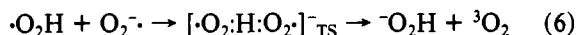


Further, this is consistent with the recent report that O_2^- forms an electron-pair donor complex with manganese(II) rather than a singlet reaction complex.³² In contrast, the high yields of singlet oxygen (based on photon counting) from the oxidation of O_2^- by $[FeCp_2]^+$, $[Mn(bpyO_2)_3]^{3+}$, and $[Mn(phen)_2O]_2^{4+}$ provide convincing evidence that a singlet transition state is favored in these redox reactions.



Such a conclusion is further supported by the singlet trapping experiments of Table II as well as by those of Mayeda and Bard.¹

The yield of singlet oxygen from the proton-induced dismutation of O_2^- is extremely low (see Tables I and II). This result is consistent with previously reported low yields of singlet oxygen from the proton-induced dismutation of O_2^- .^{33,34} One explanation which has been suggested^{35,36} for such low yields is that singlet oxygen is quenched by a rapid ($k = 1.6 \times 10^9 M^{-1} s^{-1}$) redox reaction with O_2^- . However, the conditions of the present experiments are such that this cannot account for the low singlet oxygen yield, especially in view of the high yield from the $[FeCp_2]^+ - O_2^-$ reaction for comparable concentrations of O_2^- . If the proton-induced dismutation of O_2^- occurs via a stepwise mechanism that involves a triplet transition state with electron transfer from O_2^- to $HO_2\cdot$ (eq 5 and 6), then ground-state triplet O_2 should be favored (see The-



oretical section). Because erythrocytic superoxide dismutase (SOD) catalyzes the dismutation of O_2^- to ground-state 3O_2 ,³⁷ the enzymic mechanism may also involve a triplet transition state. Alternatively, the oxidation of O_2^- by the oxidized form of SOD may involve a direct adiabatic electron transfer to give $O_2({}^3\Sigma_g^-)$, as predicted by the theoretical calculations.

Our experimental results indicate that oxidation of O_2^- by adiabatic electron transfer yields $O_2({}^3\Sigma_g^-)$ and that whether triplet or singlet state O_2 results from other oxidation and dismutation reactions of O_2^- is determined by the multiplicity of the transition state (triplet and singlet, respectively). The results of Table I and II support the conclusions that reactions of O_2^- with protons and $Fe(ClO_4)_3$ result in either triplet transition states or adiabatic electron transfer and that the $[FeCp_2]^+$, $[Mn(bpyO_2)_3]^{3+}$, and $[Mn(phen)_2O]_2^{4+}$ complexes oxidize O_2^- via a singlet transition state.

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Registry No. O_2^- , 11062-77-4; O_2 , 7782-44-7; $[Fe(Cp)_2]BF_4$, 1282-37-7; $[Mn(bpyO_2)_3](ClO_4)_3$, 75961-56-7; $[Mn(phen)_2O]_2(ClO_4)_4$, 62412-52-6; $Fe(ClO_4)_3$, 13537-24-1; $HClO_4$, 7601-90-3; $NaOCl$, 7681-52-9; H_2O_2 , 7722-84-1; $DTBQ^-$, 18802-82-9; $DPBF$, 5471-63-6; $HO_2\cdot$, 3170-83-0.

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Contribution from the Department of Chemistry,
Indiana University, Bloomington, Indiana 47401

Studies of Boranes. 47.¹ Synthesis and X-ray Crystallographic Study of Tetradecaborane(20)²

JOHN C. HUFFMAN, DAVID C. MOODY, and RILEY SCHAEFFER*

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Tetradecaborane(20) was obtained in low yield by the following synthetic route: $KB_6H_9 + B_8H_{12} \xrightarrow{Et_2O} [KB_4H_{12}] \xrightarrow{HCl} B_{14}H_{20} + H_2 + KCl$. The yellow thermochromic compound crystallizes in space group $P2_12_12_1$, with $a = 13.119$ (4), $b = 9.976$ (3), and $c = 8.963$ (3) Å (at $-164^\circ C$), with ρ (calcd) = $0.971 g/cm^3$ for $Z = 4$. The structure was solved by direct methods. Anisotropic least-squares refinement of boron positional parameters and isotropic refinement of hydrogen parameters yielded residuals of $R_1 = 0.047$ and $R_2 = 0.021$. The molecule consists of two B_8H_{12} -type fragments fused in a cis fashion and nearly possesses C_{2v} symmetry in the solid state.

