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An Ab Initio Valence Bond (VB) Calculation of the π Delocalization Energy in Borazine, $B_3N_3H_6$

Daniel Benker,[1] Thomas M. Klapötke,[1] Gerhard Kuhn,[1]
Jiabo Li,[2] and Christian Miller[1]

[1]*Chair of Inorganic Chemistry, Ludwig-Maximilian University Munich (LMU), Butenandtstrasse 5–13 (D), D-81377 Munich, Germany*

[2]*SciNet Technologies, San Diego, CA 92129, USA*

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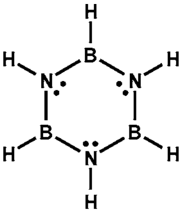
ABSTRACT: *Valence bond (VB) calculations using a double-zeta D95 basis set have been performed for borazine, $B_3N_3H_6$ and for benzene, C_6H_6 in order to determine the relative weights of individual standard Lewis structures. In the delocalized resonance scheme of borazine, the structure (**I**) with no double bonds and three lone pairs of electrons at the three nitrogen atoms is the major contributor with a structural weight of 0.17, followed by six equivalent Lewis structures with one double bond and two lone pairs at two nitrogen atoms (**II**) with weights of 0.08 each. In the case of benzene, the two Kekulé structures (**III**) contribute with structural weights of 0.15 each, followed by 12 equivalent ionic structures (**IV**) with weights of 0.03 each, followed by the three equivalent Dewar-type structures (**V**) with structural weights of 0.02 each. The values of 54.1 and 45.8 kcal mol^{-1} for the delocalization energies of borazine and benzene were estimated. Therefore, $B_3N_3H_6$ is calculated to have substantial aromatic character, similar to benzene, when we assume that the resonance energy can provide a criterion for aromaticity.* © 2005 Wiley Periodicals, Inc. Heteroatom Chem 16:311–315, 2005; Published online in Wiley InterScience (www.interscience.wiley.com). DOI 10.1002/hc.20095



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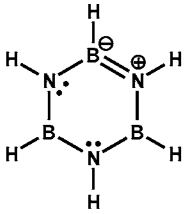

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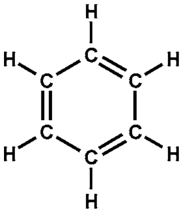

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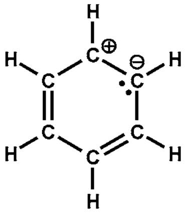

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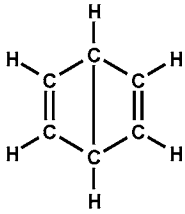

V

INTRODUCTION

The "inorganic benzene," borazine, is a textbook example of a six-π-electron six-membered ring [1–3]. Borazine, $B_3N_3H_6$ (structure **A**), was first isolated in 1926 by A. Stock and E. Pohland as a colorless liquid

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Dedicated to Professor Dr. Alfred Schmidpeter on the occasion of his 75th birthday.

Correspondence to: Thomas M. Klapötke; e-mail: tmk@cup.uni-muenchen.de.

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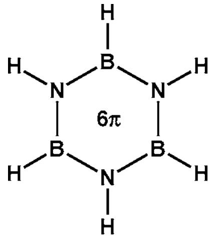
from the mixture of products obtained by the reacting B_2H_6 and NH_3 [1–3]. Borazine has a regular plane hexagonal ring structure with six π electrons and its physical properties closely resemble those of the ioselectronic compound benzene (Table. 1).



