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Identification of cyc-B₃H₃ with Three Bridging B–H–B Bonds in a Six-Membered Ring

Sheng-Lung Chou,[†] Jen-Iu Lo,[†] Yu-Chain Peng,[†] Meng-Yeh Lin,[†] Hsiao-Chi Lu,[†] Bing-Ming Cheng,^{*,†©} and John F. Ogilvie^{‡,§}

[†]National Synchrotron Radiation Research Center, No. 101, Hsin-Ann Road, Hsinchu Science Park, Hsinchu 30076, Taiwan [‡]Escuela de Quimica, Universidad de Costa Rica, Ciudad Universitaria Rodrigo Facio, San Pedro de Montes de Oca, San Jose 11501-2060, Costa Rica

[§]Department of Mathematics, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia, Canada V5A1S6

S Supporting Information

ABSTRACT: Irradiation of samples of diborane(6), B_2H_6 and B_2D_6 , separately and together, dispersed in solid neon near 4 K with tunable far-ultraviolet light from a synchrotron yielded new infrared absorption lines that are assigned to several carriers. Besides H, B, BH, BH₂, BH₃, B₂, B_2H_2 , and B_2H_4 , previously identified, a further species is assigned on the basis of quantum-chemical calculations of vibrational wavenumbers and intensities to be *cyc*-B₃H₃ (D_{3h} , singlet state) in several isotopic variants, which feature three bridging B–H–B bonds in a six-membered ring.

1. INTRODUCTION

Boron compounds have novel molecular structures. Among the boron species, boron hydrides, boranes, exhibit unique bonding features in their molecular structures and have drawn much interest because of their unique chemical properties.¹⁻⁶ The hydrides of boron and carbon have disparate molecular structures; for instance, B_2H_6 exhibits bonding patterns remarkably distinct from those of C_2H_6 . Thus, the molecular structure of diborane(6) attracts particular attention with four terminal hydrogen bonds (B–H) and two peculiar bridging hydrogen bonds (B–H–B).^{7–10} For this reason, boranes fascinate chemists for their atypical molecular structures.

An exploration of the spectra of not only compounds stable at 300 K but also the radicals and intermediate species that can be trapped in inert environments provides fascinating new knowledge about their structures, from which concepts of bonding are developed. In experiments involving the irradiation of diborane(6) dispersed in solid neon near 4 K with tunable far-ultraviolet (FUV) light from a synchrotron, we identified, among various new lines in infrared absorption spectra after photolysis, signals assigned to several boron hydrides, including BH, BH₂, BH₃, B₂H₂, and B₂H₄¹¹ from visible and ultraviolet spectra in emission or absorption, we assigned signals also to B, H, and B₂.¹²

A further new species is identified here on the basis of quantum-chemical calculations of vibrational wavenumbers and intensities of several isotopic variants, as cyc-B₃H₃ (D_{3h}) in a singlet electronic state, which features three bridging B–H–B



bonds in a novel six-membered ring. Such a structure has no precedent among diverse boron hydrides or even hydrides of other elements.

2. RESULTS AND DISCUSSION

Figure 1 shows infrared absorption spectra, over the recorded range 500-2700 cm⁻¹, of precursors B_2H_6 and B_2D_6 with B in natural abundance, dispersed in solid neon (1:1000) after deposition for 2 h at 4 K. For boron in natural abundance with two stable isotopic variants, 0.801 ¹¹B and 0.199 ¹⁰B, the ratio of species ${}^{11}B_2H_6$ or ${}^{11}B_2D_6/{}^{11}B^{10}BH_6$ or ${}^{11}B^{10}BD_6/{}^{10}B_2H_6$ or ${}^{10}B_2D_6$ is hence about 16:8:1. The spectra of B_2H_6 in natural abundance display many absorption features of which the proximity and ratios of lines enable a clear assignment to triplets of isotopic boron species containing ¹¹B₂, ¹¹B¹⁰B, and ${}^{10}\dot{B}_{2^{\prime}}$ generally in the order of increasing wavenumber. We reported a detailed analysis of the infrared and ultraviolet absorption spectra of diborane(6) dispersed in solid neon at 4 K.¹³ Figure 1 marks the notable vibrational modes observed; for instance, the lines of ${}^{11}B_2H_6/{}^{11}B_2D_6$ were recorded at 974.8/ 723.2 (ν_9), 1172.1/873.8 (ν_{18}), 1597.73/1195.0 (ν_{17}), 1855.5/ 1321.3 ($\nu_5 + \nu_{15}$), 1877.9/1475.2 (ν_8), 1990.2/1396.9 ($\nu_{13} +$ ν_{15}), 2344.9/1770.9 ($\nu_3 + \nu_{18}$), 2521.8/1846.5 (ν_{16}), and $2610.6/1977.2 (\nu_{12}) \text{ cm}^{-1}$

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Figure 1. IR absorption spectra of diborane(6) dispersed in solid neon at 4 K: (a) $B_2H_6/Ne = 1:1000$; (b) $B_2D_6/Ne = 1:1000$; and (c) $B_2H_6/Ne = 1:1000$ and $B_2D_6/Ne = 1:1000$, deposited through separate jets to preclude mixing before the formation of the deposit.

To generate various transient species, we irradiated diborane(6) dispersed in solid neon at near 4 K with tunable FUV light from the undulator of a synchrotron. Figures 2a and 3a display the partial infrared difference absorption spectra after photolysis at 121.6 nm for 76 min at 4 K from samples $B_2D_6/Ne = 1:1000$ and $B_2H_6/Ne = 1:1000$, respectively. Our difference spectra are derived upon subtracting the spectra recorded after irradiation from the spectrum before irradiation; in these spectra, the lines pointing upward indicate production and the lines pointing downward indicate destruction. In addition to the infrared absorption lines assigned previously,^{11,12} the lines in sets with similar temporal profiles of

production appeared after photolysis at specific selected wavelengths, which we discuss here.

To aid assignments of the latter lines, we undertook quantum-chemical calculations of equilibrium structures, harmonic vibrational wavenumbers, infrared intensities, and energies of selected boron hydrides (program Gaussian 09, B3LYP density functionals, both local and nonlocal terms augmented with correlation-consistent polarized-valence basis set triplet-zeta, aug-cc-pVTZ).

No stable triboron hydride is known, but among the transient species that might be trapped in solid neon, after monoboron and diboron hydrides, the most likely species are triboron hydrides. Hence, in our calculations, these species included acyclic triboron hydrides B_3H_3 (C_s) and B_3H_3 ($C_{2\nu}$) and cyclic hydrides B_3H_3 ($C_{2\nu}$), B_3H_3 (D_{3h}), and $B_3H_3^{2-}$, all of which are at least metastable; their wavenumbers and intensities are listed in the Supporting Information.

