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here. Two different studies of methyl radical recombination found the canonical rate constant to be 1.07 and 1.20 times larger.[2a,30] For C–H split in propylene the canonical and microcanonical rate constants agree to within 10%.[32] Nearly exact agreement is found between the two rate constants for surfaces with well-defined barriers and, thus, have transition states which are only weakly dependent on energy and/or temperature.[33] From these comparisons, the canonical variational transition state method is expected to be accurate for calculating the H + $CH_3 \rightarrow CH_4$ thermal rate constant.

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Theory and Experiment in Concert: Evidence for a Stable Ammoniaborene Dication (H_3NBH^{2+})[†]

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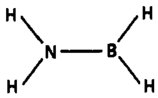
Abstract: The potential energy surfaces of the mono- and dications of aminoborane (NH_2BH_2) and ammoniaborene (NH_3BH) were explored by high level ab initio calculations. Although two minima were located on either surface, corresponding to $NH_2BH_2^{\bullet+}$, $NH_3BH^{\bullet+}$, $NH_2BH_2^{2+}$, and NH_3BH^{2+}, the theoretical analysis, in conjunction with charge stripping mass spectrometry, suggests that the only dication formed is that of ammoniaborene (NH_3BH^{2+}), requiring a Q_{min} value of 15.2 eV. NH_3BH^{2+} is predicted to be 60.6 kcal/mol more stable than the $NH_2BH_2^{2+}$ which is due to the powerful donor/acceptor interactions operative in NH_3BH^{2+}. Comparison of the $BNH_4^{\bullet+}/BNH_4^{2+}$ ions with the isoelectronic $C_2H_4^{\bullet+}/C_2H_4^{2+}$ species is made.

There has been considerable interest in aminoborane as a candidate for an inorganic analogue of ethylene.[1] Microwave spectroscopy has provided ample evidence that the neutral produced from the pyrolysis of the ammonia/borane mixture is a planar H_2NBH_2 species **1** similar to ethylene.[2]



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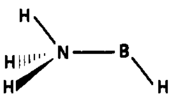

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More recently,[3b] with the aid of He I photoelectron spectroscopy and a combination of semiempirical/ab initio calculations, a twisted form of $1^{\bullet+}$ was assigned for $NH_2BH_2^{\bullet+}$. We have produced dicationic BNH_4^{2+} by applying charge stripping mass spectrometry[4] to mass-selected $BNH_4^{\bullet+}$ which in turn was produced by 70 eV electron impact ionization of aminoborane. The latter was generated as described in ref 2 and 3. Our experimental findings are complemented by ab initio MO calculations.[5] Optimized geometries, zero-point energies (ZPE), and harmonic frequencies were calculated with the 6-31G(d) basis set.[6] Minima and transition structures were characterized by having the correct number of negative eigenvalues of the Hessian matrix (no negative eigenvalue for the former and one for the latter). Single-point calculations were performed with the 6-311G(d,p) basis set.[7] Effects of valence electron correlation were incorporated by means of Møller–Plesset perturbation theory terminated at the 4th order.[8] All data reported in Figures 1 and 2 refer to this level of theory (MP4/6-311G(d,p)//6-31G(d) + ZPE). Ionization energies, IE, were calculated assuming vertical ionization. Geometries (bond

Table I. Total Energies (in hartrees) and ZPE (in kcal/mol) for Mono- and Dicationic BNH_4 Species, Transition Structures, and Some Dissociation Products

