

Dinitrogen extrusion from diazidophenylborane: Computational analysis of PhBN_x (x = 6, 4, 2) isomers

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Dedicated to Professor Dr. V. Staemmler on the occasion of his 65th birthday.

Abstract

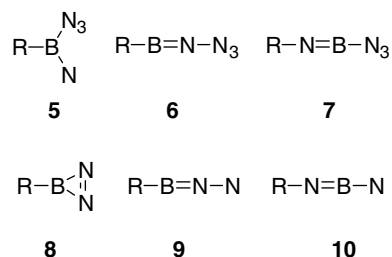
The energies and structures of possible intermediates in the dinitrogen extrusion from diazidophenylborane **4a** to give phenylborylene **11a** were determined using density functional (B3LYP), multiconfigurational (CASSCF and MRMP2), and coupled cluster (CCSD(T)) computations in conjunction with basis sets of up to cc-pVTZ quality. Formation of **11a** and nitrogen from **4a** is an exothermic process (−21 kcal mol^{−1}). The triplet electronic ground state of azidophenylborylnitrene **5a** (PhBN₄) is only 26 kcal mol^{−1} higher in energy than **4a** and the phenyl shift in **5a** to yield N-azidophenyliminoborane **7a** is highly exothermic.
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Keywords: Density functional theory computations; Azido boranes; Reactive intermediates; Borylene

1. Introduction

Azidoboranes R₂BN₃ (**1**) are versatile precursors for the formation of R₂BN products via photochemically or thermally initiated dinitrogen extrusion [1]. This reaction leads to iminoboranes **2a** for organic substituents **1a** (R = organyl), without the intermediacy of borylnitrenes [1]. On the other hand, the donor substituents in bis(diisopropylamino)azidoborane **1b** (R = N(*i*Pr)₂) stabilize the nitrene intermediate **3**, which then can be trapped [2] (see Scheme 1).

Diazidoboranes RBN₆ (**4**) with an organic substituent have received only limited attention [3–5], even though a number of highly interesting and novel compounds having RBN₄ (**5–7**), RBN₂ (**8–10**), and RB (**11**) stoichiometries could be accessible thermally or photochemically.

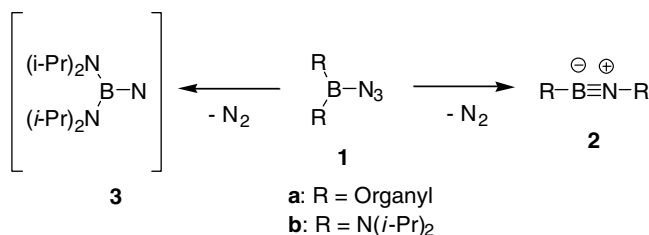


We have recently studied the photochemistry ($\lambda = 254$ nm) of **4a** (R = Ph) in a nitrogen matrix at cryogenic temperatures and observed the formation of RBN₂ (**10a**) and RB (**11**) isomers [6]. The inorganic compound **4b** (see Scheme 2) (R = Cl) was reported to lose two N₂ molecules photochemically to give **8b** in an argon matrix [7,8].

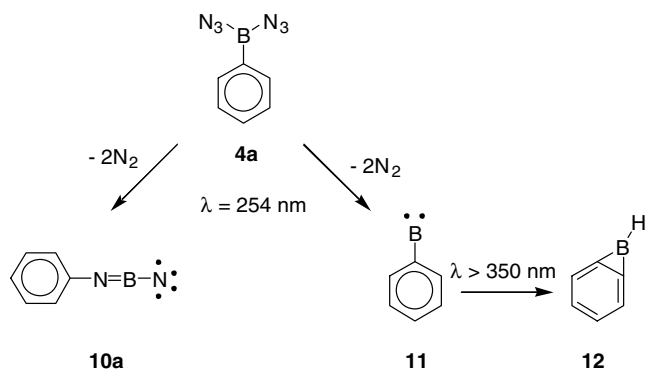
We here report the structural and energetic properties of compounds **4a–10a** in order to enhance the understanding of successive dinitrogen extrusion from **4a**. As the experimental work was done photochemically, the barriers for nitrogen extrusion are not considered here.

