Reactions of Pulsed Laser Evaporated Boron Atoms with Methane. 1. Synthesis and Characterization of a Novel Molecule with Carbon–Boron Double Bonds: HBCBH

Parviz Hassanzadeh and Lester Andrews*

Department of Chemistry, University of Virginia
Charlottesville, Virginia 22901

Received July 27, 1992

Pulsed laser assisted reaction of atoms with organic molecules for matrix isolation–FTIR spectroscopy is now opening a new channel for producing and characterizing novel molecules and new transient species. An earlier study of the reaction of concentrated methane samples with pulsed laser evaporated boron atoms reported the formation of CH_3BH.[1] The present higher resolution investigation incorporates complete isotopic substitutions and provides evidence for at least five new species. Fortunately the diagnostic 1700–1900 cm^{-1} region contains only one new product absorption. This communication presents the first observation and characterization of linear HBCBH with carbon–boron double bonds from matrix infrared spectra and ab initio calculations. Other reaction products will be detailed in a full paper. Only a few compounds with carbon–boron double bonds have been prepared, and these contain large ring substituent groups.[2-4] The present subject molecule is the simplest molecule yet characterized with carbon–boron double bonds.

A mixture of methane/argon was codeposited with laser-evaporated elemental boron using an apparatus described previously.[5,6] Several experiments were carried out with various concentrations of methane/argon from 1/400 to 5/100 and different laser powers of 10–45 mJ/pulse at the target. Typically 4–6 h of codeposition of a 1/100 mixture of methane/argon and laser power of 40 mJ/pulse at the target produced enough reaction yield for FTIR studies. The spectra of the reaction products for natural isotopic boron and enriched boron-10 with CH_4, $^{13}CH_4$, CD_4, and CH_2D_2 were collected at 0.5 cm^{-1} resolution.

The spectrum in the boron–carbon double-bond stretching region revealed absorptions at 1872.0, 1883.9, and 1895.2 cm^{-1} with 16/8/1 intensity ratios for the reaction of natural isotopic boron with natural methane. A similar experiment with 94% enriched boron-10 showed only the 1883.9 and 1895.2 cm^{-1} bands with a 1/8 intensity ratio. Similar 16/8/1 and 1/8 intensity ratio patterns from the reaction of natural isotopic boron and enriched boron-10 isotope, respectively, with $^{13}CH_4$ and CD_4 were observed. The spectra for $^{12}CH_4$ and $^{13}CH_4$ are shown in Figure 1, and the data are listed in Table I.

The B–H stretching region was dominated by the ν_3 and ν_1 modes of methane; however, reaction of deuterated methane with natural isotopic boron and enriched boron-10 revealed new bands at 2190.9, 2213.1, 2230.7 cm^{-1} with 16/8/1 intensity ratios and 2213.1 and 2230.7 cm^{-1} with 1/8 intensity ratios, respectively. These bands were as intense as the boron–carbon double-bond stretching absorptions at 1727.4, 1729.8, and 1732.2 cm^{-1}, and both series of bands grew 30% on full arc photolysis and decreased on annealing above 30 K.

The spectrum from the reaction of natural isotopic boron with CH_2D_2 showed the above CH_4 and CD_4 product bands plus new bands at 1805.9, 1805.1, 1793.4, and 1792.6 cm^{-1} for mixed H/D species with double the intensity of the pure H and D isotopes.

