Inorg. Chem. **2006**, *45*, 2494–2500

Inorganic Chemistry
Article

Theoretical Studies of Borazynes and Azaborines

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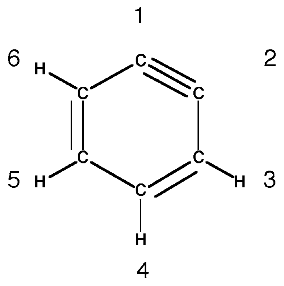
Received September 25, 2005

Four isomers of didehydroborazine, $B_3N_3H_4$, borazyne, and three isomers of azaborine, C_4H_4BN, are studied by DFT, CCSD, and CCSD(T) computational methods. The singlets of 1,2-borazyne (**I**) and 1,4-borazyne (**IV**) have angles about the boron of ca. 150°. In 1,2-azaborine (**V**), the angles are ca. 140°, while the N angles are ca. 112° except in **IV** (127°) and 1,4- azaborine (**VII**, 120°). These geometries are almost reversed in the triplets. The 1,3-borazyne (**III**) shows more bicyclic character than the corresponding *m*-benzyne, with an N–N distance of 1.7 Å. In all cases **I** was found to be lower in energy than the 2,4-borazyne (**II**), **III**, and **IV**. The order of stability of the azaborines is **V** > **VII** > 1,3- azaborine (**VI**). The nucleus-independent chemical shift (NICS) indicates that all isomers of borazyne are less aromatic than benzene and all isomers of azaborine are about as aromatic as benzene. Time-dependent DFT (TD-DFT) is used to study the excited states of the singlets. The significant structural differences between the singlet and triplet states suggest long phosphoresence lifetimes.

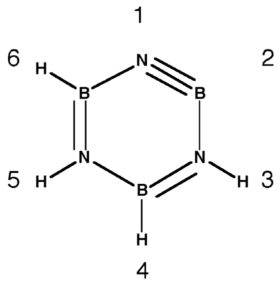
Introduction

Borazyne, $B_3N_3H_4$, can be considered the boron−nitrogen analogue of benzyne. The ortho isomer or 1,2-didehyrdoborazine (**I**) was originally proposed[1] as an intermediate in the formation of borazanaphthalene, $B_5N_5H_8$, and diborazine, $B_6N_6H_{10}$, during the photolysis of borazine, $B_3N_3H_6$. Borazyne itself was not isolated or characterized and no further studies that mention it have been reported. Borazyne should show structural similarities to benzyne, such as a shortened B−N bond evident of an increased bond order and a retention or lack of aromaticity closely related to that of the parent borazine. However, because of the polarity of the B−N bond, borazyne should show some distinctly different electronic properties analogous to the differences shown between benzene and borazine.

The loss of a hydrogen atom from a B or N atom is noted as the neutral radical in the scheme below. Finding more appropriate Lewis structures involving covalent and ionic character is one aim of this study. The electronic structure of each isomer is expected to vary widely, along with the sophistication of the theoretical method needed to accurately calculate these properties.



***o*-Benzyne**



***o*-Borazyne, I**

The synthesis and reactions of substituted borazines have been the objects of renewed interest. This blending of the traditional inorganic and organic fields has been spurred on by the many interesting mechanical and electronic properties being discovered for BN compounds in the ceramic, polymeric, and macromolecular (nanotechnological) sciences.[2] We hope that the indications of the electronic properties of borazynes reported here will generate interest in the synthesis of BN compounds through borazyne intermediates.

The presence of two atoms of widely different electronegativities is expected to influence the ionic/covalent proportions found in annular "-yne" species, favoring the ionic. There is a long history of theoretical benchmarks that have been computed for the isomers of benzyne, which are all mainly covalent in their ground states. Even in these completely uniform C atom systems, the covalent and

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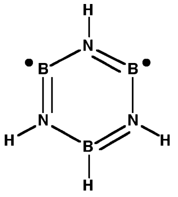

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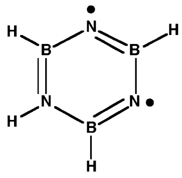
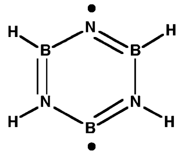


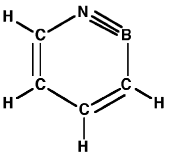
1,3-borazyne, III



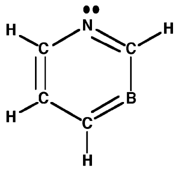
1,4-borazyne, IV

structural characteristics vary significantly for the ortho, meta, and para isomers.[3]