structure	6-31G(d)	MP4/6-311G(d,p)	ZPE[a]
H_3NBH^+	−81.15382	−81.45543 −80.87455[b]	29.5
$H_2NBH_2^+$	−81.15769	−81.44648 −80.74519[b]	26.3
$H_2NBH_2^+ \rightarrow H_3NBH^+$ TS	−81.07124	−81.39392	25.8
$H_2NBH{-}{-}{-}H^+$ TS	−81.10625	−81.42372	23.2
H_2NBH^+	−80.61302	−80.91016	21.9
H_3NBH^{2+}	−80.63102	−80.92196	29.1
$H_2NBH_2^{2+}$	−80.49264	−80.81418	25.1
$H_2NBH_2^{2+} \rightarrow H_3NBH^{2+}$ TS	−80.46794	−80.79739	23.8
$H_2NBH{-}{-}{-}H^{2+}$ TS	−80.46794	−80.79740	23.8
H_2NBH^+	−80.61302	−80.91018	21.9
$H_3N{-}{-}{-}BH^{2+}$ TS	−80.52462	−80.78613	26.2
BH^+	−24.81518[c]	−24.86374[c]	3.6
H_3N^+	−55.87324[c]	−56.06987[c]	19.8
$H{-}{-}{-}H_2NBH^{2+}$ TS	−80.48262	−80.77911	22.8
$H_3NB{-}{-}{-}H^{2+}$ TS	−80.44145	−80.74695	24.0
H_3NB^+	−80.52528	−80.83145	23.5
$H_2N{-}{-}{-}BH_2^{2+}$ TS	−80.41604	−80.69504	23.5
BH_2^+	−25.47080[c]	−25.55277[c]	10.4
H_2N^+ ($^1A_1$)	−55.12729[c]	−55.30390	10.9

[a] Scaled by a factor of 0.9. See the following: Pople, J. A.; Schlegel, H. B.; Krishnan, R.; DeFrees, D. J.; Binkley, J. S.; Frisch, M. J.; Whiteside, R. A.; Hout, R. F.; Hehre, W. J. *Int. J. Quant. Chem., Symp.* **1981**, *15*, 269. [b] Dication from fixed monocation structure. [c] *The Carnegie-Mellon Quantum Chemistry Archive, Third Edition*; Whiteside, R. A., Frisch, M. J., Pople, J. A., Eds.

[†] Dedicated to Professor Hans-Werner Wanzlick, Berlin, on the occasion of his 70th birthday.

[‡] Berlin.

[⊥] Lausanne.

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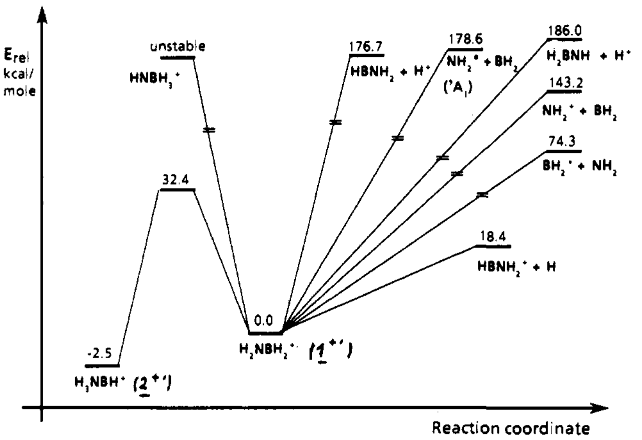


Figure 1. Potential energy diagram for unimolecular reactions of $H_2NBH_2^{\cdot+}$.

