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B,N Heterocycles

Photoisomerization of 1,2-Dihydro-1,2-Azaborine: A Matrix Isolation Study[**]

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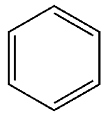
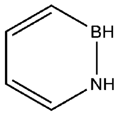
Dedicated to Professor Helge Willner on the occasion of his 65th birthday

Boron–nitrogen heterocycles have received much interest in recent years, owing to their wide applications as ligands and potential use in organic optical and electronic devices.[1,2] 1,2-Dihydro-1,2-azaborine compounds are six-membered heterocycles and are isoelectronic to benzene, with a $C{=}C$ unit replaced by a $B{=}N$ unit.[2] These compounds were initially reported in the 1960s by Dewar and by White,[3] and since 2000 examples of substituted 1,2-dihydro-1,2-azaborines[4] as well as their potential in coordination chemistry were explored by Ashe et al.[5] Interest in 1,2-dihydro-1,2-azaborine reactivity,[6] properties,[7] and applications[8] led to the synthesis and isolation of parent 1,2-dihydro-1,2-azaborine (**1**), a benzene isostere, in 2009.[9]

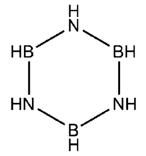
Varying analyses, including reaction calorimetry, chemical derivatization, and magnetic criteria, concluded that the aromatic character of **1** is intermediate of that between benzene and borazine, the inorganic isoelectronic relative of benzene.[6,7,9,10] Since the synthesis of **1** in 2009, examples of the types of chemistry it performs have been reported. For example, **1** readily undergoes nucleophilic aromatic substitution reactions under mild reaction conditions[11] and cationic 1,2-azaborines have recently been synthesized by Liu and coworkers.[12] To the best of our knowledge, the photochemistry of 1,2-dihydro-1,2-azaborines has not been investigated.



Benzene



1,2-Dihydro-1,2-azaborine (**1**)



Borazine

Photoisomerization reactions of aromatic molecules have been extensively explored over the past five decades, and their valence isomers have attracted vast interest from both synthetic and theoretical chemists.[13] Benzene has received the most attention, and four of its valence isomers are now well-known[14] and have been extensively investigated experimentally and theoretically.[15] Mixtures of fulvene and benzvalene are produced during benzene photolysis at 253.7 nm in solution,[14b] and Dewar benzene is observed in addition after photolysis at 204 nm in the liquid phase.[16] Fulvene is the predominant isomer produced in the gas phase.[17] Mixtures of Dewar benzene, fulvene, and benzvalene are major products in low-temperature argon matrices at 253.7 nm; however, after prolonged photolysis, reisomerizaton of benzvalene to benzene occurs.[18]

The photochemical conversion of six-membered heterocyclic aromatic compounds, such as pyridine, was first realized in 1970, when a solution of pyridine in acetonitrile was excited by a low-pressure Hg lamp.[19] Dewar pyridine was preferentially produced as an intermediate, and was found to convert back into pyridine within 15 min at room temperature. More recently, photolysis of pyridine, studied by matrix isolation IR spectroscopy, produced Dewar pyridine.[18,20]

Herein, we describe the photoisomerization of **1** in low-temperature neon, argon, or xenon matrices,[21] where photolysis products that are too unstable at room temperature can be identified spectroscopically. 1,2-Dihydro-1,2-azaborine was sublimed (−80 °C) and co-condensed with a large excess of noble gas on a cold spectroscopic window. Vibrational frequencies of **1** in neon are shown in Table 1 and Figure 1 (the complete spectrum can be found in Supporting Information). Infrared signals that are due to a small amount of tetrahydrofuran (THF), which was carried through from a precursor stage, were also observed.

The remaining IR bands were assigned to **1** based on comparison with theoretical calculations (B3LYP/6-311++G**; Figure 1). The N−H ($3463.1\ \mathrm{cm}^{-1}$) and B−H (2547.8–$2527.0\ \mathrm{cm}^{-1}$) stretching vibrations were also in agreement with previous experimental data (thin-film IR spectroscopy; N−H $3398\ \mathrm{cm}^{-1}$, B−H $2525\ \mathrm{cm}^{-1}$).[9a] The signal pair at 1540.1 and $1543.4\ \mathrm{cm}^{-1}$ has a 1:4 intensity that is typical of boron compounds with a natural isotope composition ($^{10}B/^{11}B$ 1:4.1) and is due to the $B{=}N$ stretching vibration. Strong vibrational bands were also found between 900–$550\ \mathrm{cm}^{-1}$, and are assigned as B−H (897.4, $903.4\ \mathrm{cm}^{-1}$), C−H (816.7, 709.2, $711.9\ \mathrm{cm}^{-1}$), and N−H bending modes ($574.2\ \mathrm{cm}^{-1}$).