A

Compared to benzene, the cyclic delocalization of π electrons in the borazine ring is often considered as being reduced due to the large electronegativity difference between boron (2.0) and nitrogen (3.0) [4], i.e. the π currents are more localized on the nitrogen atoms [5]. The polarity of the BN bond causes borazine to show a reactivity pattern different from benzene [4,6]. Therefore, it is also often stated in general textbooks that although it is possible to write Kekulé-type structures, the weight of chemical evidence suggests that borazine has but little aromatic character [1]. On the other hand, early studies by Fink et al. using homodesmotic equations came to the conclusion that borazine has a nonnegligible resonance energy (9.6 kcal mol^{-1}) which is close to half of the value for benzene (21.9 kcal mol^{-1}) indicating substantial aromaticity [7,8]. Whereas borazine readily undergoes several polar addition reactions which are extremely difficult with benzene [8] and let people to conclude that it has no significant aromatic character [9], more recently it was shown that for borazine, as it is the case for benzene, the dimerization is strongly endothermic due to the aromaticity of C_6H_6 and $B_3N_3H_6$ [10]. Further support for some aromatic character comes from experiments that demonstrate that borazine undergoes electrophilic aromatic substitution in the gas phase much like its organic counterpart benzene [11].

TABLE 1 Comparison of Borazine and Benzene [1]

Property	*$B_3N_3H_6$*	*C_6H_6*
M (g mol^{-1})	80.5	78.1
mp (°C)	−57	6
bp (°C)	55	80
ρ (g cm^{-3} (liquid @ mp)	0.81	0.81
Symmetry	D_{3h}	D_{6h}
Bond lengths (Å)	B–N 1.44 B–H 1.20 N–H 1.02	C–C 1.42 C–H 1.08

Density functional (DFT) calculations have also been carried out BN analogues of CC aromatic systems, and it has been shown that borazine shows aromatic character [12]. Nucleus independent chemical shift (NICS) values suggest that the aromaticity in BN-acenes, in contrast to CC acenes, shows no substantial change in the aromaticity of the individual rings. The molecular electrostatic potential (MESP) was also employed to obtain further insights into the bonding and reactivity trends of acenes and their BN analogues. The MESP topography patterns of acenes and BN-acenes are substantially different, with BN-acenes showing more localized π electron features compared to those of acenes. Recent current density calculations for borazine show that the π orbitals in $B_3N_3H_3$ are intrinsically localized [13]. Ab initio calculations of dimeric borazine $(B_3N_3H_6)_2$ have also been reported [14].

The general concept of aromaticity can be found in any textbook of theoretical organic chemistry. A conjugated ring system is usually called aromatic if its stability is considerably increased compared to that of its classical localized structure. The problem is that aromaticity is not an experimentally observable quantity and various criteria have been suggested. The criteria based on aromatic stabilization energy and ring current were previously shown to be very effective [15]. Another criterion used as a measure of aromaticity is the magnetic susceptibility exaltation (MSE) arising from the ring current [16,17]. More recently, Schleyer et al. suggested a new magnetic criterion, viz. nucleus-independent chemical shift (NICS) to probe the aromaticity in planar rings [18]. It is defined as the negative of the absolute magnetic shielding computed at the geometrical center of the ring. An alternative approach to ring current and aromaticity was developed by Karl Jug and is related to the bond order [19]. The only thing that can be concluded is that the aromaticities of benzene and borazine have been studied using all the above structural, energetic, and magnetic criteria and that all these criteria diverge quite strongly from each other [8].

In this contribution we want to address two questions: (i) What is the structural weight of the Kekulé-type and Dewar-type structures in borazine compared to benzene? and (ii) How large is the aromatic stabilization energy (ASE) in borazine compared to benzene if we assume that the resonance energy can provide a criterion for aromaticity? In order to answer these questions, we applied ab initio valence bond calculations using a D95 double-zeta basis set for all atoms.

