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Theoretical analysis of the internal rotation in aminoborane and borylphosphine

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Abstract. Using a recently proposed orbital deletion procedure and the block-localized wavefunction method, the rotational barriers in H_2BNH_2 and H_2BPH_2 are analyzed in terms of conjugation, hyperconjugation, steric effect and pyramidalization. With the zero-point energy corrections, the π-binding strengths in the planar H_2BNH_2 and H_2BPH_2 are both around 20 kcal/mol at the HF level using the $6\text{-}311 + G^{**}$ basis set. With the deactivation of the π atomic orbitals on the boron atom and the evolution from a planar structure to a 90°-twisted structure, the steric repulsion between the B—H bonds and the N—H or P—H bonds is relieved and moreover, the negative hyperconjugation from the lone electron pair or pairs on the nitrogen or phosphorus atoms to the antibonding orbital $\chi^*_{BH_2}$ of the BH_2 group stabilizes the twisted structure by 7.4(8.8) or 4.0(5.0) kcal/mol at the HF/6-31G*(6-311 + G**) level. However, the repulsive interaction between the lone pair(s) and the two BH σ bonds is so prominent that the overall steric effect contributes 20.3(22.9) and 19.3(19.8) kcal/mol to the rotational barriers in H_2BNH_2 and H_2BPH_2 with the 6-31G*(6-311 + G**) basis set. The present techniques and analyses may also give some clues to justify the parameterization in the empirical molecular mechanics methods.

Key words: Conjugation – Hyperconjugation – Orbital deletion procedure – Block-localized wavefunction method

1 Introduction

Among the aliphatic boron-nitrogen compounds, aminoborane (H_2BNH_2), formed in the thermal decomposition of H_3BNH_3 [1], has received extensive theoretical

[2–23] and experimental [24–28] attention due to its importance as a building block for complex aminoboranes. All studies have confirmed the planarity of H_2BNH_2 and the existence of a BN partial double bond. The π bonding between the nitrogen and the boron atoms also makes H_2BNH_2 well known for its hindered rotational barrier. Thus, H_2BNH_2 is not only isoelectronic but can also be considered an analogue of ethylene. However, controversies exist regarding the degree of π bonding (Ref. [18] and references therein). When the BH_2 group is attached to the amine group, the lone electron pair on the nitrogen atom may effectively interact with the vacant p_π atomic orbital on the boron atom and result in dative N→B π bonding. Since there is no unique way to evaluate the π-bond strength either theoretically or experimentally, a frequently used method is to measure the π interaction using the magnitude of the rotational barriers in the normal conformations of molecules. The contributions of other factors, such as steric and hyperconjugation effects, to the rotational barriers are not considered in such approaches.

Another analogue of ethylene is borylphosphine (H_2BPH_2). Although only a few studies [14, 22, 29–33] have been conducted, it is well recognized that the ground state, in contrast to that of H_2BNH_2, is nonplanar with a highly pyramidal phosphorus atom. Based on the analysis of bond lengths and bond orders, Allen et al. [30] suggested that there is substantial B—P double-bond character in the planar H_2BPH_2 but much less double-bond character in the nonplanar conformation. Later, Allen and Fink [31] studied the B—N and B—P π-bond energies, which are assessed as the energy difference between the planar conformation and the 90°-twisted conformation of H_2BXH_2 (X = N, P), and found that the B—P π bond is actually somewhat stronger than the B—N π bond. This is quite similar to the conclusion made by Schade and Schleyer [34] that "planarized phosphino groups are good-to-excellent p_π donors, sometimes comparable to amines."

Based on classical valence bond theory [35], the dative bond in H_2BXH_2 can be described by the following two resonance structures

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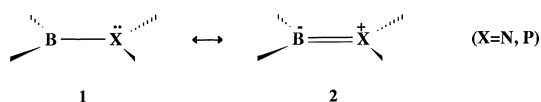
Although the above description was criticized [2] since the negative charge is misleadingly assigned to the boron atom while all theoretical population analyses have shown that the boron atom carries some positive charge in H_2BNH_2, we would like to emphasize that the above picture only reflects the partition of π electrons rather than the overall charge distribution. In the first resonance structure **1**, the p_π orbital on boron is strictly empty and the lone pair is completely located on the nitrogen or the phosphorus atom. Thus, we can safely say that structure **1** will prefer a pyramidal nitrogen or phosphorus like NH_3 or PH_3. However, the ionic resonance structure **2**, formed by the π donation from the nitrogen (phosphorus) lone pair(s) to the formally unfilled $2p_\pi$ orbital of the boron center, will tend to make the molecule planar in order to achieve the maximum overlap between π atomic orbitals, which correspondingly guarantees the maximum π-bond strength. Whether the real molecule H_2BXH_2 prefers a planar or nonplanar structure will depend on the competition between the π-bond strength and the pyramidalization ability.