Introduction

Relatively few neutral boron hydrides containing between 11 and 20 borons have been reported. Earlier studies in this area resulted in the synthesis of $n-B_{18}H_{22}$, $i-B_{18}H_{22}$, and $B_{20}H_{16}$.³ Heřmánek and co-workers later prepared $B_{16}H_{20}$ ⁴ and have reported its controlled hydrolysis to yield the first

14-boron-containing species, $B_{14}H_{18}$.⁵ More recently, however, work in this laboratory on the acid-base reactions of boron hydrides has led to a systematic method of preparation of both large and small boranes. In the range of B_{11} – B_{20} , three new hydrides have been obtained: $B_{13}H_{19}$,⁶ $B_{14}H_{22}$,⁷ and $B_{15}H_{23}$.⁸

In this paper we wish to report the planned synthesis and X-ray crystallographic study of a stable new B_{14} hydride, tetradecaborane(20), $B_{14}H_{20}$.² The synthesis takes advantage

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of the known Lewis acid character of B_8H_{12} and Lewis base character of the $B_6H_5^-$ anion.

Experimental Section

Material and Apparatus. Standard high-vacuum techniques were used throughout this investigation. The 70.6-MHz ^{11}B NMR spectra were recorded on a Varian Associates HR-220 spectrometer equipped with a "home-built" pulse apparatus. Mass spectra were recorded on a Varian Associates CH-7 mass spectrometer. All solvents used in this study were reagent grade and were dried prior to use. Hydrogen chloride was obtained from the Matheson Co. and purified by distillation through a trap at $-78^\circ C$.

Synthesis of $B_{14}H_{20}$. In a reaction vessel equipped with greaseless stopcocks, 0.4 mmol of KB_6H_5 was prepared by literature procedure.⁹ Excess B_8H_{12} (0.6 mmol)¹⁰ and 2 mL of diethyl ether were condensed into the vessel at $-196^\circ C$. The reaction solution was warmed to $-30^\circ C$; the cloudy ether solution yellowed slightly as stirring was continued for 15 min. More yellowing was observed as the solution was slowly warmed (15–20 min) to $0^\circ C$. The solution cleared briefly at approximately $-5^\circ C$ but became cloudy again at $0^\circ C$, and precipitate formed as the solution was stirred for 1 h. The volatiles were pumped from the vessel for 30 min at $0^\circ C$ and then for 15 min at room temperature; a yellow oil remained. Separation of the volatile components from the diethyl ether solvent was accomplished by fractionation into a $-78^\circ C$ trap. Mass spectral analysis of the material stopping in the $-78^\circ C$ trap indicated the presence of B_8H_{12} and diethyl ether (probably as $B_8H_{12} \cdot OEt_2$),¹¹ B_6H_{10} , $n-B_9H_{15}$, and $B_{10}H_{14}$. One milliliter of anhydrous liquid HCl was condensed on top of the yellow oily product material at $-196^\circ C$ and allowed to react for 30 min at $-78^\circ C$. When the reaction was quenched at $-196^\circ C$, only 0.10 mmol of H_2 was observed. The excess HCl was removed at $-78^\circ C$, and the material remaining in the reaction vessel, a yellow pasty solid, was allowed to warm to room temperature. The vessel was opened, and the volatile products were pumped through a $0^\circ C$ trap into one at $-196^\circ C$. After 5 h of continuous pumping, the $0^\circ C$ trap contained a white solid ($B_{16}H_{20}$) and a yellow semicrystalline solid ($B_{14}H_{20}$) embedded in a small amount of yellow oil. The material that passed the $0^\circ C$ trap and stopped at $-196^\circ C$ proved to be a mixture of $B_8H_{12} \cdot OEt_2$, B_6H_{10} , $n-B_9H_{15}$, and $B_{10}H_{14}$. These compounds were identified by mass spectra and ^{11}B NMR analysis. The boron-containing material not distilling from the reaction vessel at room temperature was dissolved in dichloromethane and filtered from the KCl also present. A ^{11}B NMR spectrum of this material indicated the presence of $B_{16}H_{20}$ and smaller amounts of $n-B_{18}H_{22}$ and $B_{14}H_{20}$.

The mixture of $B_{16}H_{20}$ and $B_{14}H_{20}$, which stopped in the $0^\circ C$ trap, was placed in an oven maintained at $32^\circ C$,¹² and larger crystals of $B_{14}H_{20}$ slowly formed over a period of several weeks. The yellow $B_{14}H_{20}$ was manually separated from the colorless $B_{16}H_{20}$ in the open air. The yield of $B_{14}H_{20}$ probably does not exceed 2%; however, accurate measurements of yield were hindered by the extremely small quantities of material obtained. Crystals of $B_{14}H_{20}$ appear to be moderately air stable; no noticeable decomposition is observed after several hours in the open air.

