The π-Electron-Accepting Ability of the Boron Atom in Ethynylboranes and Related Compounds – An Approximate Weight Computation for Resonance Structures[☆]

Vinzenz Bachler*, and Nils Metzler-Nolte*

Max-Planck-Institut für Strahlenchemie,
Stiftstrasse 34–36, D-45470 Mülheim a.d. Ruhr, Germany
Fax: (internat.) +49(0)208/306-3951
E-mail: nils@mpi-muelheim.mpg.de; bachler@mpi-muelheim.mpg.de

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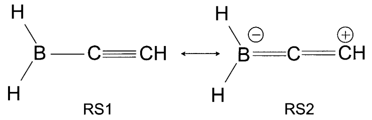
A theoretical analysis was performed to quantify the π-electron-accepting ability of the boron atom in ethynylboranes. An expansion technique was employed which permits to obtain a set of localized bonding schemes and their weights from a delocalized molecular orbital determinantal wavefunction. The derived manifold of bonding schemes is close to the classical resonance hybrid used in organic chemistry (valence-bond description). We quantified the π-electron transfer into the empty π-orbital of the boron atom by investigating nine model compounds where substituents with π-electron-donating ability are adjacent to a boron atom. This led to an ordering of the substituents according to their electron-donating ability towards boron. The boron atom hesitates to accept π-electrons from the ethynyl group in ethynylboranes in particular when good π-donors like amino groups are present. The π-electron donation from the vinyl group to the adjacent boron centre is slightly stronger than from the ethynyl group. Nitrogen lone-pair electrons are easily transferred to a neighbouring boron centre. Bonding schemes and their weights are in line with computed bond lengths and rotational barriers. Moreover, our theoretical results rationalize previous NMR and X-ray experiments and are in line with the reactivity of related compounds. It is demonstrated that bond lengths alone do not necessarily correlate with the degree of π-bonding and should be discussed with caution. The analysis is substantiated by showing that weights for covalent bonding schemes, as obtained from the simple restricted closed-shell MO determinant, correlate with bond strengths. Furthermore, a correlation of bonding-scheme weights with quantities based on the fragment orbital approach is presented. This novel correlation elucidates molecular properties which determine the extent of the π-electron transfer to the boron atom and permits a quantitative interpretation and prediction of intramolecular π-bonding.

Introduction

Ethynylboranes are characterized by a carbon−carbon triple bond directly attached to a Lewis acid boron atom[1]. Its electron-accepting ability may lead to an electron transfer from the adjacent alkynyl π-electron system into the empty π-orbital of the boron atom. This is illustrated in Scheme 1 for the parent compound ethynylborane **1a**.

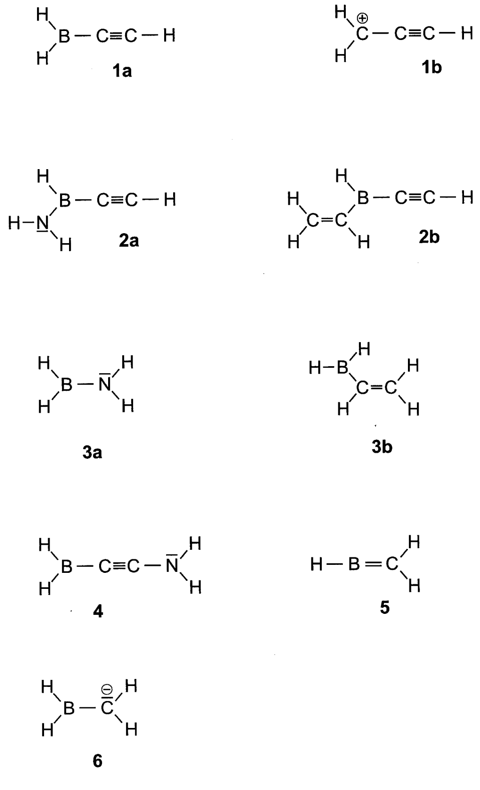
Scheme 1. Two resonance structures symbolizing the electron-accepting ability of the boron atom



The π-electron structure of ethynylborane is described by the two resonance structures RS1 and RS2 which symbolize an alkynylborane and a heteroallene, respectively. In the heteroallene resonance structure RS2 one of the two π-electrons delocalized above and below the molecular plane is transferred to the boron atom. This transfer leads to a partial double bond between the boron atom and the alkynyl group accompanied by a formal negative and a positive charge at the boron and the terminal carbon atom, respectively (see Scheme 1). The relative weights of RS1 and RS2 in the resonance hybrid for those compounds have been debated for some time. X-ray crystallographic results[2] do not show a significant lengthening of the carbon−carbon triple bond or a shortening of the boron−carbon bond. In analogy to phenyl- and vinylboranes, NMR data for ethynylboranes have been interpreted in the light of a substantial B=C double bond character[3]. Calculated bond lengths and rotational barriers[2h][2i] of several alkynylboranes support a rather weak B=C double bond. Thus, the various findings appear partially contradictory. Moreover, they permit only indirect conclusions about the electronic structure of ethynylboranes and have not been quantified in a concise manner up to now.

Ab initio quantum chemistry provides a more direct access to the electronic structure of ethynylboranes. The predominantly applied computational methods are based on the molecular orbital method[4]. There, spin-coupled electron pairs are located in molecular orbitals delocalized over the whole molecule. Scheme 1, however, represents a set of valence-bond resonance structures which describe spin-coupled electron pairs strictly localized in bonds. Thus, a valence-bond calculation for ethynylboranes would be the appropriate method for computing the weights of RS1 and RS2 contained in the valence-bond wave function. They would indicate the importance of RS1 and RS2 for the electronic structure of ethynylboranes. An alternative way is to compute a molecular orbital wave function and to analyze this wave function a posteriori in terms of resonance structures and their weights[5]. Recently, a concise method was proposed for expanding a determinantal wave function composed of delocalized molecular orbitals into a set of determinantal wave functions consisting of localized atomic orbitals[6]. The procedure permits to obtain from a delocalized molecular orbital wave function weights for localized bonding schemes which are close to the resonance structures of organic chemistry. Thus, the method is suited to discuss the frequent problem about the weight of a particular resonance structure in a resonance hybrid. In the following sections we use this technique to investigate the π-electron-accepting ability of the boron atom in ethynylboranes. We do this by obtaining weights for localized bonding schemes for a characteristic set of molecules. Our set of model compounds is represented in Scheme 2.

Scheme 2. The set of model compounds selected for quantifying the π-electron donation into the empty π-AO of boron



Ethynylborane (**1a**) is the parent compound of alkynylboranes and the main objective of our investigation. The BH_2 group is isoelectronic with the methylene cation CH_2^+. The differences in their π-electron-accepting properties are illustrated by compairing **1a** and the ethynylmethylene cation (**1b**). In **1a** and **1b**, only the ethynyl groups donate π-electrons to the BH_2 and the CH_2^+ group, respectively. However, the π-electron-donating properties of amino and vinyl groups are also well established[3b][7]. In **2a** and **2b** competitive π-electron donation may occur and we investigate the competitive electron-donating abilities of the amino, vinyl and ethynyl groups, for which aminoborane (**3a**) and vinylborane (**3b**) serve as reference compounds. Our set of model compounds comprised also 2-aminoethynylborane (**4**) where the electron attraction of the BH_2 group and the electron donation of the NH_2 group are mediated by the ethynyl group. This should lead to a push-pull π-electron transfer in **4**. In methyleneborane (**5**) the sp-hybridized boron atom itself provides a π-electron and a full carbon−boron double bond exists. In the methylborane carbanion (**6**) only a partial B=C double bond is formed which stabilizes the carbanion by delocalizing the negative charge. Compounds **5** and **6** were included in this study to put the amount of B=C double bonding (as expected from resonance structure RS2) in perspective.