To shed some light on the chemical bonding mechanism and the origin of the hindered rotational barriers in H_2BNH_2 and H_2BPH_2, we have undertaken a step-by-step study of the rotation process using a recently proposed orbital deletion procedure (ODP) [36, 37] as well as the block-localized wavefunction (BLW) [38]. The latter is a generalization of the former. In this procedure, the π-bond strengths in B—N and B—P are evaluated and compared to each other at the ab initio level.

2 Methodology

Generally the delocalization energy can be defined as the energy difference between the delocalized wavefunction and a strictly localized wavefunction. The delocalized wavefunction can be obtained with any method in which single-electron functions (or molecular orbitals in the framework of molecular orbital theory) are expanded in the whole space of primitive basis functions. The localized wavefunction, on the other hand, is used to describe the hypothetical reference where electrons are confined to some physical zones in the molecules. Examples and a discussion of this subject can be found in our recent publications [39]. In the cases of H_2BXH_2 (X = N, P), the delocalization energy (or π-bonding energy in the planar conformation and the hyperconjugation energy in the staggered conformation) is the energy difference between the delocalized case and the strictly localized case: the latter corresponds to resonance structure **1**, where the p_π orbitals of boron are completely vacant. Thus, we can perform ODP calculations where the p_π (or d_π if d polarization functions are employed) atomic orbitals centered on the boron atom are excluded from the space of basis functions [36, 37]. Since none of the standard quantum chemistry software can perform such calculations, we have slightly modified the GAUSSIAN 94 program [40]. In order to make the selected basis functions vanish in the occupied molecular orbitals, we simply set their one-electron integrals to a very high positive value (e.g., 50000 a.u.) and assign zeros to their overlap integrals with all other basis functions. Consequently, these orbitals' coefficients in the occupied molecular orbitals become negligible and do not make any noticeable contribution to the molecular energy.

This ODP method suffers from two drawbacks. First of all, it can presently only be applied at the HF level. Secondly, the local symmetry should be C_s (e.g., the trigonal-bonded boron lies in the symmetry plane and is of sp^2 hybridization mode). Fortunately, both drawbacks are acceptable in the present systems since electron correlation contributes only little to the rotational barriers in H_2BXH_2, and the restriction of H_2BX (X = N, P) in the same plane (note: BXH_2 may be pyramidal) also increases the energy by a trivial amount (less than 0.3 kcal/mol, see later). The advantage, nevertheless, is very significant since we can even optimize the strictly localized molecular structures using the GAUSSIAN 94 program. Thus, the impact of electronic delocalization on both the molecular energy and the molecular structure will be manifested distinctly.

To check whether a more flexible basis set would alter our analysis, we optimized all structures at the HF level with the 6-31G* and 6-311 + G** basis sets [41, 42]. Vibrational analyses were performed to identify the nature of each conformation. Each energy term was further corrected for the zero-point energy (ZPE), which was scaled by 0.89 [43]. All calculations apart from those we especially point out in the text were performed using the GAUSSIAN 94 program [40].

3 Results and discussion

3.1 Aminoborane

In the planar structure π conjugation exists while in the staggered structure there is hyperconjugation. Generally, the rotational barrier around the B—N bond will be affected by four factors: conjugation, hyperconjugation, steric effect and pyramidalization. Accordingly, the rotating process can be decomposed into the following four successive steps.

Step 1: Deactivate the π conjugation. Based on the optimization result of the planar aminoborane **1a** (Table 1), which is the ground state, we reoptimized the geometry of its corresponding localized structure **1b** using the ODP method. In **1b**, the π atomic orbitals centered on the boron atom have been deactivated, i.e., these orbitals have no occupation. The energy change from **1a** to **1b** is the reverse of the theoretical resonance energy as originally defined in valence bond theory [35, 39]. We denote this energy term as ΔE_1.

Step 2: Rotate the amine group to the 90°-twisted structure **1c** while the π orbitals on boron are still empty. During this step, the energy variation results mainly from the steric effect ($\Delta E_2'$) between the BH_2 group and the NH_2 group. The BN bond separation is increased in this step. However, the negative hyperconjugation from the nitrogen lone pair n_N to the antibonding orbital of π symmetry $\pi^*_{BH_2}$ in the BH_2 group will also be involved and will stabilize the system by $\Delta E_2''$. The total energy variation from **1b** to **1c** is ΔE_2 (the sum of $\Delta E_2'$ and $\Delta E_2''$). While ΔE_2 can be obtained using the ODP method, the decomposition of ΔE_2 into $\Delta E_2'$ and $\Delta E_2''$ requires a more general method, or the BLW method. At this point a brief discussion on the physical meaning of $\Delta E_2'$ is appropriate. In the present study, $\Delta E_2'$ corresponds to the rotational barrier if we keep the π orbitals on boron strictly vacant and the lone nitrogen pair strictly localized on the nitrogen atom during the whole rotation about the B—N bond. Although it is believed that Pauli repulsion makes the largest contribution to $\Delta E_2'$, other

