

The Molecular Structure of Methylenimino Borane, $\text{H}_2\text{C}=\text{N}-\text{BH}_2$, Studied by *ab initio* Calculations

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Geometry optimizations of the title compound have shown that a linear orthogonal form is preferred over a planar one by about 50 kJ mol^{-1} (12 kcal mol^{-1}). The result is in contrast to the planar structure preferred for the iso-electronic $\text{H}_2\text{B}-\text{O}-\text{BH}_2$. The important geometrical parameters of the two forms of $\text{H}_2\text{C}=\text{N}-\text{BH}_2$ are $\angle(\text{C}=\text{N}-\text{B})$ 180 and 116.4° , $r(\text{C}=\text{N})$ 1.228 and 1.255 \AA , and $r(\text{B}-\text{N})$ 1.374 and 1.476 \AA , respectively. The B-N bond length and results of the population analysis reflect the importance of dative π -bonding in the B-N bond for the preferred structure. It appears that the C=N and B-N bonds are shorter in methylenimino borane than in methylenimine and aminoborane, respectively.

The planar arrangement of the bonds to nitrogen in aminoboranes has been related to effects from dative π -bonding. Thus, when the first monomeric iminoboranes were synthesized it was said that a structural consequence of such π -bonding for compounds with two-co-ordinate nitrogen ($\text{R}_2\text{C}=\text{NBR}'_2$) would be a linear configuration at nitrogen since in a perpendicular form this would maximize the π -bonding.^{1,2} This was supported by results from infrared spectroscopic studies^{1,2} and later corroborated by infrared data for several monomeric iminoboranes, as summarized elsewhere,³ and by results of NMR spectroscopic investigations⁴⁻⁸ and semi-empirical molecular orbital calculations.⁸⁻¹⁰ Although dipole measurements are said to give

results that demonstrate the lack of $\text{N}=\text{B}$ π -bonding,^{11,12} it seems that the evidence in favour of the linear structure is substantial and it has been shown by X-ray crystallography that the structure of $\text{R}_2\text{C}=\text{N}-\text{BR}'_2$ (R=mesityl and R'=phenyl) approximates very well to an allene-like configuration: $\angle(\text{C}=\text{N}-\text{B})=173(2)^\circ$ and the dihedral angle (θ) between the $\text{R}_2\text{C}=\text{N}$ and $\text{N}-\text{BR}'_2$ planes is 87° .¹⁰ The preliminary results of a gas-phase electron-diffraction study of $(\text{CF}_3)_2\text{C}=\text{N}-\text{B}(\text{CH}_3)_2$ ¹³ initiated in connection with other studies of monomeric iminoboranes,⁶⁻⁸ suggest a similar structure for this molecule, but more elaborate testing of interdependencies between the conformational parameters and assumptions regarding the torsional orientations of the CF_3 -groups is needed to give more reliable structural data.

It has been speculated that also the derivatives of diboryloxide ($\text{H}_2\text{B}-\text{O}-\text{BH}_2$) would have allene-type structures, but electron-diffraction¹⁴ and spectroscopic^{15,16} studies showed that $[(\text{CH}_3)_2\text{B}]_2\text{O}$ has C_2 molecular symmetry in the gas phase. The molecule has $\angle(\text{B}-\text{O}-\text{B})=144(3)^\circ$ and $\phi(\text{B}-\text{O}-\text{B}-\text{C})=38(4)^\circ$ which corresponds to a dihedral angle between the two C_2B -planes of $72(7)^\circ$.¹⁴ Moreover, *ab initio* calculations for the parent molecule ($\text{H}_2\text{B}-\text{O}-\text{BH}_2$) have shown that the minimum-energy geometry corresponds to a bent ($\angle(\text{B}-\text{O}-\text{B})=127^\circ$) planar form of C_{2v} symmetry.¹⁷ Hence it was of interest to establish to which extent the iminoboranes are "true" allene analogues, *i.e.* whether the structures with angles approaching 180° at nitrogen and near perpendicular conformations in fact correspond

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to the preferred structure of the parent molecule. We have therefore studied $\text{H}_2\text{C}=\text{N}-\text{BH}_2$ by *ab initio* molecular orbital calculations, the results of which are presented in this paper. For comparison purposes we have supplemented previous *ab initio* studies of $\text{H}_2\text{C}=\text{NH}$ ¹⁸⁻²⁰ with new calculations whereas results of compatible calculations for other related molecules such as $\text{H}_2\text{B}-\text{NH}_2$, $(\text{H}_2\text{B})_2\text{NH}$ and $(\text{H}_2\text{B})_2\text{O}$ already exist.¹⁷

CALCULATION PROCEDURE AND RESULTS

The calculations were initially (A) carried out using the computer program MOLECULE²¹ which solves the Roothaan-Hall equations for a basis set of contracted Gaussian functions.