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Scheme 1. Nitrogen elimination from diorganoazidoboranes **1a** results in iminoboranes **2**, while borylnitrene **3** can be trapped in the case of **1b** [2].



Scheme 2. Photochemical extrusion of nitrogen from **4a** in a nitrogen matrix at 10 K yields **10a** and **11**, which rearranges to **12** upon longer wavelength irradiation.

2. Computational methods

Geometries were optimized and harmonic vibrational frequencies were computed using hybrid density functional theory (B3LYP) [9,10] in conjunction with the 6-311+G** basis set. These results were obtained with the GAUSSIAN-03 program [11]. Energies were refined by subsequent single energy coupled cluster computations at the CCSD(T) [12] level within the frozen-core approximation using the MOLPRO program [13]. The partially spin restricted open-shell coupled cluster theory (RHF-RCCSD(T)) was employed for triplet electronic states [14]. Correlation consistent basis sets, cc-pVDZ and cc-pVTZ, were employed in the CCSD(T) computations [15]. Due to computational limitations, the relative energy of **6a** was determined relative to that of **7a** using only the smaller cc-pVDZ basis set at the CCSD(T) level. In addition, multiconfiguration-SCF computations using a complete active space (CASSCF) were performed for nitrenes [16]. The active spaces selected depend on the systems under investigation and are detailed below. The CASSCF energies were refined by multireference Møller–Plesset perturbation theory (MRMP2) using the frozen core approximation [17–22]. All multiconfigurational computations used a 6-31G* basis set, and were done with the GAMESS program [23].

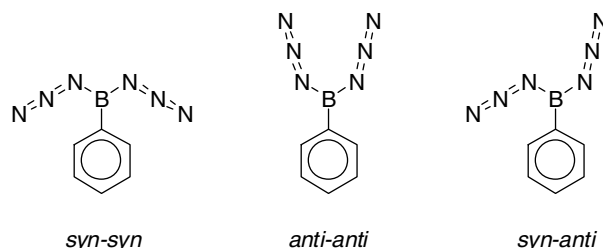
3. Results and discussion

3.1. RBN₆

Among the three different conformers considered for **4a**, the *syn-anti* (with respect to the phenyl ring) and *anti-anti*

forms are C_s and C_{2v} symmetry minima, respectively, with the former being more stable by 0.9 kcal mol⁻¹ (B3LYP/6-311+G**, see Fig. 1).

The *syn-syn* form is a saddle point in C_{2v} (4.5 kcal mol⁻¹ above *syn-anti*), but a minimum in C₂ symmetry. Here, the two planes defined by the phenyl ring and the two azido groups have a tilt angle of 43°. In all isomers the azido groups are slightly bent having angles around 168–174° at the central nitrogen atoms, while the B–N–N angles all range between 122° and 129°. The *syn-syn* isomer is the least stable, 2.3 kcal mol⁻¹ above the most stable conformer in energy. The *syn-anti* form will thus be the RBN₆ reference throughout this work.



Experimental structural data are not available for **4a**. The pentafluorophenyl derivative has a trimeric structure in the crystalline phase, but is monomeric in solution [4].

3.2. RBN₄

3.2.1. R(N₃)BN (**5**)

The primary product of N₂ loss from **4** is the borylnitrene **5**, for which two conformations are possible differing in the orientation of the azido group with respect to the phenyl ring. Alkyl- and aryl nitrenes generally prefer triplet ground states (σ¹π¹) [24,25], while for the parent borylnitrene, H₂BN, an unstable singlet state (π²) was found to be lower in energy than the triplet state by computational means [26,27]. Note that the electronic structure of borylnitrene H₂BN is different than that of typical aryl nitrenes, where the lowest energy singlet state is of (σ¹π¹) character, while the closed-shell singlet state is still higher in energy and has a σ² configuration [24,25]. The empty p orbital on boron is a good electron acceptor and thus favors the π² configuration; hence, H₂BN is isoelectronic to vinylidene H₂CC.

