Article

Revisiting the π-Back-Donation in the NHC−B≡B−NHC Molecule

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ABSTRACT: As the first thermal stable molecule with a B≡B bond, the diboryne complex protected by N-heterocyclic carbene ligands (NHC−B≡B−NHC) has attracted much interest. Researchers point out that π-back-donation highly stabilizes the B≡B bond besides σ-donation, both of which are induced by NHC ligands. In this work, details of the π-back-donation are revisited by using DFT calculations. There are two delocalized π* orbitals in NHC, and the symmetry of one π* orbital is highly adaptive to the π orbitals in B≡B bond, whereas the other cannot be involved in the π-back-donation. In staggered configuration, two orthogonal π orbitals of B≡B interact with this π* orbital in each NHC ligand, respectively, to form π-back-donations in both sides. This interaction has proven to be more intensive than π-conjunction, resulting in the lower energy of the staggered isomer compared with the eclipsed one containing greater π-conjunction. Moreover, intensity of the π-back-donation can be enhanced by reducing the energy levels of the matched π* orbitals in ligands, which gives references for the design of stable diborynes.
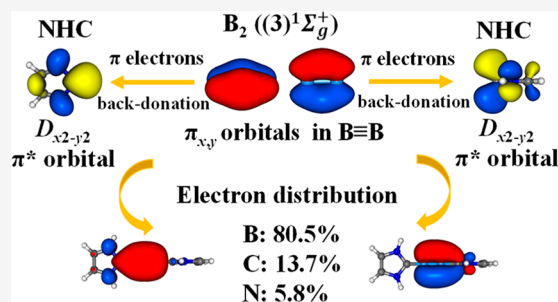
1. INTRODUCTION

Study on homoatomic multiple bonds between main group elements has always been an attractive subject in chemistry. In former times, it is generally considered that homoatomic multiple bonds are limited to certain main group atoms, such as carbon, nitrogen, and oxygen. Since the 1970s, great efforts have been made by researchers to explore homoatomic multiple bonds composed of other main-group elements in groups 13 to 15.[1−11] In 2002, the first boron−boron triple bond (B≡B) was identified in linear boron dimer (OC−B≡B−CO) protected by Lewis-base ligands, in low-temperature matrix experiments.[12,13] Following this work, theoretical investigations revealed that electronic donor ligands play an important role in formation of B≡B bond which can be described in the L → B≡B ← L formula,[14−16] and series of such species with different donor ligands (L = N_2, BO^-, PCl_3, Ge, ...) are predicted.[15−20] In 2012, a molecule with the B≡B bond protected by N-heterocyclic carbene (NHC) ligands (NHC−B≡B−NHC) was synthesized by the Braunschweig group,[21] which is the first thermal stable diboryne compound at ambient temperature. Between two boron atoms, there is a genuine triple bond consisting of one σ bond and doubly degenerate π bonds, similar to alkynes.[22,23] Quantum calculations indicate that, besides powerful electron donation, the concomitant back-donation interaction induced by NHC ligands highly stabilizes the triple bond.[24−29] In the B_2 motif, one electron pair in its antibonding $1\sigma_u^+$ orbital is pushed into its bonding $1\pi_u/1\pi_u'$ orbitals due to strong electron-donor effects of NHC, thus the B≡B bond ($1\sigma_g^+$, $1\pi_u/1\pi_u'$) exists in

this molecule. However, extra electrons in B≡B gained through the σ-donation reduce its stability, due to the electrostatic repulsion. Meanwhile, NHC ligands with unoccupied delocalized π* orbitals act as suitable π-electron acceptors, which involve B≡B in the large π delocalized bonds to receive its excessive electrons, improving stability of the molecule. Subsequently, other diboryne molecules with NHC-like ligands are investigated,[30−36] and researchers also have revealed the transition-metal-like behavior of B≡B bond with potential applications in organic chemistry as nonmetal catalysts.[37]

As mentioned above, donor−acceptor interaction is critical for the existence of the B≡B bond. Specifically, it is worth noting that the NHC−B≡B−NHC molecule with intensive π-back-donation induced by two staggered NHC ligands reaches a high stability compared with its isomers in other conformations. Therefore, more details of its π-back-donation interaction are explored in this paper using the density functional theory (DFT) method, in order to understand the nature of its stability. Our calculation reveals that adaptive orbital symmetry between the π* orbitals of ligands and π
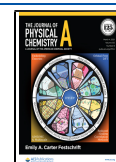
orbitals of B≡B is critical for the occurrence of intensive π-back-donation, which stabilizes the diboryne molecule.