The attribution of lines in an infrared absorption spectrum to various prospective new species within an unknown mixture is a challenging task. Our quantum-chemical calculations (Table 1) indicated that for ${}^{11}B_3D_3$, that is the dominant isotopic variant containing deuterium, two lines at 868.0 (ν_5) and 828.3 cm⁻¹ (ν_6) are characteristic of a cyclic triboron species, B₃H₃ (D_{3h}) , the molecular structure of which in a singlet electronic spin state is shown in Figure 4; the corresponding triplet state is merely a saddle point with imaginary frequencies. These calculated wavenumbers and relative intensities correlate closely with the two features in the experimental spectrum at 857.2 and 820.6 cm^{-1} , as shown in Figure 2a, according to both their wavenumbers and intensities; for comparison with the calculated ratio 0.63 of the respective intensities, the experimental ratio of integrated intensities is ~0.58, and that ratio is satisfactorily constant in various experiments with B_2D_6 . The two calculated vibrational modes are respectively ν_5 and ν_{61} both of symmetry class E'. The corresponding modes of ${}^{11}B_3H_3$



Figure 2. Partial infrared difference absorption spectra of cyc-B₃D₃ (a) after photolysis of B₂D₆/Ne = 1:1000 at 4 K and irradiation at 121.6 nm for 76 min (resolution 0.5 cm⁻¹ from 1000 co-added interferograms) and (b) from simulations. Some assignments are indicated.

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Figure 3. Partial infrared absorption difference spectrum of $cyc-B_3H_3$ (a) after photolysis of $B_2H_6/Ne = 1:1000$ at 4 K with irradiation at 121.6 nm for 76 min (resolution 0.5 cm⁻¹ from 1000 co-added interferograms) and (b) from simulations. Some assignments are indicated.

Table 1. Calculated Wavenumbers (cm^{-1}) and Intensities $(km mol^{-1})$ (within Parentheses) of Vibrational Modes and Experimental Wavenumbers (cm^{-1}) for cyc-B₃H₃ and cyc-B₃D₃ in Isotopic Variants