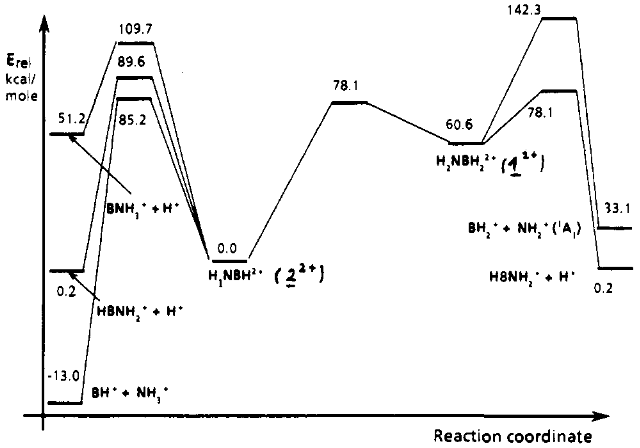
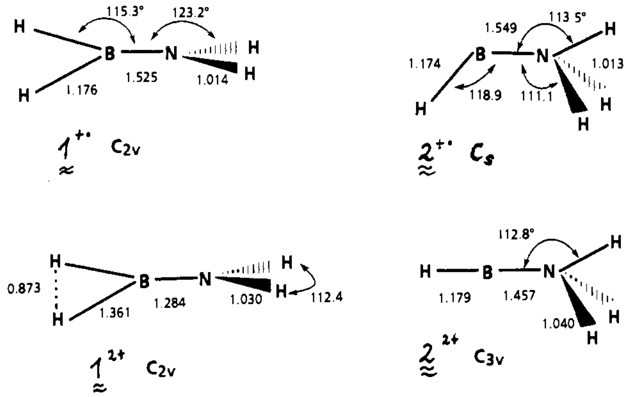


Figure 2. Potential energy diagram for BNH_4^{2+}.

length in angstrom, bond angles in degree) calculated at the 6-31G(d) level of theory for the mono- and dications of **1** and **2** are given in Chart I, and total energies are given in Table I.

Chart I



Charge stripping of $BNH_4^{\cdot+}$ gives a sharp signal due to the process $BNH_4^{\cdot+} \rightarrow BNH_4^{2+}$, and a Q_{min} value of 15.2 ± 0.2 eV was obtained. The calculated IE$_v$ for the process $\mathbf{1}^{\cdot+} \rightarrow \mathbf{1}^{2+}$ corresponds to 19.2 eV, while for the oxidation $\mathbf{2}^{\cdot+} \rightarrow \mathbf{2}^{2+}$ theory predicts a value of 15.8 eV. Obviously, charge stripping does not involve the aminoborane structure $\mathbf{1}^{\cdot+}$ but rather ionized ammoniaborene ($\mathbf{2}^{\cdot+}$). An explanation of this unexpected finding is provided by the ab initio MO calculations.

On the ground-state potential surface (Figure 1) of $BNH_4^{\cdot+}$ at the level of theory used, $\mathbf{2}^{\cdot+}$ (C_s) is calculated to be more stable than $\mathbf{1}^{\cdot+}$ (C_{2v}) by 2.5 kcal/mol. This is a further example of a class of compounds in which the most stable structure of the cation radicals is the 1,2-hydrogen shift product of the neutrals, thereby generating structures other than the classical valence structures.[9] Since neutral BNH_4 has the planar structure **1**, the initially formed ground state cation radical will also have that structure (albeit twisted[3b]). Indeed, $\mathbf{1}^{\cdot+}$ is calculated to lie in a potential well being at least 18 kcal/mol deep. The energetically most facile pathway for $\mathbf{1}^{\cdot+}$ corresponds to loss of H$^\cdot$ to generate $HBNH_2^+$.[10] All other feasible fragmentation processes of $\mathbf{1}^{\cdot+}$ have energies in excess of 70 kcal/mol above the energy of $\mathbf{1}^{\cdot+}$. The barrier for the 1,2 shift $\mathbf{1}^{\cdot+} \rightarrow \mathbf{2}^{\cdot+}$ is as high as 32.4 kcal/mol (above $\mathbf{1}^{\cdot+}$). Thus, the ground state $NH_2BH_2^{\cdot+}$ ($\mathbf{1}^{\cdot+}$) is predicted to dissociate rather than to isomerize to $\mathbf{2}^{\cdot+}$. However, as pointed out by Westwood and Werstiuk,[3b] isomerization to stable $\mathbf{2}^{\cdot+}$ may be facile if $\mathbf{1}^{\cdot+}$ is generated in its first excited state.