The lowest energy state of **5a** is the triplet of A'' symmetry, σ¹π¹. As the *anti* conformer of **5a**-³A'' is more stable than the *syn* form by 3.2 kcal mol⁻¹ (B3LYP/6-311+G**) the latter is not considered further here. The low-lying singlet states of **5a** have either the same configuration as the triplet state, ¹A'', or are of closed-shell nature, ¹A'. They can be labeled σ¹π¹ (open-shell singlet, ¹A'') or π² (closed shell singlet, ¹A'), respectively. The CASSCF(12,12)/6-31G* geometry optimizations used an all-π-electron active space in addition to the in-plane p-type orbital centered on the nitrene nitrogen atom, and the same active space was used in subsequent MRMP2/6-31G**//

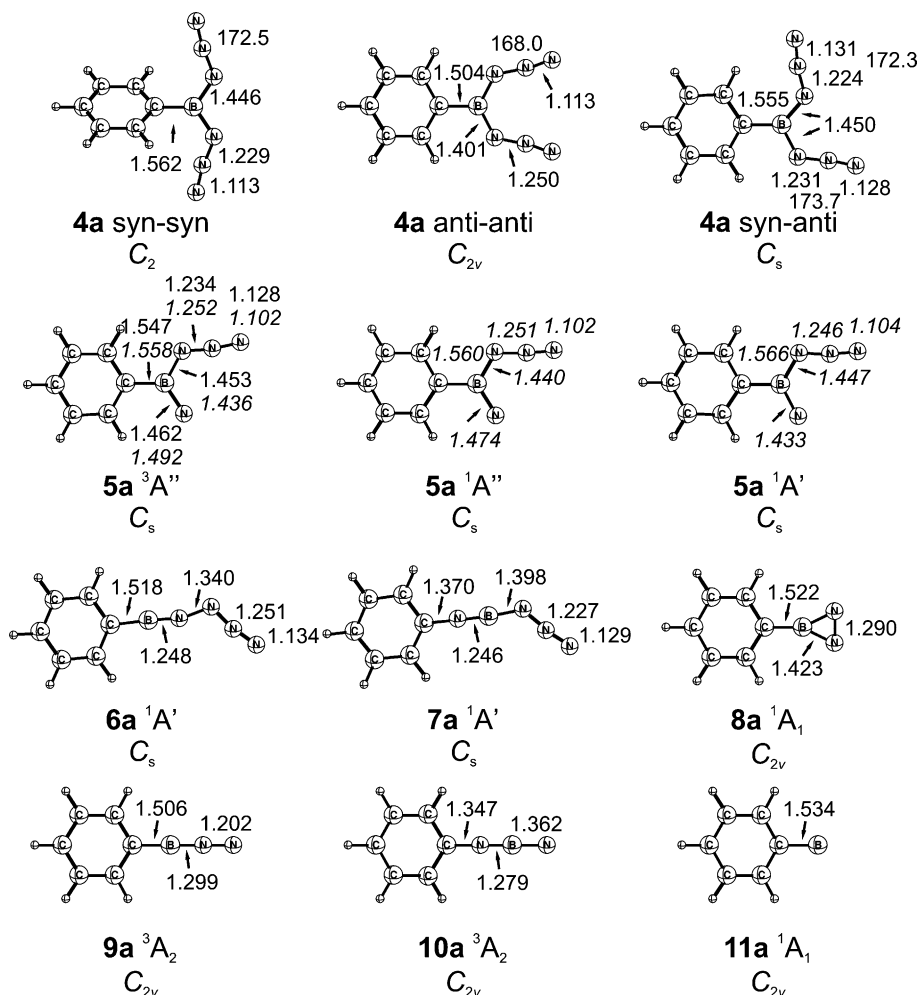


Fig. 1. Geometries of relevant stationary points considered in this work. Selected bond lengths are given in Å, bond angles in ° as computed at the B3LYP/6-311+G** (in normal print) and (12,12)-CASSCF/6-31G* (in italics) levels of theory.

