

Gas-Phase Ion Chemistry of Borazine, an Inorganic Analogue of Benzene

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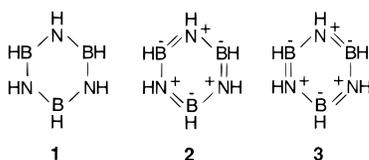
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Abstract: The gas-phase reactivity of selected ionic species with borazine and of borazine-derived ions with selected neutrals has been studied by FT-ICR and ab initio computations and related to the corresponding ion chemistry of benzene. The most basic site of borazine is at nitrogen, and its conjugate acid, $\text{H}_3\text{B}_3\text{N}_3\text{H}_4^+$, is similar in structure to the benzenium ion, as shown by ab initio calculations. $\text{H}_3\text{B}_3\text{N}_3\text{H}_4^+$ ions undergo H/D exchange of up to four hydrogens with CD_3OD and do not isomerize by stepwise 1,2-hydrogen shifts. Protonation at boron is calculated to be unfavored by 28 kcal/mol with respect to protonation at nitrogen. The $\text{H}_4\text{B}_3\text{N}_3\text{H}_3^+$ ions show the features of a $[\text{B}_3\text{N}_3\text{H}_5 \cdots \text{H}_2]^+$ complex, prone to dissociation at room temperature. The experimental gas-phase basicity of borazine is equal to 185.0 ± 1 kcal/mol. The Lewis basicity toward Me_3Si^+ places borazine into a linear correlation pertaining to model aromatic compounds. The experimental gas-phase acidity is 365.4 ± 1.5 kcal/mol. The reactions of neutral borazine with protonating, alkylating, and nitrating ions have been characterized and compared with the corresponding reactions of benzene. $\text{B}_3\text{N}_3\text{H}_5^+$ ions, retaining a cyclic structure, react similarly, in some respects, as phenylium ions, C_6H_5^+ .

Introduction

Borazine¹ is a B/N six-membered ring compound that is conceptually obtained from benzene by replacing each carbon by alternating boron and nitrogen atoms, the two neighbor elements in the second period. It follows that borazine is isoelectronic with benzene. The valence bond description of borazine comprises a saturated structure (**1**) besides two Kekulé-like structures (**2**, **3**) admitting interaction among the $2p\pi$ orbitals of adjacent B and N atoms.²



The remarkable similarity in physical properties and structure suggested borazine to be termed as the "inorganic benzene" and prompted studies aimed to ascertain the aromaticity of this heterocyclic π -electron system and to investigate its chemistry and properties. The molecular structure of gaseous borazine has been studied by electron diffraction. However, a decision between a D_{3h} structure, with large amplitude vibrations perpendicular to the ring plane, and a nonplanar C_2 model was

not possible.³ More recently, an X-ray single-crystal structure determination revealed C_2 symmetry with small deviations from the expected D_{3h} symmetry.⁴ Theoretical calculations performed by both semiempirical and ab initio methods on the isolated borazine molecule concur in assigning the molecule a planar structure with equal B–N bond lengths and a D_{3h} symmetry.^{1,5} The transmission of substituent effects through the borazine ring has been addressed by NMR studies, which indicated that the π electrons are partially delocalized.⁶ The mechanism of transmission has also been discussed in a theoretical study.⁷ The evaluation of the aromaticity of borazine has been approached by theoretical studies on energetics and magnetic properties. However, different criteria may give different answers.⁸ In the calculation of aromatic stabilization energy, the choice of the reference system is critical. The aromatic stabilization energy of borazine was found to range from about one-third to one-half of that for benzene.^{8,9} According to theoretical evaluations

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(1) Borazine is the common name for 1,3,5,2,4,6-triazatriborinine. For a note on the nomenclature of the azaborinines, see: Doerksen, R. J.; Thakkar, A. J. *J. Phys. Chem. A* **1998**, *102*, 4679.

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of magnetic properties, borazine is either moderately aromatic¹⁰ or not aromatic.⁹ An analysis of the measured electric and magnetic properties of borazine indicates that the electron delocalization is only about one-third of that in benzene.¹¹ A spin-coupled theory study of the electronic structure of borazine suggested that borazine has not any significant aromatic character.¹² In a discussion of geometric indices, borazine derivatives were found to exhibit less aromatic character than their benzene analogues.¹³ The spectral properties of borazine were the subject of a comprehensive experimental study which came to the conclusion that borazine has a planar D_{3h} structure and a delocalized π -electron system much like that of benzene.¹⁴

Chemically, however, borazine does not behave like benzene; for example, it undergoes addition reactions rather than electrophilic substitution.² Electrophilic substitution of borazine was in fact unprecedented until the first example of electrophilic substitution was recently found in the alkylation by gaseous species, such as Me_2F^+ , Me_2CH^+ , and Me_3C^+ ,¹⁵ obtained by γ -radiolysis of suitable precursors and allowed to react with borazine in a gaseous environment at atmospheric pressure. Neutral substitution products were obtained, showing that alkylation occurred at nitrogen. In continuation and completion of this study, the gas-phase ion-chemistry of borazine is now examined by FT-ICR mass spectrometry in the 10^{-8} mbar pressure range. The reactivity of borazine-derived ions with selected neutrals and of charged species with neutral borazine is reported and fundamental thermodynamic properties such as the gas-phase basicity and acidity are (re)examined. A major goal is to compare the gas-phase ion chemistry of borazine with that of benzene in the search for a link between the chemical behavior of borazine and that of the model aromatic system.

Since the original discovery by Stock in 1926,¹⁶ borazine has also gained increasing relevance for its application in the synthesis and design of new inorganic polymers and boron–nitrogen ceramics,¹⁷ which adds another facet to the interest for this molecule.

