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Phenylborylene: Direct Spectroscopic Characterization in Inert Gas Matrices

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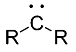
Borylenes **1**, the boron analogues of carbenes (**2**)[1] and nitrenes (**3**),[2] also termed borenes or boranediyls,[3] are highly reactive intermediates. While the chemistry of **2** and **3** is well developed, chemical trapping of the subvalent boron(I) species **1** has only been reported occasionally.[4] Direct IR spectroscopic characterizations of organoborylenes are limited to ethynylborylene HC_2B (**1a**, R = C_2H), which formed during the co-deposition of boron atoms and acetylene.[5]


1


2


3

The electronic structure of **1** is related to that of nitrenes, which have a nonbonding electron pair and two unpaired electrons described by two p-orbitals and thus generally prefer triplet electronic ground states. The two p-orbitals are unoccupied in borylenes, and consequently, singlet ground states result with a nonbonding electron pair described by a sp-type orbital.[6] Borylenes, like carbenes, can be stabilized by coordination to metal centers, and significant progress has been made in the field of transition metal−borylene complexes in recent years.[7]

Phenylborylene (**1b**) has been sought for some time, but has remained elusive to date.[3a,8] Nonetheless, computational investigation reveals that **1b** should be stable under suitable conditions, as barriers for rearrangements to benzoborirene **4** and didehydroborepine **5** are in excess of 27 kcal mol^{-1} (see Supporting Information). We here show that UV photolysis of diazidophenylborane (**6**), first synthesized and characterized by Mennekes and Paetzold in 1995,[9] provides an access to the desired **1b** as well as a nitreno-*N*-phenyliminoborane **7** (Scheme 1). The related chlorine compound, $ClBN_6$, is known to decompose into a $ClBN_2$ compound and into BCl upon irradiation in an argon matrix at 10 K.[10]

The IR spectra of the phenyl compound **6** isolated in solid inert gas matrices (Ar, Ne, N_2) are characterized by an intense group of signals centered at 2153 cm^{-1}. Irradiation ($\lambda = 254$ nm) of matrices containing **6** results in very rapid and complete disappearance of its IR signals.[11]

From a number of experiments, a set of IR bands (Table 1, Figure 1), the most prominent at 1715, 1679, and 1560 cm^{-1}, is identified which shows an identical growth behavior upon photolysis. These signals are assigned to **7** based on comparison with B3LYP/6-311+G** computations.

Scheme 1

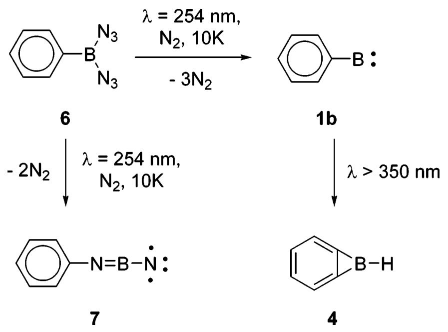


Table 1. IR Spectroscopic Data of **7** Measured in N_2 at 10 K and Computed at the UB3LYP/6-311+G** Level of Theory

	experiment		B3LYP/6-311+G**	
mode	ν_{exp} [cm^{-1}]	I_{rel}	ν_{calcd} [cm^{-1}]	I_{rel}
31 [^{10}B]	1715	0.24	1807.1	0.24
31 [^{11}B]	1679	1.00	1765.1	1.00
30	1560	0.38	1596.3	0.29
26	1314	0.13	1356.3	0.12
20	1024	0.02	1041.3	0.03
19	1009	0.03	1022.01	0.03
17	972	0.04	987.9	0.11
13	760	0.03	775.6	0.07

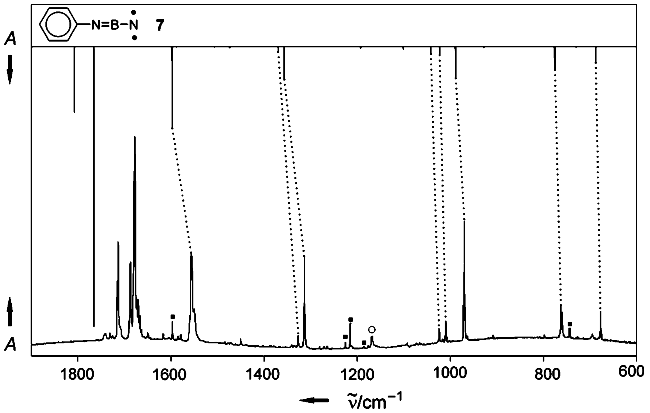


Figure 1. IR spectra obtained at 10 K in N_2 after irradiation ($\lambda = 254$ nm) of **6** (bottom). The open circle marks HN_3, while the bold squares are signals due to **1b** (see also Figure 2). The computed spectrum was obtained at the UB3LYP/6-311+G** level of theory for the $^3A_2$ state of **7**.