2. COMPUTATIONAL DETAILS

In this article, the M06-2X functional of DFT is chosen for our theoretical investigation, which is developed for main group elements.[38] Geometry optimizations and energy calculations are all carried out with def2-tzvp basis set.[39] The vibrational frequencies are checked to ensure the stability of the diborynes at the same level. Molecular orbital (MO) and natural bond orbital (NBO) analyses are performed with the same basis set to discuss their electronic structures. These calculations are carried out by using the Gaussian 09 package.[40] Adaptive natural density partitioning (AdNDP) programs[41−43] are implemented to analyze the multicenter localized bonding pattern of the complexes based on NBO results. Molecular orbital (MO) visualizations are all performed by Molekel 5.4.[44] Moreover, energy decomposition analysis in conjunction with natural orbitals of chemical valence (EDA-NOCV) computations[45−48] are carried out at BLYP/TZ2P level by using the ADF 2017.01 program package,[49,50] to provide detailed information for the strength and contribution of orbital interactions in chemical bonding.

3. RESULTS AND DISCUSSION

3.1. Geometric Structure. The NHC−B≡B−NHC complex synthesized by the Braunschweig group[21] has a linear structure with two orthogonal NHC ligands of 1,3-bis(2,6-diisopropylphenyl) imidazol-2-ylidene (IDip). To simplify the calculations, diisopropylphenyl groups in ligands are replaced by hydrogen atoms, which has little influence on the overall electronic character of this complex. The structure is optimized at the M06-2X/def2-tzvp level of theory, and vibration frequency is checked to make sure it is a true local minimum. The optimized structure with D_{2d} symmetry is shown in Figure 1. The calculated B≡B bond length is 1.445 Å, quite approaching the experimental value (1.449 Å),[21] which confirms the reliability of our calculation methods.
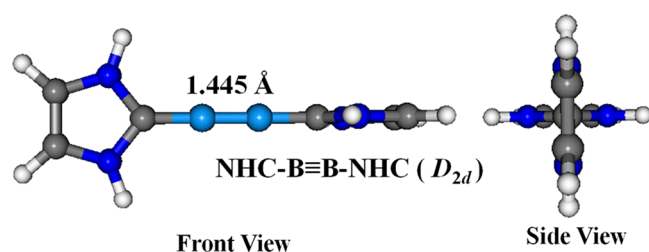

Figure 1. Optimized structure of NHC−B≡B−NHC molecule at M06-2X/def2-tzvp level of theory. The B≡B bond length is labeled.

3.2. Electronic Character. As we know, intensive π-back-donation effect plays an important part in stabilizing the B≡B bond besides σ-donation.[28,29] To understand the nature of this effect, the interaction mechanism between the triple bond and NHC ligands is explored from the view of electronic character in this section.

3.2.I. MO Analysis. MOs of ligand-free boron dimer (B_2), NHC ligands and NHC−B≡B−NHC molecule are calculated to get a general view for their electronic shells. Among them, interacting MOs and their energy levels are clearly shown in Figure 2. Two HOMOs in the B_2 motif are occupied due to

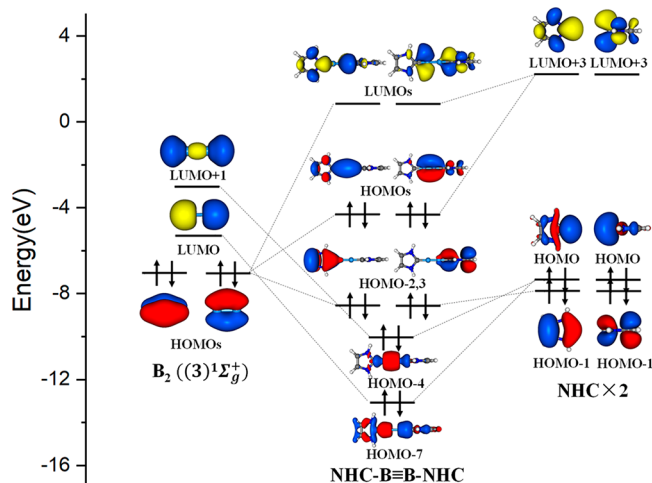one pair of its σ^* antibonding electrons being pushed into these π HOMOs by σ donor ligands.