CASSCF(12,12)/6-31G* computations (Table 1). According to these computations, the $^3A''$ state is the ground state T_0 of **5a**. The S_1 state π^2 has A' symmetry and is 24.4 kcal mol $^{-1}$ higher in energy than T_0 , while the S_2 state (A'' symmetry) is 33.6 kcal mol $^{-1}$ less favorable. This ener-

getic ordering is in contrast to that in H_2BN , where the closed-shell singlet state (π^2) is lower in energy than the triplet state ($\sigma^1\pi^1$) [26,27]. Hence, the presence of the electron donor substituents raises the energy of the singlet π^2 relative to that of the triplet state.

Geometrical parameters of the various states are in accord with their electronic structures. The BN-distances involving the nitrene atom computed at the CASSCF(12,12)/6-31G* level of theory shorten from 1.492 Å for the triplet state ($^3A''$) to 1.474 Å for the open-shell singlet ($^1A''$) and 1.433 Å for the π^2 state (1A_1).

3.2.2. $RBNN_3$ (**6**)

The formal shift of the azido group in **5a** results in the planar N-azidophenyliminoborane **6a**. Here, the Ph–B–N unit is essentially linear (177°), but the 164° angle at the imino nitrogen deviates significantly from linearity. The azido group itself also is slightly more bent than in **4a**, 169°. The BN distance of 1.248 Å is typical for an iminoborane; for comparison, in dimethyliminoborane it is 1.241 Å.

Table 1
Relative energies (kcal mol $^{-1}$) of various electronic states of **5a**, **9a**, and **10a** as computed at multiconfigurational levels of theory

	5a $^3A''$	$^1A''$	$^1A'$
CASSCF(12,12)/6-31G*	0	38.2	34.5
MRMP2/6-31G*	0	33.6	24.4
	9a 3A_2	1A_2	1A_1
CASSCF(12,12)/6-31G*	0	20.0	20.5
MRMP2/6-31G*	0	17.3	18.2
	10a 3A_2	1A_2	1A_1
CASSCF(12,12)/6-31G*	0	25.0	29.7
MRMP2/6-31G*	0	14.7	14.9

3.2.3. $RNBN_3$ (**7**)

The formal shift of the phenyl group in **5a** results in the planar N-phenylazidoiminoborane **7a**. The Ph–N–B–N part of the molecule is essentially linear (angle at imino nitrogen: 179°; angle at boron 175°), while a B–N–N angle of 127° involving the azido group is similar to that in **4a** conformers. The iminoborane BN distance of 1.246 Å is slightly shorter than for **6a**. Isomer **7a** is the most stable PhBN₄ isomer; **6a** is almost 45 kcal mol⁻¹ and ³A''-**5a** 55 kcal mol⁻¹ higher in energy.

3.3. RBN_2

3.3.1. *cyclo-RBN*₂ (**8**)

The boradiazirine **8a** is of C_{2v} symmetry and has a three-membered ring with two π electrons. It thus formally comprises a Hückel aromatic system. The N–N-distance is computed to be 1.290 Å and the equivalent BN bonds have a length of 1.423 Å. The bond angle at the boron atom is thus only 53.9°.

We have also investigated an open isomer with a long N–N-distance, which can be regarded as a bisnitrenoborane. Geometry optimizations (B3LYP/6-311+G** and CASSCF(10,11)/6-31G*) result in **8a**, unless the spin state is switched to a quintet. In the quintet state the NN bond is broken (NN distance: 2.588 Å) and the N–B–N angle is widened to 123.4°. The quintet state, however, most likely does not have any importance in the decomposition of **4a**, as it is almost 150 kcal mol⁻¹ (B3LYP/6-311+G**) higher in energy than **8a**.