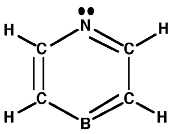
Additionally, the singlet and triplet states have been calculated for the three isomers of azaborine, C_4H_4BN, in which a B atom replaces a CH group in pyridine, producing what can be considered borapyridine. We aim to determine if C_4H_4BN chemically borapyridine or borapyridyne. The former can be classified as an *"ene"*, whereas the latter system is an *"yne"*, intermediate between the organic benzyne and inorganic borazyne. In many studies on ene species, an "organic" *pair* of two CH units is replaced with an "inorganic" *pair* of one BH unit and one NH unit. This gives a structure with a negative formal charge on the B atom and a positive one on the N atom, such as in borazine, $B_3N_3H_6$. These systems are isoelectronic with their benzene counterparts. In pyridine, C_5H_5N, a neutral N atom replaces one CH group in benzene, and the N atom lone pair in the plane of the ring governs its functionality. Also, it is isoelectronic with benzene. In borabenzene, C_5H_5B, *one* CH group in benzene is replaced by a neutral B atom with an in-plane empty orbital. Borabenzene thus has two less electrons than benzene. Azaborine can also be considered a pyridine with *one* CH group replaced by a neutral B atom, making it isoelectronic with borabenzene. However, the substitution of pairs in C_4H_4BN can be considered to start from the "inorganic" side. C_4H_4BN is chemically borazyne with *two pairs* of BH and NH groups replaced by *two pairs* of CH groups. In summary, the presence of a dicoordinate N atom makes the ene nucleophilic and a dicoordinate B atom makes the ene electrophilic, but what happens when both are present?



1,2-azaborine, V



1,3-azaborine, VI



1,4-azaborine, VII

Theoretical Methods

All calculations were carried out with the standard defaults in the Gaussian03 series of programs.[4] The 6-31G(d),[5] 6-311+G(d), and 6-311++G(d,p)[6] basis sets were used in the DFT,[7] CCSD,[8] and CCSD(T)[9] methods, but only results using the largest basis set are reported here. The DFT method used the unrestricted B3LYP functional, although in most cases a restricted B3LYP proved to be sufficient because of the ionic character and large singlet−triplet gap.

Analytical gradients were used for all optimizations and analytical frequencies were calculated in all DFT and CCSD calculations. The structures reported here have no imaginary frequencies. The CCSD(T) calculations were done using the corresponding CCSD-optimized structure. The Molekel program[10] was used for MO drawings. The Ball and Stick program[11] was used for optimized structure drawings.

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Table 1. Optimized Values for Angles and Bond Lengths (Å) Are Given for the UB3LYP and CCSD Methods Using 6-311++G** Basis Sets[a]

singlets

	angles							bonds					
	α1	α2	α3	α4	α5	α6		1	2	3	4	5	6
I							**I**						
UB3LYP	103.53	150.58	105.62	115.85	125.42	119.00	UB3LYP	1.290	1.379	1.468	1.423	1.475	1.444
CCSD	101.49	152.80	105.23	115.48	125.47	119.95	CCSD	1.296	1.386	1.469	1.428	1.478	1.452
II							**II**						
UB3LYP	110.05	126.39	121.98	113.21			UB3LYP	1.421	1.410	1.436	2.329		
CCSD	114.02	123.38	122.34	114.54			CCSD	1.430	1.422	1.438	2.399		
III							**III**						
UB3LYP	111.39	109.95	157.38	73.94			UB3LYP	1.437	1.412	1.392	1.674		
CCSD	111.23	109.50	158.80	72.18			CCSD	1.440	1.421	1.397	1.646		
IV							**IV**						
UB3LYP	127.31	118.34	104.19	147.63			UB3LYP	1.365	1.596	1.332			
CCSD	127.05	118.80	101.56	152.24			CCSD	1.377	1.587	1.336			
V							**V**						
UB3LYP	109.55	141.57	102.45	124.00	121.16	121.26	UB3LYP	1.311	1.445	1.408	1.413	1.396	1.358
CCSD	107.95	142.94	101.99	123.81	121.28	122.04	CCSD	1.317	1.457	1.409	1.423	1.397	1.367
VI							**VI**						
UB3LYP	124.47	105.56	138.57	105.38	120.71	125.30	UB3LYP	1.356	1.437	1.434	1.412	1.401	1.337
CCSD	123.02	106.61	138.58	104.41	121.48	125.90	CCSD	1.360	1.447	1.441	1.418	1.407	1.343
VII							**VII**						
UB3LYP	120.03	127.16	103.52	138.62			UB3LYP	1.337	1.419	1.428			
CCSD	119.68	127.59	103.16	138.81			CCSD	1.343	1.422	1.437			