D_{3h}	cyc- ¹¹ B ₃ H ₃		cyc- ¹⁰ B ₃ H ₃		$C_{2\nu}$	<i>cyc</i> - ¹⁰ B ¹¹ B ₂ H ₃		<i>cyc</i> - ¹⁰ B ₂ ¹¹ BH ₃	
mode (sym.)	calcd (cm ⁻¹) (int.) ^a	exp.	calcd (cm^{-1}) $(int.)^a$	exp.	mode (sym.)	calcd (cm^{-1}) $(int.)^a$	exp	calcd (cm^{-1}) $(int.)^a$	exp.
$ u_1(A_1{}')$	1319.5 (0.0)		1320.4 (0.0)		$ u_1(A_1) $	1319.5 (0.1)		1319.8 (0.0)	
$\nu_2(A_1')$	419.3 (0.0)		439.3 (0.0)		$ u_2(A_1) $	1187.8 (658)	1211.8	1188.9 (642)	1213.7
$\nu_3(A_2')$	1473.2 (0.0)		1477.8 (0.0)		$ u_3(A_1) $	1119.7 (30.7)	1145.5	1124.9 (45.4)	1148.1
$\nu_4(A_2'')$	313.9 (1020)		315.2 (1028)		$ u_4(A_1) $	457.2 (2.6)		462.4 (2.8)	
$\nu_5(E')$	1186.7 (1296)	1209.1	1189.9 (1278)	1215.7	$\nu_5(A_1)$	424.6 (0.1)		431.4 (0.2)	
$\nu_6(E')$	1120.2 (72.2)	1145.5	1125.7 (95.8)	1149.1	$\nu_6(A_2)$	192.1 (0.0)		192.6 (0.0)	
$ u_7(E') $	447.9 (2.8)		468.1 (2.9)		$ u_7(B_1) $	316.7 (1016)		317.1 (1019)	
$\nu_8(E'')$	194.3 (0.0)		194.9 (0.0)		$ u_8(B_1) $	194.5 (0.0)		194.3 (0.0)	
					$\nu_9(B_2)$	1473.8 (0.0)		1475.3 (0.0)	
					$\nu_{10}(B_2)$	1188.5 (645)	1211.8	1189.5 (656)	1213.7
					$\nu_{11}(B_2)$	1125.4 (41.9)	1149.1	1124.0 (34.4)	1148.1
					$\nu_{12}(B_2)$	454.4 (3.0)		462.5 (2.8)	
	cyc - ¹¹ B_3D_3		<i>cyc</i> - ¹⁰ B ₃ D ₃				<i>cyc</i> - ¹⁰ B ¹¹ B ₂ D ₃		
D_{3h}	<i>cyc</i> - ¹¹ B ₃ D ₃		<i>cyc</i> - ¹⁰ B ₃ D ₃		C _{2v}	<i>cyc</i> - ¹⁰ B ¹¹ B ₂ D	3	<i>cyc</i> - ¹⁰ B ₂ ¹¹ BD ₅	3
D _{3h} mode (sym.)	$\frac{cyc^{-11}B_3D_3}{\text{calcd (cm}^{-1}) \text{ (int.)}^a}$	exp.	$\frac{cyc^{-10}B_3D_3}{\text{calcd (cm}^{-1}) \text{ (int.)}^a}$	exp	$\frac{C_{2\nu}}{\text{mode (sym.)}}$	$\frac{cyc^{-10}B^{11}B_{2}D}{\text{calcd (cm}^{-1}) (\text{int.})^{a}}$	exp	$cyc^{-10}B_2^{-11}BD_3$ calcd (cm ⁻¹) (int.) ^{<i>a</i>}	exp
$\frac{D_{3h}}{\text{mode (sym.)}}$ $\nu_1(A_1')$	$\frac{cyc^{-11}B_3D_3}{\text{calcd (cm}^{-1}) (\text{int.})^a}$ 940.8 (0.0)	exp.	$\frac{cyc^{-10}B_3D_3}{\text{calcd (cm}^{-1}) (\text{int.})^a}$ 942.5 (0.0)	exp	$\frac{C_{2\nu}}{\text{mode (sym.)}}$ $\nu_1(A_1)$	$\frac{cyc^{-10}B^{11}B_2D}{\text{calcd (cm}^{-1}) (\text{int.})^a}$ 941.2 (0.2)	exp	$\frac{cyc^{-10}B_2^{-11}BD_3}{calcd (cm^{-1}) (int.)^a}$ 941.7 (0.0)	exp
$\begin{array}{c} D_{3h} \\ \hline mode \ (sym.) \\ \nu_1(A_1{'}) \\ \nu_2(A_1{'}) \end{array}$	$\frac{cyc^{-11}B_3D_3}{\text{calcd (cm}^{-1}) \text{ (int.)}^a}$ 940.8 (0.0) 415.9 (0.0)	exp.	$\begin{array}{c} cyc^{-10}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^a\\ 942.5 \ (0.0)\\ 435.3 \ (0.0)\\ \end{array}$	exp	$ \frac{C_{2\nu}}{\text{mode (sym.)}} $ $ \frac{\nu_1(A_1)}{\nu_2(A_1)} $	$\frac{cyc^{-10}B^{11}B_2D}{calcd (cm^{-1}) (int.)^a}$ 941.2 (0.2) 868.1 (237)	exp 857.2	$\frac{cyc^{-10}B_2^{-11}BD_3}{calcd (cm^{-1}) (int.)^a}$ 941.7 (0.0) 874.4 (187)	exp 862.9
$\begin{array}{c} D_{3h} \\ \hline \mathbf{mode} \ (\text{sym.}) \\ \hline \nu_1(A_1') \\ \nu_2(A_1') \\ \nu_3(A_2') \end{array}$	$\begin{array}{c} cyc.{}^{11}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^a\\ 940.8 \ (0.0)\\ 415.9 \ (0.0)\\ 1073.9 \ (0.0)\\ \end{array}$	exp.	$\begin{array}{c} cyc^{-10}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^{a}\\ 942.5 \ (0.0)\\ 435.3 \ (0.0)\\ 1080.1 \ (0.0)\\ \end{array}$	exp	$\begin{array}{c} \hline C_{2\nu} \\ \hline mode (sym.) \\ \nu_1(A_1) \\ \nu_2(A_1) \\ \nu_3(A_1) \end{array}$	$\frac{cyc^{-10}B^{11}B_2D}{\text{calcd (cm}^{-1}) (\text{int.})^{ct}}$ 941.2 (0.2) 868.1 (237) 829.6 (126)	exp 857.2 820.6	$\frac{cyc^{-10}B_2{}^{11}BD_2}{calcd (cm^{-1}) (int.)^a}$ 941.7 (0.0) 874.4 (187) 832.8 (175)	exp 862.9 823.2
$\begin{array}{c} D_{3h} \\ \hline \mathbf{mode} \ (\text{sym.}) \\ \hline \nu_1(A_1{'}) \\ \nu_2(A_1{'}) \\ \nu_3(A_2{'}) \\ \nu_4(A_2{''}) \end{array}$	cyc- ¹¹ B ₃ D ₃ calcd (cm ⁻¹) (int.) ^a 940.8 (0.0) 415.9 (0.0) 1073.9 (0.0) 231.2 (553)	exp.	$\begin{tabular}{ c c c c c c c c c c c c c c c c c c c$	exp	$\begin{array}{c} \hline C_{2\nu} \\ \hline mode (sym.) \\ \nu_1(A_1) \\ \nu_2(A_1) \\ \nu_3(A_1) \\ \nu_4(A_1) \end{array}$	$\begin{array}{c} \hline cyc^{-10}B^{11}B_2D \\ \hline calcd \ (cm^{-1}) \ (int.)^{44} \\ 941.2 \ (0.2) \\ 868.1 \ (237) \\ 829.6 \ (126) \\ 441.3 \ (1.1) \end{array}$	exp 857.2 820.6	$\begin{array}{c} cyc^{-10}B_2{}^{11}BD_2 \\ \hline calcd \ (cm^{-1}) \ (int.)^a \\ 941.7 \ (0.0) \\ 874.4 \ (187) \\ 832.8 \ (175) \\ 444.6 \ (1.2) \end{array}$	exp 862.9 823.2
$\begin{array}{c} D_{3h} \\ \hline mode \ (sym.) \\ \hline \nu_1(A_1') \\ \nu_2(A_1') \\ \nu_3(A_2') \\ \nu_4(A_2'') \\ \nu_5(E') \end{array}$	cyc- ¹¹ B ₃ D ₃ calcd (cm ⁻¹) (int.) ^a 940.8 (0.0) 415.9 (0.0) 1073.9 (0.0) 231.2 (553) 868.0 (440)	exp. 857.2	$\begin{array}{c} cyc^{-10}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^{\prime\prime}\\ 942.5 \ (0.0)\\ 435.3 \ (0.0)\\ 1080.1 \ (0.0)\\ 233.0 \ (562)\\ 875.6 \ (378) \end{array}$	exp 866.2	$\begin{array}{c} \hline C_{2\nu} \\ \hline \hline mode \ (sym.) \\ \nu_1(A_1) \\ \nu_2(A_1) \\ \nu_3(A_1) \\ \nu_4(A_1) \\ \nu_5(A_1) \end{array}$	$\begin{array}{c} \hline \\ \hline $	exp 857.2 820.6	$\begin{array}{c} cyc^{-10}B_2{}^{11}BD_2 \\ \hline calcd \ (cm^{-1}) \ (int.)^a \\ 941.7 \ (0.0) \\ 874.4 \ (187) \\ 832.8 \ (175) \\ 444.6 \ (1.2) \\ 426.5 \ (0.3) \\ \end{array}$	exp 862.9 823.2
$\begin{array}{c} D_{3h} \\ \hline mode \ (sym.) \\ \hline \nu_1(A_1') \\ \nu_2(A_1') \\ \nu_3(A_2') \\ \nu_4(A_2'') \\ \nu_5(E') \\ \nu_6(E') \end{array}$	cyc- ¹¹ B ₃ D ₃ calcd (cm ⁻¹) (int.) ^a 940.8 (0.0) 415.9 (0.0) 1073.9 (0.0) 231.2 (553) 868.0 (440) 828.3 (278)	exp. 857.2 820.6	$\begin{array}{c} cyc^{-10}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^{\alpha}\\ 942.5 \ (0.0)\\ 435.3 \ (0.0)\\ 1080.1 \ (0.0)\\ 233.0 \ (562)\\ 875.6 \ (378)\\ 834.3 \ (348)\\ \end{array}$	exp 866.2 827.3(?)	$\begin{array}{c} \hline C_{2\nu} \\ \hline \hline mode \ (sym.) \\ \nu_1(A_1) \\ \nu_2(A_1) \\ \nu_3(A_1) \\ \nu_4(A_1) \\ \nu_5(A_1) \\ \nu_6(A_2) \end{array}$	$\begin{array}{c} \hline \\ \hline $	exp 857.2 820.6	$\begin{array}{c} cyc^{-10}B_2{}^{11}BD_2 \\ \hline calcd \ (cm^{-1}) \ (int.)^a \\ 941.7 \ (0.0) \\ 874.4 \ (187) \\ 832.8 \ (175) \\ 444.6 \ (1.2) \\ 426.5 \ (0.3) \\ 140.4 \ (0.0) \end{array}$	exp 862.9 823.2