The minimum-energy geometries were determined from results of calculations for selected points on the energy surface assuming the energy to exhibit second order polynomial dependency upon the geometrical parameters. Subsequently, however, as MOLECULE was further developed so as to give a new *ab initio* gradient program MOLFORC²² which calculates the energy gradient with respect to the nuclear coordinates for a single-determinant SCF wave function and fully optimizes the molecular geometry by the force-relaxation method,²³ new calculations (B) were carried out using this computer program. Initially (A) a basis set similar in size to one earlier used for H_2BNH_2 ²⁴ was used, but in the course of the investigation a smaller basis set was found to reproduce rather well experimental molecular

Table 1. Minimum energy geometries, total energies (E_{tot}) and relative energies (ΔE) for methylenimino borane and methylenimine.^a

Type ^b	Geometrical parameters ^d	E_{tot}	ΔE
$\text{H}_2\text{C}=\text{N}-\text{BH}_2$			
A	Planar form ^c CN 1.250; BN 1.455; CNB 117.8; [CH1=CH2 1.08; NCH1=NCH2 122; BH3=BH4 1.20; NBH3=NBH4 120.] ^d	-119.31794	51.0 (12.2)
	Orthogonal (linear) form CN 1.224; BN 1.363; CNB 180 [CH1=CH2 1.08; NCH1=NCH2 122; BH3=BH4 1.20; BCH3=BCH4 120.] ^d	-119.33743	
B	Planar form CN 1.255; BN 1.476; CNB 116.4 CH1 1.086; CH2 1.090; NCH1 120.2; NCH2 124.4 BH3 1.195; BH4 1.185; NBH3 120.8; NBH4 119.1	-119.19591	46.9 (11.2)
	Orthogonal (linear) form CN 1.228; BN 1.374; CNB 180; CH1=CH2 1.086; NCH1=NCH2 121.8; BH3=BH4 1.185; NBH3=NBH4 119.3	-119.21374	
$\text{H}_2\text{C}=\text{NH}$			
B	Planar form CN 1.247 CH1 1.083; CH2 1.087; NCH1 119.5; NCH2 125.1 NH3 1.011; CNH3 110.5	-93.94904	

^a Distances in Å, angles in degrees, E_{tot} in a.u., and ΔE in kJ mol^{-1} with values in parentheses in kcal mol^{-1} .
^b See text for explanation. ^c See text for *bent* nonplanar forms of $\text{H}_2\text{C}=\text{N}-\text{BH}_2$. ^d The numbering of the atoms are given in Fig. 1. Quantities in square brackets are assumed values.

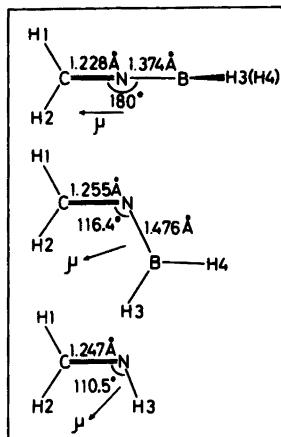


Fig. 1. Numbering of the atoms for methyleniminoborane and methylenimine. Important geometrical parameters and the directions of the dipole moments obtained in the *B*-type (see text) calculations.

geometries for H_2BNH_2 , $\text{HB}(\text{NH}_2)_2$, H_2BOH and $\text{HB}(\text{OH})_2$,¹⁷ and a similar basis set was used in the *B*-calculations. The basis sets were for the nitrogen and carbon, boron, and the hydrogen atoms, respectively: *A* ($9s, 5p, 1d$) \rightarrow $\langle 4, 3, 1 \rangle$, ($9s, 5p$) \rightarrow $\langle 4, 3 \rangle$, and ($4s, 1p$) \rightarrow $\langle 2, 1 \rangle$; and *B* ($7s, 3p, 1d$) \rightarrow $\langle 4, 2, 1 \rangle$, ($7s, 3p$) \rightarrow $\langle 4, 2 \rangle$ and ($4s$) \rightarrow $\langle 2 \rangle$. The ($9s, 5p$) and ($7s, 3p$) basis sets were those given by Huzinaga²⁵ and Roos and Siegbahn,²⁶ respectively, and the Huzinaga ($4s$) basis for the hydrogens²⁷ was scaled by a factor of 1.2.³⁰ The exponents of the polarization functions, $1d$ for carbon and nitrogen, and $1p$ for hydrogen, were 0.95 and 0.90, respectively.

