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1,2-Azaborine: The Boron-Nitrogen Derivative of *ortho*-Benzyne**

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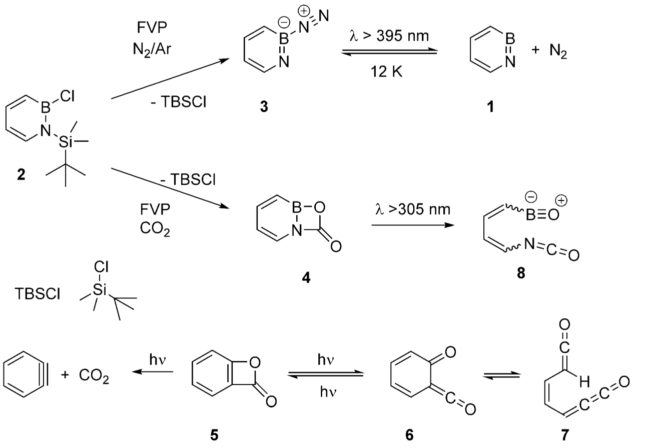
Dedicated to Professor Wolfram Sander on the occasion of his 60th birthday

Abstract: *The BN analogue of ortho-benzyne, 1,2-azaborine, is generated by flash vacuum pyrolysis, trapped under cryogenic conditions, and studied by direct spectroscopic techniques. The parent BN aryne spontaneously binds N_2 and CO_2, thus demonstrating its highly reactive nature. The interaction with N_2 is photochemically reversible. The CO_2 adduct of 1,2-azaborine is a cyclic carbamate which undergoes photocleavage, thus resulting in overall CO_2 splitting.*



Scheme 1. Generation and trapping of 1,2-azaborine (**1**) with N_2 and CO_2 by flash vacuum pyrolysis (FVP) of **2** at 800–850 °C.

The chemistry of arynes, aromatic compounds that lack two hydrogen atoms, can be traced back to 1902.[1] Since then, significant progress has turned *ortho*-benzynes, benzene derivatives that feature a highly strained triple bond, into invaluable reactive intermediates in all branches of organic synthesis.[2] Formal substitution of the triply bonded carbon atoms of *ortho*-benzyne by an isoelectronic boron–nitrogen (BN) unit results in the unknown 1,2-azaborine (**1**; Scheme 1).[3] The similarity of carbon and its BN derivatives is well documented in chemistry, including the graphite/hexagonal boron nitride and benzene/1,2-dihydro-1,2-azaborine pairs, as well as the Dewar forms of the latter.[4] However, evidence for the existence of BN arynes is scarce and indirect as it comes from a self-trapping experiment.[5] Here we show by direct spectroscopic techniques that **1** can exist as a reactive intermediate. We found that **1** can be generated by flash vacuum pyrolysis (FVP) from the precursor **2** by thermal elimination of *tert*-butyldimethylsilylchloride, and isolated in cryogenic matrices. 1,2-Azaborine spontaneously binds dinitrogen N_2 (adduct **3**) in a photochemically reversible transformation. The reaction of 1,2-azaborine with carbon dioxide (CO_2) and susbsequent irradiation results in CO_2 splitting via a cyclic carbamate (**4**) intermediate. In contrast, the cyclic CO_2 adduct of the *ortho*-benzyne, benzoxet-2-one (**5**) undergoes, among other reactions, photodecarboxylation (Scheme 1).[6] Our results show that the two heteroelements, boron and nitrogen, increase and modulate the reactivity compared to the all-carbon analogue. Our research introduces a novel class of reactive intermediates to chemistry. It may prove useful in materials and medicinal chemistry where the boron–nitrogen isoelectronic substitution is sought in order to modify the properties of electronic materials[7] or biologically active compounds.[8]

The thermally induced elimination of trialkylsilyl chlorides from suitable precursors has proven to be a reliable method for the synthesis of iminoboranes.[9] Likewise, FVP of compound **2**[10] (Scheme 1) at oven temperatures of 800–850 °C, and isolation of pyrolysis products in a large excess of argon at 6 K yielded the corresponding silyl chloride as demonstrated by comparison with the infrared spectrum of an authentic sample. Besides the silyl chloride and the unconverted precursor, at least two sets of additional signals were observed (see Figure S1 in the Supporting Information). One set of signals decreased in intensity if increasingly larger amounts of N_2 were included into the argon matrix gas, and at the same time a set of new signals appeared. The most prominent signal among them is a band at 2266 cm^{-1}. This band is reminiscent of the dinitrogen stretching vibration ν(NN) observed previously by Maier et al. for the boraben-

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zene-dinitrogen adduct. When employing $^{15}N_2$, the isotopic shift is 75 cm^{-1}, which is in good agreement with Maier et al.[11] (73.3 cm^{-1}) for borabenzene-dinitrogen, and with computations at the CCSD(T)/TZ2P level of theory. The remaining signals of **3** have, at most, slight isotopic shifts which are in agreement with theoretical calculations (see Table S1 in the Supporting Information). The computations support assignment of the structure as **3**, having end-on coordinated dinitrogen (Scheme 1).