$\begin{array}{c} D_{3h} \\ \hline mode \ (sym.) \\ \hline \nu_1(A_1') \\ \nu_2(A_1') \\ \nu_3(A_2') \\ \nu_4(A_2'') \\ \nu_5(E') \\ \nu_6(E') \\ \nu_7(E') \end{array}$	$\begin{array}{r} cyc.^{11}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^a\\ 940.8 \ (0.0)\\ 415.9 \ (0.0)\\ 1073.9 \ (0.0)\\ 231.2 \ (553)\\ 868.0 \ (440)\\ 828.3 \ (278)\\ 431.4 \ (1.5)\\ \end{array}$	exp. 857.2 820.6	$\begin{tabular}{ c c c c c c } \hline cyc-{}^{10}B_3D_3\\\hline calcd~(cm^{-1})~(int.)^{\alpha}\\ \hline 942.5~(0.0)\\ 435.3~(0.0)\\ 1080.1~(0.0)\\ 233.0~(562)\\ 875.6~(378)\\ 834.3~(348)\\ 448.6~(1.3)\\ \hline \end{tabular}$	exp 866.2 827.3(?)	$\begin{array}{c} \hline C_{2\nu} \\ \hline \hline mode \ (sym.) \\ \nu_1(A_1) \\ \nu_2(A_1) \\ \nu_3(A_1) \\ \nu_4(A_1) \\ \nu_5(A_1) \\ \nu_6(A_2) \\ \nu_7(B_1) \end{array}$	$\begin{array}{c} \hline cyc^{10}B^{11}B_2D \\ \hline calcd \ (cm^{-1}) \ (int.)^{a} \\ 941.2 \ (0.2) \\ 868.1 \ (237) \\ 829.6 \ (126) \\ 441.3 \ (1.1) \\ 420.2 \ (0.2) \\ 139.7 \ (0.0) \\ 233.5 \ (552) \end{array}$	exp 857.2 820.6	$\begin{array}{r} cyc^{-10}B_2{}^{11}BD_2 \\ \hline calcd \ (cm^{-1}) \ (int.)^a \\ 941.7 \ (0.0) \\ 874.4 \ (187) \\ 832.8 \ (175) \\ 444.6 \ (1.2) \\ 426.5 \ (0.3) \\ 140.4 \ (0.0) \\ 234.1 \ (555) \end{array}$	exp 862.9 823.2
$\begin{array}{c} D_{3h} \\ \hline mode \ (sym.) \\ \hline \nu_1(A_1') \\ \nu_2(A_1') \\ \nu_3(A_2') \\ \nu_4(A_2'') \\ \nu_5(E') \\ \nu_6(E') \\ \nu_7(E') \\ \nu_8(E'') \end{array}$	$\begin{array}{r} cyc.^{11}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^a\\ 940.8 \ (0.0)\\ 415.9 \ (0.0)\\ 1073.9 \ (0.0)\\ 231.2 \ (553)\\ 868.0 \ (440)\\ 828.3 \ (278)\\ 431.4 \ (1.5)\\ 141.1 \ (0.0)\\ \end{array}$	exp. 857.2 820.6	$\begin{array}{c} cyc^{-10}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^{\alpha}\\ 942.5 \ (0.0)\\ 435.3 \ (0.0)\\ 1080.1 \ (0.0)\\ 233.0 \ (562)\\ 875.6 \ (378)\\ 834.3 \ (348)\\ 448.6 \ (1.3)\\ 141.9 \ (0.0)\\ \end{array}$	exp 866.2 827.3(?)	$\begin{array}{c} \hline C_{2\nu} \\ \hline \hline mode \ (sym.) \\ \nu_1(A_1) \\ \nu_2(A_1) \\ \nu_3(A_1) \\ \nu_4(A_1) \\ \nu_5(A_1) \\ \nu_6(A_2) \\ \nu_7(B_1) \\ \nu_8(B_1) \end{array}$	$\begin{array}{c} \hline cyc^{10}B^{11}B_2D \\ \hline calcd \ (cm^{-1}) \ (int.)^{a} \\ \hline 941.2 \ (0.2) \\ 868.1 \ (237) \\ 829.6 \ (126) \\ 441.3 \ (1.1) \\ 420.2 \ (0.2) \\ 139.7 \ (0.0) \\ 233.5 \ (552) \\ 141.6 \ (0.0) \\ \hline \end{array}$	exp 857.2 820.6	$\begin{array}{r} cyc^{-10}B_2{}^{11}BD_2 \\ \hline calcd \ (cm^{-1}) \ (int.)^a \\ 941.7 \ (0.0) \\ 874.4 \ (187) \\ 832.8 \ (175) \\ 444.6 \ (1.2) \\ 426.5 \ (0.3) \\ 140.4 \ (0.0) \\ 234.1 \ (555) \\ 141.4 \ (0.0) \\ \end{array}$	exp 862.9 823.2
$\begin{array}{c} D_{3h} \\ \hline mode \ (sym.) \\ \hline \nu_1(A_1') \\ \nu_2(A_1') \\ \nu_3(A_2') \\ \nu_4(A_2'') \\ \nu_5(E') \\ \nu_6(E') \\ \nu_7(E') \\ \nu_8(E'') \end{array}$	$\begin{array}{c} cyc^{-11}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^a\\ 940.8 \ (0.0)\\ 415.9 \ (0.0)\\ 1073.9 \ (0.0)\\ 231.2 \ (553)\\ 868.0 \ (440)\\ 828.3 \ (278)\\ 431.4 \ (1.5)\\ 141.1 \ (0.0)\\ \end{array}$	exp. 857.2 820.6	$\begin{array}{c} cyc^{-10}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^{a}\\ 942.5 \ (0.0)\\ 435.3 \ (0.0)\\ 1080.1 \ (0.0)\\ 233.0 \ (562)\\ 875.6 \ (378)\\ 834.3 \ (348)\\ 448.6 \ (1.3)\\ 141.9 \ (0.0)\\ \end{array}$	exp 866.2 827.3(?)	$\begin{array}{c} \hline C_{2\nu} \\ \hline \hline mode \ (sym.) \\ \hline \nu_1(A_1) \\ \nu_2(A_1) \\ \nu_3(A_1) \\ \nu_4(A_1) \\ \nu_5(A_1) \\ \nu_6(A_2) \\ \nu_7(B_1) \\ \nu_8(B_1) \\ \nu_9(B_2) \end{array}$	$\begin{array}{c} \hline cyc^{10}B^{11}B_2D \\ \hline calcd \ (cm^{-1}) \ (int.)^{a} \\ \hline 941.2 \ (0.2) \\ 868.1 \ (237) \\ 829.6 \ (126) \\ 441.3 \ (1.1) \\ 420.2 \ (0.2) \\ 139.7 \ (0.0) \\ 233.5 \ (552) \\ 141.6 \ (0.0) \\ 1075.3 \ (0.0) \\ \end{array}$	exp 857.2 820.6	$\begin{array}{r} cyc^{10}B_2{}^{11}BD_2 \\ \hline calcd \ (cm^{-1}) \ (int.)^a \\ 941.7 \ (0.0) \\ 874.4 \ (187) \\ 832.8 \ (175) \\ 444.6 \ (1.2) \\ 426.5 \ (0.3) \\ 140.4 \ (0.0) \\ 234.1 \ (555) \\ 141.4 \ (0.0) \\ 1077.2 \ (0.0) \\ \end{array}$	exp 862.9 823.2
$\begin{array}{c} D_{3h} \\ \hline mode \ (sym.) \\ \hline \nu_1(A_1') \\ \nu_2(A_1') \\ \nu_3(A_2') \\ \nu_4(A_2'') \\ \nu_5(E') \\ \nu_6(E') \\ \nu_7(E') \\ \nu_8(E'') \end{array}$	$\begin{array}{c} cyc^{-11}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^a\\ 940.8 \ (0.0)\\ 415.9 \ (0.0)\\ 1073.9 \ (0.0)\\ 231.2 \ (553)\\ 868.0 \ (440)\\ 828.3 \ (278)\\ 431.4 \ (1.5)\\ 141.1 \ (0.0)\\ \end{array}$	exp. 857.2 820.6	$\begin{array}{c} cyc^{-10}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^{a}\\ \hline 942.5 \ (0.0)\\ 435.3 \ (0.0)\\ 1080.1 \ (0.0)\\ 233.0 \ (562)\\ 875.6 \ (378)\\ 834.3 \ (348)\\ 448.6 \ (1.3)\\ 141.9 \ (0.0)\\ \hline \end{array}$	exp 866.2 827.3(?)	$\begin{array}{c} \hline C_{2\nu} \\ \hline \hline mode \ (sym.) \\ \hline \nu_1(A_1) \\ \nu_2(A_1) \\ \nu_3(A_1) \\ \nu_4(A_1) \\ \nu_5(A_1) \\ \nu_6(A_2) \\ \nu_7(B_1) \\ \nu_8(B_1) \\ \nu_9(B_2) \\ \nu_{10}(B_2) \end{array}$	$\begin{array}{c} \hline cyc^{-10}B^{11}B_2D \\ \hline calcd (cm^{-1}) (int.)^{a} \\ \hline 941.2 (0.2) \\ 868.1 (237) \\ 829.6 (126) \\ 441.3 (1.1) \\ 420.2 (0.2) \\ 139.7 (0.0) \\ 233.5 (552) \\ 141.6 (0.0) \\ 1075.3 (0.0) \\ 872.7 (192) \\ \end{array}$	exp 857.2 820.6 861.6	$\begin{array}{c} cyc^{-10}B_2{}^{11}BD_2 \\ \hline calcd \ (cm^{-1}) \ (int.)^a \\ 941.7 \ (0.0) \\ 874.4 \ (187) \\ 832.8 \ (175) \\ 444.6 \ (1.2) \\ 426.5 \ (0.3) \\ 140.4 \ (0.0) \\ 234.1 \ (555) \\ 141.4 \ (0.0) \\ 1077.2 \ (0.0) \\ 871.3 \ (221) \end{array}$	exp 862.9 823.2 861.6
$\begin{array}{c} D_{3h} \\ \hline mode \ (sym.) \\ \hline \nu_1(A_1') \\ \nu_2(A_1') \\ \nu_3(A_2') \\ \nu_4(A_2'') \\ \nu_5(E') \\ \nu_6(E') \\ \nu_7(E') \\ \nu_8(E'') \end{array}$	$\begin{array}{c} cyc.^{11}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^a\\ 940.8 \ (0.0)\\ 415.9 \ (0.0)\\ 1073.9 \ (0.0)\\ 231.2 \ (553)\\ 868.0 \ (440)\\ 828.3 \ (278)\\ 431.4 \ (1.5)\\ 141.1 \ (0.0)\\ \end{array}$	exp. 857.2 820.6	$\begin{array}{c} cyc^{-10}B_3D_3\\ \hline calcd \ (cm^{-1}) \ (int.)^{a}\\ 942.5 \ (0.0)\\ 435.3 \ (0.0)\\ 1080.1 \ (0.0)\\ 233.0 \ (562)\\ 875.6 \ (378)\\ 834.3 \ (348)\\ 448.6 \ (1.3)\\ 141.9 \ (0.0)\\ \end{array}$	exp 866.2 827.3(?)	$\begin{array}{c} \hline C_{2\nu} \\ \hline \hline mode \ (sym.) \\ \hline \nu_1(A_1) \\ \nu_2(A_1) \\ \nu_3(A_1) \\ \nu_4(A_1) \\ \nu_5(A_1) \\ \nu_6(A_2) \\ \nu_7(B_1) \\ \nu_8(B_1) \\ \nu_9(B_2) \\ \nu_{10}(B_2) \\ \nu_{11}(B_2) \end{array}$	$\begin{array}{c} cyc^{-10}B^{11}B_2D\\ \hline calcd~(cm^{-1})~(int.)^{ar}\\ 941.2~(0.2)\\ 868.1~(237)\\ 829.6~(126)\\ 441.3~(1.1)\\ 420.2~(0.2)\\ 139.7~(0.0)\\ 233.5~(552)\\ 141.6~(0.0)\\ 1075.3~(0.0)\\ 872.7~(192)\\ 832.1~(168)\\ \end{array}$	exp 857.2 820.6 861.6 823.2	$\begin{array}{c} cyc^{-10}B_2{}^{11}BD_2 \\ \hline calcd \ (cm^{-1}) \ (int.)^a \\ 941.7 \ (0.0) \\ 874.4 \ (187) \\ 832.8 \ (175) \\ 444.6 \ (1.2) \\ 426.5 \ (0.3) \\ 140.4 \ (0.0) \\ 234.1 \ (555) \\ 141.4 \ (0.0) \\ 1077.2 \ (0.0) \\ 871.3 \ (221) \\ 833.1 \ (143) \end{array}$	exp 862.9 823.2 861.6 823.2

