The boron–boron triple bond in NHC→B≡B←NHC

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Quantum chemical calculations of the compound B2(NHCMe)2 and a thorough examination of the electronic structure with an energy decomposition analysis provide strong evidence for the appearance of boron–boron triple bond character. This holds for the model compound and for the isolated diboryne B2(NHCR)2 of Braunschweig which has an even slightly shorter B–B bond. The bonding situation in the molecule is best described in terms of NHCMe→B2←NHCMe donor–acceptor interactions and concomitant π-backdonation NHCMe←B2→NHCMe which weakens the B–B bond, but the essential features of a triple bond are preserved. An appropriate formula which depicts both interactions is the sketch NHCMe=B=B=NHCMe. Calculations of the stretching force constants FBB which take molecules that have genuine single, double and triple bonds as references suggest that the effective bond order of B2(NHCMe)2 has the value of 2.34. The suggestion by Köppe and Schnöckel that the strength of the boron–boron bond in B2(NHCR)2 is only between a single and a double bond is repudiated. It misleadingly takes the force constant FBB of OBBO as the reference value for a B–B single bond which ignores π bonding contributions. The alleged similarity between the B–O bonds in OBBO and the B–C bonds in B2(NHCMe)2 is a mistaken application of the principle of isolable relationship.

Introduction

In 2012, Braunschweig and co-workers reported the synthesis of the diboryne compound B2(NHCR)2 where diatomic B2 binds two N-heterocyclic carbenes (NHC) which carry bulky groups R at nitrogen.1 The X-ray structure analysis revealed a linear arrangement of the NHC ligands to the central B2 moiety and a very short B–B bond of 1.45 Å which agrees with the standard value for a triple bond (1.46 Å).2 An earlier theoretical study that was published in 2011 had predicted that the molecule has very strong bonds which can be interpreted in terms of donor–acceptor interactions NHCR→B2←NHCR where diatomic B2 is in the highly excited (3) 1Σg+ singlet state rather than in the X 1Σg− ground state (Fig. 1a and b).1

Charge donation from the ligands takes place into the empty 1σu MO (out-of-phase +,− donation) and the 2σg MO (in-phase +,+ donation) which is schematically shown in Fig. 1c. In addition to the σ-donation NHCR→B2←NHCR, π-backdonation NHCR←B2→NHCR may occur from the occupied 1πu and 1πu′ orbitals which would weaken the B≡B triple bond. An energy decomposition analysis was carried out in 2013 which suggests that 2/3 of the total orbital interactions comes from NHCR→B2←NHCR σ-donation and 1/3 comes from NHCR←B2→NHCR π-backdonation. Thus, the bond order for the B–B can be expected between 2 and 3 while the triple bond character is retained in the diboryne whose bonding situation is properly sketched with the formula NHCR=B=B=NHCR.

Very recently, Köppe and Schnöckel (KS) published in this journal a reinterpretation of the boron–boron bond in NHCR→B2←NHCR where they question the assignment of a triple bond.3 Using thermodynamic arguments and a correlation of force constants, KS suggest that the strength of the boron–boron bond in NHCR→B2←NHCR is only between a single and a double bond and that the molecule should better become described with traditional resonance structures. The conclusion of KS was made on the basis of selected experimental and calculated results. The authors write that their results ‘...generates a new interpretation which is in contrast to the triple bond donor–acceptor description visualized by arrows and which casts a critical light on the interpretation of any NHC “stabilized” molecule’. The statement was made without reference to the previous quantum chemical studies of B2(NHCR)2.4–6

We studied the paper by KS3 very carefully and noticed several flaws in their arguments which cast severe doubts on their conclusions. In the following we critically discuss the approach and the conclusions of the authors. Our counter

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arguments are presented in the same order as in the paper by KS.