	$1a^a$	$1b$	$1c^b$	$1d$	$1e^c$
HF/6-31G*					
$R(BN)$	1.389(1.391)	1.435	1.470	1.457	1.471
$R(BH)$	1.193(1.195)	1.188	1.199	1.201	1.197
$R(NH)$	0.996(1.004)	0.992	0.994	0.995	1.007
$\angle NBH$	119.4(118.9)	119.6	121.6	121.7	121.1
$\angle BNH$	123.2(122.9)	123.1	122.9	123.1	110.1
$\angle HNBH$	0.0	0.0	90.0	90.0	57.0
Dipole moment (debye)	1.82	0.38	0.99	1.19	1.64
HF/6-311+G**					
$R(BN)$	1.390	1.442	1.471	1.457	1.469
$R(BH)$	1.192	1.187	1.199	1.200	1.198
$R(NH)$	0.994	0.992	0.992	0.993	1.006
$\angle NBH$	119.4	119.4	121.4	121.5	121.0
$\angle BNH$	123.1	123.0	122.8	123.1	111.0
$\angle HNBH$	0.0	0.0	90.0	90.0	57.9
Dipole moment (debye)	1.66	0.23	0.75	0.94	1.55

[a] The data in parentheses are determined experimentally. See Ref.[28]
[b] If the $n_N \rightarrow \pi^*_{BH_2}$ negative hyperconjugation in **1c** is deactivated, the dipole moment is 0.75 or 0.55 D with the 6-31G* or 6-311+G** basis set
[c] $R(BH)$ and $\angle NBH$ for **1e** are the average values

energetic effects such as the polarization (or reorganization) energy inside the BH_2 group or the NH_2 group as well as the electrostatic interaction between the BH_2 and the NH_2 groups may also contribute to $\Delta E_2'$. Since the individual theoretical formulation for these energy terms in intramolecular interactions is not as well founded as in intermolecular interactions, for the time being we do not attempt to decompose $\Delta E_2'$ and just generally call $\Delta E_2'$ the steric effect.

Step 3: Delocalize the electrons but keep the molecular symmetry unchanged (C_{2v} symmetry with the BN bond as the C_2 axis). In this process of electronic relaxation, $\pi_{NH_2} \rightarrow B(P_\pi)$ hyperconjugation occurs and is expected to change the molecular structure to **1d**. The hyperconjugation will stabilize the system by ΔE_3. Since the π orbitals on the boron atom have been reactivated, their population will not be zero.

Step 4. Relax the molecular structure to **1e**. The nitrogen will tend to pyramidalize since the lone pair on it has a limited chance to be actively and significantly involved in bonding. In this step, the molecular symmetry will be reduced from C_{2v} to C_s. The energy variation ΔE_4 can be assumed to be small with reference to the inversion barrier in NH_3, which is only 5.8 kcal/mol as determined experimentally [44].

The above decomposition scheme is pictorialized in Fig. 1. Obviously, the rotational barrier is the sum of all individual energy terms from ΔE_1 to ΔE_4. All structures from **1a** to **1e** have been optimized and the optimized parameters are listed in Table 1, while the total energies and all energy terms are listed in Tables 2 and 3, respectively. As expected, in every step the most significant variation among the structural parameters is the central BN bond length, which is sensitive not only to the electronic structure but also to the steric effect.

The planar delocalized structure **1a** is the global minimum of the potential energy surface (PES) of H_2BNH_2, and our optimized structure is in excellent agreement with the experimental data. When the π
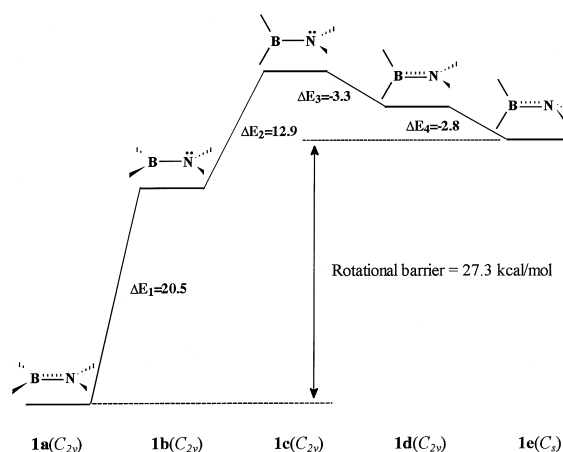

Fig. 1. Decomposition scheme for the rotational barrier in H_2BNH_2 (energy terms are evaluated at the HF/6-311+G** level with the zero-point energy corrections)

conjugation is formally switched off, the BN bond lengthens by 0.046 or 0.052 Å with the 6-31G* and 6-311+G** basis sets, respectively. Correspondingly, the energy increases by 23.0 or 20.5 kcal/mol with the ZPE corrections. In fact, ΔE_1 reflects the π-bonding strength in H_2BNH_2, and the large value indicates that there is considerable electron transfer from the nitrogen lone pair into the formally unfilled $2p_\pi$ orbital of the boron atom. We can speculate that without π bonding the planar structure will be a transition state (Table 2) and the energy minimum will correspond to a pyramidal nitrogen. We can even go further and optimize this structure using ODP by keeping the H_2BN fragment in plane, the resulting structure with the 6-31G*(6-311+G**) basis set is **1f**. However, by comparing **1b** and **1f** we find that the structural difference is very small and the energy difference is less than 0.1 kcal/mol.