Mass spectral analysis of a yellow crystalline aggregate of $B_{14}H_{20}$ yielded a base peak at 162 amu and a parent peak at 174 amu for $^{11}B_{14}H_{20}$. A 70.6-MHz ^{11}B NMR spectrum in dichloromethane solvent consisted of five doublet resonances of approximate intensity 1:2:2:1:1 (ordered from low field to high field). The chemical shifts (relative to $BF_3 \cdot OEt_2$ at 0 ppm) and coupling constants (J_{BH} , ± 10 Hz) (in parentheses) are as follows: +34.6 (150), +8.8 (160), +6.0 (160), -10.6 (150), -36.1 (160).

A similar reaction of B_8H_{12} and $(n-C_4H_9)_4NB_6H_9$ ¹³ was carried out in dichloromethane solvent at $-23^\circ C$. However, acidification of the product material failed to yield $B_{14}H_{20}$. Among the products characterized were B_6H_{10} , B_8H_{12} , $n-B_9H_{15}$, $B_{10}H_{14}$, $B_{16}H_{20}$, and $n-B_{18}H_{22}$.

Crystallography. Crystal Data. A well-formed, nearly equidimensional, single crystal of approximately 0.7 mm maximum length

was used in the crystallographic study.¹⁴ Precession photographs and a diffractometer search of the reciprocal lattice *mmm* Laue symmetry with conditions for nonextinction of $h = 2n$ for $h00$, $k = 2n$ for $0k0$, and $l = 2n$ for $00l$, consistent with space group $P2_12_12_1$ (No. 19, D_2^4). The crystal was held in a dry, cooled nitrogen stream throughout both preliminary studies and data collection. A least-squares fit of angular data from 16 reflections centered in $\pm 2\theta$ yielded cell parameters of $a = 13.119$ (4), $b = 9.976$ (3), and $c = 8.963$ (3) Å (at $-164^\circ C$), with $\rho(\text{calcd}) = 0.971$ g/cm³ for $Z = 4$. The compound is reversibly thermochromic; the yellow crystals become colorless upon cooling although there is no indication of a phase transition.

Intensity Data Collection. Data were collected by using a Picker FACS-1 diffractometer. Molybdenum $K\alpha$ radiation ($\lambda = 0.71069$ Å) and a highly oriented graphite monochromator (002 plane, $2\theta_m = 12.06^\circ$) were utilized with a continuous ($1^\circ/\text{min}$) $\theta-2\theta$ scan over a range of 2° (plus dispersion) and 20-s backgrounds at each extreme of the scan. Other diffractometer constants and data reduction formulae are given elsewhere.¹⁵ An ignorance factor of 0.05 was employed, based on prior experience. Examination of ω and 2θ scans revealed no abnormalities and indicated a crystal of suitable mosaic character. Three nearly orthogonal reflections were chosen as standards and monitored every 50 measurements. No systematic changes in intensities of the standards were observed. A total of 2114 reflections, including redundancies, were collected in the region of $1^\circ \geq 2\theta \geq 45^\circ$ and reduced to 933 unique intensities of which 487 had $I \geq 2.33\sigma(I)$. All data were utilized in the solution and refinement of the structure. No absorption corrections were necessary ($\mu = 0.38$ cm⁻¹). Preliminary scale and thermal parameters were determined by Wilson's method.¹⁶

Solution and Refinement of the Structure. Direct methods were used to assign phases to the 181 largest normalized structure factors, E_{hkl} , and an *E* map phased on these values located all boron atoms in the structure. Isotropic least-squares refinement followed by a difference Fourier synthesis was used to locate all hydrogen atoms.¹⁷ Full-matrix least squares were utilized to refine all positional parameters, anisotropic boron thermal parameters, isotropic hydrogen parameters, and an overall scale factor and isotropic extinction parameter. The function minimized was $\sum w(|F_o| - |F_c|)^2$ where $w = (4I/(\sigma(I))^2)$. A total of 913 reflections were nonzero and thus had nonzero weight in the refinement. The ratio of observations to parameters was thus 4.4:1. The final cycle yielded a goodness of fit of 0.44, indicating the errors had been overestimated. The largest Δ/σ for this cycle was 0.045. The isotropic extinction parameter refined to $3.7(2) \times 10^{-6}$, giving a maximum extinction of 9.6% for the 011 reflection. The final residuals were $R_1 = 0.047$ and $R_2 = 0.021$ where $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2]^{1/2}$. Errors in bond distances and angles were determined from the variance-covariance matrix.

A final list of observed and calculated structure factors are given in Table VII (see paragraph at end of paper regarding supplementary material).

Results and Discussion

Synthesis. Recent studies in our laboratory had established that hexaborane(10), with its two-electron boron-boron bond, could act as a moderately strong Lewis base toward a variety of Lewis acids.¹⁸ The reaction of B_6H_{10} with B_8H_{12} , however, had not yielded a stable B_{14} hydride but only resulted in the synthesis of what is best described as a 1:1 adduct, $B_6H_{10} \cdot B_8H_{12}$ ($B_{14}H_{22}$).⁷ Removal of a bridge hydrogen from B_6H_{10} increases its Lewis basicity as observed by Shore.¹⁹ Thus, as an alternate route to a B_{14} hydride, hexaborate(1-) anion might react with B_8H_{12} to form a stable B_{14} anion.