Experimental Section

Materials. Borazine was prepared from sodium borohydride and ammonium sulfate by a simple one-step procedure that has been recently described and was purified by trap-to-trap distillation.¹⁸ It was stored in the dark at low temperature. CH_4 , C_2H_6 , C_3H_8 , CF_4 , and $(\text{CH}_3)_2\text{O}$ were purchased from UCAR Specialty Gases. All other reagents were obtained from commercial sources and used as received.

Procedure. Ion–molecule reactions were investigated with a Bruker Spectrospin Apex TM 47e FT-ICR instrument, equipped with an external ion source and with a cylindrical “infinity” cell of 12 cm length and 6 cm radius situated in the bore of a 4.7 T superconducting magnet. In most experiments reagent ions were formed in the ion source in the CI configuration at $\sim 4 \times 10^{-5}$ mbar (1 mbar = 100 Pa). All ions formed were transferred into the ICR cell containing a known pressure, typically in the range of $1\text{--}4 \times 10^{-8}$ mbar, of the neutral reagent, introduced

by a needle valve from an inlet system at room temperature. The ion of interest was selected by broad band selection and quenched of excess internal and translational energy by collisions with Ar, admitted through a pulsed magnetic valve up to the peak pressure of 10^{-5} mbar. After a delay time of 0.5 s, further isolation from all other fragment or product ions was achieved by low-energy “single shots”. Mass spectra were recorded at increasing reaction time, and peak intensities were normalized to the sum of all ions detected at that reaction time. Pseudo-first-order rate constants were obtained from the slope of a logarithmic plot of reactant ion intensity and were divided by the number density of the neutral to obtain second-order rate constants. Neutral pressures were read from an ion gauge located in front of the high-vacuum turbo pump. The readings were corrected by individual response factors¹⁹ and calibrated with the reference reaction $\text{CH}_4^{++} + \text{CH}_4 \rightarrow \text{CH}_5^+ + \text{CH}_3^+$ using the value of $k = 1.1 \times 10^{-9}$ molecule⁻¹ cm³ s⁻¹ as its rate constant.²⁰ Reported values of second-order rate constants (k_{exp}) are the average of usually three experiments run at different neutral pressures. The normalized efficiency (in %) of the ion–molecule reaction is given by $k_{\text{exp}}/k_{\text{coll}}$. The collision rate constants (k_{coll}) were calculated using the parametrized trajectory theory.²¹ The product ratio from competitive reaction channels was evaluated from the ion intensities of the product ions extrapolated at initial time, to minimize interference by possible consecutive reactions. The cell and the inlet system were maintained at 25 °C, which is considered as the effective reaction temperature.

Computational Details. Density functional theory, using the B3LYP functional,²² has been used to localize the stationary points of the investigated systems and to evaluate the vibrational frequencies. The 0 K total energies of the species of interest were corrected to 298.15 K by adding translational, vibrational, and rotational contributions. The absolute entropies were calculated by using standard statistical-mechanistic procedures from scaled harmonic frequencies and moments of inertia relative to B3LYP/6-311++G(3df,3pd) optimized geometries. The 6-311++G(3df,3pd) basis set has been used.²³ The basicity of borazine has been evaluated also at coupled cluster level. Single-point energy calculations at the geometries optimized at B3LYP level with the same basis set were performed using the coupled cluster single and double excitation method²⁴ with a perturbational estimate of the triple excitations [CCSD(T)] approach.²⁵ Zero-point energy corrections evaluated at B3LYP level were added to the CCSD(T) energies. These calculations have been performed using Dunning’s correlation consistent basis set, augmented with diffuse functions, AUG-cc-pVDZ.²⁶ All calculations were performed using Gaussian 94.²⁷

Results

Reactivity of Borazine toward Gaseous Ions. The gas-phase reactions of borazine with exemplary ions are summarized in

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Table 1. Rate Constants (k_{exp}) and Efficiencies (Eff) of the Reactions of Selected Ions with Borazine

reagent ion	k_{exp}^a	Eff (%) ^b	product ion(s) (%)
CH ₅ ⁺	20	100	B ₃ N ₃ H ₅ ⁺ (75), B ₃ N ₃ H ₇ ⁺ (25)
C ₂ H ₅ ⁺	16	100	B ₃ N ₃ H ₅ ⁺ (60), B ₃ N ₃ H ₇ ⁺ (40)
<i>i</i> -C ₃ H ₇ ⁺	12	85	B ₃ N ₃ H ₇ ⁺ (100)
CF ₃ ⁺	8.9	73	B ₃ N ₃ H ₅ ⁺ (100)
(CH ₃) ₂ F ⁺	11	80	[B ₃ N ₃ H ₆ + CH ₃] ⁺ (100)
NO ₂ ⁺	12	92	[B ₃ N ₃ H ₆ + NO ₂] ⁺ (44), B ₃ N ₃ H ₇ ⁺ (56)
CH ₃ ONO ₂ H ⁺	9.0	77	[B ₃ N ₃ H ₆ + NO ₂] ⁺ (10), B ₃ N ₃ H ₇ ⁺ (90)
CH ₃ O(NO ₂) ₂ ⁺	3.9	38	[B ₃ N ₃ H ₆ + NO ₂] ⁺ (100)
D ₃ O ⁺	15	80	B ₃ N ₃ H ₆ D ⁺ (90), B ₃ N ₃ H ₅ OD ₂ ⁺ (10)
CD ₃ OD ₂ ⁺	11	70	B ₃ N ₃ H ₆ D ⁺ (90), [B ₃ N ₃ H ₅ O(CD ₃)D] ⁺ (10)
CD ₃ C ₆ D ₅ H ⁺	0.17	5	[B ₃ N ₃ H ₅ C ₇ D ₇ H] ⁺ (100)
F ⁻	14	75	B ₃ N ₃ H ₅ ⁻ (28), B ₃ N ₃ H ₄ F ⁻ (66), B ₃ N ₃ H ₆ F ⁻ (6)
CF ₃ ⁻	6.4	50	B ₃ N ₃ H ₅ ⁻ (100)
B ₃ N ₃ H ₅ ⁻	2.9	25	B ₆ N ₆ H ₁₁ ⁻ (100)

^a In units of 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. ^b The normalized efficiency, Eff = $k_{\text{exp}}/k_{\text{coll}}$, was calculated as described in the Experimental Section.

