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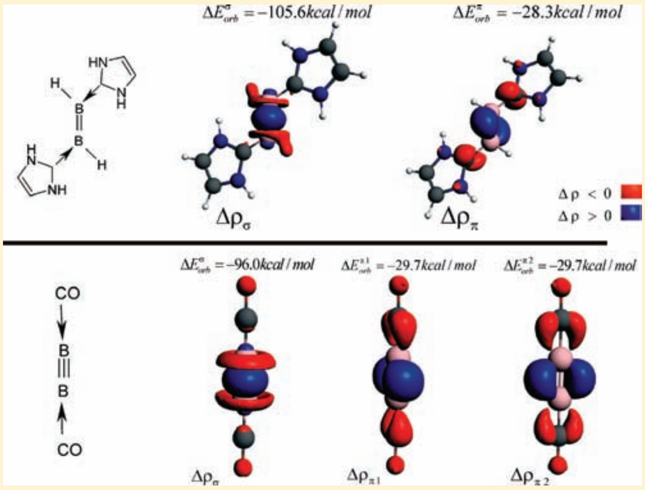
Multiple Boron−Boron Bonds in Neutral Molecules: An Insight from the Extended Transition State Method and the Natural Orbitals for Chemical Valence Scheme

Mariusz P. Mitoraj* and Artur Michalak

Department of Theoretical Chemistry, Faculty of Chemistry, Jagiellonian University, R. Ingardena 3, 30-060 Cracow, Poland



ABSTRACT: We have analyzed the character of B═B and B≡B bonds in the neutral molecules of general form: LHB═BHL (**2**-L) and LB≡BL (**3**-L), for various ancillary ligands L attached to the boron center, based on a recently developed method that combines the extended transition state scheme with the theory of natural orbitals for chemical valence (ETS-NOCV). In the case of molecules with the B═B bond, **2**-L, we have included L = PMe_3, PF_3, PCl_3, PH_3, $C_3H_4N_2$═C(NHCH)$_2$, whereas for molecules containing the B≡B connection, **3**-L, the following ligands were considered L = CO, PMe_3, PCl_3, $(Me_2NCH_2CH_2O)_2Ge$. The results led us to conclude that use of phosphorus ligands leads to strengthening of the B═B bond by 6.4 kcal/mol (for **2**-PMe_3), by 4.4 (for **2**-PF_3) and by 9.2 (for **2**-PH_3), when compared to a molecule developed on the experimental basis, **2**-$C_3H_4N_2$ ($\Delta E_{total} = -118.3$ kcal/mol). The ETS scheme has shown that all contributions, that is, (i) orbital interaction ΔE_{orb}, (ii) Pauli repulsion ΔE_{Pauli}, and (iii) electrostatic stabilization ΔE_{elstat}, are important in determining the trend in the B═B bond energies, ΔE_{total}. ETS-NOCV results revealed that both σ(B═B) and π(B═B) contributions are responsible for the changes in ΔE_{orb} values. All considered molecules of the type LB≡BL, **3**-L, exhibit a stronger B≡B bond when compared to a double B═B connection in **2**-L ($|\Delta E_{total}|$ is lower by 11.8−42.5 kcal/mol, depending on the molecule). The main reason is a lower Pauli repulsion contribution noted for **3**-CO, **3**-PMe_3, and **3**-PCl_3 molecules. In addition, in the case of **3**-PMe_3 and **3**-PCl_3, the orbital interaction term is more stabilizing; however, the effect is less pronounced compared to the drop in the Pauli repulsion term. In all of the systems with double and triple boron−boron bonds, the electronic factor (ΔE_{orb}) dominates over the electrostatic contribution (ΔE_{elstat}). Finally, the strongest B≡B connection was found for **3**-Ge [L = $(Me_2NCH_2CH_2O)_2Ge$], predominantly as a result of the strongest σ- and π-contributions, despite the highest destabilization originating from the sizable bulkiness of the germanium-containing ligand. The data on energetic stability of multiple boron−boron bonds (relatively high values of bond dissociation energies $|\Delta E_{total}|$), suggest that it should be possible to isolate experimentally the novel proposed systems with double B═B bonds, **2**-PMe_3, **2**-PF_3, **2**-PCl_3, and **2**-PH_3, and those with triple B≡B connections, **3**-PMe_3, **3**-Ge, and **3**-PCl_3.

INTRODUCTION

The chemistry of molecules containing multiple boron−boron bonds is considerably less developed compared to those of carbon−carbon derivatives.[1−6,37−41] This is primarily due to the electron-deficient character of the boron center. In addition, it was found that neutral systems containing multiple boron−boron bonds are highly reactive.[1] Accordingly, the synthesis and structural characterization of such compounds are very challenging tasks.[1−6,38−40]

