Published in final edited form as:

Angew Chem Int Ed Engl. 2012 October 22; 51(43): 10880–10883. doi:10.1002/anie.201203546.

Photoisomerization of 1,2-Dihydro-1,2-Azaborine – A Matrix Isolation Study

Sarah A. Brough^a, Ashley N. Lamm^b, Shih-Yuan Liu^b, and Holger F. Bettinger^a

Shih-Yuan Liu: lsy@uoregon.edu; Holger F. Bettinger: holger.bettinger@uni-tuebingen.de

Institut für Organische Chemie, Universität Tübingen, Auf der Morgenstelle 18, 72076 Tübingen, Germany

Department of Chemistry, University of Oregon, Eugene, OR 97403-1253, USA, lsy@uoregon.edu

Keywords

boron; heterocycles; matrix isolation; benzene; density functional calculations

Boron-nitrogen heterocycles have received much interest in recent years, due to their wide applications as ligands^[1] and potential use in organic optical and electronic devices.^[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.^[3] These compounds were initially reported in the 1960's by Dewar and White,^[4] and during the last ten years, examples of substituted 1,2-dihydro-1,2-azaborines^[1c,5] as well as their potential in coordination chemistry were explored by Ashe *et al.*^[6] Renewed interest in 1,2-dihydro-1,2-azaborine chemistry,^[1c,7] properties^[8] and applications^[9] led to the synthesis and isolation of parent 1,2-dihydro-1,2-azaborine (**1**), a benzene isostere, in 2009.^[10]

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.^[6c, 10, 11] Since the synthesis of **1** in 2009, examples of the types of chemistry it performs are appearing in the literature. For example, **1** readily undergoes nucleophilic aromatic substitution reactions under mild reaction conditions^[12] and cationic 1,2-azaborines have recently been synthesized by Liu and co-workers.^[13] To the best of our knowledge, the photochemistry of 1,2-dihydro-1,2-azaborines has never 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.^[14] Benzene has received the most attention and five of its valence isomers are now well known and have been extensively investigated experimentally^[14a,15] and theoretically^[16] in the literature. Mixtures of fulvene and benzvalene are produced after benzene photolysis at 253.7 nm in the liquid phase,^[17] and Dewar benzene is observed after photolysis at 204 nm in the condensed phase.^[15a] Fulvene is the predominant isomer produced in the gas phase.^[18] Mixtures of Dewar benzene, fulvene and benzvalene are major products in low temperature argon matrices at 253.7 nm, however after prolonged photolysis, reversion of benzvalene to benzene occurs.^[19]

The photochemical conversion of six membered heterocyclic aromatic compounds, such as pyridine was first realized in 1970, where a solution of pyridine in acetonitrile was excited by a low pressure Hg lamp.^[20] Dewar pyridine was preferentially produced as an intermediate, and was found to convert back to pyridine within 15 minutes at room temperature. More recently, photolysis of pyridine studied by matrix isolation infrared spectroscopy, produced Dewar pyridine.^[19,21]

Here, we describe for the first time photoisomerization of **1** in low temperature neon, argon, or xenon matrices,^[22] 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 (complete spectrum can be found in Supporting Information). Infrared signals 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 cm^{−1}) and B-H (2547.8-2527.0 cm^{−1}) stretching vibrations were also found to be in agreement with previous experimental data (thin film IR spectroscopy, N-H, 3460.0 cm^{−1}, B-H, 2536.0-2527.9 cm^{−1}).^[10] The signal pair at 1540.1 and 1543.4 cm^{−1} has a 1:4 intensity typical of boron compounds with a natural isotope composition (¹⁰B/¹¹B 1:4.1) and is due to the B=N stretching vibration. Strong vibrational bands were also found between 900-550 cm^{−1}, and are assigned as B-H (897.4, 903.4 cm^{−1}), C-H (816.7, 709.2, 711.9 cm^{−1}) and N-H bending modes (574.2 cm^{−1}).