Computational Methods

Applied Programs and the Expansion Technique

Quantum chemical calculations were performed by using the Gaussian 92/DFT suite of ab initio programs operating under OpenVMS[8]. The restricted Hartree-Fock (RHF) method[9] and the 6−311G** basis sets[10] were applied to optimize the geometries of the molecules.

We used the recently proposed technique[6] to expand a molecular orbital (MO) determinantal wave funtion Ψ^{mo} into N_D determinantal wave functions Ψ_i^{ao} composed of atomic orbitals (AOs).

$$\Psi^{mo} = \sum_{i=1}^{N_D} c_i \Psi_i^{ao} \qquad (1)$$

The expansion coefficients c_i in (1) are determinants of matrices which contain definite selections of the canonical MO coefficients. The weight w_i of a definite Ψ_i^{ao} in the expansion (1) was computed by means of

$$w_i = \frac{c_i^2}{\sum_{j=1}^{N_D} c_j^2} \qquad (2)$$

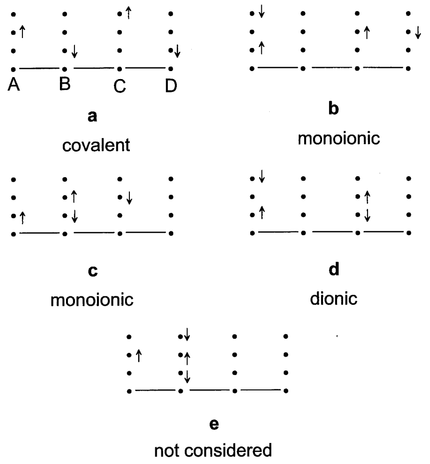
Equation 1 leads to an expansion of the delocalized wave function Ψ^{mo} into wave functions Ψ_i^{ao} which are strictly localized. Any Ψ_i^{ao} represents a definite occupation pattern of the localized atomic spin orbitals. Hence, we analyze the delocalized MO wave function in terms of local spin occupations and their weights[6]. Furthermore, local bonding schemes are obtained by drawing lines between electrons of opposite spin-localized at adjacent atoms of the molecule. These bonding schemes are close to the resonance structures drawn by organic chemists[6]. We are mainly interested in the π-electron distribution. Therefore, MO determinants Ψ^{mo} composed of π-MOs were expanded.

The Expansion Technique and Extended AO Basis Sets

We employed the extended basis set 6−311G[11] to expand Ψ^{mo} into the Ψ_i^{ao}s. We note, that eq. 1 holds also when extended basis sets are employed[6]. Thus, the Ψ_i^{ao}s contain the various groups of contracted gaussian functions which represent the π-AOs. Use of the 6−311G basis set requires a recipe for computing the total weights of the various local spin occupations.

Consider a planar molecule with four π-electrons distributed over four adjacent π-AOs. Each of them is represented by three groups of primitive gaussians. Consequently, various types of spin occupations can occur in the Ψ_i^{ao}s[12] (Scheme 3).

Scheme 3. Several types of local spin occupations occuring when the 6−311G basis is applied in the expansion technique; the occupation schemes are used to obtain local atomic spin occupations



The covalent spin occupation of type (a) describes a complete spin alternation. We obtain the total weight of the local covalent spin occupation by adding up all weights of those 81 Ψ_i^{ao}s which describe the general spin-occupation pattern given by (a). The total weight for a local monoionic spin occupation is obtained by sampling the weights for Ψ_i^{ao}s with occupation patterns of type (b). A similar sampling is performed to compute the total weight for further monoionic and diionic spin occupations resulting from cases (c) and (d), respectively. However, eq. 1 produces also Ψ_i^{ao}s for energetically unfavourable spin occupations of type (e) which allocate three electrons at one atom. Those spin occupations have very small weights and are neglected in our weight sampling.

Relating Weights and Bond Strengths

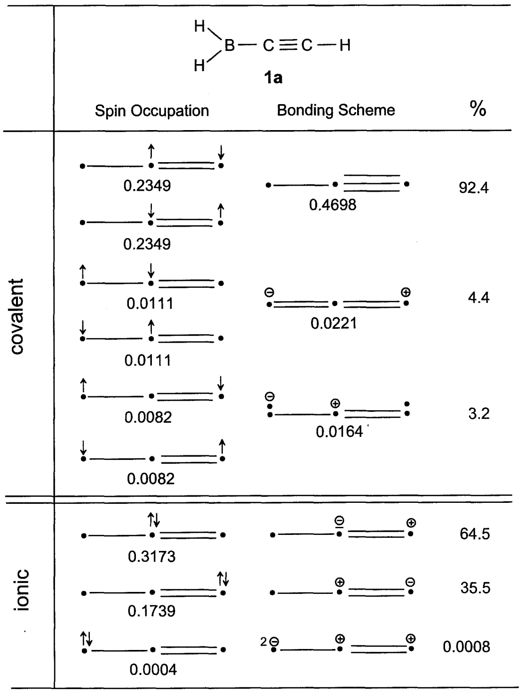
We also relate weights for bonding schemes to the strengths of the bonds designated by the bonding schemes. For this purpose the second derivatives of the molecular energy with respect to definite internal coordinates are needed. These coordinates are the bond lengths in the z-matrix[13] defining the molecular geometries. We computed the second derivatives by repeating the last step in the geometry optimization but we used an analytic hessian (FOPT=CALCALL)[8]. The second derivatives of the energy with respect to the internal coordinates of the z-matrix were printed out by means of the option IOP(1/33 = 1)[8].

Results

π-Electron Donation from the Alkynyl Group to the Isoelectronic BH_2 and CH_2^+ Groups

In ethynylborane (**1a**) the Lewis acidic BH_2 group is directly attached to the ethynyl group (see Scheme 1). Two π-electrons of this group can be transferred to the BH_2 group by partially occupying the empty π-orbital of the boron atom. Thus, two π-electrons of the ethynyl group can delocalize over three π-AOs and a partial boron−carbon π-bond can be formed (see Scheme 1). In order to investigate the extent of this π-bonding we expanded a restricted closed-shell MO determinant for the two π-electrons into the set of all 81 AO determinants. We derived local spin occupations by sampling the corresponding AO determinants as outlined above. Local spin occupations and their weights are given in the first column of Table 1.

Table 1. Bonding schemes and their weights for ethynylborane (**1a**); the covalent weights show that the boron atom hesitates to accept π-electrons from the ethynyl group



	Spin Occupation	Bonding Scheme	%
covalent	0.2349 0.2349	0.4698	92.4
	0.0111 0.0111	0.0221	4.4
	0.0082 0.0082	0.0164	3.2
ionic	0.3173		64.5
	0.1739		35.5
	0.0004		0.0008

Generally, a line in a bonding scheme represents a spin-coupled electron pair localized in bonds or at an atom by forming a lone pair[14]. In the second column of Table 1 spin occupations of the first column are converted into bonding schemes. Equal weights of spin-inverted spin occupations are added up to derive weights for bonding schemes. All covalent AO determinants give rise to three covalent bonding schemes. All ionic AO determinants make up three ionic bonding schemes (see Table 1). It is well known that expanding an uncorrelated restricted MO determinant produces weights for the covalent and ionic bonding schemes which are too small and too large, respectively[15].