triplets

	angles							bonds					
	α1	α2	α3	α4	α5	α6		1	2	3	4	5	6
I							**I**						
UB3LYP	130.27	112.17	123.57	117.94	122.79	113.04	UB3LYP	1.429	1.431	1.439	1.431	1.444	1.401
CCSD	132.88	110.89	123.42	118.12	123.10	111.56	CCSD	1.428	1.434	1.448	1.441	1.439	1.402
II							**II**						
UB3LYP	120.67	119.17	121.82	117.34			UB3LYP	1.425	1.422	1.435	2.476		
CCSD	120.64	119.12	121.88	117.38			CCSD	1.430	1.428	1.438	2.485		
III							**III**						
UB3LYP	117.86	118.32	128.05	105.34			UB3LYP	1.444	1.434	1.388	2.269		
CCSD	119.11	115.01	134.73	107.39			CCSD	1.446	1.434	1.385	2.323		
IV							**IV**						
UB3LYP	134.03	111.03	121.36	121.17			UB3LYP	1.404	1.446	1.427			
CCSD	133.47	111.18	121.57	121.04			CCSD	1.415	1.447	1.432			
V							UB3LYP	1.436	1.555	1.389	1.398	1.451	1.296
UB3LYP	117.54	120.53	116.89	119.30	121.32	124.41	CCSD	1.453	1.560	1.396	1.403	1.461	1.297
CCSD	116.40	121.14	116.87	119.05	121.34	125.20	**VI**						
VI							UB3LYP	1.331	1.551	1.527	1.373	1.427	1.348
UB3LYP	117.74	122.05	116.28	116.14	121.00	126.81	CCSD	1.336	1.560	1.538	1.376	1.435	1.352
CCSD	117.15	122.64	115.98	115.92	121.23	127.08	**VII**						
VII							UB3LYP	1.358	1.380	1.540			
UB3LYP	120.71	124.86	116.80	115.98			CCSD	1.366	1.385	1.550			
CCSD	120.14	125.22	116.93	115.56									

[a] See Figure 1 for angle and distance references.

In other studies, aromatic character is calculated using several methods,[12] including aromatic stabilization energy (ASE), magnetic susceptibilities and susceptibility anisotropies, valence-bond calculations, and nucleus-independent chemical shifts (NICS). The latter provides a rather consistent indication of aromatic character.[13] It consists of calculating the NMR shielding of a ghost atom (an atom with zero nuclear and electronic charges but with corresponding AOs) placed at a certain point relative to the molecule. The NICS(0) value is defined as the negative of the isotopic magnetic shielding constant of the Banquo[14] atom placed in the geometric center of the ring in question; the NICS(1) value is 1 Å out-of-plane above the center. Single-point gauge-independent atomic orbital (GIAO)[15] B3LYP/6-311+G(2d,p) calculations are performed with the B3LYP/6-311++G(d,p)-optimized singlet structures, as well as for borazine and benzene.

Results

Molecular Structures. The important structural parameters for the 14 singlet and triplet structures are given in