1f   **1g**
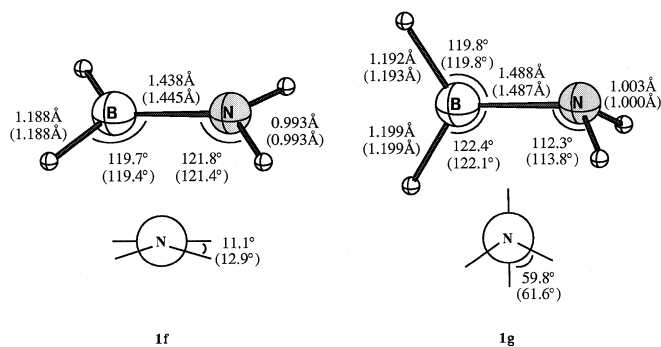
From the localized planar conformation **1b** to the localized staggered conformation **1c**, the energy increases remarkably, namely by about 12.0 kcal/mol (ZPE corrections included). This step includes two factors, the steric effect and the $n_N \rightarrow \pi^*_{BH_2}$ negative hyperconjugation. The steric contribution mainly results from the Pauli exchange, as has been very nicely demonstrated by Goodman's group [45], where the Pauli-exchange repulsion was estimated by the Badenhoop–Weinhold procedure based on the natural bond orbital method [46]. In the present form **1c**, the steric repulsion between the B—H bonds and the N—H bonds is relieved while the steric effect between the nitrogen lone pair and the opposite B—H bonds is dramatically enhanced compared with the case of **1b**. We may recall the simple case of B_2H_4 [36]. The localized staggered B_2H_4 stabilizes the system by 7.1 kcal/mol compared with the localized planar B_2H_4, which is identical to the delocalized planar structure since π electrons do not exist in this case. Taking account of this value and considering further the stabilization originating from the $n_N \rightarrow \pi^*_{BH_2}$ negative hyperconjugation effect ($\Delta E''_2$), we can estimate how strong the repulsion between the lone pair and its opposite B—H bonds is in **1c**. The $n_N \rightarrow \pi^*_{BH_2}$ negative hyperconjugation energy can be evaluated with our recently developed BLW method [38], which is used to construct strictly localized wavefunctions based on the assumption that all electrons and primitive basis functions can be partitioned into several subgroups. In a BLW, each localized molecular orbital is expanded in terms of primitive orbitals belonging to only one subgroup and the molecular orbitals belonging to the same subgroup are constrained to be mutually orthogonal, while those belonging to different subgroups are free to overlap. Thus, it is clear that the ODP method is a special case of the BLW method. If we take H_2BN as the main plane, the HF and ODP wavefunctions for the staggered H_2BNH_2 can be written as

$$\Psi(HF) = \hat{A}(\sigma 1b_1^2 1b_2^2 2b_2^2) \qquad (1)$$

Table 2. Total energies (a.u.) of H_2BNH_2[a]

	HF/6-31G*	HF/6-311 + G*
1a	−81.48910(0)	−81.51930(0)
1b	−81.45152(1)	−81.48536(1)
1c	−81.43099(1)	−81.46293(2)
1d	−81.43518(2)	−81.46750(2)
1e	−81.44219(1)	−81.47312(1)

[a] The number of imaginary frequencies is included in the parentheses

and

$$\Psi(ODP) = \hat{A}(\sigma \pi^2_{NH_2} 1b_2^2 2b_2^2) \quad , \qquad (2)$$

respectively, where σ represents the remaining molecular orbitals of a_1 symmetry and π_{NH_2} is expanded in a subspace of the entire basis, which consists of the basis functions centered on the NH_2 group. The σ molecular orbitals in $\Psi(HF)$ and $\Psi(ODP)$ will be slightly different since they are determined by the self-consistent field steps separately.

To deactivate the $n_N \rightarrow \pi^*_{BH_2}$ negative hyperconjugation effect, we construct a BLW as

$$\Psi(BLW) = \hat{A}(\sigma \pi^2_{NH_2} \pi^2_{BH_2} n_N^2), \qquad (3)$$

where π_{BH_2}, similar to π_{NH_2}, is expanded only in the basis functions of the BH_2 group and n_N is simply an optimum atomic orbital of the nitrogen atom to accommodate the lone electron pair. The π orbitals on the boron atom are still deactivated in Eq. (3) as in $\Psi(ODP)$. Thus, while the energy difference between $\Psi(HF)$ and $\Psi(ODP)$ represents the $\pi_{NH_2} \rightarrow B(p_\pi)$ hyperconjugation energy as defined earlier, the energy difference between $\Psi(ODP)$ and $\Psi(BLW)$ is the $n_N \rightarrow \pi^*_{BH_2}$ negative hyperconjugation energy $\Delta E''_2$. The overall steric effect $\Delta E'_2$ is the difference between ΔE_2 and $\Delta E''_2$ (note that ΔE_2 is positive while $\Delta E''_2$ is negative). The orbitals π_{BH_2} and n_N in Eq. (3) are not orthogonal, although both are orthogonal to all other occupied σ molecular orbitals. The calculated results of the energy contributions to ΔE_2 as well as the overlap integral between n_N and π_{BH_2} are listed in Table 4.