This problem could be alleviated by using a correlated wavefunction to obtain localized bonding schemes, the procedure for which is, however, computationally more involved. Former work has demonstrated that geometries for boron compounds are reproduced reasonably well by RHF calculations. Moreover, it was shown previously that *within the subspaces* of the covalent and ionic bonding schemes the weights can be expected to appear in correct relative order[16]. Therefore, the weights of covalent bonding schemes in Table 1 should indicate their relative importance. Because this work concentrates solely on the relative importance of covalent bonding schemes, all ionic bonding schemes have been omitted for clarity for the other compounds in this study. In the following we estimate the importance of a covalent bonding scheme by its weight precentage value, where 100% is the weight sum of all covalent bonding schemes. Table 1 shows that the two π-electrons reside mainly on the alkynyl group (92.4%). A heteroallene structure with a B=C double bond is only of minor importance (4.4%). The weight for the singlet diradicaloid bonding scheme is small (3.2%) but of comparable magnitude. These results suggest that the boron atom hesitates to accept a single π-electron from the alkynyl group. It also avoids to accept a spin-coupled electron pair as indicated by the very small weight of the respective charge-separated bonding scheme. These conclusions seem to be supported by the optimized geometries. The carbon−carbon triple bond length of the alkynyl group is 1.1927 Å, a value close to the carbon−carbon triple bond length of acetylene (1.204 Å)[17]. Thus, the C≡C bond in **1a** is in essence an acetylene triple bond. A value of 1.5250 Å is computed for the B−C bond length in **1a**. This value is close to the computed B−C bond length in BH_2-CH_3 (1.578 Å)[18]. The small bond shortening is in line with the different carbon hybridizations present in **1a** and BH_2-CH_3 (sp vs. sp^3). All results support the notion that the double-bond character of the B−C bond in **1a** is small.

In **1b** the ethynyl group is adjacent to the positively charged CH_2^+ group which is isoelectronic to the BH_2 group of **1a**, but expected to be a much stronger π-acceptor due to its positive charge. As for **1a**, the covalent AO determinants for **1b** lead to three local covalent spin occupations and bonding schemes as recorded in Table 2.

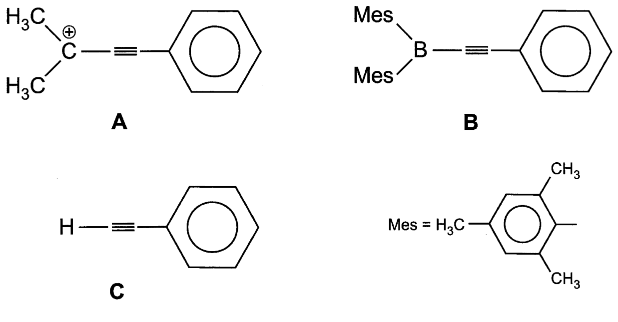
Table 2. Bonding schemes and their weights for model compound **1b**; the covalent weights indicate the two π-electrons are delocalized

Spin Occupation	Bonding Scheme	%
0.2202		42.2
0.2383		45.7
0.0633		12.1

They show that the two π-electrons are almost equally localized in the CH_2-CCH bond region (42.2%) and in the $CH_2C{\equiv}CH$ bond region (45.7%). Hence, the carbon−carbon triple bond experiences a removal of π-electrons but also positive charge is accumulated in this bond region as indicated by the first bonding scheme of Table 2. These two effects have an opposite influence on the carbon−carbon triple bond length which therefore remains unaffected. In contrast, the carbon−carbon single bond CH_2-CCH should have a significant double-bond character. Both conclusions are supported by the optimized bond lengths: The CH_2-CCH bond length of 1.3414 Å is close to the carbon−carbon bond length in ethylene (1.337 Å)[19], but the $CH_2C{\equiv}CH$ bond length is 1.2096 Å, a value near 1.204 Å which is the carbon−carbon bond length in acetylene[17]. Thus, in spite of the *massive* π-electron withdrawal from the triple bond its bond length remains virtually unchanged. This fact emphasizes that geometrical parameters are at best an indirect measure of electronic properties. The leading covalent bonding schemes of Table 2 describe the well-known delocalization of the positive charge[20] among the two terminal carbon atoms. A feature of cation **1b** seems to be its notable singlet biradical character. This is indicated by the appreciable weight of the third covalent bonding scheme (12.1%). This conclusion illustrates an advantage of the applied procedure: The singlet biradical character of a closed-shell molecule is contained in a restricted closed-shell MO determinant. However, it remains hidden but is revealed by the expansion technique[6].

The effective charge delocalization in alkynyl-substituted carbocations has been demonstrated by Olah et al.[21] using NMR spectroscopy.

Scheme 4. A set of alkynyl-substituted compounds where π-electron delocalization operates; compound **C** serves as a comparison



In **A** (see Scheme 4), the ^{13}C chemical shift of the *para*-carbon atom of the phenyl ring is $\delta_p = 145.5$ or $\Delta\delta_p = 16.8$ downfield from that of the respective carbon atom in **C**[21]. In **B**, $\Delta\delta_p$ is only 1 ppm[3d] supporting our notion that despite of their isoelectronic nature, the X−C≡C π-interaction is much weaker in ethynylboranes (X = R_2B) than in the carbocation (X = R_2C^+). By comparing the results for model compounds **1b** and **1a** we have presented two extreme cases of a strong and weak electron delocalization, respectively, which are most likely inaccessible preparatively. In those ethynylboranes known, competitive π-electron donation from other substituents to boron might diminish the

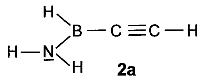
B−C≡C π-interaction even further. A quantitative estimate of these substituent effects is presented in the next section.

Competitive π-Electron Donations from the Amino, Vinyl, and Ethynyl Groups to the BH_2 Group

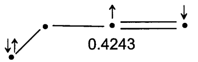
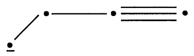
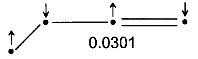
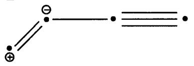
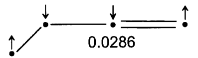
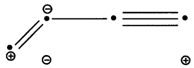
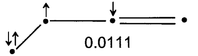
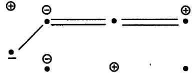
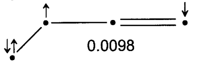
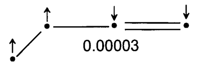
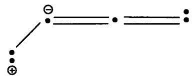
There is ample experimental evidence for the formation of a partial boron−nitrogen double bond in aminoboranes. For example, NMR spectroscopy shows a hindered rotation about the B−N bond and a rotational barrier of ca. 20 kcal/mol is measured[7f][7i] and confirmed by computational methods[22]. In aminoboranes with three-coordinate boron atoms the B−N bond length is ca. 1.40 Å and the nitrogen atom is planar[7a][7f][7i]. In related compounds with tetracoordinated boron atoms, however, the B−N bond is ca. 0.05 Å longer and the nitrogen atom is pyramidal[7a][7f][7i]. π-Electron donation from a vinyl group to a neighbouring boron centre is considered to be much weaker, but firmly established[1d]. We have calculated the relative weights for all covalent bonding schemes in amino(ethynyl)borane (**2a**) and ethynyl(vinyl)borane (**2b**) in order to determine the relative π-donating abilites of the three substituents.