Figure 2. MO interaction diagram of the NHC−B≡B−NHC molecule at the M06-2X/def2-tzvp level.

As shown in Figure 2, HOMOs of two NHCs are mainly composed of lone electron pairs, which are transferred into two unoccupied σ orbitals in B_2 (LUMO and LUMO+1) to form two occupied σ orbitals (HOMO−4,7) of NHC−B≡B−NHC. This is a typical coordination bond induced by σ-donation of the Lewis-base ligands. Two degenerate π orbitals (HOMO−2,3) in the NHC−B≡B−NHC molecule are largely delocalized, which are conjugated by π HOMOs of B_2 and HOMO−1 of the NHC ligands. Concurrently, these HOMOs of B_2 also interact with other two unoccupied π^* orbitals in NHCs (LUMO+3) to form two HOMOs and two LUMOs of NHC−B≡B−NHC. It could be inferred that the extra electrons in B≡B from σ-coordination are transferred back to NHC ligands, which form π-back-donation bonds. Therefore, σ-donation, π-conjugation, and π-back-donation between central B_2 and NHC ligands are the foundation of the electronic shell in the NHC−B≡B−NHC molecule.

3.2.II. Rotation Energies. As we know, two NHC ligands keep a staggered configuration in the ground-state of NHC−B≡B−NHC, but its isoelectronic molecule Ph−C≡C−Ph with a similar π ligand protected homoatomic triple bond has a planar structure. To reveal the reason for this difference, relative rotation energies of NHC−B≡B−NHC and Ph−C≡C−Ph are calculated, and results are plotted in Figure 3.

As we can see, for Ph−C≡C-Ph, a planar structure with two eclipsed ligands is the global minimum, which should be stabilized by large π-conjugation bonds composed of π orbitals in C≡C and Ph ligands. The energy of this molecule increases along with relative rotation of the two Ph ligands and reaches the highest point in staggered configuration, due to the destruction of its planar conjugation. The energy gap between two conformations is about 0.04 eV, which could be described as π-conjugation energy. However, for NHC−B≡B−NHC, the energy of the staggered configuration is 0.155 eV lower than the eclipsed one, although the planar configuration benefits its π-conjugation. Therefore, it is obvious that, in staggered NHC−B≡B−NHC, there are other intensive interactions besides π-conjugation. Referring to its MO diagram, it is supposed to be the back-donation of π electrons.
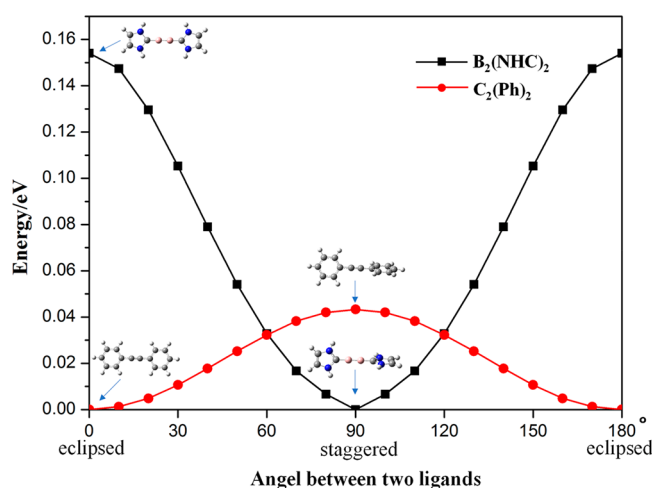
Figure 3. Rotation energies curves of NHC−B≡B−NHC (in black) and Ph−C≡C−Ph (in red) relative to their global minimums at the M06-2X/def2-tzvp level.

The intensity of this π-back-donation is larger than the energy gap between staggered and eclipsed configurations (0.155 eV) considering the opposite influence of π-conjugation, which is much larger than π-conjugation energy (0.04 eV) and critical for the stability of the B≡B bond.