In spite of above difficulties Wang et al. reported recently about the synthesis of the neutral molecule LHB═BHL (L = : C{N(2,6-$Pr^i_2C_6H_3$)CH}$_2$), that contains a boron−boron connection exhibiting double character.[7] In this study the conclusion on multiplicity was drawn from the molecular orbital analysis, bond-orders, and bond lengths.[7] However, an important detailed knowledge about the stabilizing and destabilizing factors that determine the nature of the *double* boron−boron connection in the neutral molecules of the type LHB═BHL (where L is a donor ligand) is still lacking in the literature. Accordingly, one of the main goals of this article is to perform a detailed study of the character of the B═B bond in neutral molecules LHB═BHL, based on a recently proposed combined charge and energy decomposition method, ETS-NOCV (Extended Transition State (ETS) and Natural Orbitals for Chemical Valence (NOCV)).[8−20] We will consider in our bonding analysis not only the system based on the study by Wang et al. (**2**-$C_3H_4N_2$),[7] but also the new familiar molecules of the general form LHB═BHL, where L are the phosphorus ligands exhibiting different donor/acceptor properties (**2**-PMe_3, **2**-PCl_3, **2**-PF_3, **2**-PH_3),[24,42] see Figure 1. To the best of our knowledge,

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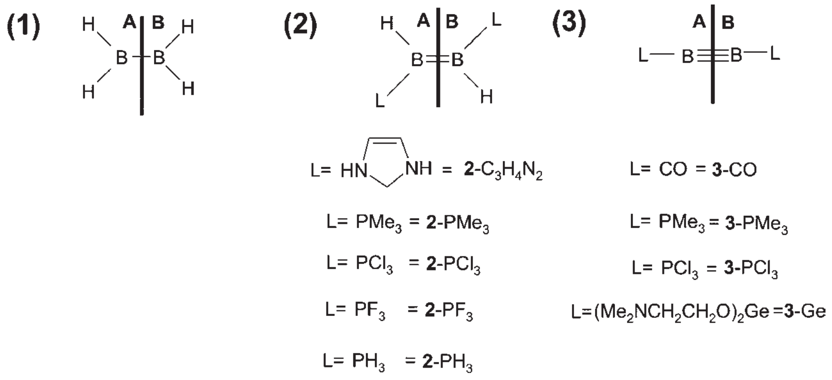

Figure 1. Molecules studied in the present work together with their abbreviations. The molecules contain single (**1**), double (**2**), and triple (**3**) boron—boron connections. A thick perpendicular line illustrates the fragmentation employed in the bonding analysis.

neither on theoretical nor experimental basis, has any phosphorus-based molecule been proposed yet that contains a multiple boron—boron connection.

Furthermore, Zhou et al. produced the OCB≡BCO molecule by decomposition of laser vaporized boron atoms with CO in an argon matrix at 8 K, in which the boron—boron connection exhibits a triple bond character.[2] The nature of the triple B≡B bond in OCB≡BCO and in other isoelectronic species were analyzed in depth and explained by Frenking et al. based on an energy decomposition study[21] as well as by Mavridis et al. based on ab initio calculations.[22] Therefore, as the second objective of our work we carried out an analysis of the triple B≡B bond not only in the pioneering OCBBCO molecule, for the purpose of comparison with previous theoretical works, but also in its phosphorus derivatives **3**-PMe$_3$, **3**-PCl$_3$, see Figure 1. Furthermore, we will extend the scope of analysis by considering a novel system (**3**-Ge) based on a germanium-containing ligand, which was found to exhibit extremely high donating power, even compared to conventional phosphanes and N-heterocyclic carbenes.[23] Finally, for the first time the character of B═B and B≡B bonds will be compared.

We believe that our results not only present a compact description of multiple BB connections but also provide supplementary knowledge useful for further experimental design of novel systems containing multiple BB connections based on phosphorus ligands.[24]

As it was mentioned in the second paragraph, we will use in the bonding analysis the ETS-NOCV method which is a merger of the energy decomposition method ETS[25,26] and the NOCV scheme.[8−14,17,19] It was demonstrated that NOCVs allow for a decomposition of the change in density upon bond formation ($\Delta\rho$) into different contributions ($\Delta\rho_k$) representing formation of specific bonding components, σ-, π-, δ-, and polarizations.[8−14,17,19] Further, amalgamation of NOCV methodology with the energy decomposition scheme ETS makes it possible to obtain the energy contributions $\Delta E_k^{\mathrm{orb}}$ to the bond energy from $\Delta\rho_k$.[15,16,18,20] Accordingly, ETS-NOCV offers a compact, qualitative (by providing deformation density contributions, $\Delta\rho_k$), and a quantitative (by providing energetic estimations $\Delta E_k^{\mathrm{orb}}$ for each $\Delta\rho_k$) picture of chemical bond formation within one common theoretical framework, even for molecules with no symmetry.[8−20]

■ COMPUTATIONAL DETAILS

All the DFT calculations presented here were based on the Amsterdam Density Functional (ADF) program.[27−29] The Becke—Perdew exchange-correlation functional[30,31] was applied. A standard double-ζ STO basis with one set of polarization functions was adopted for all atoms. Auxiliary s, p, d, f, and g STO functions, centered on all nuclei, were used to fit the electron density and obtain accurate Coulomb potentials in each SCF cycle. In our analysis each of our molecules is divided up into a two molecular fragments, A and B, as indicated by the perpendicular line in Figure 1. Subsequently we used the ETS-NOCV scheme to study single ($A\uparrow + \downarrow B$), double ($A\uparrow\uparrow + \downarrow\downarrow B$), and triple ($A\uparrow\uparrow\uparrow + \downarrow\downarrow\downarrow B$) boron—boron connections. A doublet, triplet, and quartet appeared to be the ground states for the considered fragments A and B in the systems (**1**), (**2**), (**3**), respectively, with the exceptions noted for **3**-PCl$_3$ and for **3**-Ge, where fragments appeared to be in a triplet ground state configuration. The energy required to promote the fragments in **3**-PCl$_3$ and in **3**-Ge from triplet to quadruple excited state was incorporated into the distortion energy contribution (Table 2). The contours of deformation densities were plotted based on the ADF-GUI interface.[32]