The four π-electrons in **2a** occupy two π-MOs delocalized over four π-AOs. By expanding a restricted closed-shell MO determinant we obtained a set of 4356 AO determinants for the four π-electrons. The results for the local covalent spin occupations and their weights as obtained by sampling the corresponding AO determinants are displayed in Table 3.

Table 3. Covalent bonding schemes and their weights for the amino(ethynyl)borane (**2a**)



2a

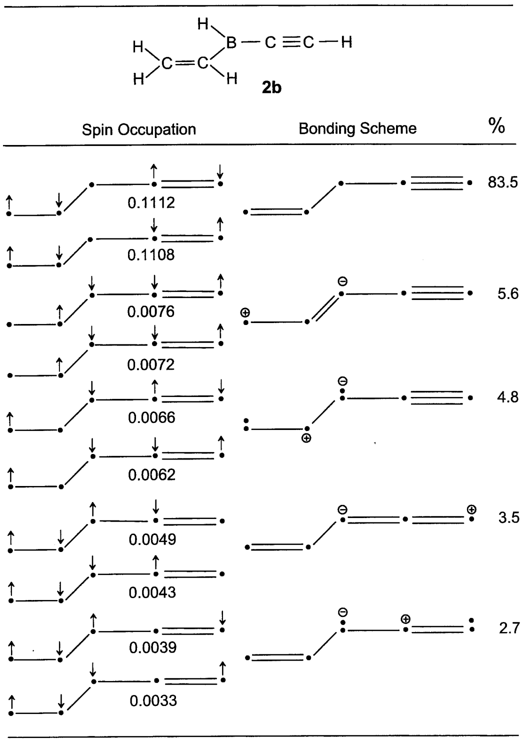
Spin Occupation	Bonding Scheme	%
		84.2
		6.0
		5.7
		2.2
		1.9
		$6.0 \cdot 10^{-5}$

As before, any line in a bonding scheme symbolizes a spin-coupled electron pair present in the corresponding local spin occupation. A single local spin occupation, however, may be compatible with various ways of drawing lines and its weight contributes to the weights of several bonding schemes[6]. Such a case is the second spin occupation in Table 3 contributing at least to a biradical scheme with a central double bond and to a scheme with a triple bond in the alkynyl group and an N=B double bond. The alkynyl carbon−carbon bond is much shorter (1.1904 Å) than the boron−carbon bond (1.5495 Å) and the bonding scheme comprising an alkynyl triple bond should be energetically much more favourable. Therefore, we attributed the weight of the second spin occupation solely to the bonding scheme with the alkyne triple and the N=B double bond (see Table 3). Similar arguments have been applied previously to derive bonding schemes from local spin occupations where the conversion is non-unique[6].

Weights in Table 3 indicate that the four π-electrons in **2a** prefer the ethynyl group and the nitrogen lone pair (84.2%). However, the boron atom accepts an electron from the nitrogen lone pair by forming a partial nitrogen−boron double bond $H_2N{=}BHCCH$ (11.7%). The formation of a π-bond between the boron atom and the ethynyl group is rather unfavourable (2.2%). The singlet biradical character of **2a** is also negligible (1.9%). In aminoborane (**3a**) (36 AO determinants for two π-electrons delocalized over two centres) the weight for the resonance hybrid with a B=N double bond is 11.2%. These results imply that the boron atom readily accepts an electron from the nitrogen lone pair, but much less from the ethynyl group. In addition, the ethynyl group is a fairly electronegative substituent at the boron centre. Its electron withdrawal through the σ bond is balanced by a slightly stronger π-electron donation from the nitrogen atom (11.7% vs. 11.2%). This idea had been advanced previously but remained unsubstantiated until now. Former computations[23] have shown that a barrier of 32.4 kcal/mol exists for a rotation about the nitrogen−boron bond. This barrier height points to a partial double-bond character and is in line with the exceptional stability of aminoboranes. Lone-pair electron donation has been exploited frequently for stabilizing otherwise inaccessible boron compounds e.g. diborane compounds[2g][24], boranes with B=C[25], B=N[26] and B=P[27] bonds. ^{13}C chemical shifts for compounds similar to **2a** have been analyzed in some detail. They are in line with an ethynyl group without electron deficit[2d][2e][2f][2h][28]. These experimental findings corroborate our theoretical result that the boron atom avoids to accept π-electrons from the C≡C triple bond provided a good π-donor like the amino group in **2a** is present. A direct comparison between two weak π-donors is possible in compound **2b** (Table 4). In **2b**, four π-electrons are distributed over five π-AOs and we obtained 11025 AO determinants.

The results in Table 4 highlight the preference of the four π-electrons for the vinyl and the ethynyl groups (83.5%). The boron atom accepts only weakly a π-electron from the vinyl group by forming the boron−carbon double bond $H_2CCH{=}BHCCH$ [5.6%, compared to 5.2% in vinylborane (**3b**)]. Electron donation from the ethynyl group by forming an $H_2CCHBH{=}CCH$ boron−carbon double bond is even less favourable (3.5%). The various singlet biradical bonding schemes appear only with small weights. However, *the vinyl group is a slightly better π-electron donator than the alkynyl group.* Our conclusions are substantiated by the optimized carbon−carbon bond lengths for the vinyl and the ethynyl group which are 1.3300 Å and 1.1921 Å, respectively. They are close to the bond lengths of ethylene (1.337

Table 4. Covalent bonding schemes and their weights for the ethynyl(vinyl)borane (**2b**); the boron atom accepts only weakly π-electrons; the π-donation is slightly stronger from the vinyl than from the ethynyl group



Å)[19] and of acetylene (1.204 Å)[17], respectively. The boron–carbon bonds $H_2CCH{-}BHCCH$ and $H_2CCHBH{-}CCH$ in **2b** have lengths of 1.5491 Å and 1.5358 Å, respectively. Again, these values reflect the trend imposed by the different hybridization states of the carbon atoms.

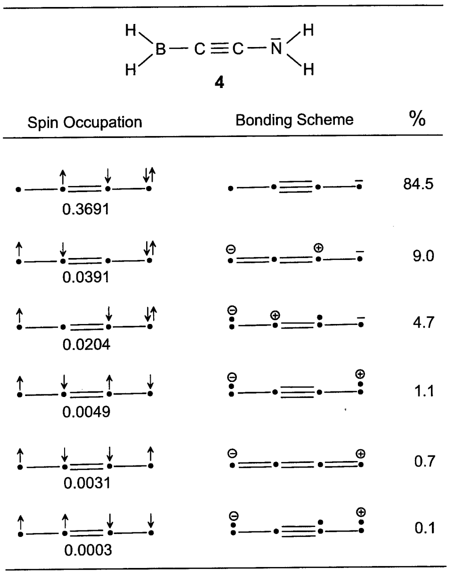
Conclusions from the Expansion Results

The following picture emerges consistantly from the above expansion results. The lone-pair electrons of an amino group are donated efficiently into the empty π-orbital of boron. Adjacent carbon–carbon double or triple bonds are an order of magnitude weaker π-electron donors. In the absence of a good π-electron donor, however, the boron centre excerts its full Lewis acidity and the extent of B=C bonding is doubled but still remains small (2.2% in **2a**, Table 3, vs. 4.4% in **1a**, Table 1). In the presence of a comparably potent π-donor, e.g. the vinyl group, an ethynyl group will only excert half of its maximal electron-donating ability (3.5%, Table 4). Moreover, the weights show that the vinyl group is more electron-donating than the ethynyl group (5.6% vs. 3.5%, Table 4). This is corroborated by ^{13}C-NMR data on dimesitylboranes[29].