3.2.III. Energy Decomposition Analysis. To confirm our inference, EDA-NOCV analysis is carried out for NHC−B≡B−NHC in two different configurations. In EDA-NOCV calculation, orbital interaction energy (ΔE_{orb}) is presented as a sum of pairwise orbital contributions, which provides quantitative insight into the strength of orbital interactions. The B$_2$ ($(3)^1\Sigma_g^+$) and NHC$_2$ are considered as fragments in the analysis, the deformation densities ($\Delta\rho(r)$) associated with pairwise orbital interactions of the four most important orbitals (two σ-donations and two π-back-donations) are shown in parts a and b of Figure 4 for staggered and eclipsed conformations, and the color code of the charge flow (red to
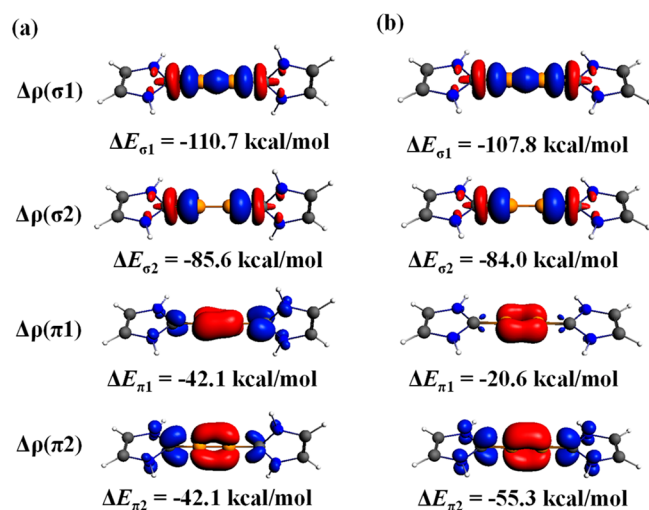
blue) visualizes the area of depletion and concentration of charge in donor−acceptor interactions. More numerical results are summarized in Table S1 of the Supporting Information. In these closely related structures, EDA results would give some references for comparison.[51,52] Obviously, the intensity of π-back-donation in staggered molecule ($\Delta E_{\pi 1} + \Delta E_{\pi 2} = -84.2$ kcal/mol) is stronger than that in eclipsed one ($\Delta E_{\pi 1} + \Delta E_{\pi 2} = -75.9$ kcal/mol), which confirms that the staggered configuration benefits the π-back-donations in NHC−B≡B−NHC.

3.2.IV. AdNDP Chemical Bonding. AdNDP localized chemical bonding is further calculated to investigate the mechanism of π-back-donation in NHC−B≡B−NHC, and the results for staggered and eclipsed conformations are shown in parts a and b of Figure 5. For the staggered molecule in
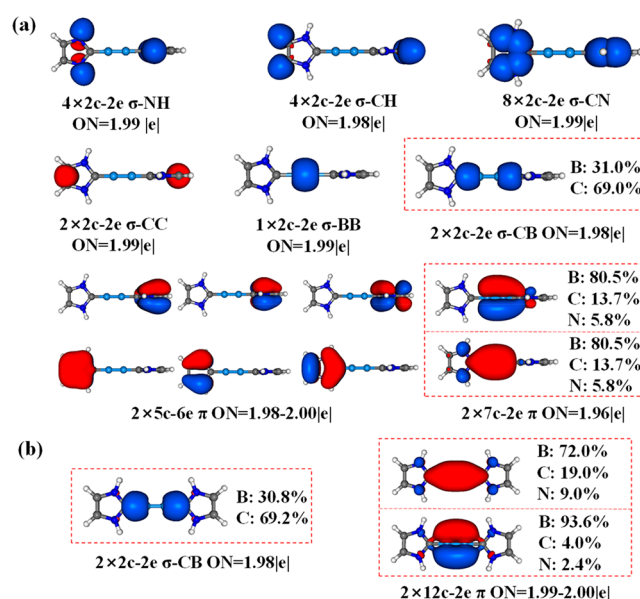

Figure 5. AdNDP localized chemical bonding of NHC−B≡B−NHC in (a) staggered configuration and (b) eclipsed configuration. The electron occupied numbers (ON) and electron distributions in chemical bonding are labeled.