"Vibrational wavenumbers are calculated with program Gaussian 09, the B3LYP method, and basis set aug-cc-pVTZ (B3LYP/aug-cc-pVTZ); the calculated vibrational wavenumbers are scaled by 0.967; and the calculated intensities are in units of km mol⁻¹.



Figure 4. Calculated structure of cyc- B_3H_3 (symmetry class D_{3h}) in a singlet state.

are calculated to have wavenumbers 1186.7 cm⁻¹ for ν_5 and 1120.2 cm⁻¹ for ν_6 , but in this case, the calculated intensity of the former is about 18 times that of the latter. Appropriate features in recorded spectra appear near 1209.1 cm⁻¹ for ν_5 and, barely visibly, 1145.5 cm⁻¹ for ν_6 , as displayed in Figure 3a.

The recorded spectrum contains contributions from the isotopic variants of boron in natural abundance; when we took into account the spectral structure of B_3H_3 resulting from these isotopes, we derived the simulated spectra, with wavenumbers slightly shifted to aid comparison, in Figures 3b and 2b, for comparison with partial difference infrared absorption spectra recorded in the region 1120–1260 cm⁻¹ after photolysis of B_2H_6 and 810–880 cm⁻¹ after photolysis of B_2D_6 in Figures 3a and 2a, respectively.

The lines attributed to cyclic B₃H₃ were detected after photolysis of B₂H₆ dispersed in neon at 1:1000 and wavelengths 121.6-180 nm but not observed at 200 and 220 nm; weak signals of cyclic B₃H₃ were also recorded after irradiation at wavelengths of only 121.6–180 nm for B_2H_6/Ne = 1:2000 and 1:10 000, with weak signals also of BH₃. With addition of hydrogen, so that initially $B_2H_6/H_2/Ne = 1:6:1000$, the lines of cyclic B₂H₂ were observed for wavelengths 121.6-180 nm, still not detected at 220 nm, and the intensity of signals of BH₃ relatively increased under the same conditions (see Supporting Information). There was no evidence for photochemical decomposition of cyclic B₃H₃ at any tested wavelength. Just as the addition of H₂ to the neon matrix promoted the production of carbon aggregates up to C₂₀ after the photolysis of $CH_{4\nu}^{14}$ the addition of H_2 with B_2H_6 in solid Ne promoted the production of cyclic B₃H₃ in our subsequent experiments.

Table 1 shows that, because ${}^{11}B_3H_3$ and ${}^{11}B_3D_3$ have a highly symmetric structure, vibrational modes ν_5 and ν_6 are the only fundamental modes that are active in infrared absorption within the range of our detection, $500-4000 \text{ cm}^{-1}$. Figure 5a,b shows that most amplitudes of the vibrational motion of the atoms in modes ν_5 and ν_6 involve the H atomic centers; as these modes are degenerate, we show only one component of each mode. The relative motions of the B and H atoms in these modes indicate that the nature of the vibrations involves both the stretching of the B–H bonds and the deformation of the B–H–B angles. The similarity of these experimental and calculated spectra of B_3H_3 and the lack of agreement for other possible species indicate the likely detection of a cyclic triborane(3) for the first time.



Figure 5. Fundamental vibrational modes (a) ν_5 and (b) ν_6 of cyc-B₃H₃; the vectors show the relative displacements of the H atoms; the small corresponding displacements of the B atomic centers are within the spheres denoting those atoms.