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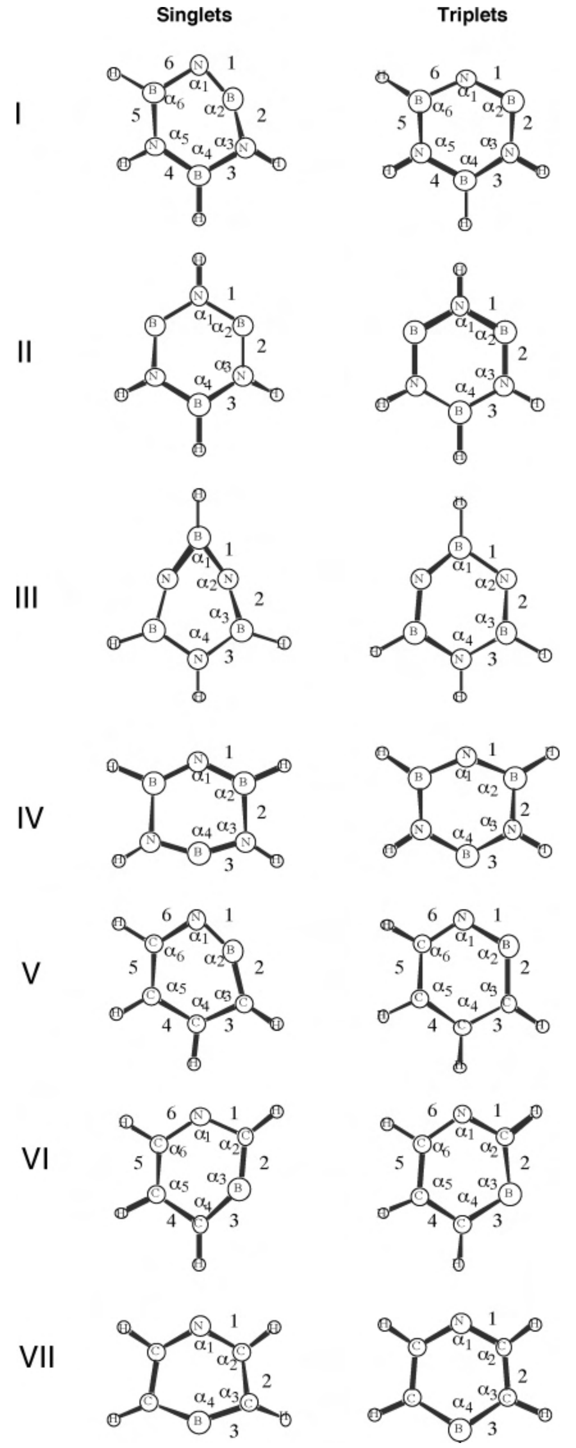

Figure 1. Optimized singlet and triplet structures for the seven isomers of $B_3N_3H_4$ and C_4H_4BN calculated with 6-311++G(d,p)/B3LYP.

Table 1, and their structures are shown in Figure 1. The molecular structures for borazyne and azaborine are similar in their deviations from the 120° angles found in sp^2-hybridized centers. The **II** and **III** isomers are particular cases and will be discussed separately at the end of this section. For singlets, the NH−B−X (X = NH, N) angle is ca. 150° for **II** and **IV**, and the CH−B−X angle isomer **V** is ca. 140°. The corresponding N angles in **I** and **V** are almost sp^3 in character, ca. 112°, but they are 127 ° in **IV** and 120 ° **VII**. In benzyne various theoretical methods give the CH−C−X angle as 127 ° in the ortho form and 125 ° in the para form. In general, azaborine can be considered intermediate in structure between benzyne and borazyne.

The geometries for triplet **I** are almost reversed with the N angle widening to more than 130 ° and the B angle decreasing to ca. 112 °. In **IV**, **V,** and **VII**, the angles are all nearly 120 °. Another singlet/triplet variation is the B−N bond length in **I** (**V**). They are lengthened from 1.29 (1.31) Å in the singlets to 1.43 (1.44) Å in triplets. In **IV** (**VII**), the B−NH bonds are lengthened from 1.33 (1.44) to 1.43 (1.55) Å, while the N−BH bonds lengthened to a lesser extent: singlet 1.37 (1.34) and triplet 1.41 (1.36) Å.

These structural changes are indicative of ortho and para singlets with high ionic character and triplets with covalent character. As noted for borabenzene,[16] the dehydrogenated B atom can be described with two nearly linear sp hybrid orbitals and a p orbital in the π system, leaving an empty p orbital as the LUMO. Figure 2 gives the HOMO−1, HOMO, LUMO, and LUMO+1 for the singlets of all seven isomers. The triplets give the same aspects, with two SOMOs replacing the singlet HOMO and LUMO (Figure 3). When a simple VSEPR theory is applied for **I** and **V**, a B atom with coordination number 2 in a linear structure denotes two single bonds and a positive formal charge. For the dicoordinate N atom in **I** and **V**, there is a formal negative charge resulting from the two lone pairs, one in the p system and the other in the plane. In the triplets, these in-plane p orbitals are singly occupied, leading to the more sp^2 situation and 120° angles.