Thermodynamic view

KS begin their discussion with a lengthy description of the energy which is required for the formation of B₂ in the excited (3) ³Σ⁺ state (which is denoted as B₂⁺⁺ in their paper) from solid boron in a gas-phase reaction which is irrelevant for the discussion of the bonding situation and for the formation and stability of the compound. The compound NHCR → B₂ ← NHCR was prepared by Braunschweig by reacting NHCR → (B₂Br₄) → NHCR with sodium naphthalenide in THF solution which gives B₂(NHCMe)₂ at BP86/def2-TZVPP.

But it was already shown in 2013³ that the donor–acceptor interactions NHCH→ B₂ ← NHCR are very strong, which should be expected in light of the low-lying vacant orbitals of B₂⁺⁺ (Fig. 1). The strong interactions do not lead to major changes in the structures of the donor and acceptor species which is easy to understand. The two vacant σ orbitals in B₂⁺⁺ are bonding and antibonding, respectively, which roughly cancel the impact of the donor–acceptor interactions on the B–B bond length. The slightly longer B–B distance in NHCH→ B₂ ← NHCR (1.45 Å) than in free B₂⁺⁺ (1.40 Å) is caused by π-backdonation from B₂ to the NH ligands. The geometry changes of the NH ligands in NHCR→ B₂ ← NHCR are likewise rather small, because they involve mainly the carbene lone-pair orbital. Thus, the structure and stability of NHCR → B₂ ← NHCR are in full accord with the bonding situation of a B≡B moiety which is stabilized by strong σ-donation of and π-backdonation to the NH ligands.

Determination and discussion of the force constants in NHCh→ B₂ ← NHCR

The main argument in the paper by KS against a triple bond character in NHCR→ B₂ ← NHCR rests on the force constants of the B–B stretching mode. The authors first discuss several molecules which may be used as reference for a B–B single bond. They choose OBBO as candidate, because it would “have a BB bonding situation similar to 1 with a linear X–B–X moiety” where 1 stands for NHCR→ B₂ ← NHCR. In order to underpin the connection between OBBO and 1 the authors refer to the isolobal relationship O−→ O− C₂H₆. Then they write that “the Lewis formula O=B−B−O is in accordance with the values of the BB and BC force constants”.

There are two major flaws in the above arguments. One flaw concerns the suggestion that the boron–boron bond in OBBO is a single bond.

8 There are two orthogonal π components in the BO moieties which conjugate over the BB fragment. Using OBBO as template for a B–B single bond ignores the contribution of B–B π-bonding. Note that the authors suggest a Lewis structure O=–B−B−O for the molecule which has an electron sextet at boron. The second flaw is the suggestion that the isolobal relationship O−→ O− C₂H₆ may be used to indicate a similar bonding situation in OBBO and NHCR→ B₂ ← NHCR. CH₂ has an electronic (1B₁) triplet ground state which is 9.0 kcal mol⁻¹ below the (1A₁) singlet state.¹⁰ Methylene is isolobal with oxygen atom, because both species have a triplet state and a similar shape and energy.¹¹ In contrast, NH has a singlet ground state which is 85 kcal mol⁻¹ below the triplet state.¹² It means that the electronic structure and the chemical reactivity of the carbene carbon atom of NHCH are very different from CH₂, which is common knowledge in chemistry.¹³ A pertinent example which demonstrates the large difference between the two carbenes is given by the compounds where they bind to a single carbon atom. C(CH₃)₂ is the parent allene H₂C−C=C=CH₂ which has a linear structure with C=C double bonds and perpendicular CH₃ planes. C(NHC₆)₂ is a carbone C₆L₂ which features two donor–acceptor bonds L−→ C ← L to a carbon atom which retains two electron lone pairs.¹⁴ The carbodibencarbene C(NHCMe)₂ has a
bond angle (NHC\textsubscript{(Me)})\textsubscript{C}–(NHC\textsubscript{(Me)}) of 132\textdegree\textsuperscript{12} which is similar to the isolobal carbodiphosphorane C[PPh\textsubscript{3}]\textsubscript{2} which has a bond angle of 135\textdegree.\textsuperscript{16} The first carbodicarbenes C(NHC\textsubscript{3})\textsubscript{2} were recently synthesized by Bertrand and by Fürstner.\textsuperscript{17} It is obvious that the isolobal relationship O=C=CH\textsubscript{2} does not hold for NHC.