After deposition, **1** was photolyzed (253.7 nm) for a total of 22 hours. The progression of the experiment was analyzed at regular intervals; however, only one set of new bands arising from a single photoproduct was detected. After 105 min, full conversion of **1** into a photoproduct was

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Table 1: Experimental (Ne, 4 K) and calculatred vibrational frequencies of **1**.[a]

ν_{exp} [cm^{-1}]	ω_{theor} [cm^{-1}][b]	Assignment
3463.1	3604.4	ν(NH)
3046.3–3008.2	3200.4–3130.5	ν(CH)
2547.8-2527.0	[^{10}B] 2630.9, [^{11}B] 2618.8	ν(BH)
1623.0-1622.3[c]	1651.7	ν(CC)
[^{10}B] 1543.4	[^{10}B] 1571.2	ν(BN)
[^{11}B] 1540.1	[^{11}B] 1568.2	
1453.6, 1460.7	1486.7	δ(in-plane CH)
1430.3	1459.4	δ(in-plane CH)
1360.6	1382.3	δ(in-plane CH)
1216.8	1241.8	δ(in-plane CH)
976.2	990.9	δ(out-of-plane CH)
[^{10}B] 903.4	[^{10}B] 924.4	δ(BH)
[^{11}B] 897.4	[^{11}B] 914.7	
816.7	830.2	δ(out-of-plane CH)
709.2, 711.9	723.1	δ(out-of-plane CH)
574.2	583.9	δ(NH)

[a] B3LYP/6-311++G**. [b] Unscaled. [c] Tentative assignment owing to overlap with H_2O bending frequencies.

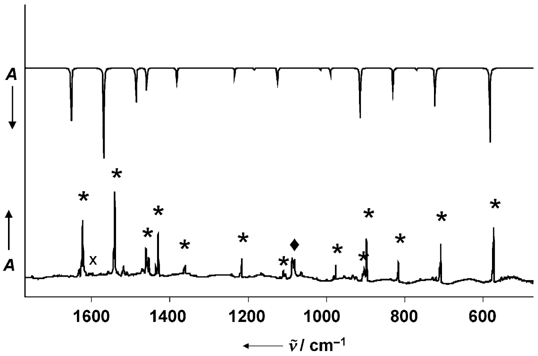


Figure 1. Observed (Ne, 4 K, bottom trace) and calculated (top trace) IR spectra for 1,2-dihydro-1,2-azaborine **1** (⋆). H_2O (x) and THF impurities (♦) are marked.

achieved (Table 2, Figure 2; for full spectra, see the Supporting Information). Impurities within the sample (THF, H_2O) did not undergo photolysis, and the signals associated with them remained unchanged after irradiation.

Matrix-controlled photochemistry of benzene at 253.7 nm produces mixtures of Dewar benzene, fulvene, and benzvalene as initial photoproducts.[18] After prolonged photolysis, higher-energy isomers are not observed, but instead photo-induced reisomerization of benzvalene to benzene.[18] It was thought that photolysis of **1** could behave in a similar way and yield mixtures of BN-fulvene **2**, BN-benzvalene **3**, and BN-Dewar **4** (Scheme 1). Theoretical calculations (MP2/6-311++G**) identify BN-fulvene **2** as the most stable isomer ($\Delta E = +17.8$ kcal mol^{-1} with respect to **1**). BN-benzvalene **3** and BN-Dewar **4** are higher in energy than **1** by +55.8 and +59.7 kcal mol^{-1}, respectively. The highly strained BN-bicyclo-2-propenyl **6** and BN-prismane **5** are +101.2 and +112.9 kcal mol^{-1} higher in energy than **1**. The possibility of constitutional isomers owing to the BN moiety was also considered, but these are all higher in energy than **2**–**6** (see the

Table 2: Comparison of vibrational frequencies after irradiation at 253.7 nm (Ne, 4 K) and calculated absorptions for **4**.[a]