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(10) Jerry Dobson and Riley Schaeffer, *Inorg. Chem.*, **7**, 402 (1968).

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(12) A similar sample placed in an oven at $45^\circ C$ led only to decomposition of the $B_{14}H_{20}$, and no crystals were obtained.

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(17) All computations were performed on a CDC6600 computer. Programs used in the solution and refinement of the structure include Woolfson's MULTAN, least squares, Fourier synthesis, and error analysis programs by A. C. Larson, and Johnson's ORTEP.

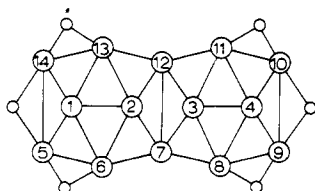
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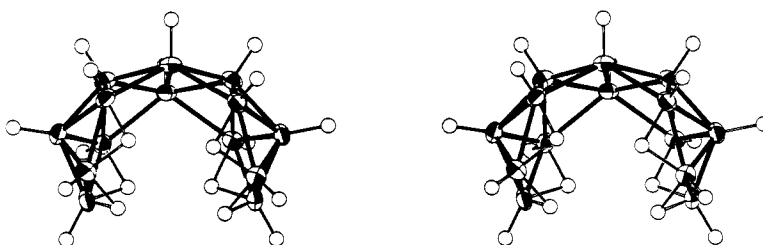
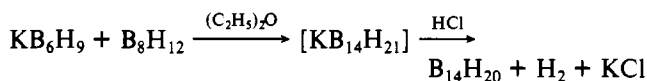
Table I. Positional and Isotropic Thermal Parameters

	x/a	y/b	z/c	$B, \text{\AA}^2$
B(1)	0.3790 (3) ^a	0.4116 (3)	0.2311 (3)	<i>b</i>
B(2)	0.4448 (2)	0.4092 (3)	0.0596 (4)	<i>b</i>
B(3)	0.4418 (2)	0.2118 (4)	-0.1852 (4)	<i>b</i>
B(4)	0.3698 (2)	0.0633 (3)	-0.2055 (4)	<i>b</i>
B(5)	0.3663 (3)	0.2520 (3)	0.3026 (4)	<i>b</i>
B(6)	0.4777 (3)	0.2882 (3)	0.1923 (4)	<i>b</i>
B(7)	0.4999 (2)	0.2648 (3)	-0.0193 (4)	<i>b</i>
B(8)	0.4656 (2)	0.0813 (3)	-0.0598 (4)	<i>b</i>
B(9)	0.3468 (3)	-0.0074 (3)	-0.0321 (4)	<i>b</i>
B(10)	0.2506 (3)	0.0819 (4)	-0.1263 (4)	<i>b</i>
B(11)	0.3091 (2)	0.2284 (3)	-0.2076 (4)	<i>b</i>
B(12)	0.3919 (2)	0.3628 (3)	-0.1127 (3)	<i>b</i>
B(13)	0.3109 (2)	0.4216 (3)	0.0543 (4)	<i>b</i>
B(14)	0.2627 (3)	0.3302 (3)	0.2141 (4)	<i>b</i>
H(1)	0.3872 (14)	0.4945 (18)	0.3052 (20)	0.35 (45)
H(2)	0.4888 (15)	0.4969 (19)	0.0502 (25)	1.07 (50)
H(3)	0.4866 (15)	0.2244 (21)	-0.2831 (21)	0.98 (49)
H(4)	0.3804 (15)	0.0024 (19)	-0.3091 (22)	0.95 (45)
H(5)	0.3702 (16)	0.2153 (18)	0.4201 (21)	1.68 (45)
H(6)	0.5508 (16)	0.2843 (21)	0.2519 (20)	1.24 (50)
H(7)	0.5806 (12)	0.2844 (18)	-0.0413 (20)	0.61 (44)
H(8)	0.5355 (17)	0.0119 (19)	-0.0555 (26)	2.03 (52)
H(9)	0.3393 (15)	-0.1123 (20)	-0.0012 (21)	1.96 (52)
H(10)	0.1753 (13)	0.0377 (18)	-0.1583 (20)	0.36 (46)
H(11)	0.2678 (15)	0.2706 (20)	-0.3089 (22)	1.51 (48)
H(12)	0.4038 (14)	0.4441 (20)	-0.1946 (22)	0.87 (47)
H(13)	0.2626 (18)	0.5113 (20)	0.0260 (22)	1.63 (50)
H(14)	0.1890 (16)	0.3507 (20)	0.2658 (21)	1.22 (50)
H(10-11)	0.2465 (17)	0.2079 (24)	-0.1064 (25)	3.18 (62)
H(9-10)	0.2648 (20)	0.0546 (23)	0.0141 (25)	3.32 (63)
H(8-9)	0.4093 (15)	0.0599 (22)	0.0506 (26)	2.28 (55)
H(5-6)	0.4296 (17)	0.1849 (24)	0.2227 (26)	2.39 (59)
H(5-14)	0.2884 (19)	0.2054 (25)	0.2385 (25)	3.08 (63)
H(13-14)	0.2573 (17)	0.3211 (22)	0.0749 (26)	2.67 (57)