Electron Donation from an NH_2 to the BH_2 Group Mediated by an Alkynyl Group

2-Aminoethynylborane (**4**) is of push-pull type and the electron transfer is mediated by the π-electrons of the alkynyl group perpendicular to the molecular plane. Due to this intramolecular electron transfer a partial $H_2B{=}CCNH_2$ double bond is expected. In order to verify this assumption we expanded a restricted MO determinant[6] for the four π-electrons and we obtained 4356 AO determinants. Subsequently, we derived covalent local spin occupations and their weights by sampling weights of the corresonding AO determinants. The results are compiled in Table 5.

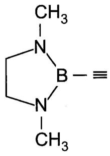
Table 5. Covalent bonding schemes and their weights for the "push-pull" 2-aminoethynylborane (**4**)



Spin occupation four is characterized by complete spin alternation and its weight can contribute to the weights of several bonding schemes. Again, we attributed the total weight solely to the bonding scheme conceived to have the lowest energy. Table 5 shows that the four π-electrons prefer the alkynyl group and the nitrogen atom by forming a lone pair (84.5%). The weight for the second bonding scheme illustrates that the boron atom accepts also a π-electron from the ethynyl group by forming a partial boron–carbon double bond (9.0%) but two π-electrons remain at nitrogen as a lone pair. This result accords with the notion that the coulomb repulsion between the nitrogen lone pair and the π-electrons of the alkynyl group is important. It is reduced when two alkynyl π-electrons leave the alkynyl group by forming the partial $H_2B{=}CCNH_2$ double bond. A push-pull character of a molecule is frequently described by resonance structures with a maximal number of covalent bonds[30] similar to the fifth bonding scheme of Table 5. Its small weight, however, shows that the formation of a completely delocalized push-pull system is highly unfavourable. The boron–carbon double-bond character in **4** (9.0%) is larger than in **1a** (4.4%). This accords with the computed boron–carbon bond lengths which are 1.4932 Å in **4** and 1.5250 Å in **1a**. Nöth et al. synthesized compound **D**[31] (see Scheme 5) which contains the "push-pull" part of model compound **4**. B=C π-bonding in **D**, however, is diminished by the two amino groups at the boron atom.

None of the spectroscopic data [δ ^{13}C, $\delta^{11}B$, ν_{CC} (IR)] of **D** are significantly different from other ethynylboranes.

Scheme 5: An alkynylborane which contains a push-pull entity; the push-pull character is dwarfed by two amino substituents at the boron centre



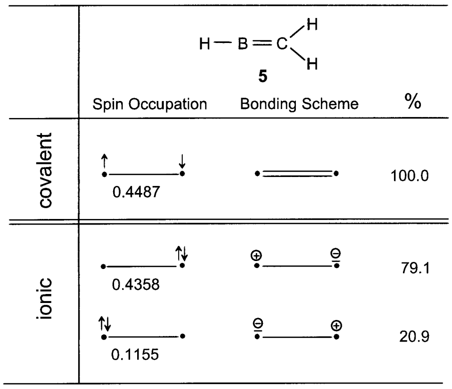
D

These findings are in line with the analysis for the model compounds **2a** and **3a**. The boron atom in **D** accepts lone-pair electrons from the adjacent nitrogen atoms but not from the ethynyl group. Accordingly, **D** could not be photodimerized to form a push-pull-stabilized cyclobutadiene[30].

Strong Carbon−Boron Double Bonds

So far we have concentrated on the formation of a partial B=C double bond through π-donation from an adjacent ethynyl or vinyl group. We will now use our expansion technique to investigate two compounds with strong B=C double bonds. In methyleneborane (**5**), the sp-hybridized boron atom provides itself one π-electron and a full boron−carbon double bond is present[32]. In contrast, the methylborane carbanion (**6**) will develop a partial (but probably strong) B=C double bond because a π-electron of the negatively charged carbon centre may be transferred to the empty π-orbital of the sp^2-hybridized boron atom. We expanded the restricted MO determinants for the two π-electrons and sets of 36 AO determinants were obtained. Weights for covalent and ionic local spin occupations were obtained by sampling the weights of the corresponding AO determinants (Tables 6 and 7).

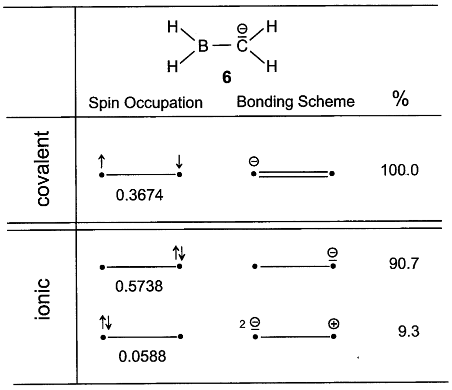
Table 6. Bonding schemes and their weights for methyleneborane (**5**)



	Spin Occupation	Bonding Scheme	%
covalent	•↑———↓• 0.4487	•═══•	100.0
ionic	•———⇅• 0.4358	⊕•———•⊖	79.1
	⇅•———• 0.1155	⊖•———•⊕	20.9

The only covalent bonding scheme for **5** evolves with a weight of 44.9% when referred to the weights of all bonding schemes. This value is close to 50% which is the weight for the covalent bonding scheme of ethylene when a restricted MO determinant is expanded[33]. The proximity of both values shows that a pronounced boron−carbon π-bond is present in methyleneborane (**5**). The π-bond in $H_2C{=}BH$ is further substantiated by its computed short bond length of 1.3741 Å. The weights for the two ionic bonding schemes show that the π-bond is polar and the electrons prefer the carbon atom. As mentioned before, when an uncorrelated wavefunction is expanded the absolute weights for all ionic bonding schemes will be overestimated at the expense of the covalent bonding schemes. Table 6 exemplifies for compound **5** that the covalent weight is only 10% smaller than the covalent weight in ethylene.

Table 7. Bonding schemes and their weights for the methylborane carbanion (**6**)



	Spin Occupation	Bonding Scheme	%
covalent	•↑———↓• 0.3674	⊖•═══•	100.0
ionic	•———⇅• 0.5738	•———•⊖	90.7
	⇅•———• 0.0588	2⊖•———•⊕	9.3