ν_{exp} [cm^{-1}]	ω_{theor} [cm^{-1}][b]	Assignment
3482.2	3615.6	ν(NH)
3117.8–2958.5	3197.0–3084.0	ν(CH)
2602.3–2566.5	[^{10}B] 2663.4, [^{11}B] 2650.4	ν(BH)
[^{10}B] 1392.8	[^{10}B] 1418.0,	ν(BN)
[^{11}B] 1374.5	[^{11}B] 1399.1	
1283.6	1298.5	δ(in-plane CH)
1229.8	1253.5	δ(in-plane CH)
1179.7	1201.8	δ(in-plane CH)
1161.0	1175.2	δ(in-plane CH)
1143.7	1164.4	δ(in-plane CH)
1039.3	1055.3	δ(in-plane CH)
995.4	1004.0	δ(in plane CH)
943.9	961.9	δ(out-of-plane CH)
911.1	924.1	δ(out-of-plane CH)
861.8	877.3	δ(out-of-plane CH)
[^{10}B] 753.0	[^{10}B] 767.8,	δ(BH)
[^{11}B] 747.6	[^{11}B] 763.1	
716.6	723.9	δ(out-of-plane CH)
582.7	590.7	δ(NH)
468.3	472.0	δ(out-of-plane CH)

[a] B3LYP/6-311++G**. [b] Unscaled.

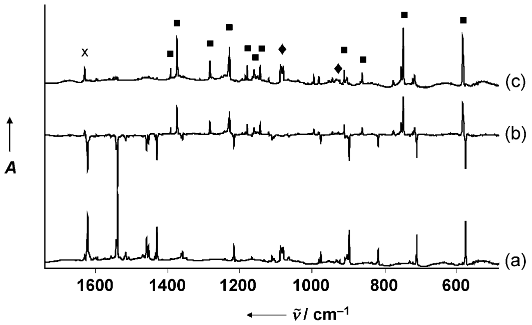
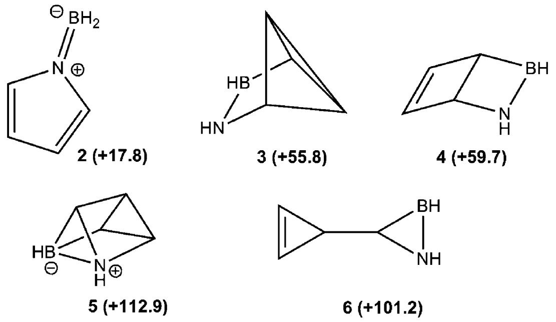


Figure 2. Observed IR spectra (Ne, 4 K) a) before and c) after irradiation (105 min, $\lambda = 253{,}7$ nm); b) difference spectrum: bands pointing downwards disappear and bands pointing upwards appear during irradiation. H_2O (x), THF (♦), BN-Dewar, **4** (■).



Scheme 1. Possible photoisomers of 1,2-dihydro-1,2-azaborine (MP2/6-311++G**). Energies [kcal mol^{-1}] relative to **1** given in parentheses.

Supporting Information). Vibrational frequencies were calculated for isomers **2**–**4** and compared with the observed IR spectrum (1700–550 cm^{-1}; Figure 3). Computed IR spectra of the constitutional isomers of **2**–**4** were also compared to the experimental spectrum; however, higher-energy isomers were not observed (for IR spectra, see the Supporting Information). The experimental spectrum is in good agreement with that of BN-Dewar form **4**, where four strong absorbances in the 1600–550 cm^{-1} region were observed (expt.: 582.7, 747.6, 1229.8, [^{11}B] 1374.5, [^{10}B] 1392.8 cm^{-1}; calcd.: 590.7, 763.1, 1253.5, [^{11}B] 1399.1, [^{10}B] 1418.0 cm^{-1}). The difference in wavenumbers between absorbances in the calculated spectrum is almost identical to that of the absorbance distances in the experimental spectrum.

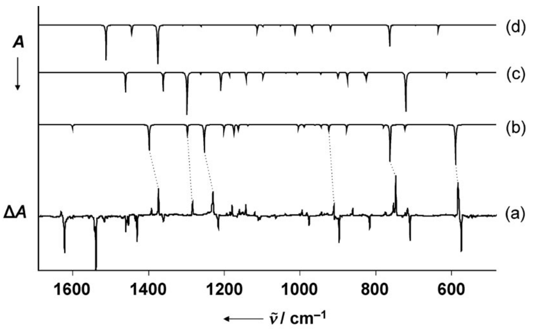


Figure 3. Observed and calculated IR spectra for isomers of **1**. a) Observed IR difference spectrum between those observed before and after 105 min UV irradiation (Ne, 4 K); b) a spectral pattern for BN-Dewar **4**; c) a spectral pattern for BN-benzvalene **3**; d) a spectral pattern for BN-fulvene **2**.