RESULTS AND DISCUSSION

In order to determine which individual standard Lewis structures are the most important ones for borazine, we performed VB calculations including the six π electrons in the active VB space. It is well known that 175 canonical VB structures contribute to the singlet ground state wavefunction for the borazine (or benzene) π electrons [20]. Resonance among these structures gives an energy which corresponds to the so-called "full-CI" limit. Here, we calculated the localized structure of borazine invoking resonance between *one* Kekulé-type structure and seven additional structures with two, one, or none π bond, respectively (Fig. 1). The delocalized energy was obtained from a VB calculation invoking resonance between 30 structures (Fig. 2), namely the *two* Kekulé-type structures, the Dewar structures as well as further structures with only two, one, or none π bond, respectively (Fig. 2). In both resonance schemes, structures of the type with a lone-pair of electrons at the B atom and no lone-pair at the N atom, i.e. B^{2-}–N^{2+}, were omitted because of their unfavorable formal charge distribution. The weights for the VB structures were calculated according to the Hiberty procedure and are also indicated in Figs. 1 and 2. Table 2 summarizes the calculated VB energies for the localized and delocalized borazine structures as well as the calculated aromatic stabilization energy (ASE), $\Delta E = E_{\text{loc}} - E_{\text{deloc}}$.

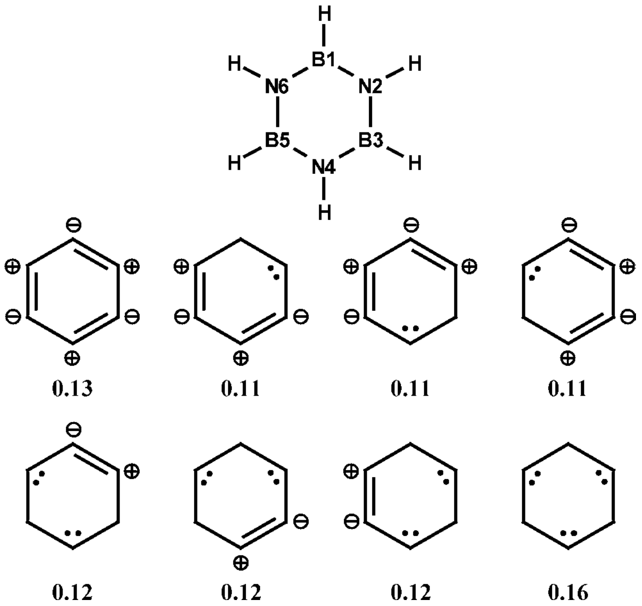


FIGURE 1 Localized VB structures for borazine. Top: numbering scheme; bottom: schematic presentation of the distribution of the 6 π electrons and calculated Hiberty structural weights.

