly occupied p_π AO from which the first π bond is formed, and a second, weaker pseudo π bond occurs by dative bonding from the sp^2 lone pair on N to the vacant sp^2 orbital on B.

The relative energies of the three idealized structures **3**–**5** were explored by *ab initio* calculations in which the bond distances (BH = 1.19, NH = 1.01, and BN = 1.30 Å) were held constant and an isotropic basis set (Table I) employed. The H–B–N and B–N–H bond angles used for **3**, **4**, and **5** were 180, 180; 180, 90; and 120, 120°, respectively. The linear geometry **3** is predicted by the calculations to be 24 kcal mol^{-1} more stable than the geometry **4** and 56 kcal mol^{-1} more stable than geometry **5**.

Since the results quoted above suggest that iminoborane does possess relatively strong π bonds, a more detailed set of calculations was carried out for the linear structure. In particular, the boron–nitrogen bond distance and both the B $2p_\pi$ and the N $2p_\pi$ orbital exponents were optimized simultaneously by a brute-force variation procedure. In agreement with previous calculations[11] for acetylene, HCN, and formaldehyde, the optimum effective nuclear charges for the $2p_\pi$ orbitals are found to be relatively low (anisotropic basis set, Table I) in comparison with those for the valence-shell σ orbitals. The predicted boron–nitrogen bond distance of 1.23 Å is quite short as expected for a triple bond but slighty longer than that of 1.21 Å in acetylene itself.[15] Thus iminoborane follows the trend established for the other B–N analogs of hydrocarbons, since the predicted distance[4] in BH_2NH_2 of 1.355 Å is longer than the C=C distance in ethylene (1.33–1.34 Å) and the distance in BH_3NH_3 (observed[15] 1.56 Å, predicted[5] 1.74 Å) is longer than that for a C–C single bond (~1.534 Å).[15]

The wave functions and energies for the linear iminoborane molecule at its equilibrium B–N separation of 2.3244 au (1.23 Å) are listed in Table II. The total bonding energy is calculated to be 0.3448 au (~216 kcal mole^{-1}) by subtracting the STO–3G atom energies[9] for B, N, and two H atoms from the calculated binding energy of −79.2864 au. In comparison, the bonding energy for acetylene is ~265 kcal mol^{-1} using the STO–3G method.[16] The energies associated with the B≡N and C≡C bonds can be estimated by subtracting from the bonding energy of HBNH one-third of the atomization energy of BH_3 plus one-third the atomization energy of NH_3 and by subtracting from the bonding energy of HCCH half of the bonding energy of CH_4, all calculated at the same STO–3G level of approximation.[17] The B≡N energy of 88 kcal mol^{-1} found by this procedure is only slightly lower than that of 94 kcal mol^{-1} for C≡C, again indicating that the bond strengths are comparable in these systems. Note that all bonding energies are much lower than experimental values, since no electron correlation effects have been allowed for in these single determinant SCF calculations.

The Mulliken population analysis[18] (Table III) for the iminoborane molecule predicts, as expected, that the nitrogen atom becomes negatively charged at the expense of the two atoms bonded to it; the excess atomic charges are



$$\overset{-0.03}{H}—\overset{+0.21}{B}\equiv\overset{-0.43}{N}—\overset{+0.25}{H}$$

TABLE III

MULLIKEN POPULATION ANALYSIS

Orbital	Gross population	Orbital	Gross population
$H_B(1s)$	1.0312	N(1s)	1.9954
B(1s)	1.9935	N(2s)	1.4716
B(2s)	0.7877	$N(2p_\pi)$	1.3875
$B(2p_\pi)$	0.6125	$N(2p_{\pi'})$	1.3875
$B(2p_{\pi'})$	0.6125	$N(2p_\sigma)$	1.1910
$B(2p_\sigma)$	0.7814	$H_N(1s)$	0.7477
Atom	**Gross population**	**Atom**	**Gross population**
H_B	1.0312	N	7.4330
B	4.7876	H_N	0.7477

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(15) L. E. Sutton, Ed., *Chem. Soc., Spec. Publ.*, **No. 11** (1958); **No. 18** (1965).

(16) Calculated using the energy for C_2H_2 determined by Pople and coworkers[9] and their atom energies for C and H.

(17) The energy for BH_3 was determined by an independent STO–3G calculation in this laboratory using the optimum STO exponents in ref 11. The NH_3 and CH_4 values were taken from ref 9.

(18) R. S. Mulliken, *J. Chem. Phys.*, **23**, 1833 (1955).