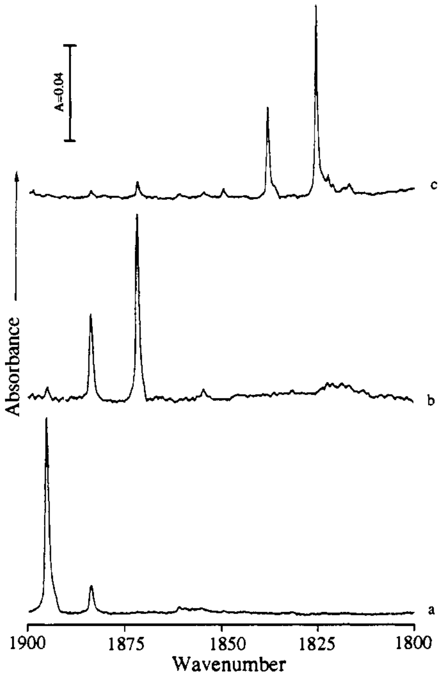


Figure 1. Infrared spectra in the 1900–1800 cm^{-1} region for laser-ablated boron atoms codeposited with Ar/CH_4 = 100/1 samples at 12 K: (a) ^{10}B (94%) + CH_4; (b) natural B (80% ^{11}B, 20% ^{10}B) + CH_4; and (c) natural B + $^{13}CH_4$.

The new HBCBH molecule is identified from isotopic shifts, isotopic intensity distribution patterns, and ab initio calculations. The reaction of methane with natural isotopic boron gave diagnostic absorptions at 1872.0, 1883.9, and 1895.2 cm^{-1} with 16/8/1 relative intensity, and only the 1883.9 and 1895.2 cm^{-1} absorptions were observed with 1/8 relative intensity for enriched boron-10. These intensity distribution patterns indicate the participation of two equivalent boron atoms in the vibrational motion. The same intensity patterns were observed at lower frequencies for reactions of $^{13}CH_4$ and CD_4. Spectra from mixtures of CH_4 and $^{13}CH_4$ were exact superimpositions of the spectra from pure isotopes, which is indicative of a product with only one carbon atom. The isotopic distribution pattern observed from the reaction of CH_2D_2 with natural isotopic boron shows that two equivalent hydrogen atoms remain in the product species. The involvement of one carbon, two equivalent boron, and two equivalent hydrogen atoms in the vibrational mode identifies the product HBCBH.

Electronic structure SCF calculations were performed for the possible reaction products of boron atoms with methane using the HONDO-7.0 program[7] and the DZP basis set. Vibrational frequencies and intensities were also calculated for the optimized structures. These calculations predict a linear structure for the HBCBH molecule with bond lengths of 1.357 and 1.164 Å for C–B and B–H, respectively. Typical B–C double-bond lengths fall in the range 1.39–1.44 Å from both experimental[2-4] and theoretical calculations.[8,9] The present SCF/DZP calculated B–C bond length for HBCBH (1.357 Å) is just shorter (by 0.03 Å) than the double-bond range and just longer (by 0.02–0.04 Å) than the calculated triple-bond value.[10] The calculated B–H bond length for HBCBH is slightly shorter (by 0.02 Å) than values calculated for organoboron anions where B_{sp} hybrid orbitals are

Table I. Observed and ab Initio Calculated Vibrational Frequencies (cm^{-1}) for the Linear HBCBH Molecule

	CH_4			$^{13}CH_4$			CD_4		
	^{10}B	$^{10/11}B$	^{11}B	^{10}B	$^{10/11}B$	^{11}B	^{10}B	$^{10/11}B$	^{11}B
ν_{BCB}[a](obsd)	1895.2	1883.9	1872.0	1849.7	1837.9	1825.4	1732.2	1729.8	1727.4
ν_{BCB}(calcd)	2037.3	2025.3	2012.5	1987.0	1974.4	1961.1	1860.7	1858.6	1856.3
ν_{BH}[b](obsd)	*c*	*c*	*c*	*c*	*c*	*c*	2230.7	2213.1	2190.9
ν_{BH}(calcd)	3014.5	3009.6	2994.2	3012.6	3008.2	2992.6	2402.8	2384.3	2359.5

[a] Predominantly antisymmetric B=C=B stretching mode. [b] Predominantly antisymmetric B—H stretching mode. [c] Covered by ν_1 of methane.

involved.[10] The calculated bond lengths for HBCBH are appropriate for a linear molecule with two carbon–boron double bonds.

The ab initio calculated vibrational frequencies are also listed in Table I. The calculated ν_{BCB} frequencies for all isotopes are converted to the observed frequency values by a constant scaling factor of 0.930, which is expected for SCF calculations. The calculated ν_{BH} frequencies require a scale factor of 0.928; the failure to observe this mode in CH_4 experiments is probably due to parent molecule absorptions. The excellent prediction of isotopic frequencies by scaled SCF calculations confirms the identification of HB=C=BH.