After deposition, **1** was photolyzed (253.7 nm) for a total of twenty two hours. The progression of the experiment was analysed at regular intervals, however, only one set of new bands due to a single photoproduct was detected. After 105 minutes, full conversion of **1** to a photoproduct was achieved (Table 2, Figure 2, full spectra available in Supporting Information). Impurities within the sample 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.^[19] After prolonged photolysis, higher energy isomers are not observed, rather photoinduced reversion of benzvalene to benzene.^[19] 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** (Figure 3). Theoretical calculations (MP2/6-311++G** level of theory) identify BN-fulvene, **2**, as the most stable isomer (ΔE = +17.8 kcal/mol), 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, respectively. The highly strained BN-bicyclo-2-propenyl (**6**) and BN-prismane (**5**) are +101.2-112.9 kcal/mol less stable than **1**. The possibility of constitutional isomers due to the BN moiety was also considered, but

these are all higher in energy than **2–6** (see Supporting Information). Vibrational frequencies were calculated for isomers **2–4** and compared with the observed infrared spectrum (1700–550 cm^{-1} , Figure 4). Computed infrared spectra of the constitutional isomers of **2–4**, were also compared to the experimental spectrum; however, higher energy isomers were not observed (infrared spectra available in 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 (experimental: 582.7, 747.6, 1229.8, [^{11}B] 1374.5, [^{10}B] 1392.8 cm^{-1} , calculated: 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.

The formation of the Dewar form, **4**, is similar to the photochemistry of matrix isolated pyridine.^[19,21] While benzene photoisomerizations are suppressed 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.^[19] 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 (CCSD(T)/cc-pVTZ, Figure 5) structure 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).^[23a] The B–N bond length is 1.397 Å, which is typical for B–N double bonds,^[24] and the carbon-carbon double bond is 1.344 Å (1.345 Å, Dewar benzene).^[23a] 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 angle and the N–C4–C1 angles are 115.4° and 116.1°, respectively. This compares well to Dewar benzene, which has a corresponding C–C–C bond angle of 116.7(6)°.^[23a]

In summary, an infrared 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 exclusively the BN-Dewar form, **4**.

The first observation of Dewar benzene was reported in 1962,^[15a, 25] a substituted Dewar borazine was initially reported in 1984,^[26, 27] and to the best of our knowledge, it 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. 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 chemistry **1** can undergo is of fundamental interest to the scientific community.

Experimental Section

1,2-Dihydro-1,2-azaborine was synthesized according to Liu *et al.*^[7] Matrix experiments were carried out according to standard techniques^[28] using a SHI CKW-21A dispex 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 minutes. 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 FT-IR spectra were measured between 4000 and 400 cm^{-1} on a Bruker V 70 spectrometer using 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.^[29] Geometries were optimized and harmonic vibrational frequencies were computed for all compounds. In addition, the geometry of **4** was optimized employing coupled cluster theory with singles, doubles, and a perturbative estimate of triples excitations [CCSD(T)]^[30] (all electrons were correlated) in conjunction with the cc-pVTZ^[31] basis set using the CFOUR program.^[32]

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

Support for this research has been provided by the Deutsche Forschungsgemeinschaft, the Fonds der chemischen Industrie, the National Science Foundation (Grant DGE-0742540; A.N.L), the National Institutes of Health (Grant R01-GM094541).