To confirm the assignment of cyclic triborane(3), we employed photolysis of a mixed sample of B_2H_6 and B_2D_6 dispersed in solid neon with selected FUV light at 4 K. Initially, we prepared a gaseous sample of $B_2H_6/B_2D_6/Ne = 1:1:1000$ at 295 K; after mixing overnight, we then deposited this gaseous mixture on a cold target at 4 K, but we observed that the IR spectrum of this precursor was complicated; with detailed analysis, we identified the lines associated with various isotopic species B_2H_6 , B_2DH_5 , $B_2D_2H_4$, $B_2D_3H_3$, $B_2D_4H_2$, B_2D_5H , and B_2D_6 . This result confirms that gaseous B_2H_6 and B_2D_6 exchange H and D freely at 295 K¹⁵ to generate in total 21 isotopic variants in our sample. Photolysis of this complicated sample produced many unknown lines.

To avoid that isotopic exchange between B_2H_6 and B_2D_6 , we adopted a scheme for co-deposition of gaseous $B_2H_6/Ne = 1:1000$ and $B_2D_6/Ne = 1:1000$; each mixture was deposited concurrently from a separate inlet at an angle of angle 90° to one another, so that mixing occurred directly above the surface of the cold target at 4 K. The IR spectrum of thus-prepared $B_2H_6/Ne = 1:1000$ and $B_2D_6/Ne = 1:1000$ recorded before photolysis is shown in Figure 1c. On comparison within Figure 1, it is observed that curve c resembles closely a sum of curves a $(B_2H_6/Ne = 1:1000)$ and b $(B_2D_6/Ne = 1:1000)$; this result indicates that isotopic exchange was avoided in this mixed sample as a result of the separate co-deposition.

Figure 6 displays the partial infrared absorption difference spectrum of the co-deposited sample for $B_2H_6/Ne = 1:1000$ and $B_2D_6/Ne = 1:1000$ upon irradiation at 121.6 nm for 76 min at 4 K. Apart from the lines recorded for isotopic variants cyc-B₃H₃ and cyc-B₃D₃, as shown in Figures 2 and 3 and listed in Table 1, other new weak lines were detected in Figure 6. As mentioned above, fragments including H, B, BH, BH₂, and BH₃ are formed in the photochemical system of B₂H₆ and D, BD, BD₂, and BD₃ are formed from B₂D₆. In addition to products cyc-B₃H₃ and cyc-B₃D₃, other isotopic variants including cyc-B₃DH₂ and cyc-B₃D₂H might be generated after photochemical decomposition of mixtures of B₂H₆ and B₂D₆ dispersed in solid neon. To identify these species, we performed further quantumchemical calculations of the vibrational modes and their intensities for cyc-B₃DH₂ and cyc-B₃D₂H; the results are listed in Table 2. For these isomers, only one geometric structure exists for isomers cyc-11B3DH2, cyc-10B3DH2, cyc-11B3D2H, and cyc-¹⁰B₃D₂H, whereas two geometric structures are possible for



Figure 6. Partial infrared absorption difference spectrum of $B_2H_6/Ne = 1:1000$ and $B_2D_6/Ne = 1:1000$ co-deposited at 4 K after photolysis at 121.6 nm for 76 min (resolution 0.5 cm⁻¹ from 1000 co-added interferograms).

 $cyc^{-11}B_2^{-10}BDH_2$, $cyc^{-11}B^{10}B_2DH_2$, $cyc^{-11}B_2^{-10}BD_2H$, and $cyc^{-11}B^{10}B_2D_2H$, named structures a and b in Table 2. For diborane(6) in natural abundance, the proportions of products $cyc^{-10}B_3DH_2$ and $cyc^{-10}B_3D_2H$ are too small to be observed in these experiments.

According to the calculated results, the most intense mode, ν_2 , of $cyc^{-11}B_3DH_2$, $cyc^{-11}B_2^{10}BDH_2$ (a), and $cyc^{-11}B^{10}B_2DH_2$ (a) and mode ν_3 of $cyc^{-11}B_2^{10}BDH_2$ (b) and $cyc^{-11}B^{10}B_2DH_2$ (b) are located in our detection range 1165–1190 cm⁻¹, but absorption from the precursors strongly interfered with, and precluded, the detection of the lines in this region for these species. On the basis of our calculations, we identified other lines for modes ν_9 and ν_{11} of $cyc^{-11}B_3DH_2$, $cyc^{-11}B_2^{10}BDH_2$ (a), and $cyc^{-11}B^{10}B_2DH_2$ (a); of modes ν_3 , ν_9 , and ν_{10} of $cyc^{-11}B_3D_2H$, $cyc^{-11}B_2^{10}BD_2H$ (a), and $cyc^{-11}B^{10}B_2D_2H$ (a); and of modes ν_1 and ν_5 of $cyc^{-11}B_2^{10}BDH_2$ (b), $cyc^{-11}B^{10}B_2DH_2$ (b), $cyc^{-11}B_2^{10}BD_2H$ (b), and $^{11}B^{10}B_2D_2H$ (b), as listed in Table 2.

The calculated standard enthalpy of formation of cyclic B_3H_3 as depicted in Figure 4 is 1240.3 kJ mol⁻¹; in comparison, the calculated enthalpy of BH is 439.2 kJ mol⁻¹ and of linear B_2H_2 $(D_{\infty h})$ is 501.7 kJ mol⁻¹. The sum of the latter enthalpies, for species already identified in our spectra, is significantly less than that calculated for cyclic B_3H_3 , shown in Figure 4, but that difference has little meaning in the context of molecular fragments dispersed in solid neon at 4 K.

Other calculated stable structures according to formula B_3H_3 include a triangular B_3 moiety with one bridging H and two terminal H's at 487.4 kJ mol⁻¹, a linear B_3 moiety with two terminal H's at one end and one terminal H at the other at 614.5 kJ mol⁻¹, and a triangular B_3 moiety ($C_{2\nu}$) of which each B has an associated terminal H atom at 526.3 kJ mol⁻¹, but in no case is there a satisfactory match between calculated and experimental wavenumbers and relative intensities of infrared spectral lines. The Supporting Information presents figures displaying the calculated molecular structures and tables of the wavenumbers and intensities of the corresponding fundamental vibrational modes.

The nonlinear hydrogen bonds in this calculated structure have little precedent as bonds within a molecule, although intermolecular hydrogen bonds of this kind are known. For any molecule, the largest calculated wavenumbers for fundamental modes are generally associated with the stretching of strong chemical bonds; for B_3H_3 in Table 1, with magnitudes explicitly 1319.5 (ν_1, A_1') , 1473.2 (ν_3, A_2') , 1186.7 (ν_5, E') , and 1120.2 $(\nu_{6'} E')$ cm⁻¹, these wavenumbers are about half of those for the terminal B–H stretching modes, about 2600 cm^{-1} , and are much smaller than even those for the stretching modes of the bridging B-H-B bonds, about 1900 cm⁻¹, for B₂H₆. Two of those four wavenumbers, for modes ν_5 and ν_{6} , correspond to the assigned experimental spectral features and their counterparts for B₃D₃; the diagram of atomic displacements in Figure 5 indicates that these modes involve both bond stretching and angular deformation. The calculated distances for B-H (0.14 nm) and B-B (0.26 nm) are likewise much larger than the corresponding distances between adjacent atomic centers in other boron hydrides, such as B-H (0.13 nm) and B-B (0.16 nm) in diborane(6). These properties are consistent with the large enthalpy of formation of this remarkable species.