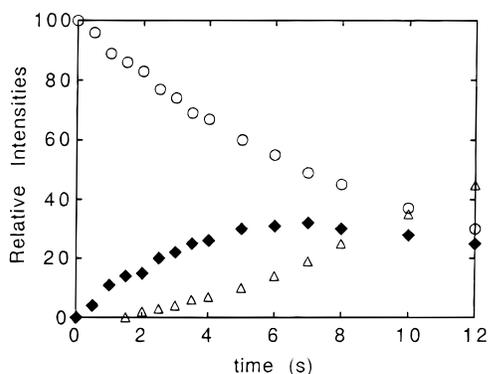
**Figure 1.** Time dependence of normalized ion intensities (◆) m/z 127; (△) m/z 82) observed after selection of CH₃O(NO₂)₂⁺ ions (○) m/z 123) in the presence of borazine at 1.3 × 10⁻⁸ mbar.

Table 1. Positive ions that are typically used as Brønsted acids in CI-MS include CH₅⁺, C₂H₅⁺, and *i*-C₃H₇⁺. Besides yielding protonated borazine the first two ions also give B₃N₃H₅⁺. This ion is also obtained from the CF₃⁺ reaction by a formal hydride transfer process. (CH₃)₂F⁺ gives a product ion corresponding to methylated borazine, the probable ionic intermediate of the *N*-methylation product obtained from the same ionic reagent under radiolytic conditions.¹⁵ The nitration of borazine was tried with several ionic reagents. Among them NO₂⁺ was found to be unreactive; protonated nitric acid and protonated methyl nitrate (H₂ONO₂⁺ and CH₃ONO₂H⁺) promoted both nitration and protonation, whereas nitrated methyl nitrate (CH₃O(NO₂)₂⁺) reacted exclusively by nitration. The [B₃N₃H₆ + NO₂]⁺ adduct reacts with neutral borazine by a subsequent H⁺ transfer step, giving B₃N₃H₇⁺, as shown by the ion intensity vs time plot in Figure 1. The competition between a D⁺ transfer and an addition–elimination pathway characterizes the reactions of D₃O⁺ and CD₃OD₂⁺, whereas protonated toluene (CD₃C₆D₅H⁺) yields exclusively the addition–elimination product. In all cases HD is lost as neutral fragment.

Negative ions such as F⁻ and CF₃⁻ react by an exclusive or major proton abstraction pathway, showing that borazine should be more acidic than HF (GA = 366 kcal/mol) and CF₃H (GA = 369 kcal/mol). Adduct ions are formed from the reaction of borazine with B₃N₃H₅⁻ and F⁻. In the latter case the addition reaction is followed by the elimination of H₂, probably driven

Table 2. Free Energy Change for the Reaction BH⁺ + B₃N₃H₆ → B₃N₃H₇⁺ + B

B	GB(B) ^a (kcal/mol)	ΔG ^o ₃₀₀ ^b (kcal/mol)
(CH ₃) ₂ O	182.7	-2.8
<i>i</i> -C ₃ H ₇ CN	184.7	-0.1
<i>i</i> -C ₄ H ₈	185.4	+1.1
(CH ₃) ₂ CO	186.9	+1.5

^a Reference 28. ^b ΔG^o₃₀₀ = -RT ln *K* was obtained from the equilibrium constant for the title reaction, $K = ([B_3N_3H_7^+][B])/([BH^+][B_3N_3H_6])$, where [B₃N₃H₇⁺]/[BH⁺] corresponds to the relative abundances of the two ions, B₃N₃H₇⁺ and BH⁺, measured when the proton transfer equilibrium is established in the FT-ICR cell and the ratio [B]/[B₃N₃H₆] is calculated from the partial pressures of the two neutrals, B and B₃N₃H₆. ΔG^o₃₀₀ is related to GB(B) by the equation ΔG^o₃₀₀ = GB(B) - GB(B₃N₃H₆).

Table 3. Free-Energy Change for the Reaction A⁻ + B₃N₃H₆ → B₃N₃H₅⁻ + AH

AH	GA(AH) ^a (kcal/mol)	ΔG ^o ₃₀₀ (kcal/mol)
C ₂ H ₂	369.8	-2.1
CH ₃ CN	365.2	-1.2
CH ₃ CO ₂ CH ₃	365.1	+0.1
CH ₃ CO ₂ C ₂ H ₅	~363.5 ^c	+1.3
(CH ₃) ₂ CO	361.9	≥2.0
CH ₃ CO ₂ H	341.5	≥2.5