Figure 4. Plots of deformation densities $\Delta\rho(r)$ with associated energies ΔE of the four most important orbital interactions for NHC−B≡B−NHC molecules in (a) staggered configuration and (b) eclipsed configuration at the BLYP/TZ2P level, considering B$_2$ ($(3)^1\Sigma_g^+$) and NHC$_2$ as the fragments. The color code of the charge flow is red → blue.

Figure 5a, one lone electron pair in the vertex carbon of each NHC ligand is donated to the central boron to form a CB σ-coordination bond with occupation number (ON) of 1.98|e|, in which boron and carbon atoms hold 31.0% and 69.0% electrons, respectively. Within central B$_2$, one 2c−2e σ-BB bond and two 7c−2e π bonds compose the B≡B bond of this molecule. Specifically, π bonds between two boron atoms should be viewed as two 7c−2e $\pi_{x,y}$ bonds, each of which is delocalized over the B$_2$ and one NHC, in order to reach the reasonable ON of 1.96|e|. In these large delocalized bonds, electron distributions are 80.5%, 13.7%, and 5.8% on boron, carbon, and nitrogen atoms, respectively; thus, 19.5% electrons in π bonds are back-donated to NHC ligands. Referring to its MO diagram, π electrons of B≡B are transferred back to LUMO+3 π^* orbitals in NHC ligands. To make this interaction feasible, adaptive symmetry between the π^* orbital of NHC and π orbitals of B≡B is critical. Moreover, as $\pi_{x,y}$ orbitals in triple bond are orthogonal, only two staggered ligands could adapt each orbital, respectively, and make π-back-donations in both sides available, which increase the stability of staggered molecule.

AdNDP chemical bonding of eclipsed NHC$-$B$\equiv$B$-$NHC is also investigated for comparation. Localized bonds inside B_2 and NHCs are similar to those for the staggered one; thus, only donor$-$acceptor bonds included in B_2-NHCs interactions are shown in Figure 5b, and more details could be found in the Supporting Information (Figure S1). Depending on our calculation, σ-CB bonds are also coordination bonds with 30.8% boron electrons and 69.2% carbon electrons, similar to those of the staggered molecule. However, two π bonds should be viewed as 12c$-$2e delocalized $\pi_{x,y}$ bonds formed by B_2 and two NHC ligands. Specifically, in the first π_x bond in parallel with two ligands, electron distributions of boron, carbon, and nitrogen are 72.0%, 19.0%, and 9.0%, indicating a significant π-back-donation. For another π_y bond perpendicular to two ligands, electrons mainly distribute in central boron atoms (93.6%); thus, the back-donation effect is obviously weakened due to the unsuitable orientation between π orbitals of B$\equiv$B and the π^* orbitals in NHC.

AdNDP calculation confirms our inference; that is, σ-donation is almost the same in staggered and eclipsed ones, but π-back-donation is affected by different configurations. Adaptive orbital symmetry between the π^* (LUMO+3) orbital of NHC and $\pi_{x,y}$ orbitals of B$\equiv$B is critical for the existence of the π-back-donation effect. In staggered configuration, π-back-donations are available for both sides, whereas for the eclipsed structure one of these back-donations could not occur due to the unsuitable orientation between donor$-$acceptor orbitals. As π-back-donation is more intensive compared with the π-conjunction effect, eclipsed NHC$-$B$\equiv$B$-$NHC with an even greater π conjunction is less stable than the staggered one.

3.3. Ligand Effect. As π-back-donations occur within π orbitals of B$\equiv$B and the π^* in NHC ligands, electronic shells of ligands are supposed to have a significant influence on the intensity of back-donation. Therefore, the ligand effect in the NHC$-$B$\equiv$B$-$NHC molecule is further discussed in this part to explore the method of improving the intensity of π-back-donations.