■ COMPUTATIONAL METHODS

Our analysis is based on the ETS-NOCV approach which is a merger of the ETS[25,26] method with the NOCV scheme.[8−14,17,19]

Historically the NOCV scheme is derived from the Nalewajski—Mrozek valence theory[33−35] as eigenvectors that diagonalizes the deformation density matrix.[8−14,17,19] It was shown[8−14,17,19] that the natural orbitals for chemical valence pairs (ψ_{-k},ψ_k) decompose the differential density $\Delta\rho$ into NOCV-contributions ($\Delta\rho_k$):

$$\Delta\rho(r) = \sum_{k=1}^{M/2} \nu_k[-\psi_{-k}^2(r) + \psi_k^2(r)] = \sum_{k=1}^{M/2} \Delta\rho_k(r) \tag{1}$$

where ν_k and M stand for the NOCV eigenvalues and the number of basis functions, respectively. Visual inspection of deformation density plots ($\Delta\rho_k$) helps to attribute symmetry and the direction of the charge flow. In addition, these pictures are enriched by providing the energetic estimations, $\Delta E_{\mathrm{orb}}(k)$, for each $\Delta\rho_k$ within the ETS-NOCV scheme. The exact formula which links the ETS and NOCV methods will be given in the next paragraph, after we briefly present the basic concept of the ETS scheme. In this method the total bonding energy $\Delta E_{\mathrm{total}}$ between interacting fragments is divided into four components:

$$\Delta E_{\mathrm{total}} = \Delta E_{\mathrm{dist}} + \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{orb}} \tag{2}$$

The first component, ΔE_{dist}, referred to as the distortion term, represents the amount of energy required to promote the separated fragments from their equilibrium geometry to the structure they will take up in the combined molecule. The second term, $\Delta E_{\mathrm{elstat}}$, corresponds to the

Table 1. Boron−Boron Bond Lengths Calculated for Molecules (1), (2), and (3)

system	L_{BB} (Å)
Single B−B	
H_2B-BH_2	1.75
Double B═B	
2-$C_3H_4N_2$	1.60
2-P(Me)$_3$	1.58
2-PCl_3	1.58
2-PF_3	1.57
2-PH_3	1.57
Triple B≡B	
3-CO	1.45
3-P(Me)$_3$	1.46
3-PCl_3	1.46
3-Ge	1.46

Table 2. ETS Energy Decomposition[a,b] of Boron−Boron Bond

	$\Delta E_{\mathrm{Pauli}}$	$\Delta E_{\mathrm{elstat}}$	ΔE_{orb}	ΔE_{dist}	$\Delta E_{\mathrm{total}}$
Single B−B					
H_2B-BH_2	125.3	−108.1	−113.6	2.4	−94.0
Double B═B					
2-$C_3H_4N_2$	173.6	−154.2	−142.9	5.2	−118.3
2-P(Me)$_3$	167.7	−141.9	−156.6	6.1	−124.7
2-PCl_3	161.4	−118.4	−167.7	8.5	−116.2
2-PF_3	155.4	−120.3	−165.2	7.4	−122.7
2-PH_3	168.1	−136.8	−163.1	4.3	−127.5
Triple B≡B					
3-CO	100.2	−97.1	−156.0	3.9	−149.0
3-P(Me)$_3$	125.8	−114.9	−176.6	8.6	−157.1
3-PCl_3	123.2	−91.5	−189.6	18.6[c]	−139.3
3-Ge	176.1	−131.3	−212.2	8.7[c]	−158.7

[a] kcal/mol. [b] $\Delta E_{\mathrm{total}} = \Delta E_{\mathrm{Pauli}} + \Delta E_{\mathrm{elstat}} + \Delta E_{\mathrm{orb}} + \Delta E_{\mathrm{dist}}$. [c] The distortion term contains the promotion energy from the doublet ground state to the quartet excited state.

classical electrostatic interaction between the promoted fragments as they are brought to their positions in the final complex. The third term, $\Delta E_{\mathrm{Pauli}}$, accounts for the repulsive Pauli interaction between occupied orbitals on the two fragments in the combined molecule. Finally, the last stabilizing term, ΔE_{orb} represents the interactions between the occupied molecular orbitals of one fragment with the unoccupied molecular orbitals of the other fragment as well as mixing of occupied and virtual orbitals within the same fragment (inner-fragment polarization). This energy term may be linked to the electronic bonding effect coming from the formation of a chemical bond.