The results of the geometry optimization are given in Table 1, whereas some results of the population analyses^{28,29} for the *B*-calculations and corresponding values for H_2BNH_2 and $\text{HN}(\text{BH}_2)_2$ obtained in compatible calculations¹⁷ are comprised in Table 2. The important geometrical parameters and the directions of the dipole moments defined as $q^- \rightarrow q^+$ are given in Fig. 1 which also shows the numbering of the atoms.

For $\text{H}_2\text{C}=\text{NH}$ only *B*-calculation on a planar form of the molecule was carried out whereas both types of calculations were performed for $\text{H}_2\text{C}=\text{N}-\text{BH}_2$.

A. $\text{H}_2\text{C}=\text{N}-\text{BH}_2$. Only $r(\text{C}=\text{N})$, $r(\text{B}-\text{N})$ and $\angle(\text{C}=\text{N}-\text{B})$ were optimized and the assumed

values used for the remainder of the geometrical parameters are given in square brackets in Table 1. Initially $r(\text{C}=\text{N})$ and $r(\text{B}-\text{N})$ were assumed to be 1.27 and 1.38 Å, respectively. For the planar form $\angle(\text{C}=\text{N}-\text{B})$ was determined to 118.8° and subsequent coupled variations of $r(\text{C}=\text{N})$ and $r(\text{B}-\text{N})$ and re-optimization of $\angle(\text{C}=\text{N}-\text{B})$ gave the minimum-energy quoted in Table 1. For the orthogonal form calculations for $\angle(\text{C}=\text{N}-\text{B})$ of 170, 175 and 180° showed that there was an energy minimum at the linear configuration and the $r(\text{C}=\text{N})$ and $r(\text{B}-\text{N})$ values obtained for $\angle(\text{C}=\text{N}-\text{B}) = 180^\circ$ are given in Table 1. The energy differences were not pronounced around the linear form as bending of the linear form by 10 and 5°, required only 5.8 and 0.01 kJ mol⁻¹ (1.4 and 0.003 kcal mol⁻¹), respectively.

B. $\text{H}_2\text{C}=\text{N}-\text{BH}_2$. The fully optimized structures of a planar and an orthogonal form are given in Table 1. The results given for the orthogonal form were obtained assuming a linear configuration. Subsequently, optimizations were carried out for a slightly bent, twisted form starting with $\angle(\text{C}=\text{N}-\text{B}) = 170^\circ$ and $\theta(\text{B}-\text{N}) = 80^\circ$ and this optimization converged to the linear orthogonal form. This confirms that the linear allene form is a minimum on the potential surface. In agreement with the *A*-calculations it was also shown that the potential surface is very flat around this minimum. For example, with $\angle(\text{C}=\text{N}-\text{B}) = 174^\circ$ and $\theta(\text{B}-\text{N}) = 86^\circ$ the total energy is only 0.13 kJ mol⁻¹ (0.03 kcal mol⁻¹) above that of the linear orthogonal structure.

DISCUSSION

The two forms of $\text{H}_2\text{C}=\text{N}-\text{BH}_2$ have quite different electron distributions: one has a B-N bond with a high degree of double bonding (see below) whereas the other has a lone pair of electrons localized on nitrogen. Thus the neglect of correlation effects, *i.e.* the use of the Hartree-Fock model, may have introduced errors not only in the total energies, but also in the energy differences. Double bonds are generally poorly described in the Hartree-Fock model giving rise to a highish $E(\text{corr})$ term which is inherently also expected for a lone pair of electrons. The resultant impact on ΔE is, however, difficult to assess, but the relatively high energy difference (Table 1) of about 50 kJ mol⁻¹ (12 kcal mol⁻¹)

Table 2. Dipole moments (μ in D), gross atomic populations (N), B–N and C=N bond distances (r in Å) and corresponding net overlap populations (n) for $\text{H}_2\text{C}=\text{N}-\text{BH}_2$ and $\text{H}_2\text{C}=\text{NH}$ compared to results for $\text{H}_2\text{B}-\text{NH}_2$ and $\text{H}_2\text{B}-\text{NH}-\text{BH}_2$ (Ref. 17) obtained with the B -type ($7s, 3p$) basis.^a