If one considers the valence-state electron configuration prior to bonding of boron to be $s^1p_\sigma{}^1p_\pi{}^1p_{\pi'}$, the gross orbital populations indicate that B has *gained* 0.225 electron in the π networks but has lost a total of 0.431 electron from the σ orbitals, almost all of the latter going to nitrogen. Thus iminoborane is analogous to aminoborane in that the σ bond is polar in the direction B^+-N^- but the π bonds effectively donate electron density to the boron atom. The charge transfers from B to N and from H_N to N are of approximately the same magnitudes but of opposite vector directions, with the result that the net dipole moment predicted for HBNH is only 0.86 D; this value is much less than that of 2.07 D predicted for aminoborane.[4]

The nature of the bonding in the HBNH species is most easily analyzed using the localized molecular orbitals (Table IV). The MO's labeled i(N) and i(B) clearly correspond almost exactly to the 1s inner-shell AO's of N and B, respectively. The remaining five bonding MO's are sufficiently localized to be characterized as two-center B–N, N–H, and B–H σ bonds (labeled b(B–N)σ, b(N–H)σ, and b(B–H)σ, respectively) and two equivalent π bonds labeled b(B–N)π and b(B–N)π', respectively (Table IV). The hybridization of the AO's and ionic character of each bond can be derived by truncating the small off-center contributions in each LMO and renormalizing the remaining molecular orbital. Thus the hybrid character of the σ-bonding orbitals of boron can be classified as $s^{1.4}p$ and $sp^{1.5}$ for the B–H and B–N bonds, respectively, in agreement with the prediction by Bent[19] that a higher degree of s character is used in the bond with the less electronegative atom. The hybrid character of the orbitals used by nitrogen to form σ bonds to B and H correspond to sp and $s^{2.3}p$, respectively.

TABLE IV
LOCALIZED MOLECULAR ORBITALS

LMO	AO 1	2	3	4	5	6	7	8	9	10	11	12
i(N)	0.0045	0.0056	−0.0225	0.0	0.0	−0.0329	1.0147	−0.0622	0.0	0.0	0.0053	−0.0261
i(B)	0.0578	−1.0068	0.0150	0.0	0.0	−0.0221	−0.0107	0.0446	0.0	0.0	−0.0007	0.0090
b(B-N)σ	0.0270	0.1173	−0.2268	0.0	0.0	−0.2748	0.0684	−0.4956	0.0	0.0	0.5058	0.1967
b(N-H)σ	−0.0193	−0.0448	0.0256	0.0	0.0	0.0249	0.0828	−0.5847	0.0	0.0	−0.3843	−0.4108
b(B-H)σ	0.5534	−0.0665	0.4069	0.0	0.0	−0.3458	0.0024	−0.0123	0.0	0.0	−0.0092	0.0052
b(B-N)π	0.0	0.0	0.0	0.0	0.4448	0.0	0.0	0.0	0.0	0.7650	0.0	0.0
b(B-N)π'	0.0	0.0	0.0	0.4448	0.0	0.0	0.0	0.0	0.7650	0.0	0.0	0.0

The gross populations for the $2p_\pi$ orbitals are identical in the localized and delocalized MO analysis, with an ionic character *i* of 39% in the direction $B^{\delta+}N^{\delta-}$ predicted for each π bond. The fact that these bonds are substantially polar does not imply that their π bonding character is weak, however. If the bonding strength of such bonds is taken to be proportional to the coefficient product C_BC_N, then one can define the effective covalent bond strength π as

$$\pi = C_BC_N/(C_BC_N)_{\max}$$

where $(C_BC_N)_{\max} = 0.5/1 + S$ where S is the overlap integral between the AO's. A plot of *i vs.* π for the case $S = 0.35$ is shown in Figure 1; this curve is not much different from that for $S = 0$ for which it can be shown that $\pi = (1 - i^2)^{1/2}$. *Thus a strong bond can result even if the ionic character is substantial.* For the π bonds in iminoborane, the ionic character of 39% only reduces the bond strength from 100 to 89%. This view of strong π character in HBNH is substantiated by a second measure of bond strength—the energy difference between the real molecule and systems in which the $2p_\pi$ AO's of boron are eliminated from the basis set. A recalculation of the energy for iminoborane, using the same orbital exponents and bond distances, with only one boron π AO, yields a structure which is 85 kcal mol^{-1} less stable than that for the triple-bond wave function.

The *ab initio* calculations presented herein indicate that while the bonds in iminoborane are substantially polarized in the expected directions, the system is sufficiently similar to acetylene in terms of the B–N bond distance, B–N bond strength, and B–N π-bond character that the boron–nitrogen bond should be considered as a triple bond. Thus the experimental difficulties in detecting and synthesizing the parent molecule are due to its chemical rather than physical instability (the activation energy required for trimerization evidently being small). It should be noted that even the trimer (benzene) of the analogous hydrocarbon is much more stable (by ~143 kcal mol^{-1} according to $\Delta H_f{}^\circ$ values) than the monomer (acetylene), so the existence of the latter is no doubt due to a high activation energy required for the 2 + 2 + 2 cycloaddition. The chemical stability of the *B*-phenyl-*N*-phenyl derivatives of iminoborane may well be due to steric hindrance in the polymerization process.

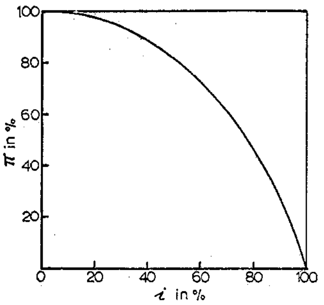

Figure 1.—Ionic character *vs.* covalent bond strength for two-center bonds.

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(19) H. A. Bent, *Chem. Rev.*, **61**, 275 (1961).