The large angle at the B atom in the singlets is the driving force for a pattern in the bond angles that is seen for the seemingly disparate cases of **I**, **IV** and **V**, **VI**, and **VII**. Taking the −B− angle as a reference, each opposite angle is on average 124° and the two adjacent angles are on average 104°, regardless of being −B−, −BH−, −N−, or −NH−.

As in benzyne, the meta isomers **II**, **III**, and **VI** are structurally different than the ortho and para isomers. The bonding and covalent character increases between the dehydrogenated meta atoms across the interior of the ring for the series **II**, **VI**, **III.** For singlets, the B···B distance in **II** is ca. 2.3 Å compared to the B−B single bond distance of 1.6 Å (H_2BBH_2, theoretical, DFT). In **VI**, the B···N distance is 2.3 Å versus the normal 1.7 Å (BH_3NH_3, theoretical, DFT). The N−N bond is 1.7 Å versus 1.4 Å (NH_2−NH_2, DFT). Thus, for **III**, the singlet−triplet excitation leads to a large distortion from a bicycliclike form to a monocyclic structure, whereas there is not much distortion for the other two dehydrogenated meta species, **II** and **VI**.

III resembles *m*-benzyne[3d] with a bicycliclike structure for the singlets and the more hexagonal ring structure for the triplets. Because of the bicyclic bonding of the two dehydrogenated N atoms, the σ OMO is, relatively, the lowest for the seven isomers, in the HOMO−2 postition. For **II**, the relatively weaker bonding in B−B and the higher energy calculated for orbitals on a B atom cause the two

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(16) Karadakov, P. B.; Ellis, M.; Gerratt, J.; Cooper, D. L.; Raimondi, M. *Int. J. Quantum Chem.* **1997**, *63*, 441.

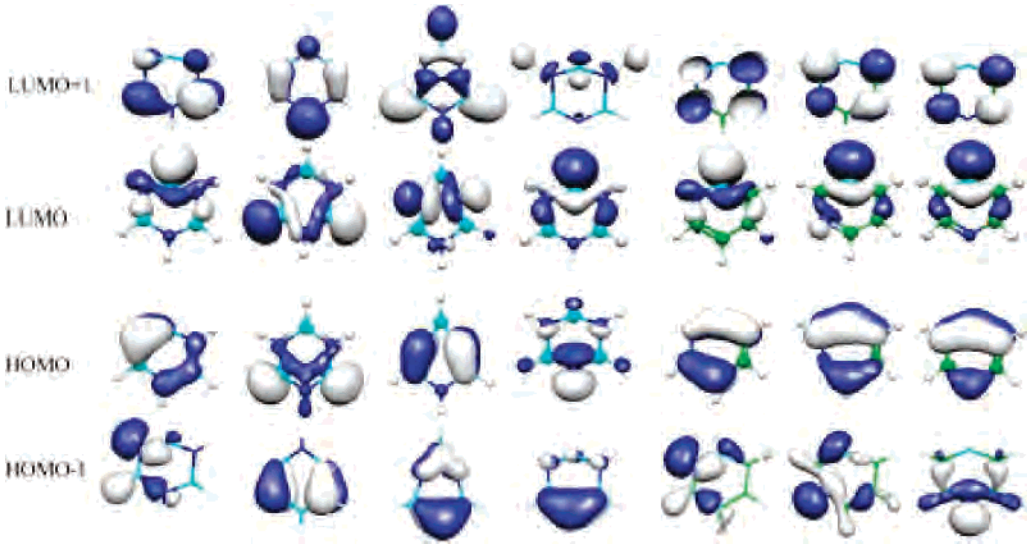

Figure 2. Highest- and next-highest-occupied and lowest- and next-lowest-unoccupied molecular orbitals calculated with 6-311++G(d,p)/B3LYP, from left to right, **I**, **II**, **III**, **IV**, **V**, **VI**, and **VII**. All molecules are oriented with the dicoordinate B atom at the top except **II** (two dicoordinate B atoms in the 3,5 positions) and **III** (two dicoordinate N atoms in the 2,6 positions).