The adduct **3** was found to be photolabile. Irradiation of **3** with the output of a high-pressure mercury lamp ($\lambda > 395$ nm) resulted in disappearance of the set of signals assigned to **3** and the concomitant growth of a set of signals which are assigned to the parent 1,2-azaborine (**1**; Figure 1). This set of signals is the same as that observed after thermolysis of **2** in the absence of dinitrogen. After photogenerating **1** from **3**, the latter could be regenerated by careful annealing of the matrix from 4 K to 12 K (Figure 1), thus indicating that the reaction of **1** + N_2 is essentially without a barrier. Both **3** and [$^{15}N_2$]-**3** behaved identically during photolysis and subsequent annealing. As expected, the bands assigned to **1** (see Table S2 in the Supporting Information) do not show any shifts in the presence of $^{15}N_2$.

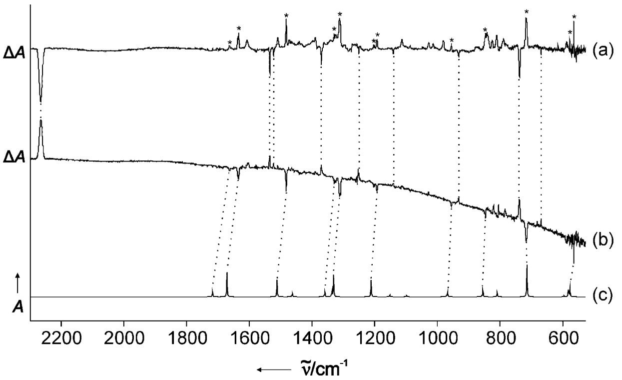

Figure 1. Generation of **1** through irradiation of **3** in Ar/N_2 (70:30). a) IR difference spectrum obtained from the pyrolysis products of **2** frozen at 6 K after two hours of irradiation with visible light ($\lambda > 395$ nm, 4 K). The decreasing signals (pointing downwards) belong to the dinitrogen adduct **3**, and the increasing signals belong to **1** (*) and **2**. b) Difference spectrum after subsequent annealing for 30 min at 12 K (starting from 4 K), thus showing reversibility of the reaction $3 \rightleftharpoons 1 + N_2$. c) Computed IR spectrum of **1** at the CCSD(T)/TZ2P level of theory.

After the successful generation of **1** and trapping with N_2, we used CO_2 as another small molecule for studying the reactivity of **1**. FVP of **2** and deposition with neat CO_2 at 52 K gave new signals in the IR absorption spectrum. The new signals which result from the reaction with CO_2 (Figure 2) can be attributed to the new species **4** by comparison with the computed spectrum (B3LYP/6-311+G**) (see Figure S2 in the Supporting Information). Very prominent is the split band at 1874/79 cm^{-1} which is associated with the carbonyl stretching vibration ν(CO) of the cyclic carbamate. Using isotopically labelled carbon dioxide, $C(^{18}O)_2$ and $^{13}CO_2$, isotopic shifts (Figure 2), which are in good agreement with calculations (B3LYP/6-311+G**), were observed (see Figure S3 and Table S3 in the Supporting Information).

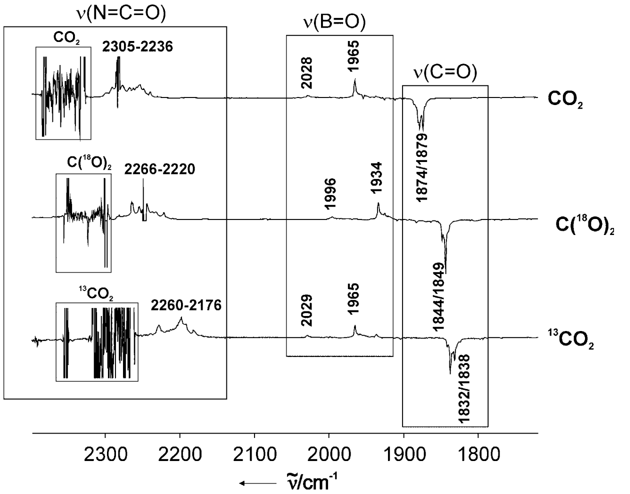

Figure 2. Difference spectra obtained upon irradiation ($\lambda > 305$ nm, 4 K) of **4**, which was generated by trapping of **1** with neat carbon dioxide at a deposition temperature of 52 K after FVP of **2** at 800 °C. Carbonyl stretching of **4** disappears (bands pointing downwards) upon irradiation with UV light, while new bands for **8** are appearing (bands pointing upwards) for natural (top), $C(^{18}O)_2$ (center), and $^{13}CO_2$ (bottom) isotopomers.