That NBH_4^{2+} exists long enough (lifetime $t > 5 \times 10^{-6}$ s) to be detected experimentally is supported by MO calculations of the isomers $\mathbf{1}^{2+}$ (C_{2v}) and $\mathbf{2}^{2+}$ (C_{3v}) (Figure 2). $\mathbf{2}^{2+}$ corresponds to the global minimum separated by a barrier of 78.1 kcal/mol from $NH_2BH_2^{2+}$ ($\mathbf{1}^{2+}$). As with the monocations, $\mathbf{2}^{2+}$ is more stable than $\mathbf{1}^{2+}$ by a now greatly enhanced value of 60.6 kcal/mol. This difference contrasts strongly to that of the isoelectronic ethylene where $C_2H_4^{2+}$ corresponds to the global minimum; CH_3CH^{2+} does not exist at all as a stable species.[11] The difference between the $C_2H_4^{2+}$ and the NBH^{42+} system may be attributed to the differing sources of stabilization. In ionized ethylene *hyperconjugation* plays a leading role which favors both the dication and monocation as a twisted form. With $HBNH_3^{2+}$, on the other hand, a type of powerful *donor–acceptor interaction* between an effective BH^{2+} acceptor and NH_3 donor dominates over hyperconjugative stabilization operative in $NH_2BH_2^{2+}$. This type of behavior is not only reminiscent of the isoelectronic system

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(1) See, for example: (a) Hoffmann, R. *J. Chem. Phys.* **1964**, *40*, 2474. (b) Armstrong, D. R.; Duke, B. J.; Perkins, P. G. *J. Chem. Soc. A* **1969**, 1566. (c) Maouche, B.; Gayoso, J. *Int. J. Quantum Chem.* **1983**, *23*, 891. (d) Kuznesof, P. M.; Schriver, D. F.; Stafford, F. E. *J. Am. Chem. Soc.* **1968**, *90*, 2557. (e) Hu, M. G.; Geanangel, R. A.; Wendtland, W. W. *Thermochim. Acta* **1978**, *23*, 249.

(2) (a) Sugie, M.; Takeo, H.; Matsumura, C. *Chem. Phys. Lett.* **1979**, *64*, 573. (b) Sugie, M.; Kawashima, K.; Takeo, H.; Matsumura, C. *Koen Yoshishu-Bunshi Kozo Sogo Tononkai* **1979**, 168.

(3) (a) Gerry, M. C. L.; Lewis-Bevan, W.; Merer, A. J.; Westwood, N. P. C. *J. Mol. Spectrosc.* **1985**, *110*, 153. (b) Westwood, N. P. C.; Werstiuk, N. H. *J. Am. Soc.* **1986**, *108*, 891.

(4) For details of the methodology, selected papers, and reviews on the subject see: (a) Rabrenovic, M.; Proctor, C. J.; Ast, T.; Herbert, C. G.; Brenton, A. G.; Beynon, J. H. *J. Phys. Chem.* **1983**, *87*, 3305. (b) Koch, W.; Maquin, F.; Stahl, D.; Schwarz, H. *Chimia* **1985**, *39*, 376. (c) Ast, T. *Adv. Mass Spectrom.* **1985**, *10A*, 471. Briefly, a Vacuum Generator ZAB-2F mass spectrometer of BE configuration was used in which the magnetic sector B precedes the electric sector E. Mass-selected $BNH_4^{\cdot+}$ ions of 8 keV kinetic energy were made to collide with O_2 at a pressure of approximately 10^{-4} Torr in the collision cell, located in the 2nd field-free region between the magnetic and electric sector. For an accurate measurement of Q_{min}, i.e., the ionization energy of the reaction $m^+ \rightarrow m^{2+} + e^-$, the energy scale was calibrated by admitting toluene as a reference compound for which Q_{min} is known to be 15.7 eV for the process $C_7H_8^{\cdot+} \rightarrow C_7H_8^{2+}$ (Dorman, F. M.; Morrison, J. D. *J. Chem. Phys.* **1961**, *35*, 575). The Q_{min} value was obtained by extrapolating to the base line of the high energy of both the main beam ($BNH_4^{\cdot+}$) and the charge-stripping peak as described by Beynon et al. (Ast, T.; Porter, C. J.; Proctor, C. J.; Beynon, J. H. *Bull. Soc. Chim. Beograd* **1981**, *46*, 135).