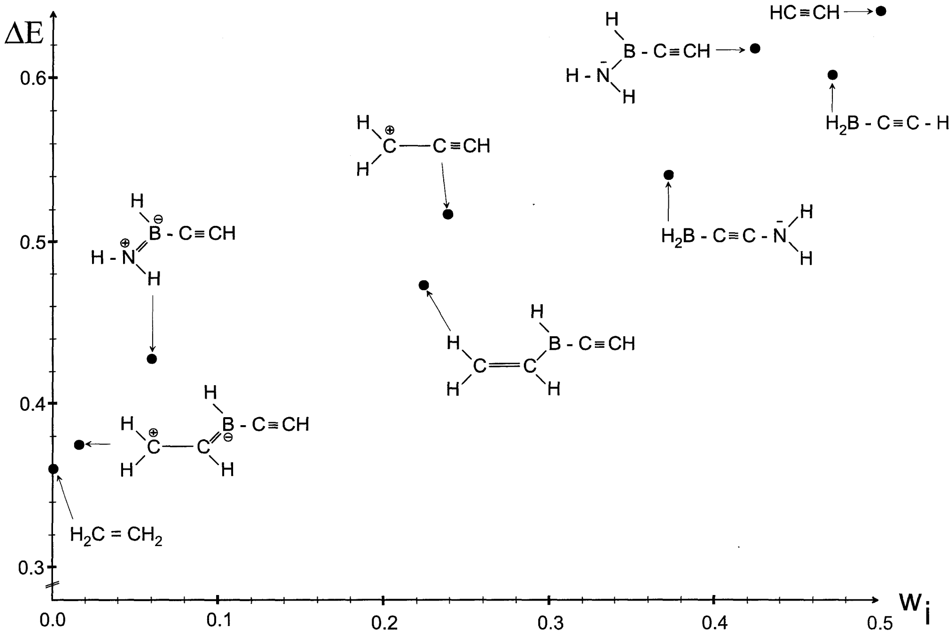
Evidently, the boron−carbon bond in **6** possesses significant double-bond character (36.7%). This supports the notion that the sp^2-hybridized boron atom efficiently stabilizes the carbanion centre by forming a partial double bond accompanied by a delocalization of the negative charge. A decrease of the negative charge at the sp^2-hybridized carbon atom is supported by ^{13}C-NMR data: For the methylene carbon atom in a dialkylmethyleneborane anion, a ^{13}C chemical shift of $\delta = 54.5$ was observed[34]. This value suggests a significant deshielding of the methylene carbon atom as a consequence of π-electron delocalization. The B=C double-bond character in **6** is also corroborated by the calculated B−C bond length of 1.4446 Å. This value is much smaller than 1.5250 Å which is the boron−carbon bond length in the alkynylborane **1a**. Moreover, a rotation about the B−C bond leads to a local minimum located 26.7 kcal/mol higher in energy than the planar ground state[35].

Computed Weights and Bond Strength

We have applied weights for localized bonding schemes to evaluate the electron-accepting ability of a boron atom bonded to a π-electron-donating group. A large electron attraction is indicated by a large weight for those covalent bonding schemes which describe a π-bond between the boron atom and the electron-donating group. Thus, we assume that the weights for covalent bonding schemes are obtained in the correct relative order. The weights were obtained by expanding a restricted closed-shell MO determinant for the π-electrons into the set of AO determinants. It is well known that expanding such an uncorrelated MO determinant leads to covalent and ionic weights which are too small and too large, respectively[15]. Expansions of correlated MO wave functions, however, produce correct weights[36]. In this section we show that even the uncorrelated restricted MO determinant leads to meaningful covalent weights whose relative magnitudes correlate with bond strengths.

Consider the leading bonding scheme RS1 for **1a**. It locates two π-electrons into the C=C bond region and an alkynyl group is indicated. A large or a small weight for this bonding scheme designates the triple bond as strong or weak, respectively. A measure for the C≡C triple-bond strength at the equilibrium geometry is the energy increase ΔE which occurs when the bond is elongated by an amount ΔR (see Appendix for details). Figure 1 correlates this energy increase ΔE with the computed weights for all covalent bonding schemes of Tables 1−7 with at least one C≡C triple bond.

Figure 1. A correlation between weights for bonding schemes and computed ΔE values; bonding schemes are considered where at least one C≡C triple bond occurs

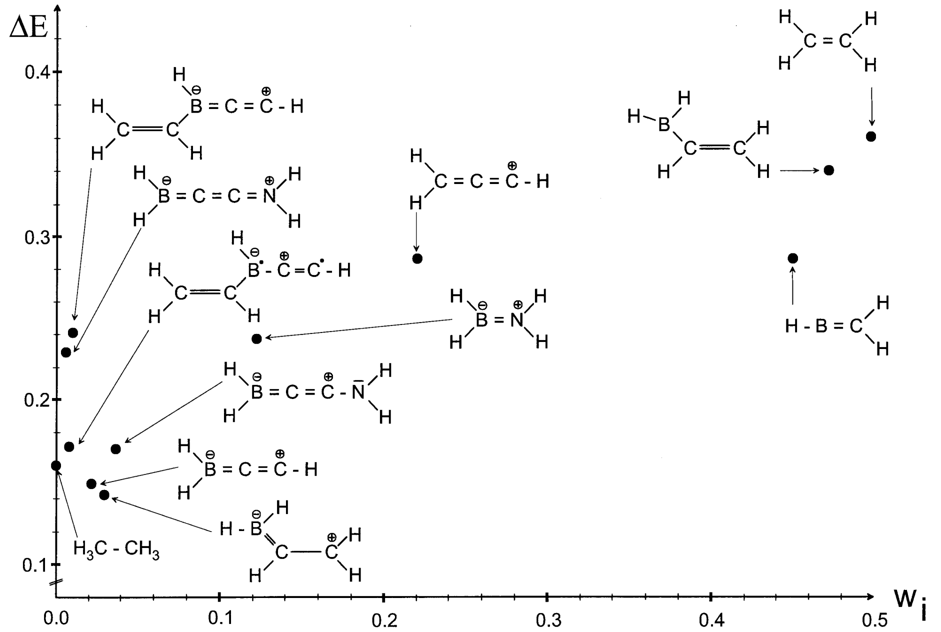


On the abscissa their weights are given and on the ordinate the corresponding energy increases ΔE are recorded (computed by means of eq. 5 or eq. 9). The needed second derivatives were obtained at the RHF/6−311G** level of theory as described in "Computational Methods". Figure 1 shows that a correlation exists between ΔE values and the weights for covalent bonding schemes. The entry for acetylene (0.5) confines the rightmost upper end of the correlation line. In our context, ethylene can be considered as an acetylene molecule devoid of one π-bond and we attribute weight zero to ethylene. Its entry marks the leftmost lower end of the correlation line. The fact that acetylene and ethylene are members of the correlation line supports a qualitative weight rationalization. All leading covalent bonding schemes for **1a**, **2a**, and **4** locate two π-electrons into the alkynyl groups. Their entries appear near acetylene, which shows that the π-systems in **1a**, **2a** and **4** are acetylene-like. The leading covalent bonding scheme for **2b** locates two π-electrons into the alkynyl but also two π-electrons into the vinyl group (see Figure 1). Its intermediate weight shows that both groups are relevant. At the leftmost lower part of the correlation line, different covalent bonding schemes of **2a** and **2b** appear. They attribute two π-electrons to the ethynyl group and two π-electrons to the N=B and C=B double bonds, respectively. Their small weights, however, indicate that an occurrence of N=B, and C=B double bonds in combination with an ethynyl C≡C triple bond is unfavourable in **2a** and **2b**. The small weights suggest the notion that the ΔE values for these bonding schemes are determined by the bonds which remain when the π-bonds of the bonding schemes are not drawn. Thus, the small ΔE values should be determined by the strongest remaining bond which is the double bond of the alkynyl groups and hence appear near the value for ethylene (see Figure 1).

A similar treatment was carried out for bonding schemes with double bonds. On the abscissa of Figure 2, weights are recorded for covalent bonding schemes of Tables 1−7 which comprise at least one double bond.