The crucial evidence for the existence and detection of such a bizarre species in its several isotopic variants is the undeniable match of calculated and experimental wavenumbers and relative intensities, which provides confidence in our identification. The differences between the calculated and experimental data are entirely comparable with those of B_2H_6 itself, for which the mean magnitude of deviation between the scaled harmonic and experimental wavenumbers for the gaseous state is about 17 cm⁻¹ (cf. Supporting Information).

3. EXPERIMENTAL SECTION

The apparatus for photochemical experiments on solid samples using FUV light from a synchrotron was described previously.^{16,17} The radiation for photolysis was selected from an undulator on beamline 21A2 attached to the 1.5 GeV synchrotron in Taiwan Light Source at the National

Table 2. Calculated Wavenumbers	(cm ⁻¹) and Intensities (km mol ⁻¹) (withi	n Parentheses) of Vibrational Modes and
Experimental Wavenumbers (cm ⁻¹) for cyc-B ₃ H ₂ D and cyc-B ₃ HD ₂ in Isotopi	c Variants

$C_{2\nu}$	cyc- ¹¹ B ₃ DH ₂		cyc- ¹⁰ B ₃ DH ₂		$cyc^{-10}B^{11}B_2DH_2(a)$		<i>cyc</i> - ¹⁰ B ₂ ¹¹ BDH ₂ (a)	
mode (sym.)	calcd (cm^{-1}) $(int.)^{a}$	exp.	calcd (cm^{-1}) $(int.)^{a}$	exp.	calcd (cm ⁻¹) (int.) ^a	exp.	calcd (cm ⁻¹) (int.) ^a	exp.
$\nu_1(A_1)$	1266.3 (0.9)		1268.0 (0.5)		1266.6 (1.4)		1267.6 (0.2)	
$\nu_2(A_1)$	1185.6 (671)		1188.3 (674)		1186.7 (673)		1187.2 (672)	
$\nu_3(A_1)$	860.7 (8.9)		868.8 (10.1)		860.8 (8.8)		868.8 (10.2)	
$\nu_4(A_1)$	437.9 (2.2)		456.5 (2.2)		449.5 (1.9)		448.5 (2.2)	
$\nu_5(A_1)$	417.4 (0.0)		437.0 (0.1)		420.1 (0.3)		430.8 (0.1)	
$\nu_6(A_2)$	191.3 (0.0)		191.8 (0.0)		191.3 (0.0)		191.8 (0.0)	
$\nu_7(B_1)$	292.5 (855)		293.8 (864)		293.1 (858)		293.2 (861)	
$\nu_8(B_1)$	151.4 (12.2)		152.1 (12.2)		151.5 (12.5)		151.9 (11.9)	
$\nu_9(B_2)$	1407.6 (120)	1391.5	1412.0 (119)		1409.8 (120)	1394.3	1409.9 (120)	1394.3
$\nu_{10}(B_2)$	1124.1 (3.8)		1130.4 (3.3)		1128.1 (4.1)		1126.4 (3.0)	
$\nu_{11}(B_2)$	899.4 (345)	884.2	903.1 (349)		899.5 (345)	884.2	903.1 (350)	887.3
$\nu_{12}(B_2)$	447.9 (2.4)		468.1 (2.5)		454.1 (2.6)		462.1 (2.4)	
$C_{2\nu}$	cyc- ¹¹ B ₃ D ₂ H		cyc- ¹⁰ B ₃ D ₂ H		$cyc-{}^{10}B{}^{11}B_2D_2H(a)$		$cyc^{-10}B_2^{-11}BD_2H(a)$	
mode (sym.)	calcd (cm^{-1}) $(int.)^{a}$	exp.	calcd (cm^{-1}) $(int.)^{a}$	exp.	calcd (cm^{-1}) $(int.)^a$	exp.	calcd (cm^{-1}) $(int.)^a$	exp.
$ u_1(A_1) $	1204.6 (2.0)		1207.7 (1.8)		1204.7 (1.9)		1207.6 (1.9)	
$\nu_2(A_1)$	894.3 (16.1)		900.9 (18.1)		894.5 (13.4)		900.7 (20.7)	
$\nu_3(A_1)$	852.8 (342)	841.9	855.6 (344)		855.0 (347)	845.4	853.4 (339)	841.9
$\nu_4(A_1)$	442.6 (1.9)		461.8 (1.8)		449.6 (1.7)		458.3 (1.8)	
$ u_5(A_1) $	416.5 (0.0)		435.9 (0.0)		423.0 (0.1)		426.1 (0.2)	
$\nu_6(A_2)$	139.0 (0.0)		139.8 (0.0)		139.0 (0.0)		139.8 (0.0)	
$\nu_7(B_1)$	267.9 (684)		269.3 (693)		268.2 (687)		269.1 (689)	
$\nu_8(B_1)$	166.0 (27.5)		166.8 (27.0)		166.8 (27.0)		166.0 (27.5)	
$\nu_9(B_2)$	1325.9 (265)	1312.3	1330.1 (264)		1326.3 (264)	1312.3	1329.7 (265)	1315.2
$\nu_{10}(B_2)$	959.8 (289)	947.4	964.7 (290)		963.2 (285)	952.4	961.4 (294)	948.3
$\nu_{11}(B_2)$	839.5 (19.3)		848.9 (23.3)		844.7 (24.5)		843.5 (18.1)	
$\nu_{12}(B_2)$	432.2 (1.9)		449.5 (1.9)		436.8 (2.0)		445.2 (1.8)	
Cs	$cyc^{-10}B^{11}B_2DH_2(b)$		$cyc^{-10}B_2^{-11}BDH_2(b)$		$cyc^{-10}B^{11}B_2D_2H(b)$		$cyc^{-10}B_2^{-11}BD_2H(b)$	
mode (sym.)	calcd (cm^{-1}) $(int.)^{a}$	exp.	calcd (cm^{-1}) $(int.)^{a}$	exp.	calcd (cm^{-1}) $(int.)^a$	exp.	calcd (cm^{-1}) $(int.)^{a}$	exp.
$ u_1(A') $	1410.4 (120)	1394.3	1411.5 (120)	1395.6	1327.4 (263)	1313.3	1327.8 (262)	1313.3
$\nu_2(A')$	1267.0 (1.0)		1267.7 (0.6)		1207.1 (2.2)		1207.2 (2.1)	
$ u_3(A')$	1187.5 (673)		1188.2 (674)		960.5 (292)	948.3	963.8 (289)	952.4
$ u_4(A')$	1126.6 (3.6)		1127.8 (3.3)		898.5 (18.5)		898.8 (15.9)	
$\nu_5(A')$	898.7 (345)	884.2	900.7 (346)	884.2	853.6 (340)	841.9	855.9 (345)	845.4
$\nu_6(A')$	862.2 (8.5)		866.0 (10.6)		840.2 (18.9)		845.5 (24.1)	
$ u_7(A') $	453.9 (2.5)		462.2 (2.4)		451.0 (1.8)		455.5 (1.8)	
$ u_8(A') $	449.4 (2.0)		452.6 (2.1)		439.6 (1.8)		445.1 (1.6)	
$ u_9(A') $	420.2 (0.3)		427.7 (0.3)		419.8 (0.2)		427.6 (0.3)	
$ u_{10}(A'') $	292.1 (860)		292.5 (863)		267.7 (689)		267.9 (692)	
$ u_{11}(A'')$	192.6 (0.0)		192.9 (0.0)		164.3 (26.8)		165.1 (26.3)	
$\nu_{12}(A'')$	150.1 (11.8)		150.3 (11.6)		140.3 (0.0)		140.3 (0.0)	

^{*a*}Vibrational wavenumbers are calculated with program Gaussian 09, the B3LYP method, and basis set aug-cc-pVTZ (B3LYP/ aug-cc-pVTZ); the calculated vibrational wavenumbers are scaled by 0.967; and the calculated intensities are in units of km mol⁻¹.