(5) The GAUSSIAN 82 series of programs was used throughout. Calculations were performed on a Cray-1M computer: Binkley, J. S.; Frisch, M.; Raghavachari, K.; DeFrees, D.; Schlegel, H. B.; Whiteside, R.; Fluder, E.; Seeger, R.; Pople, J. A. GAUSSIAN 82, Release H, Department of Chemistry, Carnegie-Mellon University, Pittsburgh, 1984.

(6) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213.

(7) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650.

(8) Raghavachari, K.; Frisch, J.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 4244 and references cited therein.

(9) For further examples see: (a) Frisch, M. J.; Raghavachari, K.; Pople, J. A.; Bouma, W. J.; Radom, L. *Chem. Phys.* **1983**, *75*, 323. (b) Schwarz, H. *Mass Spectrosc.* (*Tokyo*) **1984**, *32*, 3. (c) Radom, L.; Bouma, W. J.; Nobes, R. H.; Yates, B. F. *Pure Appl. Chem.* **1984**, *56*, 1831. (d) Hammerum, S. *Mass Spectrom. Rev.*, in press.

(10) A barrier of 3 kcal/mol above the dissociation products $HBNH_2^+$ + H$^\cdot$ was initially calculated at the 6-31G(d) level; this barrier disappears at our level used.

(11) Lammertsma, K.; Barzaghi, M.; Olah, G. A.; Pople, J. A.; Kos, J. A.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 5252.

CNH_3^{2+},[12a,d] but it also seems to constitute a general stabilization principle for many other dications.[12b,c]

The dication $\mathbf{1}^{2+}$ exists also in a well. Both charge separation to generate H^+ and $HBNH_2^+$ as well as isomerization to $\mathbf{2}^{2+}$ would require an activation energy of 17.5 kcal/mol. But nevertheless, $\mathbf{1}^{2+}$ cannot be generated by vertical electron removal from $\mathbf{1}^{\bullet+}$. According to the ab initio calculations, vertical ionization of $\mathbf{1}^{\bullet+}$ leads to a species located 22.7 kcal/mol *above* the dissociation/isomerization transition states of $NH_2BH_2^{2+}$. In contrast, vertical removal of an electron from $NH_3BH^{\bullet+}$ ($\mathbf{2}^{\bullet+}$) generates a dication with an energy of 29.7 kcal/mol above the ground state H_2NBH^{2+} but still well *below* the transition state energies for further reactions of NH_3BH^{2+}. This is further evidence that electron impact ionization of **1** leads to the ground state of $\mathbf{1}^{\bullet+}$ *and* (presumably via the first excited state of $\mathbf{1}^{\bullet+}$) to excited $\mathbf{2}^{\bullet+}$; the latter, upon charge stripping, serves as actual precursor to generate the new donor–acceptor complex H_3NBH^{2+} ($\mathbf{2}^{2+}$). This interpretation is substantiated by a comparison of the $Q_{\min}$ value (15.2 eV) with the theoretically predicted ionization energy (15.8 eV), as the difference of 0.6 eV is in excellent agreement with the 0.7 eV calculated for the energy difference between the ground and first excited state of $\mathbf{1}^{\bullet+}$.[3b]

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(12) (a) Koch, W.; Heinrich, H.; Schwarz, H. *J. Am. Chem. Soc.* **1986**, *108*, 5400. (b) Koch, W.; Frenking, G.; Gauss, J.; Dieter, C. *J. Am. Chem. Soc.* **1986**, *108*, 5808. (c) Koch, W.; Schwarz, H. Proceeding of the NATO ASI "Structure, Reactivity and Thermochemistry of Ions" Ausloos, P., Lias, S. P., Eds., Reidel Publisher: Dordrecht, 1987; p 413. (d) Wong, M. W.; Yates, B. F.; Nobes, R. H.; Radom, L. *J. Am. Chem. Soc.*, in press.