The large steric contribution to the rotational barrier (Table 4) clearly shows the strong repulsion between the lone pair on the nitrogen atom and the BH_2 group. We can expect that the repulsion between the two lone pairs is the dominant feature. This point of view is supported by the case of N_2H_4.[1] If we optimize the planar and the staggered conformations of N_2H_4 at the HF/6-31G* level, the latter will be 22.1 kcal/mol more stable than the former. Surely, electronic delocalization is involved in the above data. With the same geometries, we can screen the electronic delocalization effect by localizing the lone pairs strictly on the two nitrogen atoms using the BLW method. The staggered N_2H_4 is still 10.3 kcal/mol more stable than the planar conformation.

In the next step connecting structures **1c** and **1d**, the direct hyperconjugation between the N—H bonds (forming a π_{NH_2} orbital) and the vacant p_π of the boron atom is very moderate. ΔE_3 is only about −3.3 to −3.6 kcal/mol, which is in good agreement with studies on substituted methyl boranes. The central BN bond shortens by 0.013 Å. As pointed out earlier, the nitrogen lone pair can hyperconjugate with the nearby antibonding orbital $\pi^*_{BH_2}$ and stabilizes the staggered structure by 7.4–8.8 kcal/mol. However, the repulsion between the lone pair on the nitrogen atom and the two

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[1] The HF/6-31G* energies for the plane and the staggered N_2H_4 are −111.116482 a.u. and −111.151778 a.u., respectively. With the same geometries and the same basis set, the BLW energies −111.103129 a.u. and −111.119508 a.u., respectively

Table 3. Energy partition for the rotational barrier (*RB*) in H$_2$BNH$_2$[a]

	ΔE_1	ΔE_2	ΔE_3	ΔE_4	RB
HF/6-31G*	23.6 (23.0)	12.9 (12.0)	−2.6 (−3.6)	−4.4 (−3.6)	29.5 (27.8)
HF/6-311+G**	21.3 (20.5)	14.1 (12.9)	−2.9 (−3.3)	−3.5 (−2.8)	29.0 (27.3)

[a] Energy terms with zero-point energy corrections are included in the parentheses

Table 4. Energy contributions to ΔE_2 (kcal/mol) and the overlap integral $S\langle \pi_{BH_2}|n_N\rangle$ in staggered H$_2$BNH$_2$

|	$\Delta E_2'$	$\Delta E_2''$	ΔE_2	$S\langle \pi_{BH_2}|n_N\rangle$
HF/6-31G*	20.3	−7.4	12.9	0.1602
HF/6-311+G**	22.9	−8.8	14.1	0.1699

σ_{BH} bonds prevails over the attractive hyperconjugation. Thus, the nitrogen in **1d** will prefer to be pyramidal to alleviate the steric repulsion.

The real transition state in the PES of H$_2$BNH$_2$ is **1e**, whose symmetry is C_s. The pyramidalization energy is around −3 kcal/mol. If we deactivate the boron p_π atomic orbitals and reoptimize **1e**, we obtain structure **1g**. The energy difference between **1c** and **1g** is only 3.2–2.0 kcal/mol. These data are somewhat smaller than the experimentally determined inversion barrier of NH$_3$ of 5.8 kcal/mol [44] and imply that there may still be a residual $n_N \rightarrow \sigma_{BH}^*$ hyperconjugation effect.

One may question why the BN bond lengthens while we claim that the steric effect is relieved due to pyramidalization. We believe the main reason should be the change of the hybridization mode of the nitrogen atom, namely from sp^2 in **1d** to sp^3 in **1e**. This conclusion can also be derived from the lengthening of the NH bonds from **1d** to **1f** and in both cases of the BN and NH bonds the variation is of the same magnitude.

In summary, the rotational barrier in H$_2$BNH$_2$ is 27.5 and 27.3 kcal/mol with ZPE corrections at the levels of HF/6-31G* and HF/6-311+G**, respectively. These values are slightly lower than the values obtained at higher levels taking account of electron correlations: the barrier is 31.7 kcal/mol at the MP2(full)/6-31G* level with ZPE correction.