^a GA(AH) corresponds to ΔG₃₀₀ for the process AH → H⁺ + A⁻. Data are from ref 28. ^b ΔG^o₃₀₀ = -RT ln *K* was obtained from the equilibrium constant for the title reaction, $K = ([A^-][B_3N_3H_6])/([B_3N_3H_5^-][AH])$, where [A⁻]/[B₃N₃H₅⁻] corresponds to the relative abundances of the two ions, A⁻ and B₃N₃H₅⁻, measured when the proton transfer equilibrium is established in the FT-ICR cell, and the ratio [B₃N₃H₆]/[AH] is calculated from the partial pressures of the two neutrals, B₃N₃H₆ and AH. ΔG^o₃₀₀ is related to GA(AH) by the equation ΔG^o₃₀₀ = GA(B₃N₃H₆) - GA(AH). Only upper limits are reported for AH = (CH₃)₂CO and CH₃CO₂H. With these reference acids the title reaction was too thermodynamically unfavored to yield a meaningful ratio of ion abundances. ^c Reference 31.

by the large exothermicity associated to the formation of a strong B–F bond (e.g., the F₃B–F⁻ bond energy amounts to ~80 kcal/mol).²⁸

Thermodynamic Acid–Base Properties of Borazine. The gas-phase basicity (GB) of borazine at 300 K has been determined by approaching the proton-transfer equilibrium between protonated borazine and a reference base of known GB. The equilibrium constants evaluated from the abundances of the protonated species and the concentrations of the neutrals were checked to be unaffected by changes in the relative concentration of borazine and reference base. The data collected in Table 2 lead to a GB value of 185.0 ± 1 kcal/mol, which is in excellent agreement with the 184.7 value reported in the NIST compilation.²⁸ This updated evaluation is derived from an experimental ICR determination, once the GB values of the reference bases used have been corrected to the new standards.²⁹

The Lewis basicity of borazine has been determined with respect to the Me₃Si⁺ ion, in the framework of a trimethylsilyl cation affinity (TMSA) scale that has been established for classes of compounds including amines, oxygenated organic compounds, and aromatic compounds.³⁰ A ΔG^o value of 0.06 ±

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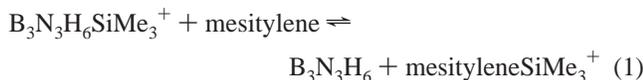
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Table 4. Rate Constants (k_{exp}) and Efficiencies (Eff) of the Reactions of [Borazine-H]⁺ and [Borazine+H]⁺ Ions with Selected Neutrals (N)

reagent ion	N	k_{exp}^a	Eff (%) ^b	product ion(s) (%)
B ₃ N ₃ H ₅ ⁺	H ₂ O	4.1	22	B ₂ N ₃ H ₆ ⁺ (100)
B ₃ N ₃ H ₅ ⁺	CH ₃ OH	3.0	19	B ₂ N ₃ H ₅ CH ₃ ⁺ (88), B ₃ N ₃ H ₅ OCH ₃ ⁺ (12)
B ₃ N ₃ H ₅ ⁺	CH ₃ F	1.5	10	B ₃ N ₃ H ₄ F ⁺ (100)
B ₃ N ₃ H ₅ ⁺	C ₂ H ₆	0.4	3	B ₃ N ₃ H ₇ ⁺ (100)
B ₃ N ₃ H ₇ ⁺	D ₂ O			
B ₃ N ₃ H ₇ ⁺	CD ₃ OD	0.56	4	B ₃ N ₃ H ₆ D ⁺ (60), B ₃ N ₃ H ₆ OCD ₃ ⁺ (40)
B ₃ N ₃ H ₆ D ⁺	<i>c</i> -C ₅ H ₁₀ NH	15	100	<i>c</i> -C ₅ H ₁₀ NHD ⁺ (48), <i>c</i> -C ₅ H ₁₀ NH ₂ ⁺ (52)
B ₃ N ₃ H ₇ ⁺	CD ₃ C ₆ D ₅	1.0	7	B ₃ N ₃ H ₆ C ₇ D ₇ ⁺ (100)

^a See footnote a, Table 1. ^b See footnote b, Table 1.

0.03 kcal/mol was obtained for the Me₃Si⁺ transfer equilibrium between borazine and mesitylene (eq 1) established in the FT-ICR cell at 300 K.



Under the assumption that the entropic contribution to ΔG° may be neglected, $-\Delta H^\circ$ for the association reaction $\text{Me}_3\text{Si}^+ + \text{B}_3\text{N}_3\text{H}_6 \rightarrow \text{B}_3\text{N}_3\text{H}_6\text{SiMe}_3^+$, namely the TMSA of borazine, is computed to be equal to 31.1 kcal/mol.

The gas-phase acidity (GA) of borazine has been determined by the usual equilibrium method, using the compounds listed in Table 3 as reference acids. The average of the ΔG° values obtained from the proton-transfer equilibria combined with the reported GA of the reference acids yields a GA value of 365.4 \pm 1.5 kcal/mol.

Reactivity of Borazine-Derived Ions. Ions formally corresponding to [Borazine-H]⁺ and [Borazine+H]⁺ can be obtained by any of the hydride abstraction or proton-transfer reactions listed in Table 1. These ions have been characterized by studying their reactivity with selected neutrals (Table 4). The reaction of B₃N₃H₅⁺ ions, formed by CH₄-CI in the external ion source, with XOH (X = H, CH₃) occurs by a major pathway leading to B₂N₃H₅X⁺ as ionic product and to BOH as (probable) neutral fragment. The reaction of B₃N₃H₅⁺ with CH₃F yields a product ion where a fluorine atom has formally replaced a former hydrogen atom, whereas B₃N₃H₅⁺ gains two hydrogen atoms from the reaction with ethane.