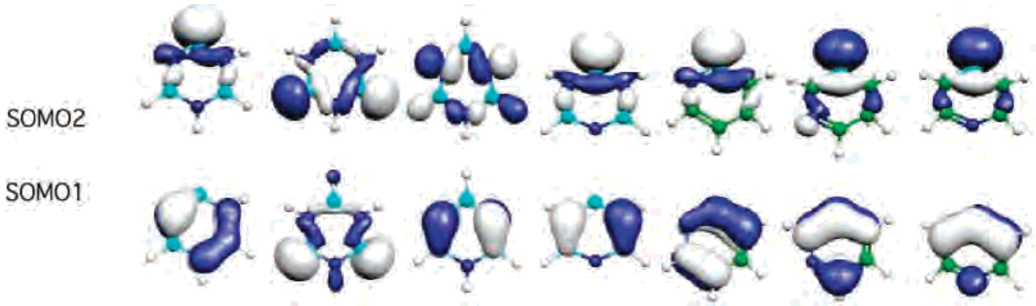

Figure 3. Highest and next-highest singly occupied molecular orbitals calculated with 6-311++G(d,p)/B3LYP, from left to right, **I**, **II**, **III**, **IV**, **V**, **VI**, and **VII**. All molecules are oriented with the dicoordinate B atom at the top except **II** (two dicoordinate B atoms in the 3,5 positions) and **III** (two dicoordinate N atoms in the 2,6 positions).

Table 2. Energies, E, for **I** (−239. Ha) and **V** (−234. Ha) According to the Theoretical Method Using the 6-311++G** Basis Set, the Energies Relative to the ortho Isomers, E_{rel} (kcal/mol), for the Singlets and Triplets of the Other Isomers, and the Calculated Singlet−Triplet Gaps, E_{rel} (kcal/mol), for Each Individual Isomer and Method

	E (**I**)	E_{rel} (**IV**)	E_{rel} (**II**)	E_{rel} (**III**)	E (**V**)	E_{rel} (**VI**)	E_{rel} (**VII**)
			$\Delta E_{isomer-orthosinglet}$				
UB3LYP	0.45273	32.13	51.59	37.51	0.46408	25.80	21.09
CCSD	0.75715	35.47	46.71	39.93	0.77287	27.71	21.43
CCSD(T)	0.79199	34.65	36.01	37.57	0.81606	26.67	21.34
			$\Delta E_{isomer-orthotriplet}$				
UB3LYP	0.36302	−4.04	−14.32	8.03	0.38042	10.39	15.06
CCSD	0.66950	−3.45	−15.54	20.78	0.69461	10.11	14.94
CCSD(T)	0.70005	−3.43	−15.70	19.40	0.73166	9.93	19.84
			$\Delta E_{triplet-singlet}$				
UB3LYP	56.30	20.12	−9.61	26.81	52.50	37.09	46.46
CCSD	55.00	16.07	−7.25	35.85	49.11	31.51	42.62
CCSD(T)	57.70	19.62	5.99	39.52	52.96	36.22	51.46

single electrons to be described by a pair of degenerate sp^2 orbitals (Figure 2). The HOMO is symmetric, and the LUMO is antisymmetric. The gap (HOMO → LUMO) (Table 3) is 0.08 Ha (2.2 eV), whereas the gap for the $\sigma^* \leftarrow n$ transition for **III** (HOMO−2 → LUMO) (not given in the table) is 0.29 Ha (7.9 eV). The gaps for the $\sigma^* \leftarrow n$ transitions for the other isomers, which involve an N atom and a B atom, range from 0.16 (4.4 eV) to 0.26 Ha (7.7 eV).

Energetics. A property where borazyne and benzyne may differ is in the singlet−triplet energy gap. A number of computational and experimental studies report the singlet−triplet gap in *o*-benzyne to be ca. 35 kcal/mol.[17] Since borazine has a larger HOMO−LUMO gap than benzene, one might expect the singlet−triplet gap to be larger in borazyne than in benzyne if the excitations are from the π system. It is more difficult to predict gaps that involve the in-plane hybrid orbitals of the B and N atoms in borazyne compared to those involving the two C atoms in benzyne.

The energies of the optimized structures relative to the singlet ortho isomers of borazyne and azaborine, calculated by various methods, are found in Table 2. In each case, the singlet **I** was found to be lower in energy than the singlet **II**, **III**, and **IV** isomers. For azaborine, the ortho form is more stable than the para and meta forms by ca. and ca. 27 kcal/mol, respectively. The results are largely independent of method and basis set. The DFT and CCSD(T) results are quite close. For all molecules except **II**, the singlet is lower in energy then the triplet. The sign of this triplet−singlet gap in **II** depends on method. The DFT and CCSD correlation method, which does not include triple excitations,

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[17] Lindh, R.; Bernhardsson A.; Schütz, M. *J. Phys. Chem. A* **1999**, *103*, 9913 and references therein.