3.3.2. $RBNN$ (**9**)

The N-nitrenophenyliminoborane **9a** has a linear R–B–N–N arrangement (C_{2v} symmetry). The active space in multiconfiguration computations comprised 12 orbitals (six π orbitals of the phenyl ring and two orthogonal sets of p-type orbitals at the B–N–N unit) and 12 electrons, i.e., CASSCF(12,12). Qualitative analysis of the molecular orbitals of **9a** (and also **10a**, vide infra) indicates that the two exocyclic allyl-type orthogonal π-systems of the B–N–N unit being occupied by six electrons favor a triplet electronic ground state of A₂ symmetry (Fig. 2).

This analysis is confirmed by the MRMP2/6-31G**//CASSCF(12,12)/6-31G* computations (Table 1). The ³A₂ state is lowest, and the singlet states having A₂ and A₁ symmetries are 17.3 and 18.2 kcal mol⁻¹ higher in energy, respectively. The BN distance, 1.299 Å, in ³A₂-**9a** is significantly longer than that of a typical iminoborane (1.241 Å in MeBNMe), while the NN distance, 1.202 Å, is much longer than in a typical organic diazo compound (1.137 Å in diazomethane).

3.3.3. $RNBN$ (**10**)

The N-phenylnitrenoiminoborane **10a** is a constitutional isomer of **9a** and shares very similar structural and electronic features: it also has C_{2v} symmetry with a linear R–

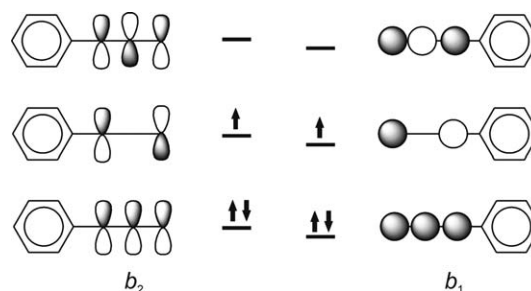


Fig. 2. Schematic representation of the two orthogonal allyl-type systems of the –B–N–N (**9a**) or –N–B–N (**10a**) units neglecting the different sizes of the orbital coefficients.

N–B–N arrangement and a triplet electronic ground state of A₂ symmetry (see also Fig. 2). The singlet states having A₂ and A₁ symmetries are 23.6 and 25.6 kcal mol⁻¹ higher in energy, respectively. Compared to ³A₂-**9a**, the BN bond length of the iminoborane unit is shorter, 1.279 Å, while the B–N distance involving the nitrene atom is longer (1.362 Å) in ³A₂-**10a**.

3.3.4. Energetics

The Hückel aromatic **8a** is most stable among the PhBN₂ isomers, followed by ³A₂-**9a** (19.4 kcal mol⁻¹) and ³A₂-**10a** (27.6 kcal mol⁻¹) as computed at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G** level of theory.

3.4. Thermodynamics of dinitrogen extrusion from PhBN₆

The complete denitrogenation of **4a** according to PhBN₆ → PhB + 3N₂

is an exothermic process, ΔH(0 K) = –21.2 kcal mol⁻¹, according to the CCSD(T)/cc-pVTZ//B3LYP/6-311+G** computations (see Fig. 3). The bisazido compound **4a** is thus clearly a high-energy molecule and only sizeable barriers towards loss of nitrogen make it kinetically stable.

The extrusion of the first nitrogen molecule is endothermic by about 50 kcal mol⁻¹ to give an excited singlet state of the azidophenylborylnitrene ¹A'-**5a**. This singlet state is expected to be short lived for two reasons. First, there is a lower lying triplet state available through intersystem crossing, and second, there are rearrangements possible to give **6a** and **7a**. In particular the shift of a phenyl group from the boron to the nitrene nitrogen atom to give **7a** is extremely favorable thermodynamically: it is exothermic by about 80 kcal mol⁻¹ with respect to the singlet state of **5a**. Formation of **6a**, in contrast, is only exothermic by about 36 kcal mol⁻¹. Absorption of a second photon by **7a** is then expected to give **10a**, the most prevalent isomer observed in our experiment [6].