Finally, another interesting aspect is the dipole moment of H$_2$BNH$_2$. In the ground state **1a** the calculated dipole moment is 1.82–1.66 D, compared with the experimental value of 1.844 D [47]. Although all population analyses have shown that the nitrogen carries negative charges while the boron carries positive charges, the polarity of the dipole moment is along the BN axis and is in the direction of B$^-$—N$^+$. We can formally decompose the total dipole moment in the ground state of H$_2$BNH$_2$ into four contributions: $\delta_{BN}(\sigma)$ from the BN σ bond (induction); $\delta_{BN}(\pi)$ from the BN π dative bond; δ_{BH_2} from the BH$_2$ group or the two B—H σ bonds (the hydrogen atoms carry only a little negative charge); and δ_{NH_2} from the NH$_2$ group (the hydrogen atoms carry positive charges). Their directions can be depicted as follows:
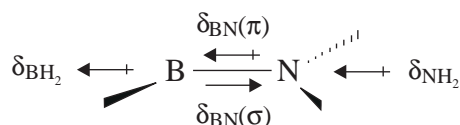
δ_{BH_2}, $\delta_{BN}(\pi)$ and δ_{NH_2} have the same polarity while $\delta_{BN}(\sigma)$ is of the opposite polarity. For the delocalized conformation **1a**, the total dipole moment is $\delta_{BH_2} + \delta_{BN}(\pi) + \delta_{NH_2} - \delta_{BN}(\sigma)$ and is equal to 1.82(1.66) D evaluated at the HF/6-31G*(6-311+G**) level (see Table 1). With the deactivation of p_π orbitals on the boron, $\delta_{BN}(\pi)$ becomes zero and the total dipole moment changes to $\delta_{BH_2} + \delta_{NH_2} - \delta_{BN}(\sigma)$, which is reduced to only 0.38(0.23) D as shown in Table 1 for the localized planar structure **1b**. With the rotation about the B—N bond from **1b** to **1c**, however, although the boron p_π orbitals are deactivated, the $n_N \rightarrow \pi_{BH_2}^*$ negative hyperconjugation and the polarization due to the steric effect will make significant contributions and will increase the dipole moment by about 0.6 D. If we keep the geometry of **1c** unchanged and switch off the electronic delocalization fully using the BLW method, the dipole moment changes to 0.75(0.54) D with the 6-31G*(6-311+G**) basis set, which indicates that the $n_N \rightarrow \pi_{BH_2}^*$ negative hyperconjugation increases the dipole moment by 0.24(0.21) D. Similarly, comparison of **1c** and **1d** reveals that the $\pi_{NH_2} \rightarrow B(p_\pi)$ hyperconjugation will contribute 0.2 D more to the molecular dipole moment.

3.2 Borylphosphine

It is known that the ground state of H$_2$BPH$_2$ is not planar and that it possesses a highly pyramidal phosphorus atom opposite a slightly pyramidal boron atom. Consequently, the initial step for the decomposition of

$$\delta_{BH_2} \longleftrightarrow \overset{\delta_{BN}(\pi)}{\underset{\delta_{BN}(\sigma)}{B \rightleftharpoons N}} \longleftrightarrow \delta_{NH_2}$$
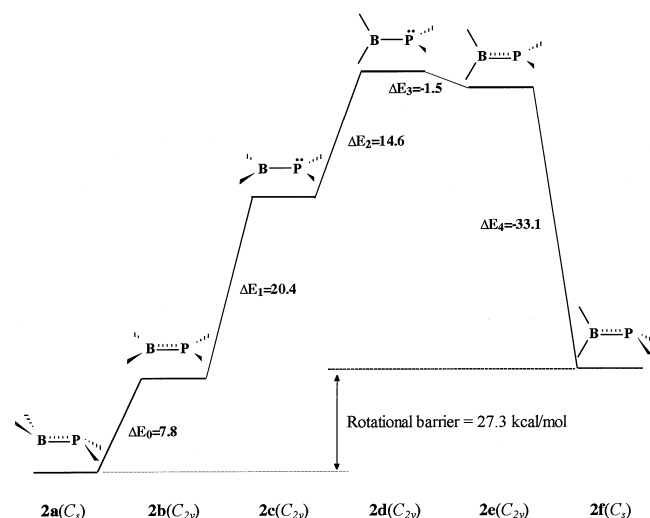

Fig. 2. Decomposition scheme for the rotational barrier in H$_2$BPH$_2$ (energy terms are evaluated at the HF/6-311+G** level with the zero-point energy corrections)