B₃N₃H₇⁺ ions, formed by C₃H₈-CI in the external ion source, have been allowed to react with D₂O and CD₃OD to examine possible H/D exchange processes. D₂O is unreactive but CD₃OD promotes deuterium incorporation into protonated borazine. A parallel reaction with CD₃OD gives an addition-elimination product ion, involving loss of HD. A similar process is observed when B₃N₃H₇⁺ reacts with perdeuterated toluene. Multiple deuterium incorporation has been promoted by prolonged reaction times allowed to B₃N₃H₆D⁺ ions formed by D⁺ transfer from CD₃OD₂⁺ to borazine in the presence of neutral CD₃OD. A sequence of consecutive steps of D-incorporation is observed, which ends with the formation of B₃N₃H₃D₄⁺ ions (Figure 2).

D⁺ transfer from D₃O⁺ to borazine in the ion source gave B₃N₃H₆D⁺ ions, which were assayed in the FT-ICR cell by their reaction with a strong base (piperidine, PA = 228 kcal/mol).²⁸ The branching ratio for the formation of *c*-C₅H₁₀NHD⁺ and *c*-C₅H₁₀NH₂⁺ is close to one, suggesting the presence of one hydrogen and one deuterium atom in equivalent positions in the reagent ion.

Computational Results. The optimized geometry of B₃N₃H₆, of *D*_{3h} symmetry, is reported in Figure 3 together with the experimental values.³ The calculated geometrical parameters are in good agreement with the experimental ones and are comparable with those previously evaluated at MP2/6-31G* level,^{5b}

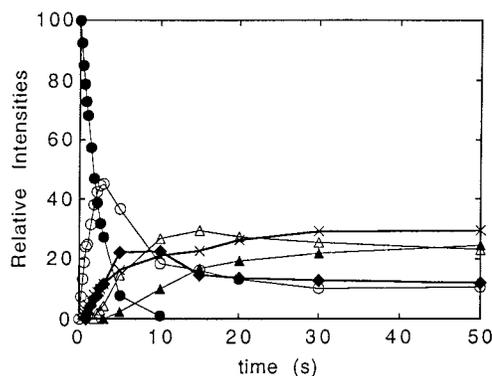


Figure 2. Time dependence of normalized ion intensities [(○) *m/z* 83; (◆) *m/z* 84; (△) *m/z* 85; (▲) *m/z* 86; (×) *m/z* 115] observed after selection of CD₃OD₂⁺ ions [(○) *m/z* 38] in the presence of CD₃OD at 6.0 \times 10⁻⁸ mbar and borazine at 1.0 \times 10⁻⁸ mbar.

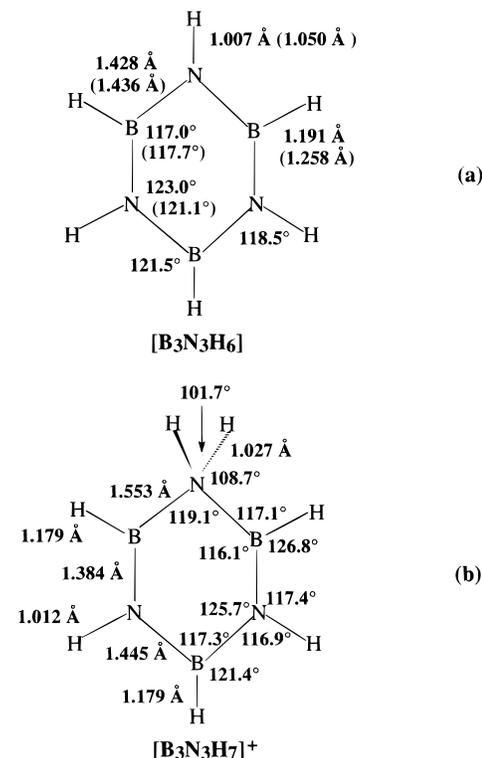


Figure 3. Optimized geometries of borazine (a) and protonated borazine (b). The experimental geometry of borazine is reported in parentheses. Bond lengths in Å, angles in degrees.

while a worse performance was shown by the computations at HF level.^{5d-f} The vibrational frequencies are in reasonable agreement with the experimental values and with those previously computed at MP2/6-31G* level.^{5b}

The preferred protonation site is the nitrogen atom and the optimized structure of [B₃N₃H₇]⁺ in *C*_{2v} symmetry is shown in

Table 5. Energetics of Some Processes Involving Borazine

	ΔE_0^a	$\Delta H_{298.15}^a$	$\Delta G_{298.15}^a$
$B_3N_3H_7^+ \rightarrow B_3N_3H_6 + H^+$	189.5 ^b 190.8 ^c	191.1 ^b 192.4 ^c	183.4 ^b 184.7 ^c 185.0 ^d 184.7 ^e
$[B_3N_3H_5 \cdots H_2]^+ \rightarrow B_3N_3H_6 + H^+$	159.1 ^b	163.8 ^b	156.4 ^b
$[B_3N_3H_5 \cdots H_2]^+ \rightarrow B_3N_3H_5^+ + H_2$	1.4 ^b	6.8 ^b	-1.7 ^b

^a Values are in kcal/mol. ^b B3LYP/6-311++G(3df,3pd)//B3LYP/6-311++G(3df,3pd) ^c CCSD(T)/AUG-cc-pVDZ//B3LYP/AUG-cc-pVDZ ^d Experimental value, this work. ^e Experimental value, ref 28.