Synchrotron Radiation Research Center (NSRRC). This beamline provides pseudocontinuous FUV light with photon flux of ~ 10^{16} photons s⁻¹ (2% bandwidth); after absorption by Ar (pressure 1.33 kPa) and a filter, crystalline LiF for 121.6 nm, CaF₂ for 130, 140, and 155 nm, silica (Suprasil) for 165 and 175 nm, and quartz for 185, 190, and 200 nm, to suppress harmonics from the undulator, the selected FUV light delivers about ~ 10^{15} photons s⁻¹.

IR absorption spectra were recorded with an interferometric spectrometer (Bomem DA8) equipped with a KBr beamsplitter and a HgCdTe detector (cooled to 77 K) to span the spectral range $500-4000 \text{ cm}^{-1}$; spectra were typically recorded with 1000 scans and with a resolution of 0.5 cm⁻¹. Gaseous samples comprising diborane(6) in neon were deposited on a cold KBr

disc window; a closed-cycle refrigerator (Janis RDK-415) cooled the KBr substrate to ~4 K within an enclosure evacuated to <4 μ Pa. Before and after irradiation of the sample for cumulative periods from 2 to 6 h in a programmed sequence, we recorded IR spectra at each stage of the experiment. Difference spectra, that is, the absorbance curve after irradiation of a sample with FUV light for some period minus the absorbance curve before irradiation, emphasize the variation of the chemical composition resulting from photolysis.

Gaseous B_2H_6 or B_2D_6 (Voltaix, chemical purities B_2H_6 99.99% and B_2D_6 99.8%) was received as 10% in He and degassed at liquid nitrogen temperature before dilution in neon. Gaseous neon (Scott Specialty Gases, purity 99.999%) was used without purification.

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4. CONCLUSIONS

Irradiation of diborane(6) dispersed in solid neon at 4 K with FUV radiation selected from a synchrotron as a source yielded infrared absorption lines due to a new boron-hydride species that we assign, on the basis of quantum-chemical calculations of vibrational wavenumbers and intensities, to a carrier *cyc*-B₃H₃ (D_{3h}) that contains three bridging B–H–B bonds in a sixmembered ring. The cumulative spectral evidence for the existence of B₃H₃ in its several isotopic variants provides a strong basis for our assignment to this unprecedented species.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.6b00396.

Additional data related to this work (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: bmcheng@nsrrc.org.tw.

ORCID

Bing-Ming Cheng: 0000-0002-8540-6274

Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Eisch, J. J. Boron-carbon multiple bonds. *Adv. Organomet. Chem.* **1996**, *39*, 355–391.

(2) Braunschweig, H.; Kupfer, T. Recent developments in the chemistry of antiaromatic boroles. *Chem. Commun.* **2011**, 47, 10903–10914.

(3) Mesbah, W.; Präsang, C.; Hofmann, M.; Geiseler, G.; Massa, W.; Berndt, A. Dianions of tetraboranes(4): puckered aromatic fourmembered rings and their reactions with conservation of aromaticity. *Angew. Chem., Int. Ed.* **2003**, *42*, 1717–1719.

(4) Hofmann, M.; Berndt, A. $(\pi + \sigma)$ -double aromatic and π,σ -mixed aromatic boron compounds with two electrons delocalized over three centers. *Heteroat. Chem.* **2006**, *17*, 224–237.

(5) Kupfer, T.; Braunschweig, H.; Radacki, K. The triboracyclopropenyl dianion: the lightest possible main-group-element hückel π Aromatic. *Angew. Chem., Int. Ed.* **2015**, *54*, 15084–15088.

(6) Böhnke, J.; Braunschweig, H.; Constantinidis, P.; Dellermann, T.; Ewing, W. C.; Fischer, I.; Hammond, K.; Hupp, F.; Mies, J.; Schmitt, H. -C; Vargas, A. Experimental assessment of the strengths of B–B triple bonds. J. Am. Chem. Soc. **2015**, 137, 1766–1769.

(7) Longuet-Higgins, H. C. The structure of some electron-deficient molecules. J. Chem. Soc. 1946, 139–143.

(8) Longuet-Higgins, H. C.; Bell, R. P. The structure of the boron hydrides. J. Chem. Soc. 1943, 250-255.

(9) Eberhardt, W. H.; Crawford, B.; Lipscomb, W. N. The valence structure of the boron hydrides. J. Chem. Phys. 1954, 22, 989-1001.

(10) Lipscomb, W. N. Boron Hydrides; W. A. Benjamin. Inc.: New York, 1963.

(11) Chou, S.-L.; Lo, J.-I.; Peng, Y. C.; Lin, M.-Y.; Lu, H.-C.; Cheng, B.-M.; Ogilvie, J. F. Identification of diborane(4) with bridging B–H– B bonds. *Chem. Sci.* **2015**, *6*, 6872–6877.

(12) Lo, J.-I.; Chou, S.-L.; Peng, Y. C.; Lin, M.-Y.; Lu, H.-C.; Cheng, B.-M.; Ogilvie, J. F. Ultraviolet and infrared spectra of diboron in solid neon at 4 K. *ChemPhysChem* **2017**, *18*, 124–127.

(13) Peng, Y.-C.; Chou, S.-L.; Lo, J.-I.; Lin, M.-Y.; Lu, H.-C.; Cheng, B.-M.; Ogilvie, J. F. Infrared and ultraviolet spectra of diborane(6): B_2H_6 and B_2D_6 . J. Phys. Chem. A **2016**, 120, 5562–5572.

(14) Lin, M.-Y.; Lo, J.-I.; Chou, S.-L.; Peng, Y. C.; Lu, H.-C.; Cheng, B.-M.; Ogilvie, J. F. Vacuum-ultraviolet photolysis of methane at 3 K: synthesis of carbon clusters up to C_{20} . J. Phys. Chem. A **2014**, 118, 3438–3449.

(15) Maybury, P. C.; Koski, W. S. Kinetics of two exchange reactions involving diborane. J. Chem. Phys. **1953**, 21, 742–747.

(16) Chou, S.-L.; Lo, J.-I.; Lin, M.-Y.; Peng, Y. C.; Lu, H.-C.; Cheng, B.-M. Production of N_3 upon photolysis of solid nitrogen at 3 K with synchrotron radiation. *Angew. Chem., Int. Ed.* **2014**, *53*, 738–741.

(17) Lo, J.-I.; Chou, S.-L.; Peng, Y. C.; Lin, M.-Y.; Lu, H.-C.; Cheng, B.-M. Formation of N_3 , CH_3 , HCN, and HNC from the far-uv photolysis of CH_4 in nitrogen ice. *Astrophys. J., Suppl. Ser.* **2015**, 221, 20.