We searched for a molecule which possesses a genuine B–B single bond. The vast experimental information which has been accumulated about boron compounds clearly shows that boron atoms in stable molecules have at least partially filled four valence AOs which makes the search for an experimental value of species with a B–B single bond futile. We therefore looked for a model compound with a genuine B–B single bond that can be calculated with an accuracy that rivals experimental values. A suitable species is planar H\textsubscript{2}B\textsubscript{2}BH\textsubscript{2} where the p(\pi) orbitals of boron are vacant. The planar (D\textsubscript{3h}) structure is a transition state for the rotation about the B–B bond of B\textsubscript{2}H\textsubscript{4} which has a perpendicular (D\textsubscript{2d}) equilibrium structure. The B–B bond in the D\textsubscript{2d} energy minimum structure has been calculated to be much shorter (1.623 \textgreek{\AA}) than in the planar form (1.752 \textgreek{\AA}) which is due to significant hyperconjugation that was estimated from the energy difference between the D\textsubscript{2d} and D\textsubscript{2h} structures (17.3 kcal mol\textsuperscript{−1}).\textsuperscript{18} The reported B–B bond length of 1.65 \textgreek{\AA} for OBBO which is much shorter than in planar B\textsubscript{2}H\textsubscript{4} (1.752 \textgreek{\AA}) indicates a substantial degree of B–B \pi-bonding which makes the molecule unsuitable as reference for a single bond.

We calculated the force constant for the B–B stretching mode in planar H\textsubscript{2}B\textsubscript{2}BH\textsubscript{2} and took the value of F\textsubscript{BB} = 2.49 mdyn \textgreek{\AA}\textsuperscript{−1} as reference value for a B–B single bond. A related molecule with a genuine B–B double bond is HBBH in the (\Sigma^\text{g}−) triplet state which has a B–B \sigma bond and two singly occupied B–B \pi orbitals. The calculated force constant for the B–B stretching mode in planar H\textsubscript{2}B\textsubscript{2}BH\textsubscript{2} and took the value of F\textsubscript{BB} = 5.38 mdyn \textgreek{\AA}\textsuperscript{−1} which is taken as reference value for a B=B double bond. The reference value for a B=B triple bond comes from the calculated force constant for the (3) \Sigma^\text{g}− state of B\textsubscript{2} which has the value of F\textsubscript{BB} = 7.62 mdyn \textgreek{\AA}\textsuperscript{−1}. The B–B force constants in mdyn \textgreek{\AA}\textsuperscript{−1} of the hydroboranes for a single bond (2.49; planar B\textsubscript{2}H\textsubscript{4}), double bond (5.38, triplet B\textsubscript{2}H\textsubscript{3}) and triple bond (7.62; (3) \Sigma^\text{g}− B\textsubscript{2}) exhibit the same ratio 1 : 2 : 3 as the force constants F\textsubscript{CC} for the C–C bonds in the analogous hydrocarbons which were given by KS as 4.4 (C\textsubscript{2}H\textsubscript{6}), 9.1 (C\textsubscript{2}H\textsubscript{4}) and 15.6 (C\textsubscript{2}H\textsubscript{2}).\textsuperscript{3} The regular increase of the force constant is at first sight a bit surprising, since the additional components of the multiple bonds are \pi bonds which are weaker than \sigma bonds. Along with the addition of \pi bonding, there is a concomitant change in the hybridisation of the \sigma bond which enhances the overall bonding and leads to the approximate relation 1 : 2 : 3.\textsuperscript{19}