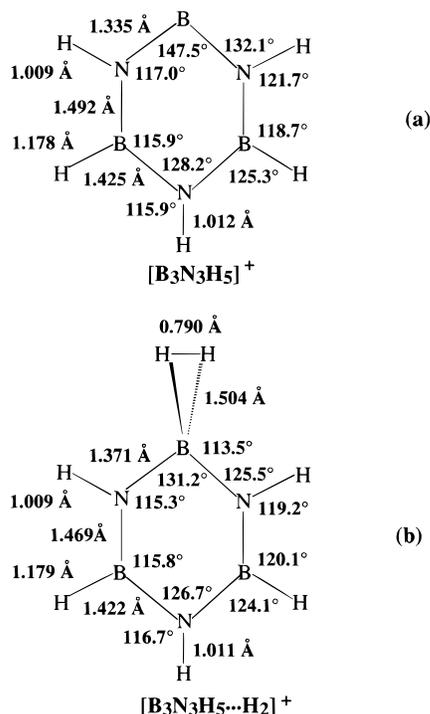
**Figure 4.** Optimized geometries of $[B_3N_3H_5]^+$ (a) and its adduct with H_2 (b). Bond lengths in Å, angles in degrees.

Figure 3. The gas-phase basicity of borazine at 298.15 K is computed to be equal to 183.4 kcal/mol at B3LYP/6-311++G(3df,3pd) level, as reported in Table 5. The protonation at boron gives an adduct $[B_3N_3H_5 \cdots H_2]^+$ which dissociates into $[B_3N_3H_5]^+$ and H_2 in an exoergic process at 298.15 K (Table 5). The optimized geometries of $[B_3N_3H_5 \cdots H_2]^+$ and $[B_3N_3H_5]^+$ are shown in Figure 4.

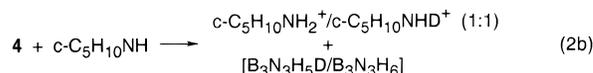
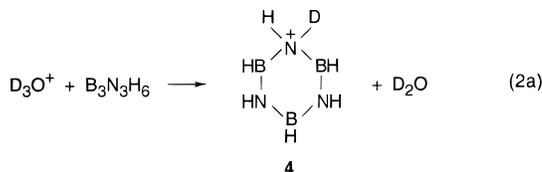
The GB of borazine has been evaluated also at the coupled-cluster level, using the less extended basis set AUG-cc-pVDZ, and is computed to be equal to 184.7 kcal/mol. Taking into account correlation effects and basis set incompleteness, the GB of borazine is estimated to amount to 185.3 ± 1 kcal/mol, at variance with the substantially lower GB that has been obtained by ab initio computations at 4-31G level.²⁹

Discussion

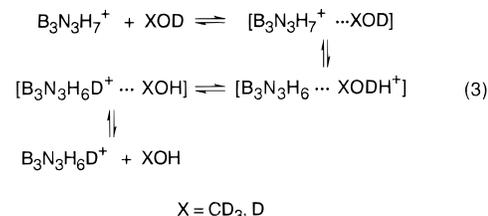
Protonation of Borazine. Structure and Reactivity of $[B_3N_3H_7]^+$ Ions. Ions corresponding to protonated borazine, $[B_3N_3H_7]^+$, that are stable with respect to dissociation, can be obtained from a variety of gaseous Brønsted acids, such as $i\text{-C}_3\text{H}_7^+$, C_4H_9^+ ,³² $(\text{CH}_3)_2\text{OH}^+$, $i\text{-C}_3\text{H}_7\text{CNH}^+$, $t\text{-C}_4\text{H}_9^+$, $(\text{CH}_3)_2\text{-}$

COH^+ . The GB of 185.0 kcal/mol for borazine, that has been determined by the equilibrium method, compares very well with a previous measurement by the same technique and agrees with a qualitative estimate based on the occurrence of proton transfer from $[B_3N_3H_7]^+$ to ammonia and failure to observe proton transfer to 2-butyne.^{32b} The agreement with the GB value obtained by two different computational approaches is excellent, when the $[B_3N_3H_7]^+$ ion is identified as nitrogen-protonated borazine.

The geometry of nitrogen-protonated borazine reveals little structural change with respect to neutral borazine with the exception of the geometry at the tetrahedral nitrogen. Therefore it closely resembles the geometry of the most favored protonated form of benzene,³³ so that nitrogen-protonated borazine may be viewed as an inorganic analogue of benzenium ion (C_6H_7^+). However, the similar structure is not paralleled by similar reactivity. Gaseous benzenium ions are known to undergo a relatively fast randomization process of the seven hydrogens at the rate of $\sim 10^9$ s⁻¹ at 310 K, by way of consecutive 1,2-hydrogen migration steps.³⁴ No evidence for such a process is found for protonated borazine. In fact, $B_3N_3H_6D^+$ ions, obtained by D^+ transfer from D_3O^+ (eq 2a) are found to transfer H^+/D^+ to a strong base in approximately 1:1 ratio (eq 2b). This result suggests that the primary labeled ion (4) does not undergo any intramolecular hydrogen migration process.



The study of H/D exchange reactions performed on $B_3N_3H_7^+$ ions led to the same conclusion. The H/D exchange mechanism involves consecutive H^+/D^+ transfer processes (such as the one shown in eq 3) within ion-neutral complexes formed with a suitable reagent, namely a molecule of close GB containing a deuterium atom at the protonation site.