As shown in Figure 6a, there are three bonding π orbitals and two antibonding π^* orbitals in the NHC ligand, which could be viewed as super S, P_x, P_y, D_{xy} and $D_{x^2-y^2}$ from their orbital shapes. As the orbital symmetry of $D_{x^2-y^2}$ is adaptive to π orbitals in triple bond, π electrons of B$\equiv$B are back-donated into this $D_{x^2-y^2}$ π^* orbital (LUMO+3) rather than the D_{xy}

π^*orbital (LUMO+1). Therefore, it could be inferred that the lower energy level of this π^* orbital would benefit π-back-donations. To verify our inference, H atoms connected with N are substituted by other R groups with different electronegativity (R = CN, Cl, I), to change energy levels of MOs in NHC. Energy levels of $D_{x^2-y^2}$ orbitals (E_{π^*}), ratios of electron-back-donations (back-donation %), and binding energies ($E_b = 2E_{B(NHC)} - E_{B^2(NHC)^2}$) of NHC ligands with different R groups (R = CN, Cl, I, H) are calculated and shown in Figure 6b. More details are given in Table S2. With increasing electronegativity of R substituent groups, E_{π^*} goes down, and the corresponding back-donation ratio rises up, which confirms our inference. As the intensity of σ-donations (Table S2) and delocalized interactions are close in these diborynes with the same series NHC ligands, E_b increases along with intensity of π-back-donations, which indicates higher stability of the molecules. This gives references for design of other stable diboryne molecules by regulating electrons character of ligands. However, π bonding characters in B$\equiv$B are weakened due to the loss of its π-electrons through back-donations, confirmed by the longer B$\equiv$B bond lengths (Table S2).

3.4. Other Diborynes. Electronic characters of other diborynes obtained in experiments, X$-$B$\equiv$B$-$X (X = CO, Saturated (Sat.) NHC, cAAC), are also investigated here to discuss their π-back-donations. All of these ligands are strong electron-donors and better π-acceptors than NHC. AdNDP chemical bonding of these diborynes are investigated, and their B$\equiv$B bonds and C$-$B coordination bonds are shown in parts a$-$c of Figure 7, respectively. As we can see, B$\equiv$B bonds also exist in these molecules, which include one σ and two degenerate π bonds with π-back-donation characters. Moreover, σ-coordination bonds are formed between ligands and B_2 motifs, induced by σ-donor ligands. Energy levels of the π^* orbitals of these ligands involved in π-back-donations (E_{π^*}) and back-donation ratios are also calculated and shown in Table 1. More details are given in Table S2 and Figure S2. As better π-acceptors, adaptive orbital symmetry and lower E_{π^*} of CO, Sat. NHC, and cAAC make π-back-donations more intensive (higher back-donation ratios) compared with NHC. However, OC$-$B$\equiv$B$-$CO is less thermally stable than NHC$-$B$\equiv$B$-$NHC in experiments, perhaps due to the geometric shielding effect of NHC ligands. Moreover, as π-back-donations are stronger in diborynes with Sat. NHC, cAAC ligands, their π bonds in B$\equiv$B are weakened, which leads to their greater reactivity with H_2.[53−55]

4. CONCLUSIONS

In this paper, details of π-back-donation in NHC$-$B$\equiv$B$-$NHC molecule are theoretically investigated to reveal the nature of its high stability. MO analysis indicates that combined effect of σ-donation, π-back-donation, and π-conjugation is critical for the existence of the B$\equiv$B bond. The rotation energy of NHC$-$B$\equiv$B$-$NHC compared with the isoelectronic Ph$-$C$\equiv$C$-$Ph implies that intensive π-back-donation exists in its staggered configuration, which is stronger than π-conjugation. EDA-NOCV analysis also confirms that π-back-donation is more intensive in the staggered configuration than in the eclipsed one. Localized chemical bonding patterns further reveal that there are two π^* orbitals in NHC, only one of them ($D_{x^2-y^2}$) could interact with π orbitals in the B$\equiv$B bond due to their adaptive orbital symmetry. As two π orbitals in triple bond are orthogonal, the staggered configuration of ligands makes the π-back-donations in both sides feasible.
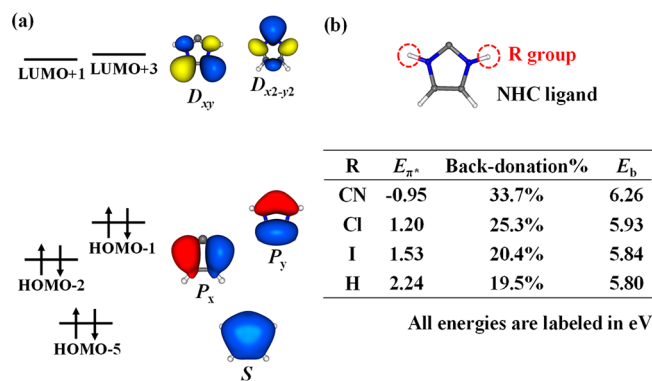