Table 3. First and Second Vertical Transition Singlet and Triplet Energies and State Designations for Borazyne and Azaborine Isomers Calculated with TD-DFT/6-311++G(d,p) and the First Two HOMO and LUMO Energies (a.u.) with Their Symmetry Designations and Orbital Type[a]

	E_{rel} (**I**)	E_{rel} (**IV**)	E_{rel} (**II**)	E_{rel} (**III**)	E_{rel} (**V**)	E_{rel} (**VI**)	E_{rel} (**VII**)	$B_3N_3H_6$
state								
T_1	268.0 A′	490.3 A1	(−)823.8 B2	328.7 B1	363.5 A″	456.0 A″	396.0 B1	207.3
T_2	265.0 A″	328.2 B1	457.5 A2	270.1 B2	347.4 A′	389.2 A′	333.1 A1	198.8
S_1	246.5 A″	399.4 A1	458.5 B2	275.0 B1	328.8 A″	399.3 A″	352.2 B1	194.1
S_2	228.9 A′	317.0 B1	397.7 B1	238.0 B2	278.9 A′	309.4 A′	311.6 A2	187.6 E″
orbital								
LUMO+1	−0.015 A′ σ^*	−0.020 A1 σ^*	−0.015 B1 π	−0.030 B1 π	−0.043 A″	−0.047 A″	−0.035 A2	.001 E″
LUMO	−0.048 A′ σ^*	−0.086 A1 σ^*	−0.085 B2 σ^*	−0.032 B2 σ^*	−0.062 A′	−0.078 A′	−0.084 A1	−0.007 A1′
HOMO	−0.283 A″ π	−0.226 A1 n	−0.165 A1 n	−0.262 A2 π	−0.247 A″	−0.243 A″	−0.264 B1	−0.289 E″
HOMO-1	−0.286 A′ n	−0.269 B1 π	−0.308 A2 π	−0.312 B1 π	−0.292 A′	−0.261 A′	−0.265 A1	−0.332 E′×94 [b]

[a] The three principal orbital transitions in different isomers have particular symmetry designations: $(\sigma^* \leftarrow N)$ A′ (all isomers), A1(**VII**, **IV**), B2(III, II); $(\sigma^* \leftarrow \pi)$ A″ (all), A2(**VII**), B1(**VII**, **IV**, **III**); $(\pi^* \leftarrow N)$, A2(**II**), B1(**II**). [b] Corresponds to first degenerate MO pair below two degenerate E″ HOMOs.

Table 4. Selected Calculated Vibrational Frequencies (uncorrected)

I	**II**	**III**	**IV**	$B_3N_3H_6$
1834s	1490s	1587	1801	1480s

V	**VI**	**VII**	C_5H_5B	C_5H_5N
1709s	1608w	1629m	1629m	1623w

Table 5. Nucleus-Independent Chemical Shift (NICS) Values Calculated at Ring Centers, NICS(0), and at 1 Å above the Ring Center, NICS(1), at the B3LYP/6-311+G(2d,p) Level[a]

	I	**IV**	**II**	**III**	**V**	**VI**	**VII**	$B_3N_3H_6$
NICS(0)	−5.0	−7.5	−4.0	−20.6, −10.9, −39.7, −54.1	−10.4	−10.5	−12.0	−1.5
NICS(1)	−3.3	−4.7	−3.7	−7.5, −6.9, −8.2, −9.1	−9.3	−9.9	−10.3	−2.8

[a] The **III** values are for measurements at six-membered, five-membered, and three-membered ring centers and midway between N1 and N3.

favor the triplet. The CCSD(T), which includes triple excitations in a perturbative way, favors the singlet. There were no calculated imaginary frequencies for the triplets with C_{2v} structures for **II**, **III**, **IV**, and **VII** and the triplets for **I**, **V**, and **VI** maintain C_s symmetry with the DFT and CCSD methods. These isomers can clearly provide more food for benchmark calculations and tests of theoretical methods.