The corresponding ΔE values are given on the ordinate. Figure 2 shows that a fair correlation between weights and ΔE values exists. The ethylene entry confines the righmost upper part of the correlation line with a weight of 0.5 and ethane (attributed weight zero) delimits the leftmost lower part of the correlation line. The dominating covalent bonding schemes for **3b** and **5** appear near the ethylene entry (see Figure 2). This proximity shows that the π-bonds in **3b** and **5** are similar to the strong π-bond in ethylene. The bonding schemes for the $H_2C{=}CCH$ double bond in **1b** and the $H_2N{=}BH_2$ double bond in **3a** appear at the middle of the correlation line. This intermediate location, between ethylene and ethane, shows that these π-bonds have a significant single-bond character. The covalent bonding schemes for C=B double bonds in **1a**, **3b** and **4** are located at the lower left part of the correlation line. Their small weights show that drawing of double bonds is unjustified. These boron−carbon bonds are in essence single bonds and the entries appear near ethane. The location of two π-electrons

Figure 2. A correlation between weights for bonding schemes and computed ΔE values; the bonding schemes comprise at least one C=C double bond



into the vinyl group combined with a singlet biradical arrangement of the remaining two π-electrons is unfavourable for **2b**. The corresponding bonding scheme appears with a small weight (see Figure 2). At the lower leftmost part of the correlation line, deviations are found for two covalent bonding schemes of **2b** and **4**. They both locate four π-electrons into two π-bonds. However, their small weights show that they should be regarded as *two* single bonds. This may explain the deviation from the correlation line where small ΔE values are determined by only *one* single bond.

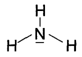
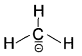
Discussion and Conclusion

In the previous sections we have evaluated the π-electron-accepting ability of an sp^2-hybridized boron atom bonded to a π-electron-donating entity. The π-electron-attraction can be viewed as an intramolecular π-electron transfer. It leads to a partial B=X double bond where X is an atom of the electron-donating substituent. This double-bond character increases in the sequence of model compounds **1a** < **3b** < **3a** < **6**. Our analysis is rooted in the framework of valence-bond theory. An alternative way, however, is to analyse the π-bond character of the B=X bonds by means of the qualitative perturbational approach in terms of fragment molecular orbitals[38]. In the following we show that a correlation between computed weights and quantities based on the fragment-orbital approach exists. This correlation leads to an elucidation of factors which are responsible for the extent of the B=X double-bond character.

Consider the parent ethynylborane (**1a**) where an intramolecular π-electron transfer may occur from the alkynyl group to the BH_2 group. The acceptor (A) fragment orbital is the lowest unoccupied molecular orbital (LUMO) of the borane BH_3. The donor (D) orbital is one of the degenerate π-orbitals of acetylene. Electron transfer occurs within the model compound **1a** which can be viewed as donor acceptor complex (DA). The π-electron transfer transforms the π-orbital of D into the π-orbital of (DA). This occurs by mixing the LUMO of A into the π-orbital of D[38]. An efficient π-electron transfer is manifested by an π-orbital energy in (DA) which is significantly lower than in D[38]. For model compounds **1a**, **3b**, **3a**, **1b** and **6** the operation of this concept is illustrated in Table 8.

In the first column the computed orbital energies of the acceptor fragment orbitals are recorded. These are the LUMOs of BH_3 and of CH_3^+. In the third column the energies of the donor fragment orbitals of the reference donor molecules D are given. Electron transfer in the model compounds (DA) leads to new π-orbitals and their computed MO energies are given in column two. The energy differences ΔE between the π-orbital energies in (DA) and (D) are recorded in column four. The ΔE values show the intramolecular electron transfer increases in the sequence **1a** < **3b** < **3a** < **6**. This ordering accords with the weights for the corresponding covalent bonding schemes. However, the ΔE value for compound **1b** is far too large and incompatible with the intermediate weight for the covalent bonding scheme. The donor orbitals for the substituted boranes are energy lowered only by mixing in the acceptor orbitals of BH_3 and the overall net charges of (D) and (DA) are identical. In **1b**, however, a positive charge is present which is absent in the donor fragment (D). This leads to an additional energy lowering of the donor π-orbital and the ΔE value is exaggerated. A better interpretation is given in the following by interrelating computed weights to quantities derived from the fragment molecular orbital approach. Any bonding scheme for the B=X double bonds is charcterized by a definite expansion coefficient c_i (see eq. 1). For the

Table 8. The fragment orbital approach as applied to a selection of model compounds; they are considered as donor acceptor molecules (DA) where a π-electron donation occurs from the donor fragments D to the acceptors fragments A; the relevant MO energies ε and the energie decreases ΔE are given

A	(AD)	D	ΔE	$\frac{1}{\varepsilon_D{}^o - \varepsilon_A{}^o}$	lg $\frac{\Delta E}{\varepsilon_D{}^o - \varepsilon_A{}^o}$
BH_3 ε_5 =0.06701 (LUMO)	$H_2B-C\equiv CH$ ε_g = -0.42235	$HC\equiv CH$ ε_7 = -0.41440	-0.00795	-2.0772	-1.782
	$H_2B-CH=CH_2$ ε_{11} = -0.39237	$H_2C=CH_2$ ε_8 = -0.37678	-0.01559	-2.2533	-1.454
	$H_2B-\bar{N}H_2$ ε_8 = -0.43956	 ε_5 = -0.38496	-0.0546	-2.2125	-0.918
	$H_2B-\overset{\ominus}{\bar{C}}H_2$ ε_8 = -0.06231	 ε_5 = 0.03434	-0.09665	-30.6091	0.471
$CH_3^{\oplus}$ ε_5 = -0.28526 (LUMO)	$H_2C=C=\overset{\oplus}{C}H$ -0.70486	$HC\equiv CH$ ε_7 = -0.41440	-0.29046	-7.7435	0.352

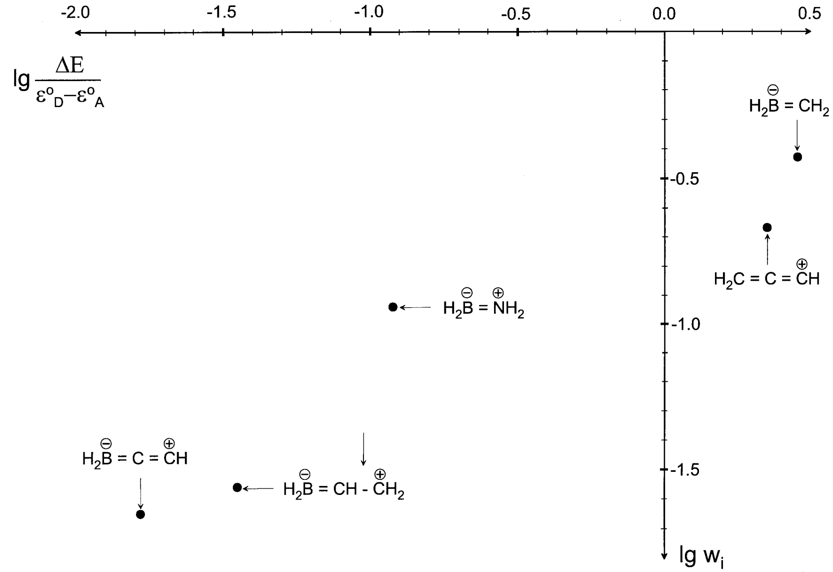
molecules in Table 8, c_i is simply the product between the π-MO coefficients $c_{\mu\pi}$ and $c_{\nu\pi}$.