Fractional Bonds: Relations among Their Lengths, Strengths, and Stretching Force Constants

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Abstract: A simple modification of the Morse equation is shown to yield several relationships among bond lengths, energies, and stretching force constants that have been established empirically over the years. The adjustable parameters can be assigned to yield reasonable agreement with experimental observations. The Morse equation can also be adapted to deal with the energy variation along reaction paths involving changes in more than one bond length. The relationships derived provide a rationale for the strong dependence of reaction rate on small changes in ground-state structure that has been observed for several systems.

The study of chemical bonds in terms of dissociation energies D, equilibrium interatomic distances r_e, and stretching force constants k has led over the years to a number of empirical relationships involving the notion of fractional bonds. Thus the Pauling bond order (or fractional bond number)[1] n is defined in terms of the difference between an interatomic distance r, a standard "single bond" distance r_0, and an empirical constant c

$$r = r_0 - c \ln n \tag{1}$$

In the remarkably successful bond-energy–bond-order (BEBO) method developed by Johnston and Parr[2] expressions of the type

$$D(n) = D_0 n^p \tag{2}$$

are used where p is a number close to unity (0.8–1.1 for various types of bond). Stretching force constants for a wide variety of diatomics, including covalent, polar, and van der Waals molecules, have been found[3] to correlate with bond distance according to

$$r = a - b \ln k \tag{3}$$

We point out here that these three relationships may all be derived in a simple and intuitive way by what we have called the CNPE method.[4]

The Modified Morse Equation. The Morse equation

$$V(r - r_0) = D_0\{1 - \exp[-B(r - r_0)]\}^2 - D_0 = D_0\{\exp[-2B(r - r_0)] - 2\exp[-B(r - r_0)]\} \tag{4}$$

is known to provide a good approximation to the potential energy of many classes of chemical bonds. For fractional bonds we merely multiply the attractive term by the bond number[5] or, more generally, by some power of it,[6] leaving the repulsive terms unaltered, to obtain

$$V(r - r_0) = D_0\{\exp[-2B(r - r_0)] - 2n^q \exp[-B(r - r_0)]\} \tag{5}$$

With the modified Morse eq 5 the quantities describing the properties of fractional bonds become

$$r_e(n) = r_0 - qB^{-1} \ln n \tag{6}$$

$$D(n) = D_0 n^{2q} \tag{7}$$

$$k(n) = 2B^2 D_0 n^{2q} \tag{8}$$

Equation 6 is evidently the same as the Pauling eq 1 with $qB^{-1} = c$; eq 7 has the same form as the empirical relationship (2). Moreover, combining (6) and (8) leads to

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[†] University of Berne.

[‡] E.T.H. Zurich.

(1) Pauling, L. *J. Am. Chem. Soc.* **1947**, *69*, 542.

(2) (a) Johnston, H. S. *Adv. Chem. Phys.* **1960**, *3*, 131. (b) Johnston, H. S.; Parr, C. *J. Am. Chem. Soc.* **1963**, *85*, 2544.

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(4) Complete Neglect of Practically Everything. We modestly disclaim any priority for the invention or development of this method, the origins of which seem to be shrouded in obscurity.

(5) Dunitz, J. D. *X-ray Analysis and the Structure of Organic Molecules*; Cornell University Press: Ithaca, New York, 1979; p 347.

(6) We could also multiply the repulsive term by some factor, leaving the attractive term unaltered, or we could multiply both attractive and repulsive terms by different factors, to obtain slightly different equations. However, in the spirit of the CNPE method,[4] it is only the general idea that matters.

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