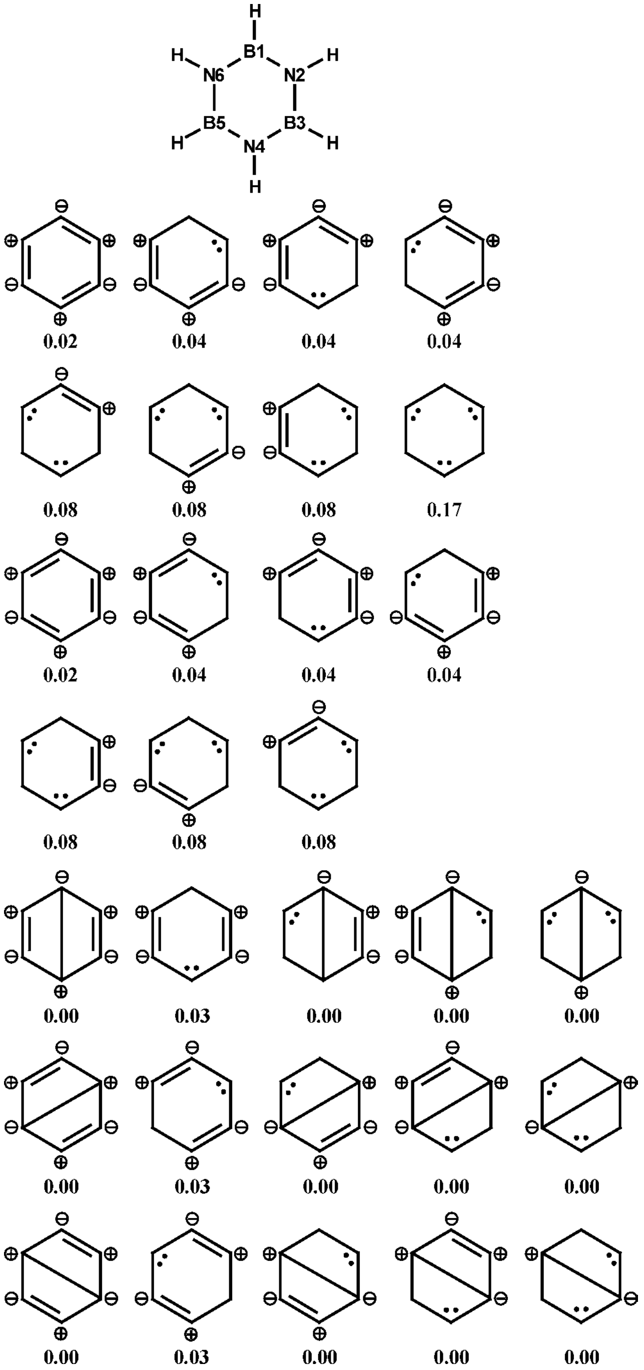


FIGURE 2 Delocalized VB structures for borazine. Top: numbering scheme; bottom: schematic presentation of the distribution of the 6 π electrons and calculated Hiberty structural weights.

In a similar fashion, we also estimated the delocalization energy in benzene by assuming that the delocalization energy, *E*(localized)–*E*(delocalized) for C_6H_6 is proportional to the ASE. With the geometries as indicated in Table 1 for C_6H_6, all canonical Lewis structures that do not involve any of C^+—C^+,

TABLE 2 Localized and Delocalized VB Energies for Borazine and Benzene and Calculated Aromatic Stabilization Energies (ASE), $\Delta E = E_{\mathrm{loc}} - E_{\mathrm{deloc}}$

	$B_3N_3H_6$	C_6H_6
No. of localized structures	8	15
$-E^{\mathrm{VB}}$(localized) (a.u.)	240.988085	230.590891
No. of delocalized structures	30	55
$-E^{\mathrm{VB}}$(delocalized) (a.u.)	241.074396	230.663981
$\Delta E = ASE$ (kcal mol^{-1})	54.1	45.8

$\mathrm{C^-}$—$\mathrm{C^-}$, $\mathrm{C^+}$—$\mathrm{C^+}$—$\mathrm{C^+}$, and $\mathrm{C^-}$—$\mathrm{C^-}$—$\mathrm{C^-}$ were included in the calculations. There are respectively 15 and 55 such structures for *E*(localized) and *E*(delocalized). We thereby calculate values of 54.1 and 45.8 kcal mol^{-1} for the delocalization energies of borazine and benzene, respectively. Therefore, $B_3N_3H_6$ is calculated to have substantial aromatic character, similar to benzene, when we assume that the resonance energy can provide a criterion for aromaticity. Recently, the aromatic stabilization energy (ASE) of benzene has been estimated to be 33 kcal mol^{-1} [21] which is of the same order of magnitude and compares well with our calculated value of 45.8 kcal mol^{-1}.

It is interesting to note that for benzene the two Kekulé-type structures are the most important individual contributors to the resonance scheme while for borazine the Kekulé-type structure is less important. Nonetheless, the delocalization energies are comparable for both compounds with that for borazine being even slightly greater. This apparent contradiction may be explained by the fact that the six equivalent Lewis structures for borazine with one double bond and two lone pairs at two nitrogen atoms with weights of 0.08 each correspond to a highly delocalized structure and alone account for nearly 50% of the structural weights in the borazine resonance scheme.

Although our findings are in accord with the results of previous spin-coupled VB descriptions of borazine in so far that most of the electron density remains at the N atom [22], we cannot confirm the reported weights of the different Rumer structures reported by Gerratt et al. [22]. The question as to whether that there is considerable aromaticity in borazine remains open and also depends on the question whether the assumption that the resonance energy can provide a criterion for aromaticity is correct or not.