D_2O is ineffective because of its much lower GB with respect to that of borazine, which makes proton transfer from $B_3N_3H_7^+$ ions within the complex too unfavorable on energetic grounds. CD_3OD is successful in carrying out a stepwise exchange process, which, however, does not proceed beyond the incor-

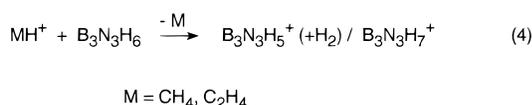
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poration of four D-atoms. This process is clearly displayed by the plot of ion abundances vs time of Figure 2, where the reaction of CD_3OD_2^+ ions with borazine yields $\text{B}_3\text{N}_3\text{H}_6\text{D}^+$ ions which undergo stepwise exchange reactions ending with the formation of $\text{B}_3\text{N}_3\text{H}_3\text{D}_4^+$ ions. It is clear that the sites involved in the protonation of borazine are only three, the N-atoms, as indicated both by the computational results and by the fact that electrophilic attack by alkylating ions is directed at nitrogen, yielding the corresponding substitution products. The protonation at boron is thermodynamically unfavored by 28 kcal/mol at B3LYP/6-311++G(3df,3pd) level of calculation (Table 5). Moreover the B-protonated species shows the features of a $[\text{B}_3\text{N}_3\text{H}_5\cdots\text{H}_2]^+$ adduct and is expected to evolve by the entropically favored dissociation of H_2 . Nevertheless, strong Brønsted acids, such as CH_5^+ ($\text{GB}(\text{CH}_4) = 124.4$ kcal/mol)²⁸ and C_2H_5^+ ($\text{GB}(\text{C}_2\text{H}_4) = 155.7$ kcal/mol),²⁸ are able to protonate also the B-atom, yielding $\text{B}_3\text{N}_3\text{H}_5^+$ ions in comparable amounts with respect to $\text{B}_3\text{N}_3\text{H}_7^+$ (eq 4).



The involvement of the B-atom in the formation of $\text{B}_3\text{N}_3\text{H}_5^+$ ions is further supported by previous CH_4 -CI and C_2H_6 -CI experiments using $\text{D}_3\text{B}_3\text{N}_3\text{H}_3$, showing that the hydrogen atom removed from borazine was originally bound to the B atom.^{32a}

Gas Phase Reactions of Borazine with Positively Charged Ions. The reactivity of selected cations with gaseous borazine has been examined. Most of them react with benzene, yielding the ionic intermediates of electrophilic substitution products (arenium ions).³⁵ The alkylation of borazine has indeed been observed from the reaction of carbenium ions ($i\text{-C}_3\text{H}_7^+$, $t\text{-C}_4\text{H}_9^+$) and a halonium ion ($(\text{CH}_3)_2\text{F}^+$) in radiolytic experiments at atmospheric pressure, which allowed us to obtain neutral N-substitution products.¹⁵ In the pressure range of 10^{-8} mbar in the FT-ICR cell, carbenium ions are known to react predominantly by proton transfer. $\text{B}_3\text{N}_3\text{H}_7^+$ is in fact the only ionic product from the reaction of $i\text{-C}_3\text{H}_7^+$ with borazine. However, a highly efficient methyl transfer process from $(\text{CH}_3)_2\text{F}^+$ yields $[\text{B}_3\text{N}_3\text{H}_6 + \text{CH}_3]^+$, the ionic intermediate of N-methylborazine obtained from the radiolytic reaction.¹⁵

Another example of typical electrophilic aromatic substitution is nitration. Gaseous NO_2^+ is unable to perform nitration, giving only charge and formal O^+ transfer products with benzene and being unreactive with borazine. "Solvated" forms of NO_2^+ , such as XNO_2^+ ($\text{X} = \text{H}_2\text{O}, \text{CH}_3\text{OH}, \text{CH}_3\text{ONO}_2$), are on the contrary well-behaved nitrating agents, yielding $[\text{B}_3\text{N}_3\text{H}_6 + \text{NO}_2]^+$ ions.³⁶ Whereas the nitration of benzene yields a nitrobenzenium ion that evolves by hydrogen migration to the nitro group,³⁶ by far the most basic site in nitrobenzene, more basic than benzene itself, the $[\text{B}_3\text{N}_3\text{H}_6 + \text{NO}_2]^+$ species is subsequently deprotonated by neutral borazine, as evidenced from the ion abundance vs time plot of Figure 1.

The reaction of Me_3Si^+ with simple aromatic compounds has been studied in detail, and the ionic adduct has been characterized as a σ -complex with a Si-C covalent bond. Moreover, the TMSA values for the association reaction to aromatic compounds and amines have been found to respond to linear correlations when plotted against the PA values of the neutrals.³⁰

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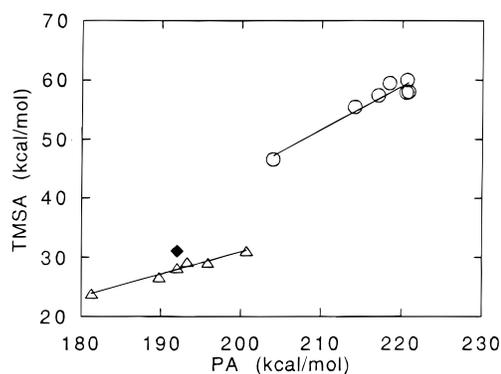
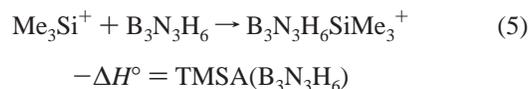
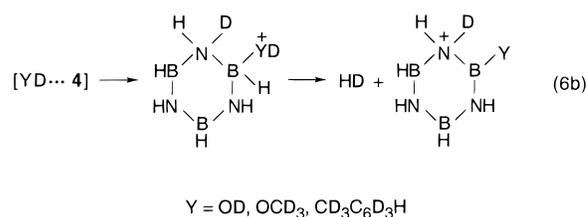
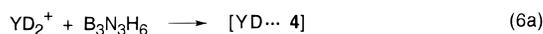


Figure 5. The correlation between proton affinities (PA) and trimethylsilylium affinities (TMSA): (O) amines; (Δ) aromatic compounds; (\blacklozenge) borazine.