^a Figures in parentheses throughout this paper refer to error in least significant digit. ^b Refined anisotropically.

Figure 1. Connectivity diagram with numbering system for B₁₄H₂₀.

The reaction of B₈H₁₂ with (*n*-C₄H₉)₄NB₆H₉ in dichloromethane solvent, however, failed to yield a B₁₄ species. The products obtained suggested that appreciable decomposition of the starting materials had occurred even though the reaction was run at -23 °C. The stabilization of B₈H₁₂ by the formation of a weak adduct with diethyl ether had been previously established.¹⁰ If B₆H₉⁻ proved to be a strong enough base to displace the ether, then perhaps a stable B₁₄ anion could be formed without B₈H₁₂ decomposition. The reaction scheme utilized is

Figure 2. Stereoscopic view of B₁₄H₂₀. The hydrogens have been given artificial *B*'s of 1.0 Å², and thermal ellipsoids for borons are drawn at the 50% probability level.Table II. Anisotropic^a Thermal Parameters (×10³) for Borons

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
B(1)	49 (3)	45 (4)	47 (4)	-5 (4)	-4 (4)	-12 (4)
B(2)	37 (3)	47 (4)	58 (4)	-5 (4)	-2 (4)	2 (4)
B(3)	31 (3)	66 (4)	42 (4)	7 (4)	4 (4)	-3 (4)
B(4)	44 (3)	52 (3)	40 (3)	8 (4)	-1 (4)	-14 (4)
B(5)	56 (3)	63 (4)	44 (3)	-7 (4)	8 (4)	-5 (4)
B(6)	45 (3)	50 (4)	49 (4)	-15 (4)	-8 (4)	-5 (4)
B(7)	35 (3)	53 (4)	46 (4)	-7 (4)	2 (3)	9 (4)
B(8)	47 (3)	52 (4)	40 (4)	3 (4)	7 (4)	-5 (4)
B(9)	61 (3)	54 (4)	54 (4)	-9 (4)	6 (4)	-7 (4)
B(10)	56 (3)	51 (4)	49 (4)	-3 (4)	1 (4)	-21 (4)
B(11)	42 (3)	51 (4)	42 (4)	3 (4)	2 (3)	4 (4)
B(12)	33 (3)	43 (3)	50 (3)	-3 (4)	6 (3)	3 (4)
B(13)	45 (3)	36 (4)	50 (4)	-1 (4)	-1 (4)	-9 (4)
B(14)	58 (3)	50 (4)	42 (4)	8 (4)	5 (4)	-17 (4)

^a Anisotropic thermal parameters are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$.

Table III. Bonded Distances (Å)

B(1)-B(2)	1.763 (4)	B(13)-B(14)	1.812 (5)
B(1)-B(5)	1.724 (4)	B(1)-H(1)	1.07 (2)
B(1)-B(6)	1.820 (5)	B(2)-H(2)	1.05 (2)
B(1)-B(13)	1.822 (5)	B(3)-H(3)	1.06 (2)
B(1)-B(14)	1.736 (5)	B(4)-H(4)	1.12 (2)
B(2)-B(6)	1.749 (5)	B(5)-H(5)	1.12 (2)
B(2)-B(7)	1.760 (4)	B(6)-H(6)	1.10 (2)
B(2)-B(12)	1.755 (5)	B(7)-H(7)	1.10 (2)
B(2)-B(13)	1.761 (4)	B(8)-H(8)	1.15 (2)
B(3)-B(4)	1.766 (5)	B(9)-H(9)	1.09 (2)
B(3)-B(7)	1.753 (4)	B(10)-H(10)	1.12 (2)
B(3)-B(8)	1.748 (4)	B(11)-H(11)	1.14 (2)
B(3)-B(11)	1.760 (4)	B(12)-H(12)	1.10 (2)
B(3)-B(12)	1.767 (4)	B(13)-H(13)	1.13 (2)
B(4)-B(8)	1.822 (4)	B(14)-H(14)	1.09 (2)
B(4)-B(9)	1.733 (4)	B(5)-H(5-6)	1.29 (2)
B(4)-B(10)	1.727 (5)	B(5)-B(5-14)	1.26 (2)
B(4)-B(11)	1.829 (4)	B(6)-H(5-6)	1.24 (2)
B(5)-B(6)	1.802 (5)	B(8)-H(8-9)	1.25 (2)
B(5)-B(14)	1.756 (5)	B(9)-H(9-10)	1.31 (3)
B(6)-B(7)	1.933 (4)	B(9)-H(8-9)	1.29 (2)
B(7)-B(8)	1.919 (5)	B(10)-H(10-11)	1.27 (2)
B(7)-B(12)	1.914 (4)	B(10)-H(9-10)	1.30 (2)
B(8)-B(9)	1.809 (5)	B(11)-H(10-11)	1.24 (2)
B(9)-B(10)	1.760 (5)	B(13)-H(13-14)	1.24 (2)
B(10)-B(11)	1.804 (5)	B(14)-H(5-14)	1.31 (2)
B(11)-B(12)	1.924 (5)	B(14)-H(13-14)	1.25 (2)
B(12)-B(13)	1.927 (4)		