In the combined ETS-NOCV scheme[15,16,18,20] the orbital interaction term (ΔE_{orb}) is expressed in terms of NOCV's eigenvalues (v_k) as follows:

$$\Delta E_{\mathrm{orb}} = \sum_{k} \Delta E_{\mathrm{orb}}(k) = \sum_{k=1}^{M/2} v_k[-F^{\mathrm{TS}}_{-k,-k} + F^{\mathrm{TS}}_{k,k}] \qquad (3)$$

where $F^{\mathrm{TS}}_{k,k}$ are diagonal Kohn−Sham matrix elements defined over NOCV with respect to the transition state (TS) density (at the midpoint between density of the molecule and the sum of fragment densities). The above components $\Delta E_{\mathrm{orb}}(k)$ provide the energetic estimation of $\Delta\rho_k$ that may be related to the importance of a particular electron flow channel for the bonding between considered molecular fragments (see Figure 1 for fragmentation details).

RESULTS AND DISCUSSION

Molecules Containing the B═B Bond. Let us first discuss the total bond energies, $\Delta E_{\mathrm{total}}$, originated from the ETS energy decomposition scheme. In line with our expectations, all considered systems of the type LHB═BHL exhibit a considerably shorter (by 0.15−0.18 Å depending on the system) and stronger ($|\Delta E_{\mathrm{total}}|$ is higher by 22.2 − 33.5 kcal/mol) boron−boron bond compared to H_2B-BH_2 with a single B−B bond, see Table 1 and Table 2. A similar trend on bond energies was found by Frenking and co-workers when comparing the familiar molecule HB═BH with H_2B-BH_2.[36] It is clear from Table 2 that B═B bond energies ($\Delta E_{\mathrm{total}}$) increase (in absolute kcal/mol values) by 6.4 (for **2**-PMe_3), by 4.4 (for **2**-PF_3), and by 9.2 (for **2**-PH_3) when compared to the molecule studied by Wang et al.,[7] **2**-$C_3H_4N_2$ ($\Delta E_{\mathrm{total}} = -118.3$). In the case of **2**-$PCl_3$, the double boron−boron connection appeared to be slightly weaker ($|\Delta E_{\mathrm{total}}|$ is lower by 2.1 kcal/mol) than in **2**-$C_3H_4N_2$. Thus, use of phosphorus ligands leads to similar (in the case of **2**-PCl_3) or even higher energetic stability (for **2**-PH_3, **2**-PF_3, **2**-PMe_3) relatively to that of molecule derived from the experiment, **2**-$C_3H_4N_2$. Accordingly, we believe that it should be possible to isolate experimentally such new phosphorus derivatives containing a double boron−boron bond. It was also found by Alkorta and co-workers that use of L = CO, NH_3, SH_2, ClH leads to formation of stable E-conformers of neutral LHB═BHL.[43]

An important question that arises at this point is about stabilizing and destabilizing factors that determine B═B bond energies, $\Delta E_{\mathrm{total}}$. According to the data collected in Table 2 the orbital interaction term, ΔE_{orb}, becomes noticeable more stabilizing (by 13.7−24.8 kcal/mol, depending on the molecule) when going from **2**-$C_3H_4N_2$ to phosphorus derivatives (**2**-PMe_3, **2**-PCl_3, **2**-PF_3, **2**-PH_3). In addition, the Pauli repulsion term, $\Delta E_{\mathrm{Pauli}}$, appeared to be less destabilizing (by 5.5−18.2 kcal/mol) for phosphorus analogues. The electrostatic contribution acts in the opposite direction, that is, leading to weakening of the B═B bond, which is less stabilizing as we descend the 2-L group from **2**-$C_3H_4N_2$ toward phosphorus-containing molecules. It is also clear from Table 2 that the geometry distortion component, ΔE_{dist}, varies relatively slightly (<3.5 kcal/mol). In summary of the changes in all bonding contributions, the total B═B bond energies noted for phosphorus-containing species fall in a quite narrow range, from −116.2 (for **2**-PCl_3) up to −127.5 kcal/mol (for **2**-PH_3).

In the following paragraphs the origin of the changes in ΔE_{orb} values will be discussed based on the ETS-NOCV method (eq 3).

Let us start from the qualitative and quantitative characteristics of the B═B bond that emerges from NOCV-based deformation density contributions, $\Delta\rho_k$, (eq 1) and the corresponding energies, $\Delta E_k^{\mathrm{orb}}$(eq 3), for the molecule studied by Wang et al.,[7] **2**-$C_3H_4N_2$. The deformation densities $\Delta\rho_k$ are depicted in such a way that red marks depletion (outflow) of electron density on bond formation, whereas dark blue color indicates electron density accumulation (inflow). It is evident from panel A of Figure 2 and Table 3 that predominantly two deformation density contributions, $\Delta\rho_\sigma$, $\Delta\rho_\pi$, capture the formation of the B═B bond.