References

1. a) Ly HV, Tuononen HM, Parvez M, Roesler R. Chem. Commun. 2007;4522–4524. b) Ghesher I, Piers WE, Parvez M, McDonald R. Organometallics. 2004; 23:3085–3087. c) Ashe AJ III, Fang X. Org. Lett. 2000; 2:2089–2091. [PubMed: 10891237]
2. a) Bendikov M, Wudl F, Perpichka DF. Chem. Rev. 2004; 104:4891–4945. [PubMed: 15535637] b) Jaska CA, Emslie DJH, Bosdet MJD, Piers WE, Sorensen TS, Parvez M. J. Am. Chem. Soc. 2006; 128:10885–10896. [PubMed: 16910684] c) Mansell SM, Norman NC, Russel CA. Dalton Trans. 2010; 39:5084–5086.
3. For reviews see: Campbell PG, Marwitz AJV, Liu S-Y. Angew. Chem. Int. Ed. 2012; 51:6074–6092. Bosdet MJD, Piers WE. Can. J. Chem. 2009; 87:8–29. Liu Z, Marder TB. Angew. Chem. Int. Ed. 2008; 47:242–244.
4. White DG. J. Am. Chem. Soc. 1963; 85:3634–3636. b) Culling GC, Dewar MJS, Marr PA. J. Am. Chem. Soc. 1964; 86:1125–1127.
5. Ashe AJ III, Fang X, Fang X, Kampf JW. Organometallics. 2001; 20:5413–5418.
6. a) Pan J, Kampf JW, Ashe AJ III. Organometallics. 2004; 23:5626–5629. b) Pan J, Kampf JW, Ashe AJ III. Organometallics. 2006; 25:197–202. c) Pan J, Kampf JW, Ashe AJ III. J. Organomet. Chem. 2009; 694:1036–1040.
7. a) Abbey ER, Zakharov LN, Liu S-Y. J. Am. Chem. Soc. 2008; 130:7250–7252. [PubMed: 18479099] b) Paetzold P, Stanescu C, Stubenrauch JR, Bienmüller M, Englert U. Z. Anorg. Allg. Chem. 2004; 630:2632–2640.
8. a) Silva PJ, Ramos MJ. J. Org. Chem. 2009; 74:6120–6129. [PubMed: 19627164] b) Tanjaroon C, Daly A, Marwitz AJV, Liu S-Y, Kukolich S. J. Chem. Phys. 2009; 131:224312. [PubMed: 20001041] c) Del Bene JE, Yáñez M, Alkorta I, Elguero J. J. Chem. Theory Comput. 2009; 5:2239–2247. d) Kranz M, Clark T. J. Org. Chem. 1992; 57:5492–5500.
9. Campbell PG, Zakharov LN, Grant DJ, Dixon DA, Liu S-Y. J. Am. Chem. Soc. 2010; 132:3289–3291. [PubMed: 20214402]
10. a) Marwitz AJV, Matus MH, Zakharov LN, Dixon DA, Liu S-Y. Angew. Chem. Int. Ed. 2009; 48:973–977. b) Chrostowska A, Xu S, Lamm AN, Maziere A, Weber CD, Dargelos A, Baylere P, Graciaa A, Liu S-Y. J. Am. Chem. Soc. 2012; 134:10279–10285. [PubMed: 22616808]