We were not able to isolate the B₁₄ anion since large amounts of other products were also present; however, acidification of this impure material did generate the new boron hydride B₁₄H₂₀ in low yield.

Since only extremely small quantities of the pure material were obtained, the reaction chemistry of B₁₄H₂₀ was not pursued and structural studies were limited to mass spectra analysis, ¹¹B NMR, and X-ray crystallography. A discussion of the crystallographic results, along with the relationship of the solid-state structure to that suggested by the ¹¹B NMR

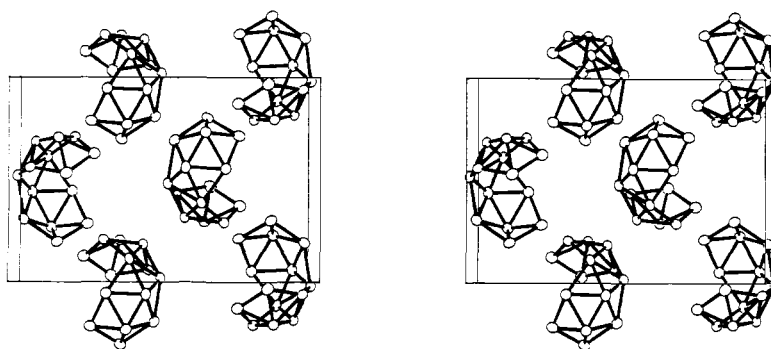


Figure 3. Stereoscopic view of the molecular packing of $B_{14}H_{20}$, viewed down the b axis. Hydrogens have been omitted for clarity.