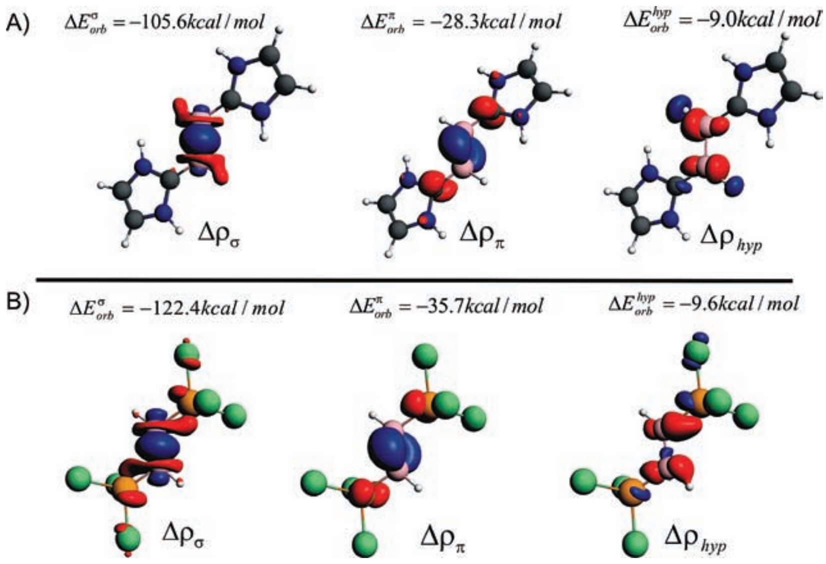

Figure 2. Contours of deformation density contributions $\Delta\rho_{\sigma}$, $\Delta\rho_{\pi}$, $\Delta\rho_{\text{hyp}}$ describing double boron−boron bond in **2**-$C_3H_4N_2$ (Panel A) and in **2**-PCl_3 (Panel B). The numerically smallest contour values are ±0.003 a.u. The very last components, $\Delta\rho_{\text{hyp}}$, were plotted with the smaller contour values, ± 0.0008 a.u., to improve the visibility. In addition the corresponding energies $\Delta E^{\sigma}_{\text{orb}}$, $\Delta E^{\pi}_{\text{orb}}$, $\Delta E^{\text{hyp}}_{\text{orb}}$ are shown.

Table 3. Orbital Interaction Energy ΔE_{orb} Decomposition Based on the ETS-NOCV Scheme (kcal/mol)

	ΔE_{orb} [a]	$\Delta E^{\sigma}_{\text{orb}}$	$\Delta E^{\pi 1}_{\text{orb}}$	$\Delta E^{\pi 2}_{\text{orb}}$	$\Delta E^{\text{rest}}_{\text{orb}}$ [b]
		Single B−B			
H_2B-BH_2	−113.6	−109.4			−4.2
		Double B=B			
2-$C_3H_4N_2$	−142.9	−105.6	−28.3		−9.0
2-$P(Me)_3$	−156.6	−109.0	−37.7		−9.9
2-PCl_3	−167.7	−122.4	−35.7		−9.6
2-PF_3	−165.2	−118.4	−38.6		−8.2
2-PH_3	−163.1	−114.1	−40.0		−9.0
		Triple B≡B			
3-CO	−156.0	−96.0	−29.7	−29.7	−0.6
3-$P(Me)_3$	−176.6	−99.0	−36.0	−36.0	−5.6
3-PCl_3	−189.6	−112.5	−35.7	−35.7	−5.7
3-Ge	−212.2	−118.0	−41.6	−41.9	−10.7

[a] $\Delta E_{\text{orb}} = \Delta E^{\sigma}_{\text{orb}} + \Delta E^{\pi 1}_{\text{orb}} + \Delta E^{\pi 2}_{\text{orb}} + \Delta E^{\text{rest}}_{\text{orb}}$. [b] $\Delta E^{\text{rest}}_{\text{orb}} = \Delta E_{\text{orb}} - (\Delta E^{\sigma}_{\text{orb}} + \Delta E^{\pi 1}_{\text{orb}} + \Delta E^{\pi 2}_{\text{orb}})$.

It is clearly seen from the figure, that they represent σ- and π-components. The strength of σ-bond ($\Delta E_{\text{orb}}{}^{\sigma} = -105.6$ kcal/mol) is nearly four times larger than the strength of π-contribution ($\Delta E^{\pi}_{\text{orb}} = -28.3$ kcal/mol). This can be directly related to better overlap of orbitals involved in the formation of the σ-bond. The remaining, non-negligible, stabilization of the B=B bond, by −9.0 kcal/mol, comes from the hyperconjugative contribution, $\Delta\rho_{\text{hyp}}$, that is, intrafragment polarization, which is based on the electron transfer from the B−H bonding orbital into the vacant σ*(B−H). The pure ETS scheme analysis performed by Frenking and co-workers for the familiar molecule, HB=BH ($D_{\infty h}$ symmetry), revealed that the σ-contribution (−111.1 kcal/mol) is only twice more important compared to π-bonding (−54.4 kcal/mol).[36]

To obtain an insight into the influence of L = PX_3 (X = Me, Cl, F) on the strength of individual σ- and π-contributions of the B=B bond in LHB=BHL molecules, the quantitative bonding characteristics originated from ETS-NOCV are presented in Table 3. In addition, based on an example of **2**-PCl_3, visual representation of deformation density contributions together with the corresponding energies are depicted in panel B of Figure 2. We can see from panel B of Figure 2 that both σ-($\Delta E^{\sigma}_{\text{orb}} = -122.4$ kcal/mol) and π-contributions ($\Delta E^{\pi}_{\text{orb}} = -35.7$ kcal/mol) of the B=B bond in **2**-PCl_3 are considerably stronger (more stabilizing) than the corresponding components in **2**-$C_3H_4N_2$ (by −16.8 kcal/mol and −7.4 kcal/mol, respectively). The same is true for other phosphorus-containing molecules, that is, both σ- and π-bonds are stronger compared to **2**-$C_3H_4N_2$, Table 3. This fact is directly responsible for more pronounced stabilization originated from the total orbital interaction term (ΔE_{orb}) noted in the case of phosphorus molecules **2**-PX_3 (X = Me, H, F), Table 2 and Table 3. An increase in the strength of π-bonding when going from **2**-$C_3H_4N_2$ to phosphorus-containing molecules can be related to more pronounced overlap between the orbitals constituting the π(B=B) bond. Finally, it should be noted that for phosphorus-containing molecules the electronic factor (ΔE_{orb}) dominates over the electrostatic contribution (ΔE_{elstat}).