The mechanism for reaction of B atoms with CH_4 will be considered in detail after all of the products are identified. Semiempirical calculations predict that B inserts into a C–H bond in CH_4 without activation energy.[11] Two successive B atom insertions into C–H bonds in methane, which must be highly exothermic reactions, followed by H_2 elimination are required for the formation of HBCBH.

None of the frequencies reported for carbon–boron double bonds are due to an isolated C=B subgroup.[2,3] The present SCF/DZP calculations predict antisymmetric and symmetric B=C=B stretching modes at 2012 and 1196 cm^{-1}, respectively. The average value scaled by 0.93 is 1492 cm^{-1}, which represents a prototype C=B subgroup stretching fundamental. It is perhaps noteworthy that SCF/DZP calculations for H_2C=BH predict the double-bond stretching mode at 1608 cm^{-1}, which scales (× 0.93) to 1495 cm^{-1}.

Acknowledgment is made for financial support from NSF Grant CHE 91-22556.

---

(1) Jeong, G. H.; Boucher, R.; Klabunde, K. J. *J. Am. Chem. Soc.* **1990**, *112*, 3332.

(2) Klusic, H.; Berndt, A. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 877.

(3) Glaser, E.; Hanecher, E.; Noth, H.; Wager, E. *Chem. Ber.* **1987**, *120*, 659.

(4) Boese, R.; Paetzold, P.; Tapper, A. *Chem. Ber.* **1987**, *120*, 1069.

(5) Burkholder, T. R.; Andrews, L. *J. Chem. Phys.* **1991**, *95*, 8697.

(6) Hassanzadeh, P.; Andrews, L. *J. Phys. Chem.*, in press.

(7) Dupuis, M.; Watts, J. D.; Villar, H. D.; Hurst, G. J. B. *Comput. Phys. Commun.* **1989**, *52*, 415. Dupuis, M.; Rhys, J.; King, H. F. *J. Chem. Phys.* **1976**, *65*, 111.

(8) Cook, C. M.; Allen, L. C. *Organometallics* **1982**, *1*, 246.

(9) Frenking, G.; Schaefer, H. F., III *Chem. Phys. Lett.* **1984**, *109*, 521.

(10) Alberts, I. L.; Schafer, H. F., III *Chem. Phys. Lett.* **1990**, *165*, 250.

(11) Lebrilla, C. B.; Maier, W. F. *Chem. Phys. Lett.* **1984**, *105*, 183.

Formaldehyde Preferentially Interstrand Cross-Links Duplex DNA through Deoxyadenosine Residues at the Sequence 5′-d(AT)

Huifang Huang, Marjorie S. Solomon, and Paul B. Hopkins*

Department of Chemistry
University of Washington
Seattle, Washington 98195

Received July 17, 1992

Formaldehyde is a toxic substance ubiquitous in living systems and the environment.[1] From dietary sources alone, the average adult human consumes up to an estimated 14 mg of formaldehyde per day.[1] Formaldehyde is a DNA-denaturing[2] and interstrand-cross-linking agent.[3] We report here that formaldehyde preferentially forms dA-to-dA cross-links as in **1** at the dinucleotide sequence 5′-d(AT) in certain AT-rich sequences of duplex DNA.

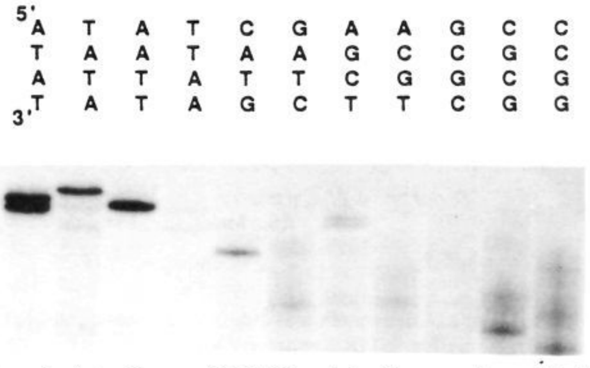


Figure 1. Autoradiogram of DPAGE analysis of interstrand-cross-linked products from formaldehyde-treated partially 5′-^{32}P-labeled [5′-d-(TACAACN$_4$GTTGT)]$_2$, N$_4$ as indicated.[4]