Table IV. Bonded Angles (Deg) Involving Only Borons

B(2)-B(1)-B(5)	111.0 (2)	B(5)-B(6)-B(7)	129.5 (2)
B(2)-B(1)-B(6)	58.4 (2)	B(2)-B(7)-B(3)	114.2 (2)
B(2)-B(1)-B(13)	58.8 (2)	B(2)-B(7)-B(6)	56.3 (2)
B(2)-B(1)-B(14)	110.3 (2)	B(2)-B(7)-B(8)	139.5 (2)
B(5)-B(1)-B(6)	61.0 (2)	B(2)-B(7)-B(12)	56.9 (2)
B(5)-B(1)-B(13)	109.0 (2)	B(3)-B(7)-B(6)	143.5 (2)
B(5)-B(1)-B(14)	61.0 (2)	B(3)-B(7)-B(8)	56.6 (2)
B(6)-B(1)-B(13)	102.7 (2)	B(3)-B(7)-B(12)	57.4 (2)
B(6)-B(1)-B(14)	107.0 (2)	B(6)-B(7)-B(8)	105.4 (2)
B(13)-B(1)-B(14)	61.2 (2)	B(6)-B(7)-B(12)	104.8 (2)
B(1)-B(2)-B(6)	62.4 (2)	B(8)-B(7)-B(12)	103.4 (2)
B(1)-B(2)-B(7)	124.2 (3)	B(3)-B(8)-B(4)	59.3 (2)
B(1)-B(2)-B(12)	125.3 (2)	B(3)-B(8)-B(7)	56.9 (2)
B(1)-B(2)-B(13)	62.3 (2)	B(3)-B(8)-B(9)	107.3 (2)
B(6)-B(2)-B(7)	66.8 (2)	B(4)-B(8)-B(7)	113.0 (2)
B(6)-B(2)-B(12)	121.0 (3)	B(4)-B(8)-B(9)	57.0 (2)
B(6)-B(2)-B(13)	108.2 (3)	B(7)-B(8)-B(9)	129.9 (2)
B(7)-B(2)-B(12)	66.0 (2)	B(4)-B(9)-B(8)	61.9 (2)
B(7)-B(2)-B(13)	117.1 (2)	B(4)-B(9)-B(10)	59.3 (2)
B(12)-B(2)-B(13)	66.4 (2)	B(8)-B(9)-B(10)	107.7 (2)
B(4)-B(3)-B(7)	125.0 (3)	B(4)-B(10)-B(9)	59.6 (2)
B(4)-B(3)-B(8)	62.5 (2)	B(4)-B(10)-B(11)	62.3 (2)
B(4)-B(3)-B(11)	62.5 (2)	B(9)-B(10)-B(11)	107.4 (2)
B(4)-B(3)-B(12)	123.7 (2)	B(3)-B(11)-B(4)	58.9 (2)
B(7)-B(3)-B(8)	66.5 (2)	B(3)-B(11)-B(10)	107.4 (3)
B(7)-B(3)-B(11)	119.9 (3)	B(3)-B(11)-B(12)	57.1 (2)
B(7)-B(3)-B(12)	65.9 (2)	B(4)-B(11)-B(10)	56.8 (2)
B(8)-B(3)-B(11)	108.7 (3)	B(4)-B(11)-B(12)	112.2 (2)
B(8)-B(3)-B(12)	117.7 (2)	B(10)-B(11)-B(12)	128.8 (2)
B(11)-B(3)-B(12)	66.1 (2)	B(2)-B(12)-B(3)	113.7 (2)
B(3)-B(4)-B(8)	58.3 (2)	B(2)-B(12)-B(7)	57.1 (2)
B(3)-B(4)-B(9)	110.0 (2)	B(2)-B(12)-B(11)	142.7 (2)
B(3)-B(4)-B(10)	110.6 (2)	B(2)-B(12)-B(13)	56.9 (2)
B(3)-B(4)-B(11)	58.6 (2)	B(3)-B(12)-B(7)	56.7 (2)
B(8)-B(4)-B(9)	61.1 (2)	B(3)-B(12)-B(11)	56.8 (2)
B(8)-B(4)-B(10)	108.6 (2)	B(3)-B(12)-B(13)	138.5 (2)
B(8)-B(4)-B(11)	102.6 (2)	B(7)-B(12)-B(11)	104.8 (2)
B(9)-B(4)-B(10)	61.1 (2)	B(7)-B(12)-B(13)	102.9 (2)
B(9)-B(4)-B(11)	107.4 (2)	B(11)-B(12)-B(13)	104.1 (2)
B(10)-B(4)-B(11)	60.9 (2)	B(1)-B(13)-B(2)	58.9 (2)
B(1)-B(5)-B(6)	62.1 (2)	B(1)-B(13)-B(12)	112.9 (2)
B(1)-B(5)-B(14)	59.8 (2)	B(1)-B(13)-B(14)	57.1 (2)
B(6)-B(5)-B(14)	106.9 (2)	B(2)-B(13)-B(12)	56.6 (2)
B(1)-B(6)-B(2)	59.2 (2)	B(2)-B(13)-B(14)	107.0 (3)
B(1)-B(6)-B(5)	56.9 (2)	B(12)-B(13)-B(14)	130.8 (2)
B(1)-B(6)-B(7)	112.1 (2)	B(1)-B(14)-B(5)	59.2 (2)
B(2)-B(6)-B(5)	108.1 (2)	B(1)-B(14)-B(13)	61.8 (2)
B(2)-B(6)-B(7)	56.8 (2)	B(5)-B(14)-B(13)	108.1 (2)

spectrum, is contained in the following section.

Description of the Structure. Tetradecaborane(20) is a conjuncto borane which can be described as two octaborane(12) molecules sharing two borons. A connectivity diagram showing the numbering scheme utilized is given in Figure 1, and a stereoscopic view of the molecule is shown in Figure 2. The unit cell packing viewed down the β axis is shown in Figure 3. Final positional and thermal parameters are listed in Tables I and II, and important distances and angles are given in Table III-V. A more extensive table of angles in-

Table V

A. Intramolecular Nonbonded H-H Distances (Å)			
H(5-6)-H(5-14)	1.87 ^a	H(14)-H(13-14)	1.95
H(6)-H(5-6)	1.89	H(5)-H(5-14)	1.95
H(10-11)-H(9-10)	1.89	H(5)-H(5-6)	1.96
H(5-14)-H(13-14)	1.91	H(14)-H(5-14)	1.97
H(9-10)-H(8-9)	1.92	H(8)-H(8-9)	1.97
H(9)-H(9-10)	1.94	H(10-11)-H(13-14)	1.98
H(11)-H(10-11)	1.94	H(10)-H(10-11)	1.99
H(10)-H(9-10)	1.95	H(9)-H(8-9)	2.00
H(13)-H(13-14)	1.95	H(8-9)-H(5-6)	2.00
B. Intermolecular Nonbonded H-H Distances (Å)			
H(12)-H(14)	2.41 ^a	H(7)-H(13-14)	2.56
H(1)-H(8)	2.47	H(4)-H(7)	2.61
H(8)-H(12)	2.47	H(10)-H(5-14)	2.64
H(4)-H(9-10)	2.54	H(2)-H(10)	2.65
H(6)-H(10)	2.55	H(11)-H(13)	2.66
H(7)-H(10-11)	2.55	H(5)-H(10)	2.69