11. a) Carion R, Liégeois V, Champagne B, Bonifazi D, Pelloni S, Lazzeretti P. *J. Phys. Chem. Lett.* 2010; 1:1563–1568. b) Campbell PG, Abbey ER, Neiner D, Grant DJ, Dixon DA, Liu S-Y. *J. Am. Chem. Soc.* 2010; 132:18048. [PubMed: 21141893]
12. Lamm AN, Garner EB III, Dixon DA, Liu S-Y. *Angew. Chem. Int. Ed.* 2011; 50:8157–8160.
13. Marwitz AJV, Jenkins JT, Zakharov LV, Liu S-Y. *Angew. Chem. Int. Ed.* 2010; 49:7444–7447.
14. a) Harman PJ, Kent JE, O'Dwyer MP, Griffith DWT. *J. Phys. Chem.* 1981; 85:2731–2733. b) Noyes WA Jr, Al-Ani KE. *Chem. Rev.* 1974; 1:29–43. c) Dunkin, IR.; Allen, NS.; Horspool, WM.; Gilbert, A. *Photochemistry*. Dunkin, IR., editor. Vol. 36. Cambridge: RSC Publishing; 2007. p. 91–132.
15. a) Ward HR, Wishnok JS. *J. Am. Chem. Soc.* 1968; 90:1085–1086. b) Kent JE, Harman PJ, O'Dwyer MP. *J. Phys. Chem.* 1981; 85:2726–2730. c) Billups WE, Haley MH. *Angew. Chem. Int. Ed.* 1989; 28:1711–1712.
16. a) Li Z, Rogers DW, McLafferty FJ, Mandziuk M, Podosenin AV. *J. Phys. Chem. A.* 1999; 103:426–430. b) Schulman JM, Disch RL. *J. Am. Chem. Soc.* 1985; 107:5059–5061. c) Newton MD, Schulman JM, Manus MM. *J. Am. Chem. Soc.* 1974; 96:17–23.
17. Wilzbach KE, Ritscher JS, Kaplan L. *J. Am. Chem. Soc.* 1967; 89:1031–1032.
18. Kaplan L, Wilzbach KE. *J. Am. Chem. Soc.* 1967; 89:1030–1031.
19. Johnstone DE, Sodeau JR. *J. Phys. Chem.* 1991; 95:165–169.
20. Wilzbach KE, Rausch DJ. *J. Am. Chem. Soc.* 1970; 92:2178–2179.
21. Kudoh S, Takayanagi M, Nakata M. *J. Photoch. Photobio. A.* 1999; 123:25–30.
22. Due to the higher quality, the neon data are discussed in the paper. Experiments performed in argon or xenon gave similar results, spectra and band tables can be found in the Supporting Information.
23. Experiment: McNeill EA, Scholer FR. *J. Mol. Struct.* 1976; 31:65.; for representative computations, see: Priyakumar UD, Dinadayalane TC, Sastry GN. *New J. Chem.* 2002; 26:347–353. Li Z, Rogers DW, McLafferty FJ, Mandziuk M, Podosenin AV. *J. Phys. Chem. A.* 1999; 103:426–430.
24. Paetzold P. *Pure Appl. Chem.* 1991; 63:345.
25. a) Van Tamelen EE, Pappas SP. *J. Am. Chem. Soc.* 1962; 84:3789–3791. b) Van Tamelen EE. *Angew. Chem. Int. Ed.* 1965; 4:738–745. c) Van Tamelen EE, Pappas SP, Kirk KL. *J. Am. Chem. Soc.* 1971; 93:6092–6101.
26. a) Paetzold P, Von Plotho C, Schmid G, Boese R. *Z. Naturforsch., B: Chem. Sci.* 1984; 39:1069–1075. b) Steuer HA, Meller A, Elter G. *J. Organomet. Chem.* 1985; 295:1–6. c) Paetzold P, Kiesgen J, Krahe K, Meier HU, Boese R. *Z. Naturforsch., B: Chem. Sci.* 1991; 46:853–860. d) Münster J, Paetzold P, Schröder E, Schwan H, Von Bennigsen T. *Z. Anorg. Allg. Chem.* 2004; 630:2641–2651.
27. For reviews see: Paetzold P. *Adv. Inorg. Chem.* 1987; 31:123–170. Paetzold P. *Phosphorus, Sulfur Silicon Relat. Elem.* 1994; 93–94:39–50.
28. Dunkin, IR. *Matrix-Isolation Techniques*. New York: Oxford University Press; 1998.
29. Frisch, et al. *GAUSSIAN 09*, Revision C.01. Wallingford, CT (USA): Gaussian Inc.; 2010.
30. a) Raghavachari K, Trucks GW, Pople JA, Head-Gordon M. *Chem. Phys. Lett.* 1989; 157:479–483. b) Bartlett RJ, Watts JD, Kucharski SA, Noga J. *Chem. Phys. Lett.* 1990; 165:513–522. c) Scuseria GE. *J. Chem. Phys.* 1991; 94:442–447.
31. Dunning TH. *J. Chem. Phys.* 1989; 90:1007–1023.
32. Stanton, JF., et al. *CFOUR*, Coupled-Cluster techniques for Computational Chemistry. for the current version, see <http://www.cfour.de>

Figure 1. Observed (Ne, 4K, bottom trace) and calculated (top trace) infrared spectra for 1,2-dihydro-1,2-azaborine **1** (*). H₂O (x) and THF (♦) impurities are marked.

Figure 2. Observed infrared spectra (Ne, 4K); (a) before, (c) after irradiation (105 minutes, $\lambda = 253.7$ nm); (b) difference spectrum, bands pointing downwards disappear, bands pointing upwards appear during irradiation. H_2O (x), THF (♦), BN-Dewar, **4** (■)

Figure 3.

Possible photo isomers of 1,2-dihydro-1,2-azaborine (MP2/6-311++G**). Energies (in kcal mol⁻¹) relative to **1** given in parentheses.

Figure 4.

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

Figure 5. Optimized geometrical structure of BN-Dewar, **4** (CCSD(T)/cc-pVTZ). Bond lengths are in Å.

Table 1Vibrational Frequencies (cm^{-1}) of 1,2-Dihydro-1,2-Azaborine **1** from Experiment (Ne, 4 K) and Theory^[a]

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

^[a] B3LYP/6-311++G**,^[b] Unscaled,^[c] Tentative assignment, due to overlap with H₂O bending frequencies

Table 2

Comparison of Vibrational Frequencies (cm^{-1}) after Irradiation at 253.7nm (Ne, 4 K) and Calculated Wavenumbers (cm^{-1}) for BN-Dewar, 4^[a]

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

^[a] B3LYP/6-311++G**,

^[b] Unscaled