Identification of the Borirene Molecule, (CH)₂BH: Matrix Isolation FTIR and DFT Calculations for Five Vibrational Modes of Six Isotopic Molecules

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According to molecular orbital (MO) theory, the simplest aromatic ring contains two π-electrons. For hydrocarbons, this condition is satisfied in the cyclopropenyl cation $C_3H_3^+$, in which the carbons form a three-membered ring. Volpin et al.[1] considered the possibility of a neutral aromatic species in which trivalent boron replaced a carbon to form borirene, (CH)₂BH. Ab initio studies of borirene and its derivatives show that this molecule is indeed aromatic, as the B−C bond lengths are shorter than those of typical B−C single bonds and the C−C bond length is longer than a normal C=C double bond.[2-4] The isolation of borirene has to date eluded scientists, although Eisch et al. have generated substituted borirenes in the laboratory.[5,6]

Matrix isolation spectroscopy has been used to identify the borirene radical, (CH)₂B, following reactions of laser-ablated boron atoms with acetylene.[7,8] Because acetylene has only two hydrogen atoms, the closed-shell borirene molecule with three hydrogens was not formed. However, reacting laser-ablated boron with ethylene allows formation of, among other products, the borirene molecule. Infrared spectra and DFT/BP86 calculations for six isotopic (CH)₂BH molecules are presented here.

Mixtures of ethylene/argon (1/200) were codeposited at 10 K with laser-ablated boron atoms [ⁿB (80% ¹¹B, 20% ¹⁰B) and ¹⁰B (94% ¹⁰B, 6% ¹¹B) using 30 mJ pulses of 1064 nm laser light as described previously.[7-10] Spectra for reaction of each boron isotopic sample with C₂H₄, ¹³C₂H₄, and C₂D₄ were collected at 0.5 cm⁻¹ resolution. Following deposition, the matrix was subjected to broadband UV photolysis for 30 min, annealing to 25 and 35 K, and spectra were recorded after each step to correlate band intensities.

Figure 1 presents the 1210−1120 cm⁻¹ region of the spectrum following 2 h deposition for six isotopic reagent combinations. Absorptions in this region are due to B−C₂ ring stretching modes. Borirene radical bands are observed as minor peaks in the spectra, for example, at 1170.6 cm⁻¹ in Figure 1b (labeled E); these bands *decrease* on photolysis and reappear on annealing as observed previously.[7,8] The strongest band in each
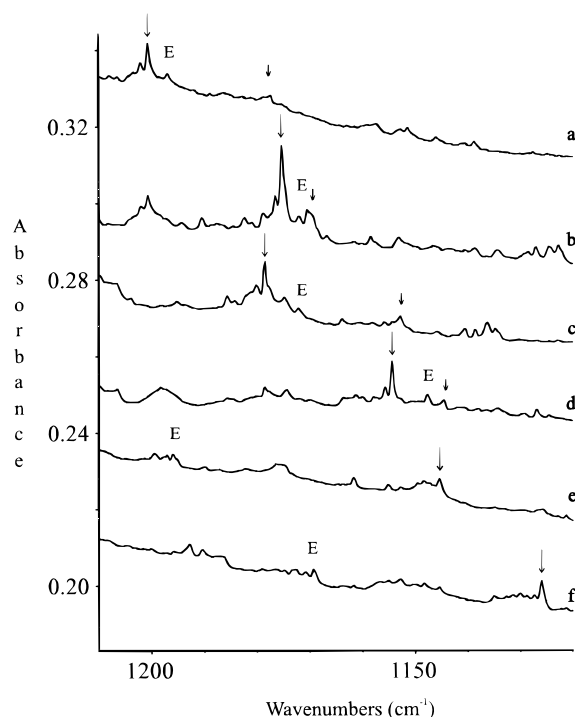
Figure 1. Matrix infrared spectra in the 1210−1120 cm⁻¹ region following pulsed laser ablation of B atoms codeposited with Ar/C₂H₄ (200/1) samples on a CsI window at 10 K; (a) ¹⁰B + ¹²C₂H₄, (b) ⁿB + ¹²C₂H₄, (c) ¹⁰B + ¹³C₂H₄, (d) ⁿB + ¹³C₂H₄, (e) ¹⁰B + ¹²C₂D₄, and (f) ⁿB + ¹²C₂D₄. Arrows indicate (CH)₂BH product absorptions.

spectrum is due to the symmetric B−C₂ ring stretching mode of borirene (long arrows); each absorption has a blue side band. The strong absorptions *increase* 15% on broad-band photolysis and another 20% on 25 K annealing. Table 1 presents the frequencies for six isotopic absorptions of borirene. Note with natural boron (Figure 1b) the 1:4 relative boron isotopic product band intensities indicate the participation of a single boron atom in this vibrational mode.