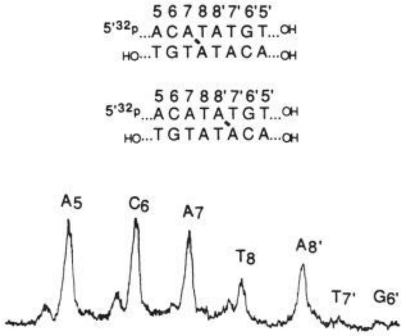
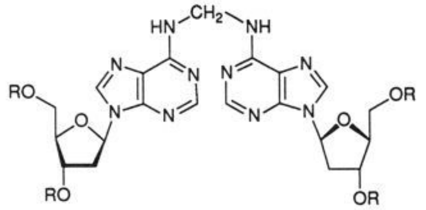


Figure 2. DPAGE analysis of partially 5′-^{32}P-labeled, formaldehyde-cross-linked [5′-d(TACAACATATGTTGT)]$_2$ following treatment with iron(II) EDTA/ascorbic acid/H_2O_2[5] reveals indicated sites of interstrand cross-linking.



1 R= DNA chain

2 R=H

A panel of self-complementary, 5′-^{32}P-radiolabeled duplexes 5′-d(TACAACN$_4$GTTGT) (Figure 1) was exposed to 25 mM formaldehyde (pH 6.0, 25 mM NaCl, 50 mM sodium phosphate buffer, 25 °C, 9 days). Each of the duplexes afforded several interstrand-cross-linked products (DPAGE), but the duplexes containing N$_4$ = ATAT and AATT preferentially afforded respectively two equiabundant products and one product, consistent with cross-linking centered on the shared 5′-d(AT) sequence.[4] A

---

(1) WHO Task Group on Environmental Health Criteria for Formaldehyde. Environmental Health Criteria 89, Formaldehyde; World Health Organization: Geneva, 1989.

(2) (a) McGhee, J. D.; von Hippel, P. H. *Biochemistry* **1975**, *14*, 1281, 1297. (b) McGhee, J. D.; von Hippel, P. H. *Biochemistry* **1977**, *16*, 3267, 3276.

(3) (a) Feldman, M. Ya. *Prog. Nucleic Acid Res. Mol. Biol.* **1973**, *13*, 1. (b) Freifelder, D.; Davison, P. F. *Biophys. J.* **1963**, *3*, 49. (c) van der Eb, A. J.; van Kestern, L. W.; van Brugger, E. F. J. *Biochim. Biophys. Acta* **1969**, *182*, 530. (d) Chaw, Y. F. M.; Crane, L. E.; Lange, P.; Shapiro, R. *Biochemistry* **1980**, *19*, 5525.

(4) Single strands and end-cross-linked products common to all DNAs are omitted in Figure 1 (see: Weidner, M. F.; Sigurdsson, S. Th.; Hopkins, P. B. *Biochemistry* **1990**, *29*, 9225). Because 5′-^{32}P-phosphorylated and excess hydroxyl-terminal strands were admixed, the symmetry of the two 5′-d(AT) sites in N$_4$ = ATAT is broken and two products are observed.[5b] Yields (%) of the major cross-linked product in each lane/total yield of cross-linked products exclusive of end-cross-linked products (phosphorimager) were as follows: ATAT 0.31 and 0.38/1.44; TATA 0.18/0.93; AATT 0.35/0.91; TTAA 0.04 and 0.04/0.39; CATG 0.16/0.91; GATC –/2.02; AGCT 0.08/1.19; ACGT –/1.45; GCGC –/1.14; CGCG 0.19/1.76; CCGG 0.18/2.03. These yields emphasize the distinction between *duplexes* which are efficiently cross-linked (N$_4$ = GATC and CCGG) and *specific sites within duplexes* [5′-d(AT)], which are preferentially cross-linked.

0002-7863/92/1514-9240$03.00/0