METHODS

The VB program package VB2000, version 1.7.1 (running under LINUX) was used for all VB calculations [23–29]. VB2000 is an ab initio electron structure package for performing modern VB calculations; it is based on a highly efficient VB algorithm—the so-called algebrant algorithm [24,25]. A major feature of VB2000 is the implementation of modern VB theory at ab initio level using the algebrant algorithm. The VB methods used in this study were the VB(X) method (with X VB electrons) which is implemented in the VB2000 program package. In VB2000 each "structure" becomes a spin-coupling scheme, involving pairs of electrons occupying rather localized, strongly overlapping orbitals.

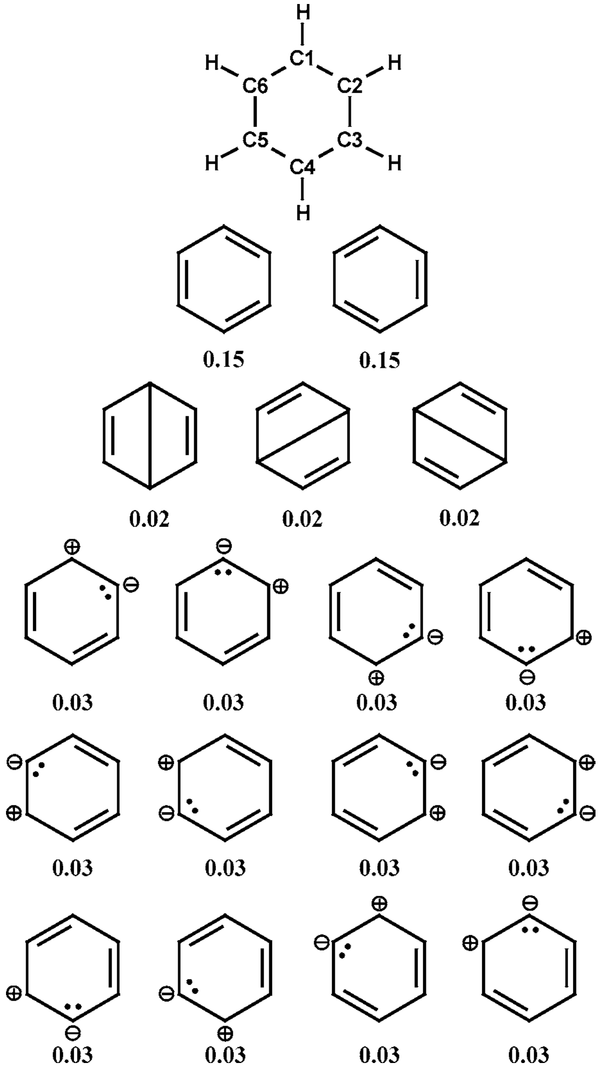


FIGURE 3 Selected and important delocalized VB structures for benzene. Top: numbering scheme; bottom: schematic presentation of the distribution of the 6 π electrons and calculated Hiberty structural weights.

The weights for the VB structures were calculated according to the Hiberty [30a–d] procedure, with $W_i = C_i^2/\Sigma C_i^2$. For a resonance scheme according to the wavefunction ψ (Eq. (1)) the Hiberty weights also account for the overlap integral (Eqs. (2)–(4)).

$$\psi = c_1\psi_1 + c_2\psi_2 \tag{1}$$

$$C_1^2 + C_2^2 + 2C_1C_2S_{12} = 1 \tag{2}$$

$$C_1^2 + C_2^2 = 1 - 2C_1C_2S_{12} \tag{3}$$

$$w_1 = \frac{c_1^2}{1 - 2c_1c_2S_{12}} \approx c_1^2(1 + 2c_1c_2S_{12}) \tag{4}$$

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