Also in Table 1 are the results of density functional theory (DFT) calculations on borirene using the BP86 functional[11,12] with the 6-311G* basis sets[13,14] in the Gaussian 94 program package.[15] In previous studies of the reaction of beryllium atoms with hydrogen cyanide, calculations using the BP86 functional predicted frequencies better than the B3LYP functional,[16] and this is also the case for borirene.[17] Agreement between experiment and theory is also excellent for the symmetric B−C₂ ring stretching mode of borirene with all predictions 4 ± 1 cm⁻¹ higher than the observed values. This excellent agreement between calculated and observed frequencies (i.e., the isotopic shifts) for six isotopic molecules clearly identifies this diagnostic mode of the borirene molecule.

Also in Table 1 are observed and calculated frequencies for four other strong infrared absorptions of borirene. As with the

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Table 1. Observed and Calculated Isotopic Frequencies (cm^{-1}) for Borirene

B-C-H	11-12-1	10-12-1	11-13-1	10-13-1	11-12-2	10-12-2
obs	1175.3[a]	1200.7	1154.4	1178.6	1126.0	1145.4
calc	1179.2	1205.4	1158.0	1183.1	1129.0	1150.4
obs	1169.5[a]	1177.6	1144.6	1152.9		
calc	1157.9	1166.8	1132.6	1141.6	1079.1	1092.1
obs	2639.6[a]	2656.3	2643.6	2659.2	2006.1	2029.9
calc	2668.2	2683.3	2668.1	2683.2	2006.0	2031.3
obs	832.5[a]	843.4	823.5	833.9		
calc	842.5	852.1	838.7	848.4	692.0	703.7
obs	653.0[a]	653.7	651.6	652.3	481.6	482.7
calc	642.1	643.0	640.8	641.7	471.9	473.1

[a] Peak absorbances: 1175.3 cm^{-1} (0.020 au), 1169.5 (0.004), 2639.6 (0.016) plus absorbance shared by Fermi component at 2669.5 (0.002), 832.5 (0.025), 653.0 (0.006).

Table 2. DFT/BP86 Vibrational Frequencies (cm^{-1}) and Infrared Intensities (km/mol) for (^{12}CH)$_2$^{11}BH

symmetry	frequency	intensity	symmetry	frequency	intensity
B$_1$	642.1	15	B$_2$	1157.9	15
B$_2$	761.9	4	A$_1$	1179.2	45
B$_1$	842.5	54	A$_1$	1500.9	0
A$_1$	869.9	11	A$_1$	2668.2	82
B$_2$	875.2	24	B$_2$	3095.1	23
A$_2$	985.4	0	A$_1$	3120.7	8

symmetric B$-$C$_2$ ring stretching mode in Figure 1, these absorptions also have a blue side band, and they increase 15% on photolysis and 20% on annealing to 25 K. The weaker predominantly antisymmetric B$-$C$_2$ ring stretching mode (short arrows) also appears in Figure 1, and it can be assigned to borirene because of matching photolysis and annealing behavior, band contour, and DFT isotopic frequency calculations. This time the observed bands for four isotopic molecules are 11 ± 1 cm^{-1} higher than calculated (the 1169.5 cm^{-1} shoulder is resolved when the 1170.6 cm^{-1} E band is decreased on photolysis), but the deuterium counterpart is too weak to be observed. Note that the calculated and observed ^{10}B and ^{13}C shifts for these two B$-$C$_2$ stretching modes of A$_1$ and B$_2$ symmetry are different as expected.

The two lower frequency peaks at 832.5 and 653.0 cm^{-1} for natural isotopes are due to out-of-plane hydrogen deformation modes. DFT calculations agree very well with the experimental values with residuals on the order of 10 cm^{-1}. Isotopic frequencies for boron, carbon, and hydrogen are predicted 10 ± 1 cm^{-1} lower than observed for the 653.0 cm^{-1} mode, which is nearly harmonic, but not as precisely for the more anharmonic 832.5 cm^{-1} mode.