The reaction of borazine with Me_3Si^+ (eq 5) has therefore been assayed in order to probe whether its chemistry conformed to the behavior of an aromatic compound or of a simple amine. The position of borazine in the TMSA vs PA plot of Figure 5 is in line with those of simple aromatic compounds, supporting the view of borazine as an inorganic counterpart of benzene.



Few other gaseous cations react with borazine by an addition-elimination pathway which may be described by eq 6, on the basis of the higher GB of borazine with respect to neutral Y. These reactions are not known in the chemistry of benzene. Still, they may be viewed as driven by the elimination of a hydrogen molecule, restoring the borazine nucleus. This ring system thus appears to be endowed with a certain degree of thermodynamic stability.



Gas-Phase Reactions of Borazine with Negatively Charged Ions. The reactions of borazine with negative ions have been less extensively investigated than those with positive ions. The gas-phase acidity of borazine (ΔG_{300}°), measured from proton-transfer equilibria with reference acids, is found equal to 365 kcal/mol, compared with a recent evaluation of 393 kcal/mol for the gas-phase acidity of benzene.³⁷ Deprotonation can involve either the hydrogen bound to boron or the hydrogen bound to nitrogen. Which of these alternatives occurs may not be answered by the present experiments and is the object of studies in progress.

The presence of the electron-deficient boron atoms confers borazine a somewhat higher reactivity toward negative ions with

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respect to benzene. In fact, borazine displays addition reactions that are unknown in the gas-phase chemistry of the carbocyclic analogue.

Structure and Reactivity of $B_3N_3H_5^+$ Ions. The formation of $B_3N_3H_5^+$ ions following protonation at boron has already been discussed. The optimized structure shown in Figure 4 shows that $B_3N_3H_5^+$ retains a cyclic structure, in many ways similar to that of the phenylium ion, $C_6H_5^+$, from formal hydride abstraction from benzene. Alternatively, $B_3N_3H_5^+$ ions may be formed by the reaction of borazine with CF_3^+ , a process estimated exothermic by ~ 60 kcal/mol. The analogy with phenylium ion is that it is not only structural but that it also extends to some aspects of reactivity. For example, the formation of $B_3N_3H_7^+$ from the reaction with ethane is paralleled by the formation of $C_6H_7^+$ from phenylium ions.³⁸ Some other reactions, such as those with methanol and water leading to $B_2N_3H_5-CH_3^+$ and $B_2N_3H_6^+$, respectively, are peculiar to $B_3N_3H_5^+$ ions and are probably driven by the high stability of the accompanying neutral fragment, BOH.

Conclusions

The gas-phase ion chemistry of borazine presents both remarkable analogies and interesting differences with that of benzene, an isoelectronic and aromatic organic molecule. The issue of the extent of aromaticity of borazine is currently a debated topic, and one scope of the present work has been to search for reactivity patterns that could confirm or disprove a distinct aromatic character of this molecule. The reactivity study in the gas phase was motivated by the absence of specific interactions, such as, for example, those of the electron-deficient B-atoms with donor centers of solvents and counterions, that could significantly obscure the reactivity properties of borazine. The attack of the proton, the prototypical electrophile, is directed at the N-atom, the most basic site according to *ab initio* calculations. The experimental GB value was found equal to 185.0 kcal/mol. Whereas the optimized structure of protonated borazine is close to that of the benzenium ion, its reactivity with exchange reagents shows that hydrogen equilibration does

not occur within $B_3N_3H_7^+$, at variance with the complete scrambling of all seven H's that is known to take place within $C_6H_7^+$ in the time scale of mass spectrometric experiments.^{35b,c} This result is ascribed to the high barrier associated to a 1,2-hydrogen-shift mechanism that should proceed via a B-protonated species. Calculations predict $H_4B_3N_3H_3^+$ to lie ~ 28 kcal/mol higher in energy than $H_3B_3N_3H_4^+$. Accordingly, protonation at boron, followed by cleavage of H_2 , is observed only by the strongest among the Brønsted acids used. The electrophilic attack at nitrogen is clearly shown by alkylating ions which lead to N-alkylborazines, the neutral products obtained from radiolytic experiments at atmospheric pressure.¹⁵ These products represent also the first evidence for an electrophilic substitution on the borazine ring. They proceed by way of the charged intermediates detected in the FT-ICR kinetic experiments, which may be viewed as inorganic analogues of arenium ions. The same kind of intermediates are probably formed by Me_3Si^+ addition, a reaction that places borazine in the correlation line for model aromatic compounds. Also an exemplary electrophilic reaction, the attack by nitrating ions, proceeds in the gas phase in a closely similar way as observed for benzene, with the formation of $B_3N_3H_6NO_2^+$ adducts from solvated forms of the nitronium ion.

Passing to negative ion chemistry, the gas-phase acidity of borazine has been found to be equal to 365 kcal/mol by proton transfer equilibria with reference acids. Borazine has therefore proved to be both more basic and more acidic than benzene (GB(benzene) = 173.4 kcal/mol, GA(benzene) = 393 kcal/mol).^{28,37}

In conclusion, in many respects the gas-phase ion chemistry of borazine has shown a remarkable similarity to that of benzene under similar conditions, so that at least from a reactivity standpoint it appears legitimate to denote it as "inorganic benzene".

Acknowledgment. The authors acknowledge the Italian Ministero dell'Università e della Ricerca Scientifica e Tecnologica and the Consiglio Nazionale delle Ricerche for financial support and are grateful to Professor Fulvio Cacace for many helpful discussions.

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