In Table 3, we give the UB3LYP TD-DFT excitation energies of the first two vertical singlet and triplet excited states based on the 6-311++G(d,p)-optimized ground-state singlet geometry. Descriptions of the excited states in terms of the predominant orbital excitations from the two LUMOs and two HOMOs are also given in Table 3. Except for **II**, there are two types, $\sigma^* \leftarrow n$ and $\sigma^* \leftarrow \pi$. The σ^* MO is of unusually low energy compared to the π^* MOs. The first σ^* MO can be described as being between an unoccupied p AO on a B atom with sp hybridization and an sp^2 hybrid orbital on the B atom (Figure 1), which results in a bond angle of ca. 150°. Thus, the two excitations to the σ^* MO are either from the N atom lone pair, n, or from the ring π system. For all structures, both the vertical-transition TD-DFT method and methods with geometry optimization give the same nature of the first two triplet states in regards to orbital participation and energy ordering.

Although borazyne and azaborine are expected to be intermediates, significant vibrational bands are also reported in Table 4. In borazine, the strongest stretch is calculated to be at 1480 cm^{-1} (unadjusted calculated value), corresponding to a BN stretch. In **I** and **V**, the stretch between the dehydrogenated B−N atoms is calculated to be as strong at 1834 and 1709 cm^{-1}, respectively, indicating the higher bond order in an yne. In **IV** and **VII**, only −B− is increased in bond order as indicated by the increase in wavenumber. That for −N− remains nearly what was found in the borazine BH−NH. Although the triplet is the ground state in DFT calculations for **II**, the −B− stretches in the singlet are near the values for borazine BH−NH. The increase for −N− in **II** reflects the bicyclic bonding of the bridgehead N atoms.

Aromaticity. An indication of aromatic character can be obtained from the NICS(0) and NICS(1) values reported in Table 5. The NICS(0) values give an indication of the participation of the ring current of the σ system to the overall ring current, while the NICS(1) values are essentially from the π system. The B3LYP/6-311+G(d,p) literature values[5c] for benzene and borazine are also reported here for comparison to those in Table 4. Slight enhancements of the aromaticity were found[5c] for the change between an ene and an yne, benzene versus benzyne for example: NICS(0) benzene (−7.6), *o*-benzyne (−17.8), *m*-benzyne (−15.4), *p*-benzyne (−19.3); NICS(1) benzene (−9.8), *o*-benzyne (−12.5), *m*-benzyne (−11.7), *p*-benzyne (−14.0).[3j] The values for borazine recalculated here with B3LYP/6-311+G(2d,p) indicate very low aromaticity (viz. NICS(0), −1.5; NICS(1), −2.8). These values reflect those calculated for the π and total current densities induced by a magnetic field in borazine.[13b,18] The values calculated here for azaborines reflect the trends in benzyne; there is an increase for NICS(0) and an increase in NICS(1) to the value calculated for benzene. While there is an increase in NICS(0) for **I**, **IV**, and **II** (UB3LYP), there is a decrease for NICS(1) to values indicating nonaromaticity. The **III** isomer appears to be aromatic with a NICS(1) value of −7.5. Since this isomer is nearly bicyclic, the measurements were calculated at three places in addition to the geometric center of the six-membered outer ring. There was one at the center of the five-membered ring, three-membered ring, and midway between N1 and N3. Corresponding NICS(1) values were also calculated. The four NICS(1) values ranged from −7 to −9, indicating aromatic cyclic structures.

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(18) Fowler P. W.; Steiner E. *J. Phys. Chem. A* **1997**, *101*, 1409.

In conclusion, there are major structural differences between the singlet and triplet species of most borazyne and azaborine isomers. This undoubtedly leads to long phosphorescence lifetimes. Since excited singlet state geometries need to be optimized, fluorescence studies of borazyne and azaborine are in progress. Both theoretical methods gave only minor structural differences. The relative energy values were also consistent for both theoretical methods.

In comparison to borazine, which absorbs in the far UV, some isomers of borazynes are expected to absorb in the near UV−vis. The calculated vibrational frequencies indicate an increase in bond order between the ortho BN atoms in both borazyne and azaborine.

The MOs delineate a clear picture of a nucleophilic N atom and electrophilic B atom in every case except **II** and **III**. This indicates that azaborine can be designated *borapyridine* in the meta and para isomers. However, the amount of bond order as indicated in the increased vibrational frequency indicates the case for the name *borapyridyne* (or azaboryne)- in the ortho isomer.

Acknowledgment. L.A.B. wishes to acknowledge the US National Science Foundation for a computer equipment grant (MRI NSF-DMR0116315).

Supporting Information Available: Expanded version of Table 2. This material is available free of charge via the Internet at http://pubs.acs.org.

IC051649D