The highest frequency absorption in Table 1 corresponds to the strong B$-$H stretching mode of borirene. For carbon-12 products with hydrogen, the calculated frequencies and boron-10 shift are reasonably close to the experimental values. These calculations are in better agreement with the values for the products with carbon-13 and deuterium, however. For the carbon-13 isotopic molecules, the observed frequencies are actually *higher* than their carbon-12 counterparts. The reason for this unusual isotopic shift is that (^{12}CH)$_2$BH has a Fermi resonance caused by the interaction of a combination band with the B$-$H stretching fundamental. According to Table 2, the A$_1$ bands at 1179.2 cm^{-1} (the B$-$C$_2$ stretching mode) and 1500.9 cm^{-1} (the C$-$C stretching mode) can have a combination band near 2680 cm^{-1}, the sum of the fundamentals. This combination band is likely to fall above and close in frequency to the B-H stretching mode at 2639.6 cm^{-1}, also of A$_1$ symmetry, and thereby perturb this vibrational mode to a lower frequency than would otherwise be observed. The combination band in turn acquires intensity in this mixing and can be observed at 2669.5 cm^{-1} for the ^{11}B molecule. For the

(^{13}CH)$_2$^{11}BH molecule, the calculated B$-$H stretching mode is only 0.1 cm^{-1} lower than for ^{12}C, while the sum of the calculated ring B$-$C$_2$ and C$-$C stretching modes is 56 cm^{-1} lower than the calculated B$-$H stretching mode. Therefore, the combination band for the carbon-13 product falls too low to perturb the B$-$H stretching fundamental.

Although BP86 calculations tend to overestimate bond lengths,[18] the calculated borirene geometry agrees well with the previous MP2/DZP structure.[7,8] The BP86-calculated B$-$C bond length of 1.48 Å is clearly shorter than a typical B$-$C single bond, in agreement with previous calculations.[2−4,7,8] Similarly, the calculated C$-$C bond length of 1.36 Å is longer than that expected for a C$=$C double bond. The geometry again suggests that borirene is aromatic. These calculations predict this molecule to be more stable than its aliphatic isomers, BH$_2$CCH and CH$_2$CBH, further suggesting that its aromatic nature is effecting this relative stability.[17]

The BP86 harmonic frequency calculations predict five fundamentals of borirene 28, 4, and 10 cm^{-1} higher and 11 and 11 cm^{-1} lower than observed, and infrared intensities in reasonably good agreement with experimental values (Table 1). However, even more important, the calculated isotopic frequencies for each fundamental have the same deviation (±1 cm^{-1}, except for the 2639.6 cm^{-1} B$-$H stretching and 832.5 cm^{-1} wagging modes, which have larger anharmonicities). This means that the isotopic shifts are correctly calculated. Since isotopic substitution at all atomic positions characterizes normal vibrational modes, the matching of calculated and observed isotopic shifts as a measure of normal modes provides a "fingerprint" identification for the new borirene molecule.
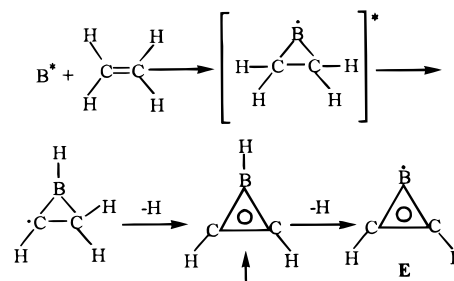
The reaction of atomic boron with ethylene is a complicated process particularly in view of the excess energy present in laser-ablated boron atoms.[7,8] Two mechanisms are possible: (1) insertion into a C$-$H bond, which leads ultimately to the above aliphatic isomers,[17] and (2) addition to the π-bond to form the cyclic borirane radical BC$_2$H$_4$, which rearranges and dissociates during the relaxation process. The borirane radical is formed in an exothermic reaction (-40 kcal/mol),[19] and this energized radical rearranges to the cyclic isomer ⌐BHCHCH$_2$, which is calculated to be more stable (-10 kcal/mol).[20] This cyclic radical eliminates H to form borirene ($+33$ kcal/mol)[17] and, in some cases, another H to give the borirene radical.[7,8] The increase of borirene absorptions on annealing suggests that the exothermic formation of cyclic BC$_2$H$_4$ and ⌐BHCHCH$_2$ provides the energy to eliminate H and form borirene from the B + C$_2$H$_4$ reaction.

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