Table 5. Optimized Bond Lengths (Å) and angles (deg) for H_2BPH_2

	2a[a]	2b	2c[b]	2d	2e	2f[c]
HF/6-31G*						
$R(BP)$	1.903	1.808	1.888	1.965	1.961	1.973
$R(BH)$	1.187	1.184	1.181	1.185	1.185	1.188
$R(PH)$	1.399	1.380	1.377	1.377	1.378	1.409
∠PBH	119.9	118.5	118.7	120.3	120.4	120.6
∠BPH	103.0	124.9	123.0	122.5	122.5	95.2
∠HPBH	42.1	0.0	0.0	90.0	90.0	47.2
Dipole moment (debye)[d]	0.91	1.05	−0.96	−0.59	−0.55	1.13
HF/6-311+G**						
$R(BP)$	1.901	1.806	1.892	1.967	1.963	1.973
$R(BH)$	1.187	1.184	1.181	1.185	1.185	1.188
$R(PH)$	1.403	1.384	1.379	1.379	1.380	1.413
∠PBH	119.6	118.3	118.5	120.0	120.1	120.5
∠BPH	103.1	124.8	122.8	122.4	122.4	95.0
∠HPBH	41.8	0.0	0.0	90.0	90.0	47.3
Dipole moment (debye)[d]	0.89	1.14	−1.01	−0.69	−0.65	1.10

[a] The dihedral angles H_2BP and H_2PB are 187.1°(187.0°) and 102.9°(103.5°) with 6-31G*(6-311+G**)
[b] If the $n_P \rightarrow \pi^*_{BH_2}$ negative hyperconjugation in **2d** is deactivated, the dipole moment is −0.67 or −0.77 D with the 6-31G* or 6-311+G** basis set
[c] $R(BH)$ and ∠PBH for **2f** are the average values
[d] The negative values for **2c**, **2d** and **2e** indicate that the dipole moments are along the BP axis and have the polarity of B^+—P^-, in contrast to the polarity of B^-—P^+ in **2b**

the rotational barrier (Fig. 2) of H_2BPH_2 is the planarization from **2a** with the symmetry of C_s to **2b** with the symmetry of C_{2v}; the corresponding energy variation is defined as ΔE_0. The subsequent steps are the same as in the analysis of H_2BNH_2, and the full decomposition scheme is shown in Fig. 2. The optimized bond lengths and angles, the total energies and the energy partition for the rotational barrier are listed in Tables 5–7.

For **2a**, the BH_2 group is only slightly folded and if we place H_2BP in the same plane, the HF energy increases by only 0.26 and 0.25 kcal/mol with the 6-31G* and 6-311 + G** basis sets, respectively. Using ODP, we can evaluate the π conjugation energy $\Delta E'_0$ in **2a** and find that it is only 6.3–6.8 kcal/mol (without ZPE corrections). Compared with the planar conformation **2b**, the B—P and P—H bonds in **2a** are about 0.1 and 0.02 Å longer, respectively. Apparently, this is partially due to the variation of hybridization mode for the phosphorus atom. The significant shortening of the central bond from **2a** to **2b**, however, is due to the stronger π bonding between the boron and the phosphorus atoms. Our results clearly show that the phosphorus atom can form a planar structure with strong π bonds: the π-bonding energy in the planar conformation of H_2BPH_2 is 20 kcal/mol and is in fact as strong as the B—N π bond. This is in accord with previous arguments [34]. Since the energy variation ΔE_2 from **2c** to **2d** is very strong while the $\pi_{PH_2} \rightarrow B(p_\pi)$ hyperconjugation effect ΔE_3 is very weak, the usual measurement [20] to evaluate the π-bond strength using the energy difference between planar H_2BXH_2 and the 90°-twisted H_2BXH_2 leads to large errors.

Similar to the treatment of H_2BNH_2, ΔE_2 can be further decomposed into two terms, namely the steric effect $\Delta E'_2$ and the $n_P \rightarrow \pi^*_{BH_2}$ negative hyperconjugation $\Delta E''_2$. Taking H_2BP as the main plane, we can construct the HF and ODP wavefunctions for staggered H_2BPH_2 as

Table 6. Total energies (a.u.) of H_2BPH_2[a]

	HF/6-31G*	HF/6-311+G**
2a	−367.70403(0)	−367.73661(0)
2b	−367.68992(1)	−367.72394(1)
2c	−367.65850(1)	−367.69195(1)
2d	−367.63408(1)	−367.66843(1)
2e	−367.63408(1)	−367.66843(1)
2f	−367.69004(1)	−367.72261(1)

[a] The number of imaginary frequencies is included in parentheses

$$\Psi(HF) = \hat{A}(\sigma 1b_1^2 1b_2^2 2b_2^2 3b_2^2) \qquad (4)$$

and

$$\Psi(ODP) = \hat{A}(\sigma \pi_{PH_2}^2 1b_2^2 2b_2^2 3b_2^2), \qquad (5)$$

and the BLW wavefunction as

$$\Psi(BLW) = \hat{A}(\sigma \pi_{PH_2}^2 \pi_{BH_2}^2 1n_P^2 2n_P^2), \qquad (6)$$

where π_{BH_2} is expanded with the basis functions centered on the BH_2 group and $1n_P$ and $2n_P$ are two optimum atomic orbitals on the phosphorus atom. While π_{BH_2} is nonorthogonal to both $1n_P$ and $2n_P$, the latter two are orthogonal to each other. Calculation results are listed in Table 8.