Molecules Containing the B≡B Bond. Let us now focus our attention on the bonding in the OCB≡BCO molecule. In line with expectations, the total B≡B bond energy, $\Delta E_{\text{total}} = -149.0$ kcal/mol, is considerably more stabilizing (by 21.5 − 32.8 kcal/mol, depending on the system) compared to ΔE_{total} noted for molecules with a double B=B bond, Table 2. Our calculated value of ΔE_{total} for OCB≡BCO is in good agreement with that previously reported by Frenking et al.,[21] −149.7 kcal/mol, and by Mavridis et al., −146.3 kcal/mol.[22] One might expect that the main factor responsible for the relatively higher stabilization of the B≡B bond in OCB≡BCO when compared to the B=B connections is the presence of three dominant bonding components, that is, one σ(BB) and the two equivalent π-(BB) contributions, presented in the panel A of Figure 3. However, this is not the case. It is clear from Table 2 and Table 3 that the total orbital interaction term, $\Delta E_{\text{orb}} = -156.0$ kcal/mol, characterizing the B≡B bond in OCB≡BCO is lower in magnitude (in absolute values) than in

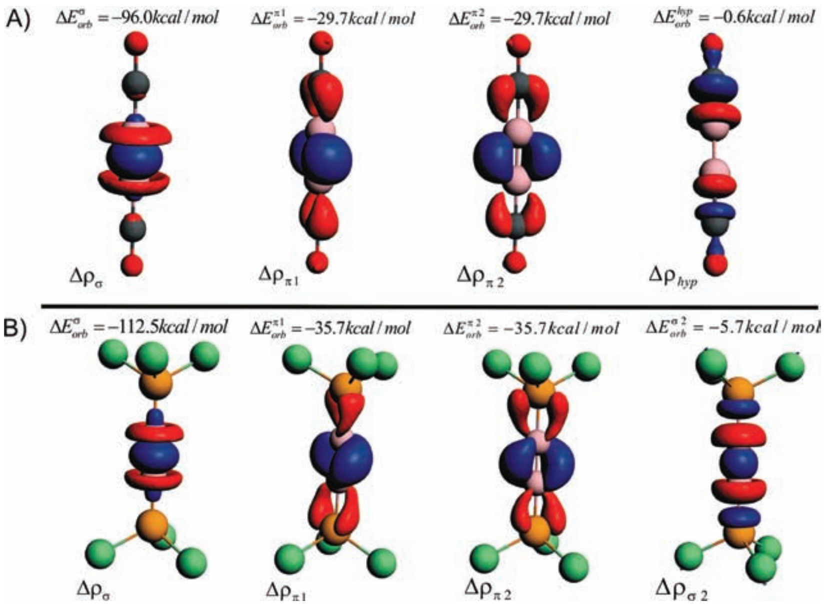

Figure 3. Contours of deformation density contributions $\Delta\rho_{\sigma}$, $\Delta\rho_{\pi 1}$, $\Delta\rho_{\pi 2}$, $\Delta\rho_{hyp}$ describing the triple boron−boron bond in **3**-CO (Panel A) together with the corresponding energies ΔE^{σ}_{orb}, $\Delta E^{\pi 1}_{orb}$, $\Delta E^{\pi 2}_{orb}$, ΔE^{hyp}_{orb}. In addition, panel B displays deformation density contributions together with the corresponding energies that characterize the triple boron−boron bond in **3**-PCl_3. The numerically smallest contour values are ±0.003 a.u. The very last components ($\Delta\rho_{hyp}$ and $\Delta\rho_{\sigma 2}$) were plotted with the smaller contour values, ± 0.008 a.u., to improve the visibility.