Characteristic of **7** is a pair of signals at 1715 and 1679 cm^{-1} with 1:4 intensities corresponding to the natural $^{10}B/^{11}B$ composition. Both of these signals are split considerably and show pronounced fine structure, more so in argon and least in neon, possibly due to the two molecules of N_2 lying within the same matrix cage. The nitrene **7** prefers a triplet electronic ground state, $^3A_2$, according to computations.[12] This is confirmed by electron spin resonance (ESR) measurements. Irradiation ($\lambda = 254$ nm) of **6** isolated in argon at 10 K results in an ESR signal with zero-field splitting parameters, $|D/hc| = 1.240$ cm^{-1} and $|E/hc| = 0.0021$ cm^{-1}.[13]

In nitrogen and, to a lesser extend, in neon matrices, another set of bands (Table 2) shows a growth behavior different from that of **7**. These bands are assigned to the borylene **1b** based on comparison with computations and deuterium labeling (see Supporting Information). The 1225/1215 cm^{-1} pair has the 1:4 intensity pattern typical for natural boron isotope composition, and according to the B3LYP

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Table 2. IR Spectroscopic Data of **1b** Measured in N_2 at 10 K and Computed at the B3LYP/6-311+G** Level of Theory

	Experiment		B3LYP/6-311+G**	
mode	ν_{exp} [cm^{-1}]	I_{rel}	ν_{calcd} [cm^{-1}]	I_{rel}
25	1597	0.60	1630.6	0.32
19 [^{10}B]	1225	0.24	1250.5	0.24
19 [^{11}B]	1215	1.00	1239.5	1.00
18	1186	0.06	1202.8	0.14
9	798	0.07	807.9	0.08
8	743	0.20	755.2	0.26

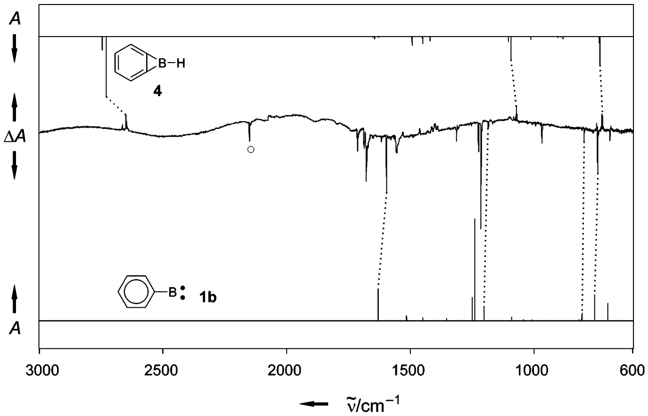

Figure 2. Difference spectra (middle) measured at 10 K after photolysis (350−450 nm) of the matrix depicted in Figure 2. Bands pointing down disappear, bands pointing upward increase upon irradiation. The open circle marks HN_3. The IR spectra for **4** (top) and **1b** (bottom) were computed at the B3LYP/6-311+G** level of theory.

Table 3. IR Spectroscopic Data of **4** Measured in N_2 at 10 K and Computed at the B3LYP/6-311+G** Level of Theory

	Experiment		B3LYP/6-311+G**	
mode	ν_{exp} [cm^{-1}]	I_{rel}	ν_{calcd} [cm^{-1}]	I_{rel}
26 [^{10}B]	2662	0.21	2743.0	0.24
26 [^{11}B]	2647	1.00	2727.9	1.00
17 [^{10}B]	1084	0.16	1105.0	0.10
17 [^{11}B]	1073	0.73	1094.2	0.39
8	728	0.53	733.8	0.47

computations, this band corresponds to the ν(C−B) stretching vibration.The features due to **1b** are rapidly bleached by longer wavelength irradiation (λ = 350−450 nm) with concomitant growth of a further set of signals.[14] Two signals of this set (2647, 1073 cm^{-1}) can already be detected after the initial 254 nm irradiation. These bands are typical of a ν(B−H) stretching vibration and a ring breathing mode of a benzoborirene.[15] Hence, this set is assigned to **4**, and this assignment is also supported by comparison with computations (Table 3).

The ground state of C_{2v} symmetric **1b** is a singlet state ($^1A_1$), but due to the two vacant orbitals on boron, two different triplet states, $^3B_1$ and $^3B_2$, need to be very similar in energy. This is confirmed by CCSD(T)/cc-pVTZ computations, which give singlet−triplet energy splittings of 36.1 and 36.9 kcal mol^{-1}, respectively. According to eq 1, the phenyl substituent (R = C_6H_5) stabilizes the singlet state ($\Delta E_S(1) = -2.7$ kcal mol^{-1}) and destabilizes the $^3B_1$ state ($\Delta E_T(1) = +2.6$ kcal mol^{-1}), resulting in an increased singlet−triplet gap compared to BH (calcd 30.8, exp 29.8 kcal mol^{-1}).[6a]

$$BH + RBH_2 \rightarrow RB + BH_3 \qquad (1)$$

In conclusion, this work demonstrates that Paetzold's[9] bisazidophenylborane is a precursor for opening the chemistries of hitherto unknown reactive intermediates of $C_6H_5BN_2$ and C_6H_5B stoichiometries. While the rearrangement to an iminoborane derivative[16] is competing with phenylborylene formation, this system will nonetheless allow future reactivity studies of **1b**.

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Supporting Information Available: Technical details, complete tables of vibrational data, enlarged IR spectra, ESR spectra, and Cartesian coordinates and energies of stationary points. This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) An unknown photolabile intermediate with an absorption at 2050 cm^{-1} is formed initially, but also quantitatively bleached by the time **6** is decomposed completely.

(12) The $^1A_2$ and $^1A_1$ states are 15 kcal mol^{-1} higher in energy. See: Bettinger, H. F. *J. Organomet. Chem.* **2006**, accepted for publication.

(13) Upon longer irradiation, another signal ($|D/hc| = 0.870$ cm^{-1} and $|E/hc| = 0.0007$ cm^{-1}) can be detected (see Supporting Information). While its origin is unclear, we note that the C_6H_5BNN isomer also has a triplet ground state ($^3A_2$), and B3LYP/6-31G* computations show a larger delocalization of spin density from the terminal N than in **7**, consistent with a smaller *D* value.

(14) Additional bands form during irradiation, but their origin is not clear beyond doubt at this time.

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