$$c_\iota = c_{\mu\pi}c_{\nu\pi} \qquad (3)$$

Here, μ and ν refer to an AO of boron and of the adjacent atom X, respectively. The boron coefficients $c_{\mu\pi}$ are much smaller than the coefficients $c_{\nu\pi}$ for atom X. Moreover, $c_{\nu\pi}$ can be reasonably approximated by the unperturbed MO coefficient of the donor orbital. The small boron coefficients $c_{\mu\pi}$, however, are determined in the perturbational fragment approach by a first-order improvement of the donor MO[38]. This improvement is proportional to a first-order coupling integral divided by the energy difference between the donor and the acceptor orbital, namely $(\varepsilon_D - \varepsilon_A)$[39]. Weights w_i are proportional to the squares of the expansion coefficients c_i (see eq. 2). Therefore, the w_i should correlate linearly with a quantity which is the square of the first-order coupling integral divided by the square of $(\varepsilon_D - \varepsilon_A)$. The computed ΔE values of Table 8 can be considered as second-order perturbation energies[40]. The analytic form of the second-order perturbation energies[40] and the above reasoning leads us to conclude that the w_i values should correlate linearly with ΔE divided by $(\varepsilon_D - \varepsilon_A)$. The logarithm of the $\Delta E/(\varepsilon_D - \varepsilon_A)$ values are recorded in the last column of Table 8. Figure 3 shows that they correlate reasonably with the logarithms of the w_i values.

This correlation leads immediately to an explanation of the relative ordering of weights in terms of properties of the fragment orbitals. A small weight for the B=X double bond is expected provided the ΔE values are small and the energy difference $(\varepsilon_D - \varepsilon_A)$ is large. This situation holds for ethynylborane (**1a**) and vinylborane (**3b**). Large ΔE values supplemented by a small energy difference $(\varepsilon_D - \varepsilon_A)$ determine large B=X weights. This is valid for the ethynyl carbocation

Figure 3. A correlation between bonding-scheme weights and a quantity based on the fragment molecular orbital approach



1b and the borane carbanion **6**. Aminoborane (**3a**) represents an intermediate case. Thus, a large B=X double-bond character is expected provided the donating fragment has a low π-electron ionization potential. This is certainly true for the carbanion fragment in **6**. The π-electron ionization potential of acetylene (11.4 eV)[41] and ethylene (10.5 eV)[41] are larger and the B=C double-bond character in **1a** and **3b** is rather small. Due to the ionization potentials, however, the B=C double-bond character in **3b** should be slightly larger than in **1a**. This accords with the corresponding weights which are 4.4% in **1a** and 5.2% in **3b**. Moreover, the extent of the double-bond character is also determined by the energy of the acceptor orbital. The high energy of the BH_3 acceptor orbital implies a small weight for the B=C double bond in ethynylborane (**1a**). On the contrary, the low energy of the acceptor orbital of CH_3^+ leads to a rather large weight for the C=C double bond in **1b**. The derived qualitative explanation holds also for the π-bond present in a planar borylphosphane H_2B-PH_2. The optimized geometry of H_2B-PH_2 is characterized by a pyramidal phosphanyl group and the lone pair at the PH_2 group is oriented away from the BH_2 group. Therefore, only a weak B=P π-bond is present in H_2B-PH_2 at the equilibrium geometry[42]. However, computational results at a *planar* C_{2v} geometry of H_2B-PH_2 indicate a B=P bond slightly *stronger* than the B=N bond in **3a**[43]. This finding is in line with the concepts determining the correlation line of Figure 3. The 3p electrons at the planar PH_2 fragment have a lower ionization potential than the 2p electrons at the NH_2 fragment. Consequently, the weight for the B=P bond should be larger than the weight for the B=N bond.

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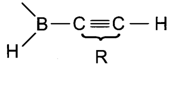
Appendix

Consider a bonding scheme with one bond of length R (exemplified for **1a** in Scheme 6).

Scheme 6. A bonding scheme where only one π-bond is indicated; the only bond parameter is the bond length R



The energy E at a bond length R, elongated by ΔR, is given up to second order in ΔR by

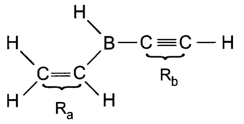
$$E(0+\Delta R)=E(0)+\left(\frac{dE}{dR}\right)^0\Delta R+\frac{1}{2}\left(\frac{d^2E}{dR^2}\right)\Delta R^2+.. \quad (4)$$

If we assume an optimized geometry for **1a**, the first derivative in eq. 4 vanishes. Furthermore, we apply a reference elongation with a squared norm of unity. Thus, ΔR^2 is unity and the energy increase ΔE is given by

$$\Delta E = E(0+1)-E(0)=\frac{1}{2}\left(\frac{d^2E}{dR^2}\right)^0 \quad (5)$$

We see, ΔE is given by half of the curvature when the reference elongation is applied. A representative covalent bonding scheme for two π-bonds is the leading scheme for the ethynyl(vinyl)borane (**2b**) represented in Scheme 7.

Scheme 7. A bonding scheme where two π-bonds are indicated; the two bonds have the bond lengths R_a and R_b



It locates four π-electrons into two π-bonds such that a C≡C triple and a C=C double bond is formed. A measure for their combined bond strength is the energy increase resulting when the two bonds are stretched by ΔR_a and ΔR_b (see Scheme 7). The energy up to second order in ΔR_a and ΔR_b at the distorted geometry is given by eq. 6.

$$E(0+\Delta R_a,0+\Delta R_b)=E(0,0)+\frac{1}{2}\left(\frac{\delta^2E}{\delta R_a^2}\right)^{00}\Delta R_a^2+\frac{1}{2}\left(\frac{\delta^2E}{\delta R_b^2}\right)^{00}\Delta R_b^2+\ldots \quad (6)$$

Here, we have applied the Taylor expansion for a function depending on two parameters[37]. The expansion is simplified by the vanishing of the first derivatives implied by the use of optimized geometries. Moreover, we neglected the mixed second derivatives. This is suggested by the fact that the double and the triple bonds are well separated. A coupling between the two bonds should be negligible. Again, a reference elongation is chosen such that the squared norm of the elongation vector is unity. Thus, we have

$$\Delta R_a^2+\Delta R_b^2=1 \quad (7)$$

Moreover, we partition the elongations such that eq. 8 holds.

$$\Delta R_a^2=\Delta R_b^2=\frac{1}{2} \quad (8)$$

Based on these assumptions, we obtain an energy increase ΔE given by eq. 9.

$$\Delta E=E\left(0+\sqrt{\frac{1}{2}},0+\sqrt{\frac{1}{2}}\right)-E(0,0)=\frac{1}{4}\left[\left(\frac{\delta^2E}{\delta R_a^2}\right)^{00}+\left(\frac{\delta^2E}{\delta R_b^2}\right)^{00}\right] \quad (9)$$

The ΔE given by eq. 5 and eq. 9 are based on a different number of bond elongations, namely one and two, respectively. The squared norm of both elongations, however, is equal and unity. This property permits us to compare bonding schemes with a different number of bonds by computing ΔE values. Our notion is that covalent bonding schemes with large (small) weights indicate strong (weak) bonds and they should be characterized by large (small) ΔE values. In Figure 1, weights for bonding schemes and ΔE values are correlated.

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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