phosphorus-containing molecules **2**-PX_3 (X = Me, F, Cl, H). It implies lower stabilization of the B≡B bond when considering solely the electronic factor (ΔE_{orb}). In addition, according to Table 2, stabilization of B≡B bond in OCB≡BCO originating from the electrostatic contribution ($\Delta E_{elstat} = -97$ kcal/mol) is considerably lower (in absolute values by 23.2−57.1 kcal/mol, depending on the system) in relation to ΔE_{elstat} noted for LHB=BHL molecules. As it can be seen from Table 2, the main factor responsible for the higher stabilization of the triple bond in OCB≡BCO versus the double bond in LHB=BHL is the Pauli repulsion term, ΔE_{Pauli}, which appeared to be significantly lower (less destabilizing) (by 55.2 − 73.4 kcal/mol) in the former case. It is an interesting result in the light of a comparison of C=C versus C≡C bond strength, where the main factor responsible for increasing of bond energies ($|\Delta E_{total}|$) is the orbital interaction contribution.[15,36] It is important to note that the ΔE_{Pauli} term, calculated at the BP86 level of theory by Frenking and coworkers, for HB=BH amounts only to 116.3 kcal/mol,[36] whereas our calculated values of ΔE_{Pauli} based on exactly the same computational details, for familiar systems HLB=BHL, are significantly higher, that is, 155.4−173.6 kcal/mol. It evidently shows that the presence of ancillary ligands L attached to boron atoms introduces additional destabilization of the B=B bond, predominantly via interaction of the B=B bonding orbitals with the occupied orbitals characterizing B−L bonds. Thus, ancillary ligands L act here not only as donor/acceptor agents, but at the same time they also cause relatively strong destabilization of B=B that originates from the Pauli repulsion term. In all of the systems with triple boron−boron bonds, the electronic factor (ΔE_{orb}) dominates over the electrostatic contribution (ΔE_{elstat}), similar to what was noted in the case of B=B connections.

Considering an influence of phosphorus ligands on the characteristics of triple B≡B bond in **3**-PMe_3 and **3**-PCl_3, one might notice an increase in stability of B≡B when considering solely the orbital interaction term, ΔE_{orb}. The data in Table 3 originated from ETS-NOCV calculations proves that such increase in absolute values of ΔE_{orb} is related to increase in the strength of both σ- and π-contributions to B≡B bond. Accordingly, an incorporation of phosphorus ligands leads finally to strengthening of B≡B bond in the case of **3**-PMe_3. Despite very high electronic stabilization, $\Delta E_{orb} = -189.6$ kcal/mol, weakening of total B≡B bond strength is observed for **3**-PCl_3 ($|\Delta E_{total}|$ is lower by 9.7 kcal/mol) when compared to **3**-CO, see Table 2. This is related to (i) the highest value of the distortion term (18.6 kcal/mol), which contains promotion energy from the doublet ground state to the quartet excited state of considered fragments, (ii) the relatively high Pauli repulsion contribution, and (iii) the low stabilization stemming from the electrostatic contribution, ΔE_{elstat}.

Concerning the system **3**-Ge, it is evident from Table 2 that use of the germanium-containing ligand leads to the strongest B≡B connection among all of considered molecules. The main stabilizing factor is the orbital interaction term, which exhibits the lowest value, $\Delta E_{orb} = -212.2$ kcal/mol. ETS-NOCV based results collected in Table 3 and Figure 4, lead to the conclusion that the highest stabilization from ΔE_{orb} originates from the strongest σ- and π-components of the B≡B bond. It was expectable because the germanium ligand was found to exhibit extremely high donating power.[23] In addition, the electrostatic attraction is important in making the B≡B bond in **3**-Ge the strongest in the considered series **3**-X (X = CO, PMe_3, PCl_3, $Me_2NCH_2CH_2O)_2Ge$). The highest destabilization of the B≡B connection in **3**-Ge coming from the Pauli repulsion term, $\Delta E_{Pauli} = 176.1$ kcal/mol, related to the sizable bulkiness of germanium ligands, is unable to diminish the total stabilization originating from both orbital interaction term and electrostatic attraction.

Finally, as it can be seen from Figure 5, the ratio $\Delta E^{\pi}_{orb}/\Delta E^{\sigma}_{orb}$, that estimates relative strength of π/σ contributions, is notably higher (by ~0.1) when applying PMe_3 and germanium-containing ligands, as compared to CO and PCl_3. It clearly indicates the more pronounced role of π-bonding in the formed case. In addition, our calculated ratio π/σ for

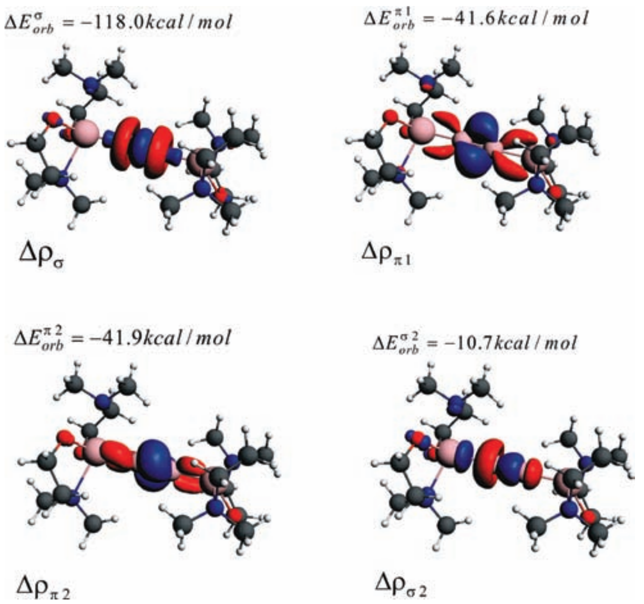

Figure 4. Contours of deformation density contributions $\Delta\rho_{\sigma}$, $\Delta\rho_{\pi 1}$, $\Delta\rho_{\pi 2}$, $\Delta\rho_{\sigma 2}$ describing the triple boron−boron bond in **3**-Ge together with the corresponding energies $\Delta E^{\sigma}_{\text{orb}}$, $\Delta E^{\pi 1}_{\text{orb}}$, $\Delta E^{\pi 2}_{\text{orb}}$, $\Delta E^{\text{hyp}}_{\text{orb}}$. The numerically smallest contour values are ±0.003 a.u. The very last component, $\Delta\rho_{\sigma 2}$, was plotted with the smaller contour values, ± 0.008 a.u., to improve the visibility.