The mechanisms of phenylborylene **11** formation are unclear, but could either involve **6a** or direct dinitrogen loss from **5a**, to give **9a** and possibly **8a**. Based on the well-known photochemical instability of organic diazo and diazirine systems, the corresponding boron compounds should also readily lose the last N₂ molecule to give **11**.

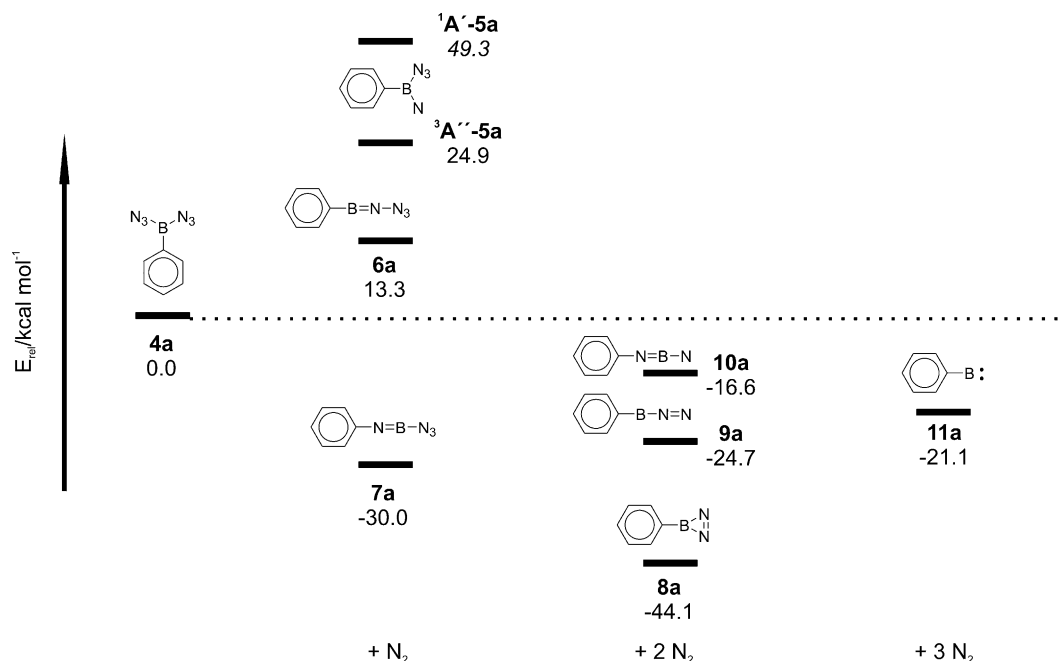


Fig. 3. Schematic representation of the relative energies (kcal mol^{-1}) of $\text{C}_6\text{H}_5\text{BN}_6$, $\text{C}_6\text{H}_5\text{BN}_4 + \text{N}_2$, $\text{C}_6\text{H}_5\text{BN}_2 + 2\text{N}_2$, and $\text{C}_6\text{H}_5\text{B} + 3\text{N}_2$ isomers (not drawn to scale) as computed at the CCSD(T)/cc-pVTZ//B3LYP/6-311+G** level of theory. The energies given for **9a** and **10a** are for the most stable triplet states. The energy given for **6a** is based on comparison with **7a** at the CCSD(T)/cc-pVDZ level. The energy given for the $^1\text{A}'$ state of **5a** is based on MRMP2/6-31G**/CASSCF(12,12)/6-31G* computations for this nitrene.

4. Conclusion

The computational analysis of the PhBN_x ($x = 6, 4, 2$) systems reveals that the decomposition of bisazido-phenylborane **4a** to give phenylborylene **11a** and three nitrogen molecules is a strongly exothermic process. The first intermediate, not detected experimentally, is an azido-borylnitrene **5a**, which has a triplet electronic ground state. A highly exothermic phenyl shift and subsequent cleavage of the remaining azide group provides a rationalization for the experimental observation of nitreno-iminoborane **10a**.

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Appendix A. Supporting information

Cartesian coordinates and absolute energies of stationary points. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.01.017](https://doi.org/10.1016/j.jorganchem.2006.01.017).

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