By comparing the data in Tables 4 and 8, we can see that the $n_P \rightarrow \pi^*_{BH_2}$ negative hyperconjugation effect in H_2BPH_2 is somewhat weaker than that in H_2BNH_2 but the steric interactions are very close in the two systems. It is well known that the electron repulsive interaction between two atomic orbitals, or more generally between two strictly localized orbitals such as lone pairs [45, 48], is roughly proportional to the square of the overlap integral between these two orbitals. In other words, the larger the square of the overlap integrals, the more electron repulsive force is assumed between the two orbitals. In the present cases of H_2BNH_2 and H_2BPH_2, we

Table 7. Energy partition for the rotational barrier RB in H_2BPH_2[a]

	ΔE_0	ΔE_1	ΔE_2	ΔE_3	ΔE_4	RB
HF/6-31G*	8.9 (8.6)	19.7 (20.3)	15.3 (15.1)	−0.4 (−1.7)	−34.7 (−34.1)	8.8 (8.2)
HF/6-311+G**	8.0 (7.8)	20.1 (20.4)	14.8 (14.6)	−0.4 (−1.5)	−33.6 (−33.1)	8.9 (8.2)

[a] Energy terms with zero-point energy corrections are included in parentheses

Table 8. Energy contributions to ΔE_2 (kcal/mol) and the overlap integrals in staggered H_2BPH_2

	$\Delta E_2'$	$\Delta E_2''$	ΔE_2	$S\langle\pi_{BH_2}|1n_P\rangle$	$S\langle\pi_{BH_2}|2n_P\rangle$
HF/6-31G*	19.3	−4.0	15.3	0.1144	0.1081
HF/6-311+G**	19.8	−5.0	14.8	0.1180	0.1113

can see that this rule is valid. The square of the overlap integral between π_{BH_2} and n_N listed in Table 4 is very close to the sum of the squares of the overlap integrals between π_{BH_2} and $1n_P$ as well as between π_{BH_2} and $2n_P$ as shown in Table 8. The data in Tables 1 and 5, however, indicate that in H_2BPH_2 the B—P bond length is more sensitive to the steric effect than the B—N bond in H_2BNH_2.

The dipole moment analysis for H_2BPH_2 is similar to that for H_2BNH_2. The $P \rightarrow B$ dative bond results in the polarity of the dipole moment in **2b** being $B^-—P^+$. With the deactivation of the π orbitals on the boron atom, the polarity even reverses to $B^+—P^-$ in **2c** and this polarity is preserved in **2d** and **2e** since the changes of the dipole moment due to the steric and the $n_P \rightarrow \pi^*_{BH_2}$ negative hyperconjugation effects are relatively small.

The most impressive difference between the decomposition schemes for H_2BNH_2 and H_2BPH_2 (Figs. 1, 2) is the structural relaxation energy ΔE_4, which roughly corresponds to the pyramidalization energy of the nitrogen and the phosphorus atoms. A more accurate evaluation for H_2BPH_2 is achieved by deleting boron p_π orbitals after placing the H_2BP fragment in a plane and then optimizing the planar structure (resulting in **2c**) and its corresponding relaxed structure. The energy variation is $\Delta E_0' + \Delta E_0 + \Delta E_1$, which is about 35 kcal/mol, is comparable with the inversion barrier of PH_3 (experimental and theoretical values are 31.5 and 35.1 kcal/mol, respectively [49]). The significant difference between the barrier heights for NH_3 and PH_3 has been adequately rationalized by simple molecular orbital theory [50].

4 Conclusions

The ODP and BLW methods can not only calculate the conjugation energy at the ab initio level, but also are able to differentiate other factors such as hyperconjugation and steric effects. Our results indicate that the π-binding strengths in planar H_2BNH_2 and H_2BPH_2 are very close. Moreover, the analysis in the decomposition scheme of the rotational barriers shows that it is not appropriate to evaluate the π-bond energies in the above or other systems simply by using their rotational barriers between planar conformations and the 90°-twisted conformation [20] since the steric effect and the hyperconjugation effect, although they are opposite, are

involved and do not cancel each other. The basic difference between the structures of H_2BNH_2 and H_2BPH_2 lies in the very different role of the lone electron pair(s) of the nitrogen and phosphorus atoms, similar to the cases of NH_3 and PH_3. The analysis presented in this work is also very useful for judging the parameterization in molecular mechanics methods [51, 52], where the force field is normally expressed as the summation of bonded and nonbonded terms. The latter deals directly with the electronic delocalization. For example, Leroy et al. [53] recently determined a series of bond-energy terms in compounds containing dative, single, double and/or triple boron-nitrogen, where the energy difference between the BN double bond and the single bond is 16.27 kcal/mol and a dative $N \rightarrow B$ bond is fitted to be 17.58 kcal/mol. However, up to now there have been few direct means to justify these empirical terms which are based on chemical intuition and which are fitted to ab initio or experimental data, although the molecular mechanics method is being widely used nowadays. The present work sheds some light on this important area.

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