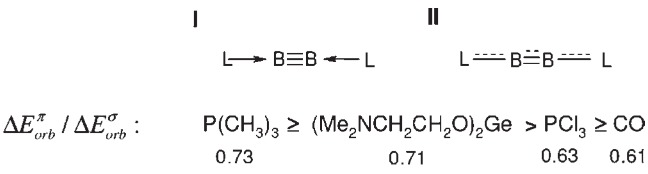

Figure 5. Valence structures characterizing LBBL molecules together with the relative strength of π/σ−contributions.

L═CO, is the same as reported previously by Frenking et al. based on the original ETS scheme.[36]

CONCLUDING REMARKS

In the present study the character of B═B and B≡B bonds in the neutral molecules of the general form LHB═BHL (**2**-L) and LB≡BL (**3**-L) was described based on a recently proposed ETS-NOCV method. For the first time, systems with double and triple BB bonds were compared. For a qualitative depiction of charge transfer channels (σ, π, and polarizations) we used deformation density contributions, $\Delta\rho_k$, originating from NOCVs. To provide a quantitative picture of B═B and B≡B bond formation, the ETS-NOCV scheme was applied to obtain energetic estimates, ΔE_k, associated with each charge rearrangement, $\Delta\rho_k$. Various ancillary ligands L attached to the boron center, characterized by different donor/acceptor properties, were considered in the case of molecules with B═B bond, **2**-L, L = PMe_3, PF_3, PCl_3, PH_3, $C_3H_4N_2$ and for molecules containing the B≡B connection, **3**-L, L = CO, PMe_3, PCl_3, $(Me_2NCH_2CH_2O)_2Ge$.

The results led us to conclude that use of phosphorus ligands leads to the strengthening of the B═B bond by 6.4 kcal/mol (for **2**-PMe_3), by 4.4 (for **2**-PF_3), and by 9.2 (for **2**-PH_3) when compared to the molecule originated from the experiment **2**-$C_3H_4N_2$ ($\Delta E_{\text{total}} = -118.3$ kcal/mol). In the case of **2**-PCl_3, the double boron−boron connection appeared to be slightly weaker ($|\Delta E_{\text{total}}|$ is lower by 2.1 kcal/mol) than in **2**-$C_3H_4N_2$. It shows that use of phosphorus ligands leads to comparable stability of **2**-PX_3 systems relative to the molecule based on experiment, **2**-$C_3H_4N_2$ ($|\Delta E_{\text{total}}|$ falls in the range 116.2−127.5 kcal/mol). Thus, it should be possible to isolate experimentally such new phosphorus derivatives containing a double boron−boron bond. The ETS scheme also revealed that all contributions, that is, (i) orbital interaction ΔE_{orb}, (ii) Pauli repulsion ΔE_{Pauli}, and (iii) electrostatic stabilization ΔE_{elstat}, are important in determining the trend in the B═B bond energies, ΔE_{total}. ETS-NOCV data shows that both σ(B═B) and π(B═B) components are responsible for the changes in $|\Delta E_{\text{orb}}|$ values when going from **2**-$C_3H_4N_2$ to phosphorus-containing species.

All of considered molecules LB≡BL, **3**-L, exhibit a stronger B≡B bond in relation to the double B═B connection in the case of **2**-L ($|\Delta E_{\text{total}}|$ is lower by 11.8−42.5 kcal/mol, depending on the molecule). The main reason is the lower Pauli repulsion term noted for **3**-CO, **3**-PMe_3, and **3**-PCl_3 molecules. The effect is the most pronounced for **3**-CO. In the case of **3**-PMe_3 and **3**-PCl_3, in addition, the orbital interaction term is more stabilizing compared to **2**-L; however, the effect is less important than the drop in the Pauli repulsion contribution. It is an interesting result in the light of a comparison of C═C versus C≡C bond energies, for which the main factor responsible for increasing of total bond strength was the orbital interaction term.[15,36] In the case of **3**-Ge, the strongest B≡B connection was found, predominantly as a result of the strongest σ- and π-contributions, despite the highest destabilization originating frmo the sizable bulkiness of the germanium-containing ligand L = $(Me_2NCH_2CH_2O)_2Ge$, see Figure 4. Finally, it should be pointed out that the new proposed derivatives **3**-Ge, **3**-PMe_3, and **3**-PCl_3 are stable (i.e., they exhibit high $|\Delta E_{\text{total}}|$ values, in the range 139.3 up to 158.7 kcal/mol) as compared to the already isolated molecule **3**-CO with $|\Delta E_{\text{total}}|$ = 149.9 kcal/mol. Accordingly, these results suggest the possibility for experimental development of such new derivatives containing a triple B≡B connection.

AUTHOR INFORMATION

Corresponding Author

*E-mail: mitoraj@chemia.uj.edu.pl.

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