Fig. 2 shows a correlation diagram between the force constants and the bond orders of the reference compounds H\textsubscript{2}B–BH\textsubscript{2} [planar], HB=\textsubscript{B}B (\Lambda \Sigma^\text{g}−) and B\textsubscript{2} [(3) \Sigma^\text{g}− B\textsubscript{2}] which exhibits a linear correlation coefficient of R\textsuperscript{2} = 0.995. The calculated force constant F\textsubscript{BB} = 3.5 for OBBO suggests a bond order of 1.35, which indicates a significant contribution of \pi bonding. The force constant F\textsubscript{BB} = 6.0 which was calculated by KS for NHC→B\textsubscript{2}←NHC now indicates an effective bond order for the B–B bond of 2.34. This is in agreement with the classification as a molecule which has a B≡B triple bond that is weakened by \pi-backdonation. The assignment of the much lower bond order of 1.5 for the complex which was suggested by KS is misleading, because it arbitrarily uses a bond order of 1.0 for OBBO, which neglects the \pi contribution to the B–B bond.

### Bonding analysis of NHC→B\textsubscript{2}←NHC

The above discussion provides information about the relative strength of the B–B bond in the complex NHC\textsubscript{6}→B\textsubscript{2}←NHC\textsubscript{6} compared with reference compounds which were chosen by KS (OBBO) and by us (planar H\textsubscript{2}BBH\textsubscript{2}, triplet HBBH and (3) \Sigma^\text{g}− B\textsubscript{2}) which, however, does not give insight into the nature of the bonding. Quantitative information is available form EDA-NOCV\textsuperscript{20} (Energy Decomposition Analysis\textsuperscript{21} combined with Natural Orbitals for Chemical Valence)\textsuperscript{22} calculations. The advantage of the recently developed EDA-NOCV method over the EDA procedure which we used in our earlier bonding analysis\textsuperscript{4} of NHC\textsubscript{Me}→B\textsubscript{2}←NHC\textsubscript{Me} is, that the orbital interactions are broken down to a sum of pairwise contributions which provides detailed information about the strength of specific pairs of orbitals. The results give a complete picture of the bonding between the interacting fragments which can be connected with classical bonding models of chemistry. A helpful feature of the EDA-NOCV method is, that the results of the calculations can not only numerically be expressed but that the impact of the pairwise orbital interactions on the electronic structure can also graphically be visualized. Details of the calculations are given in ESL.\textsuperscript{4} For further information about the EDA-NOCV method\textsuperscript{23} and recent examples we refer to the literature.\textsuperscript{24}

Table 1 gives the numerical data of the EDA-NOCV calculations of the complex NHC\textsubscript{Me}→B\textsubscript{2}←NHC\textsubscript{Me} for the interactions between the acceptor (3) \Sigma^\text{g}− B\textsubscript{2} (for the choice of the latter excited state of B\textsubscript{2} see ref. 4) and the donor (NHC\textsubscript{Me})\textsubscript{2} at the geometry of the complex. The instantaneous interaction energy \Delta E\textsubscript{int} = −307.5 kcal mol\textsuperscript{−1} is very large and overcompensates the electronic excitation energy of B\textsubscript{2} of 106.4 kcal mol\textsuperscript{−1}. The interaction energy \Delta E\textsubscript{int} comprises the Pauli repulsion \Delta E\textsubscript{Pauli} (259.0 kcal mol\textsuperscript{−1}) and the binding interactions which comes from the Coulombic attraction \Delta E\textsubscript{elstat} (−252.3 kcal mol\textsuperscript{−1}) and
Table 1 Results of the EDA-NOCV calculations for NHCMo→B2→NHCM in 2 at BP86/TZ2P using the fragments B2[(3) 1Σg+] and (NHCM)2 as interacting species. All energy values in kcal mol⁻¹. Calculated NBO partial charge of B2 in e