The carbon analogue of **4** is benzoxetone (**5**), which is known to be in a photochemical equilibrium with the α-oxoketene **6** (Scheme 1). Prolonged irradiation of **5** leads to *ortho*-benzyne.[6a,b] Recently the reversible rearrangement of **6** into the ketene **7** was reported to proceed at high temperatures.[6d] Irradiation of **4** with UV light ($\lambda > 305$ nm) did not result in loss of CO_2. Rather, **4** underwent ring opening through a retro [2+2] cycloaddition to give **8**, that is, a boron-nitrogen analogue of **7** (Scheme 1).

All signals of **4** disappeared simultaneously while new signals in the range 2303–2236 cm^{-1} of the isocyanate group of **8** and the signals 1965 and 2208 cm^{-1} of the BO unit[12] appeared (Figure 2). The structure of **8** could be confirmed again through the use of isotopically labelled carbon dioxide and is in excellent agreement with the corresponding computed isotopic shifts (B3LYP/6-311+G**; see Table S4 in the Supporting Information). Further irradiation with $\lambda = 254$ nm leads to decomposition of **8** to an unknown product.

The most remarkable structural feature of **1** is the distortion of the hexagon with a small angle at N and a wide angle at boron in the singlet ground state, as noted previously.[3,5] This feature can be rationalized by the difference in electronegativity: the more electronegative N atom prefers to have a lone pair (HOMO-1) in the molecular plane, while the more electropositive B atom prefers an empty in-plane orbital (LUMO) which has a strong p character (Figure 3a). The natural bond orbital (NBO) analysis arrives at occupancies of 1.80 e^- and 0.22 e^- for the lone pair and empty orbitals, respectively, and a pronounced $n(N) \rightarrow n^*(B)$ interaction [$E(2) = 27.6$ kcal mol^{-1}] according to the second-order perturbation estimate of the donor–acceptor interaction in the NBO basis. The natural charges obtained from the NBO

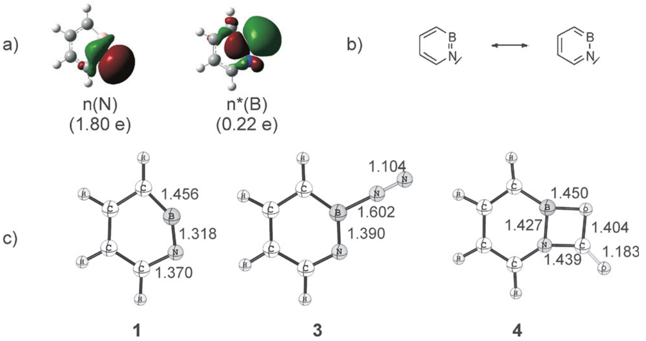

Figure 3. a) Natural bond orbitals (NBOs) and their occupation numbers which describe the in-plane part of the BN linkage as computed at the B3LYP/6-311+G** level of theory. b) Resonance forms of 1,2-azaborine. c) Structures and selected bond lengths in Å of molecules **1**, **3**, and **4** as computed at the CCSD(T)/TZ2P level of theory, $r(N_2) = 1.103$ Å.

analysis on N and B are large (−0.79 on N and +0.97 on B) while the Wiberg bond index between B and N is only 1.46. These data make the resonance forms (Figure 3b) a more reasonable description of the electronic structure of **1** than does the BN triple bond, despite the isoelectronic relationship with *ortho*-benzyne. In a sense, the boron and nitrogen centers in **1** may be regarded as an internal frustrated Lewis pair.[13] The empty n_B* orbital is responsible for the pronounced Lewis acidity of **1** and allows binding of such a poor Lewis base as N_2. According to CCSD(T)/TZ2P+ZPVE computations, the binding energy is 6.0 kcal mol^{-1}. The B–N_2 distance is 1.602 Å, and the N–N distance is hardly elongated (Figure 3c). In contrast, the endocyclic B–N distance is increased from 1.318 Å in **1** to 1.390 Å in **3**. Note that the B–N distance in *tert*-butyl(*tert*-butylimino)borane is 1.258(4) Å and ranges between 1.330–1.340 Å in some of its N-heterocyclic carbene adducts.[9a,14] With the ambiphilic CO_2 molecule both the electron-deficient boron and the electron-rich nitrogen centers are involved in binding with an overall binding energy of 29 kcal mol^{-1}, as calculated at the CCSD(T)/TZ2P + ZPVE(B3LYP/6-311+G**) level of theory.

In summary, we have established the first synthesis and characterization of 1,2-azaborine, the BN analogue of *ortho*-benzyne. 1,2-Azaborine can be generated by flash vacuum thermolysis and can exist under cryogenic matrix isolation conditions as demonstrated by direct spectroscopic techniques. 1,2-Azaborine has a very Lewis-acidic boron center that undergoes reversible binding of a dinitrogen molecule, and also spontaneously binds CO_2. The research described herein opens the wide and uncharted field of BN aryne chemistry and is expected to allow access to novel boron–nitrogen-doped molecular architectures of importance in medicinal and materials chemistry.

Keywords: ab initio calculations · arynes · boron · matrix isolation · nitrogen heterocycles

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