R	E_{π^*}	Back-donation%	E_b
CN	-0.95	33.7%	6.26
Cl	1.20	25.3%	5.93
I	1.53	20.4%	5.84
H	2.24	19.5%	5.80

All energies are labeled in eV

Figure 6. (a) π and π^* orbitals and their energy levels in NHC ligand and (b) energy levels of $D_{x^2-y^2}$ orbitals (E_{π^*}), electron-back-donations ratios (back-donation %), and binding energies ($E_b = 2E_{B(NHC)} - E_{B_2(NHC)_2}$) of NHC-B$\equiv$B-NHC with R groups substituted NHC ligands (R = CN, Cl, I, H) at the M06-2X/def2-tzvp level.
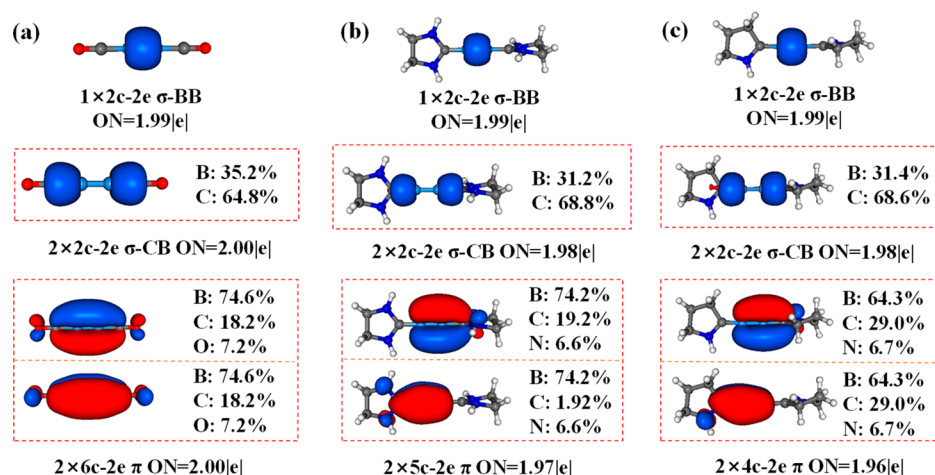
Figure 7. AdNDP localized chemical bonding (including B≡B bonds and C−B coordination bonds) of (a) OC−B≡B−CO, (b) Sat. NHC−B≡B−NHC, and (c) cAAC−B≡B−cAAC. The electron occupied numbers (ON) and electron distributions in chemical bonding are labeled.

Table 1. Energy Levels of the π^* Orbitals (E_{π^*}) and Electron-Back-Donation Ratios (Back-Donation %) of X−B≡B−X (X = CO, NHC, Sat. NHC, and cAAC) at the M06-2X/def2-tzvp Level

X−B≡B−X	X = CO	X = NHC	X = Sat. NHC	X = CAAC
E_{π^*} (eV)	0.53	2.24	1.60	0.99
back-donation (%)	25.4%	19.5%	25.8%	35.7%

Thus, the staggered molecule is more stable than the eclipsed one although the planar structure benefits π-conjugation. The following discussion on ligand effect indicates that high electronegative substitutes reduce the energy levels of the matched π^* orbitals in NHCs, resulting in stronger π-back-donations. Further investigation of other stable diborynes also confirms that adaptive symmetry and lower energy level of ligands' π^* orbitals would benefit π-back-donations and improve the stability of the molecules. This study would give a reference for the design of new diboryne complexes.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c10207.

> Numerical results of the EDA-NOCV calculations, electron-donation radios, B≡B bond lengths and binding energies of diborynes with NHC−R_2 (R = CN, Cl, I, H) ligands and CO, saturated NHC, cAAC ligands, AdNDP localized chemical bonding of eclipsed NHC−B≡B−NHC, and the π^* MOs of CO, saturated NHC, and cAAC ligands (PDF)

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Notes

The authors declare no competing financial interest.

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