<table>
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<tr>
<th>Interacting fragments</th>
<th>B2(NHCM)2</th>
<th>B2[(3) 1Σg+] and (NHCM)2</th>
</tr>
</thead>
<tbody>
<tr>
<td>ΔE_{INT}</td>
<td>−307.5</td>
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</tr>
<tr>
<td>ΔE_{Pauli}</td>
<td>259.0</td>
<td></td>
</tr>
<tr>
<td>ΔE_{Coh}</td>
<td>−252.3 (44.5%)</td>
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</tr>
<tr>
<td>ΔE_{orb}</td>
<td>−314.2 (55.5%)</td>
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</tr>
<tr>
<td>ΔE_{ex}L→B2→L (+,+) donation</td>
<td>−112.7 (35.9%)</td>
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</tr>
<tr>
<td>ΔE_{ex}L→B2→L (+,−) donation</td>
<td>−86.9 (27.7%)</td>
<td></td>
</tr>
<tr>
<td>ΔE_{ex}L→B2→L π-backdonation</td>
<td>−48.0 (15.3%)</td>
<td></td>
</tr>
<tr>
<td>ΔE_{ex}L→B2→L π'-backdonation</td>
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<td></td>
</tr>
<tr>
<td>ΔE_{orb}</td>
<td>−24.2 (7.7%)</td>
<td></td>
</tr>
<tr>
<td>η(B2)</td>
<td>−0.36</td>
<td></td>
</tr>
</tbody>
</table>

The value in parenthesis gives the percentage contribution to the total attractive interactions ΔE_{Coh} + ΔE_{orb}. The value in parenthesis gives the percentage contribution to the total orbital interactions ΔE_{orb}.

the covalent (orbital) term ΔE_{orb} (−314.2 kcal mol⁻¹). The EDA-NOCV calculations suggest that the donor–acceptor bonds NHCM→B2→NHCM have a slightly more covalent (55.5%) character than electrostatic character (44.5%). The breakdown of the orbital term ΔE_{orb} into pairwise contributions between occupied and vacant MOs of the fragments provide quantitative insight into the σ-donation NHCM→B2→NHCM and π-backdonation NHCM→B2→NHCM. The associated charge flow can be visualized through the deformation densities Δρ_{σ} − Δρ_{π} that are shown in Fig. 3, left column. The colour code indicates the direction of the charge flow red→blue. The occupied and vacant orbitals which are connected to the deformation densities are displayed in the three columns at the right side of Fig. 3. There are strongly stabilizing contributions from the in-phase (+,+) NHCM→B2→NHCM σ-donation into the LUMO + 1 of (3) 1Σg+ B2 (ΔE_{ex1} = −112.7 kcal mol⁻¹) while the out-of-phase (+,−) donation into the energetically lower-lying LUMO is a bit smaller (ΔE_{ex2} = −86.9 kcal mol⁻¹) which is due to the better overlap of the former (+,+) donation. There two contributions of the NHCM→B2→NHCM π'-backdonation are clearly smaller (ΔE_{ex1} = −48.0 kcal mol⁻¹ and ΔE_{ex2} = −42.4 kcal mol⁻¹) than the σ-donation. Since both components, σ-donation and π-backdonation significantly contribute to the bonding, a more appropriate notation for the bonding interactions is the formula NHCM→B2→NHCM. Since the π'-backdonation weakens the boron–boron bond, a smaller bond order below 3 but above 2 is expected, which is in agreement with the effective bond order of 2.34 that was derived from the force constants.