	$\text{H}_2\text{C}=\text{N}-\text{BH}_2$		$\text{H}_2\text{C}=\text{NH}$	$\text{H}_2\text{N}-\text{BH}_2$	$\text{H}_2\text{B}-\text{NH}-\text{BH}_2$
	Orthogonal ^b	Planar	Planar	Planar	Planar
$ \mu $ ^c	2.21	2.05	2.08	2.00	1.23
$N(\text{N})$	7.48	7.54	7.45	7.88	7.93
σ	4.77	6.46	6.36	6.18	6.35
π	1.10(z); 1.61(y)	1.08	1.09	1.70	1.58
$N(\text{B})$	4.65	4.53	—	4.64	4.60
σ	4.33	4.40	—	4.34	4.39
π	0.33(y)	0.13	—	0.30	0.21
$N(\text{C})$	6.17	6.18	6.24	—	—
σ	5.28	5.40	5.33	—	—
π	0.89(z)	0.78	0.91	—	—
$\overline{N(\text{H}_\text{C})}$	0.78	0.79	0.80	—	—
$\overline{N(\text{H}_\text{B})}$	1.06	1.08	—	1.07	1.06
$N(\text{H}_\text{N})$	—	—	0.71	0.67	0.65
$r(\text{B}-\text{N})$	1.374	1.476	—	1.398	1.435
$n(\text{B},\text{N})$	0.86	0.71	—	0.82	0.71
σ	0.54	0.60	—	0.52	0.50
π	0.32(y)	0.11	—	0.30	0.21
$r(\text{C}=\text{N})$	1.228	1.255	1.247	—	—
$n(\text{C},\text{N})$	1.13	1.13	1.17	—	—
σ	0.62	0.68	0.65	—	—
π	0.51(z)	0.45	0.52	—	—

^a Subscripts for H indicate the atoms to which the hydrogens are bonded. ^b π is considered to involve p_y for BH_2 and p_z for CH_2 , thus giving two π components for nitrogens, p_y interacting with BH_2 and p_z with CH_2 . ^c Experimental counterparts are $\mu_a=1.325$ and $\mu_b=1.53$ D,³⁴ 1.844(5) D,³⁰ and 1.245(17) D³⁵ for $\text{H}_2\text{C}=\text{NH}$, H_2NBH_2 and $\text{H}_2\text{B}-\text{NH}-\text{BH}_2$, respectively.

suggests that such effects cannot reverse the calculated conformational preference for the molecule. Hence it is concluded that an allene-type structure of $\text{H}_2\text{C}=\text{N}-\text{BH}_2$ is clearly favoured over a planar form. This is in contrast to the results for the isoelectronic $\text{H}_2\text{B}-\text{O}-\text{BH}_2$ which has a planar minimum energy geometry in which one lone pair of electrons remains uninvolved in bonding and the other is shared equally between the two BH_2 groups.¹⁷

Larger basis sets are known to yield the shorter bond distances, and this accounts for the differences in bond lengths obtained in the two sets of calculations (Table 1). For $r(\text{B}-\text{N})$ in the planar form the discrepancy is of the magnitude encountered for $\text{H}_2\text{B}-\text{NH}_2$ in which $r(\text{B}-\text{N})$ is 1.378 and 1.398 Å for A -²⁴ and B -type¹⁷ calculations, respectively. The difference in $r(\text{B}-\text{N})$ is less for the orthogonal form and it is marginal for $r(\text{C}=\text{N})$. The calculated structure with B -basis

for $\text{H}_2\text{B}-\text{NH}_2$ ¹⁷ is in good agreement with the experimental one which has $r_s(\text{B}-\text{N})=1.391(2)$ Å.³⁰ However, the calculated $r(\text{C}=\text{N})$ of 1.247 Å in $\text{H}_2\text{C}=\text{NH}$ is shorter than the experimental counterpart³¹ by 0.026 Å. Consequently, the C=N bond length of 1.228 Å in $\text{H}_2\text{C}=\text{N}-\text{BH}_2$ is probably calculated too short. However, 1.374 Å should give a relatively good estimate of $r(\text{B}-\text{N})$ in the iminoborane, and it appears consistent with the somewhat unprecisely determined experimental values of 1.38(2) and 1.35(2) Å in $\text{R}_2\text{C}=\text{N}-\text{BR}'_2$ with R/R' equal to mesityl/phenyl¹²⁰ and CF_3/CH_3 ,¹³ respectively. The short B–N bond shows that it has strong π -bonding, and this is supported by results from the population analysis (Table 2). Corresponding quantities for the planar form reflect the slight possibility for the C=N bond to donate π -electrons to the BH_2 -group. It appears that the C=N and B–N bonds in methyleniminoborane

are shorter than the corresponding bonds in H₂C=NH and H₂BNH₂. This trend may be rationalized by the hybridization changes of nitrogen as related to the bonding in ethylene and allene which have $r(\text{C}=\text{C})$ values of 1.335(3)³² and 1.312 Å,³³ respectively.

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