The formation of the Dewar form **4** is similar to the photochemistry of matrix-isolated pyridine.[18,20] While benzene photoisomerizations are supressed in solid xenon, pyridine solely produces the Dewar form in both argon and xenon. This was taken as a strong indication of the involvement of a triplet state in the photoisomerization of pyridine.[18] We observe that **1** yields its Dewar form also in solid xenon, indicating that the photochemistry in inert gas matrices differs from that of benzene. Further photochemical and photophysical investigations of **1** in other environments are highly desirable.

In the optimized structure (CCSD(T)/cc-pVTZ; Figure 4) of BN-Dewar **4**, the C3−C4 bridging bond distance is 1.573 Å. This compares well with the experimental electron-diffraction structure of Dewar benzene (1.574(5) Å).[22] The B−N bond length is 1.397 Å, which is typical for B−N double bonds,[23] and the carbon-carbon double bond is 1.344 Å (1.345 Å, Dewar benzene).[22] The long B−C bond (1.610 Å) and the short N−C bond length (1.472 Å) result in a distortion of the corresponding four-membered ring. The B-C3-C2 and the N-C4-C1 angles are 115.4° and 116.1°, respectively. These values compare well to Dewar benzene, which has a corresponding C-C-C angle of 116.7(6)°.[22]

In summary, an IR spectrum of 1,2-dihydro-1,2-azaborine **1** in low-temperature neon matrices has been obtained and analyzed. The observed spectrum compared well with that of the DFT calculation. Subsequent photolysis of **1** was found to produce the BN-Dewar form **4** exclusively.

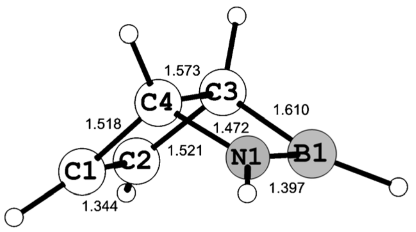
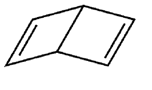
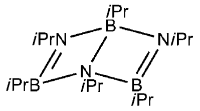


Figure 4. Optimized geometrical structure of BN-Dewar **4** (CCSD(T)/cc-pVTZ). Bond lengths are in Å.

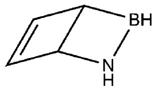
The first observation of Dewar benzene was reported in 1963,[14a,24] a substituted Dewar borazine was initially reported in 1984,[25,26] and to the best of our knowledge, this is the first time that the Dewar isomer (**4**) of 1,2-dihydro-1,2-azaborine **1** has been observed. Computed harmonic vibrational frequencies of **4** compared well to that of the observed spectrum, and no other valence isomers were detected. The development of benzene mimics, such as **1**, is an increasingly important and emerging area of chemistry and the discoveries of the type of reactivity **1** can undergo is of fundamental interest to the scientific community.



Dewar benzene



iPr-substituted
Dewar borazine



Dewar 1,2-dihydro-
1,2-azaborine

Experimental Section

1,2-Dihydro-1,2-azaborine was synthesized according to Liu et al.[9a] Matrix experiments were carried out according to standard techniques[27] using a SHI CKW-21A displex closed-cycle helium cryostat. 1,2-Dihydro-1,2-azaborine was sublimed from a glass flask at −80 °C (EtOH/Julabo FT902 immersion cooler) and co-condensed with a large excess of neon 5.0 (Westfalen), argon 6.0 (Westfalen), or xenon 4.0 (Westfalen), which was dosed to 2.0 sccm by a mass flow controller (MKS mass flow PR400B) prior to being condensed onto a cold CsI window (Ne and Ar 4 K, Xe 25 K). Deposition occurred for a total of 180 min. Matrix photolysis was achieved using a low-pressure mercury lamp (UVP, 253.7 nm), and light was transmitted through a quartz window present in the vacuum shroud. All FTIR spectra were measured between 4000 and 400 cm^{-1} on a Bruker V70 spectrometer at a resolution of 0.5 cm^{-1}. All calculations were performed with the Gaussian 09 program suite using either the functional B3LYP or second-order Møller–Plesset perturbation (MP2) theory with the implemented 6-311++G** basis set.[28] Geometries were optimized and harmonic vibrational frequencies were computed for all of the compounds. Furthermore, the geometry of **4** was optimized employing coupled-cluster theory with singles, doubles, and a perturbative estimate of triple excitations [CCSD(T)][29] (all electrons were correlated) in conjunction with the cc-pVTZ[30] basis set using the CFOUR program.[31]

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