The numerical results of the EDA-NOCV calculations and the graphical display of the deformation densities together with the molecular orbitals provide a bridge between heuristic bonding models of chemistry and a quantum chemical analysis of the electronic structure of the investigated complex. The calculated energy values are not observable data, but they arise from an unambiguously defined partitioning scheme which is not very sensitive to the level of theory. The value of the EDA-NOCV method lies in the fact that it establishes a quantitative classification scheme where comparisons can be made with related compounds. Explanations for experimental findings and predictions for new compounds can be made for different ligands L and atoms E in complexes L→E2→L as well as for compounds L→E→L by considering the electronic states of E2 or E and the donor strength of L. This has been shown for numerous complexes of atoms E of group 13,4,5,6,27 group 1414,15,26 and group 15,16,27. The same approach has recently been used to predict stable beryllium compounds L→B2→L.28

We would like to make a comment on the use of the different notations which were used by KS and by us for describing the bonding situation in B2(NHCR)2 (see Scheme 1). The two formulas are not just different writing styles but they refer to different bonding situations between B2 and the NHCR moieties. The notation with arrows NHCR→B2→B2→NHCR indicates heterolitic cleavage of neat bonds while the notation with dashed lines as suggested by KS suggests conjugation over electron-sharing bonds which cleave homolytically. The latter description is appropriate for molecules such as 1,2-butadiene where rupture of the C=C bonds yields radicals. Cleavage of the B–NHCR bonds gives closed-shell fragments. Recognizing the difference between the two types of bonding has led to the discovery of carbones CL2 as a peculiar class of organic compounds and related systems which exhibit unusual geometries and reactivities and to the prediction of novel compounds.29
Finally, we want to point out that two recent papers by Braunschweig just appeared where the strength of the B–B triple bond in the original diboryne \( \text{B}_2(\text{NHCR})_2 \) and in the slightly changed species \( \text{B}_2(\text{NHCR}_0)_2 \) with slightly less bulky substituents \( R_0 \) than \( R \) has experimentally been assessed.\(^{30}\) One paper shows that the observed B–B stretching modes of the Raman spectra nicely fit into the established trend of the C=C and N=N stretching frequencies of alkynes and dinitrogen.\(^{30}\)a The second paper reports \( ^{11}\text{B}–^{11}\text{B} \) spin–spin (\( J \)) coupling constants which indicate that the bonding description in terms of a triple bond is justified.\(^{30}\)b Thus, theory and experiment agree that \( \text{B}_2(\text{NHCR})_2 \) contains has significant boron–boron triple bond character.

**Summary and conclusion**

The results of this work can be summarized as follows. The calculated data and the thorough bonding analysis of the compound \( \text{B}_2(\text{NHCMe})_2 \) provide convincing evidence for the appearance of significant boron–boron triple bond character in the model compound and in the isolated diboryne \( \text{B}_2(\text{NHCMe})_2 \) of Braunschweig which has an even slightly shorter B–B bond. The bonding situation is best described in terms of NHCMe \( \rightarrow \text{B}_2 \leftarrow \text{NHCMe} \) donor–acceptor interactions and concomitant \( \pi \)-back donation NHCMe \( \leftarrow \text{B}_2 \rightarrow \text{NHCMe} \) which weakens the B–B bond, but the essential features of a triple bond are preserved. An appropriate formula which depicts both interactions is the sketch \( \text{NHCMe} \rightleftharpoons \text{B} \rightleftharpoons \text{NHCMe} \).

Calculations of the stretching force \( F_{\text{BB}} \) constants which take molecules that have genuine single, double and triple bonds suggest that the effective bond order of \( \text{B}_2(\text{NHCMe})_2 \) has the value of 2.34. The suggestion by Köppe and Schnöckel that the strength of the boron–boron bond in \( \text{B}_2(\text{NHCH})_2 \) is only between a single and a double bond which should be described with a Lewis structure that has a \( \sigma \) bond and a delocalized \( \pi \) bond is repudiated. It misleadingly takes the force constant \( F_{\text{BB}} \) of \( \text{OBBO} \) as reference value for a B–B single bond which ignores \( \pi \) bonding contributions. The alleged similarity between the B–O bonds in \( \text{OBBO} \) and the B–C bonds in \( \text{B}_2(\text{NHCMe})_2 \) is a mistaken application of the principle of isolable relationship.

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