^a The errors for the distances reported in this table only are ± 3 in least significant digit.

volving hydrogens (Table VI) is available (see paragraph at end of paper regarding supplementary data). All hydrogen positions were refined isotropically and were considered well determined on the basis of thermal parameters, estimated errors from the variance-covariance matrix, and the consistency of B-H_i bonded and H-H nonbonded distances.¹⁹

Several structural features are unique to this molecule. Most noteworthy is that the present molecule is the first conjuncto borane to occur in a cis configuration. All other structurally characterized "fused-fragment" boranes ($B_{13}H_{19}$, $B_{16}H_{20}$, n - $B_{18}H_{22}$, and i - $B_{18}H_{22}$)^{6,20-22} occur with the open faces in a trans configuration.

Boron-boron distances and angles for the two B_8 fragments, other than those involved in the juncture of the two cages (i.e., B(7) and B(12)), agree favorably with those of B_8H_{12} or the corresponding fragment in n - B_9H_{15} .²³ All hydrogen bridges are symmetrical, within the accuracy of the data. One feature of special interest is the geometry of the borons around the juncture. The B(3)-B(7)-B(12):B(2)-B(7)-B(12) interplanar angle of $176^\circ 58'$ is the most nearly planar angle yet observed in a borane. This can be compared to an interplanar angle of $138^\circ 11'$ for an ideal icosahedron. The nearly planar angle is easily explained on the basis of nonbonded intramolecular contacts. As shown in Table V, the H(10-11)-H(13-14) and N(5-6)-H(8-9) distances of 1.98 and 2.00 Å force the cage to "open".

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(23) In a private communication, W. N. Lipscomb has indicated that the localized molecular orbitals for $B_{14}H_{20}$ indeed resemble those of n - B_9H_{15} .

Table VIII

$\rho, e/\text{\AA}^3$	x/a	y/b	z/c	relative location
0.141	0.444	0.344	-0.037	B(2)-B(7)-B(12)
0.130	0.349	0.373	-0.039	B(2)-B(12)-B(13)
0.127	0.391	0.272	-0.167	B(3)-B(11)-B(12)
0.121	0.476	0.310	0.069	B(2)-B(6)-B(7)
0.119	0.432	0.359	0.156	B(1)-B(2)-B(6)
0.117	0.977	0.187	-0.070	<i>a</i>
0.116	0.323	0.403	0.160	B(1)-B(13)-B(14)
0.113	0.502	0.290	-0.271	B(3) ^b
0.112	0.369	0.293	-0.142	B(3)-B(11)-B(12)
0.104	0.514	0.029	-0.106	B(8) ^b
0.100	0.402	0.399	0.100	B(1)-B(2)-B(13)

^a More than 2 Å from any boron atom. ^b Not located in B-B-B face, but close (within 1.5 Å) to designated B.

The resultant strain on the bonding environment around B(7) and B(12) accounts for not only the planarity of the junction but also the rather long B-B distances involving these borons. One might expect this juncture to be a reactive site for the molecule, but the paucity of sample precluded reaction studies. The molecule nearly possesses C_{2v} symmetry in the solid state; however, nonbonded constraints cause significant deviations such that the actual molecular symmetry observed is only C_2 . The significance of nonbonded interactions on the structures of boranes is discussed more fully elsewhere.²⁴ The

(24) (a) John C. Huffman, Ph.D. Thesis, Indiana University, 1974; (b) John C. Huffman, manuscript in preparation.

observance of only five resonances in the room-temperature ¹¹B NMR spectra of B₁₄H₂₀ is consistent with a molecule of approximate C_{2v} symmetry.

A final difference Fourier synthesis revealed the 11 peaks over 0.1 e/Å³ which are listed in Table VIII. It is to be noted that, for all peaks above 0.1 e/Å³, only one is not associated with the boron cage, and most lie in B-B-B triangles, suggestive of residual electron density from three-center bonding. Similar peaks have been observed in other borane structures,²⁵ and X-N (X-ray-neutron) difference maps have shown similar features for decaborane(14).²⁶

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Registry No. B₁₄H₂₀, 55823-36-4; KB₆H₉, 12447-66-4; B₈H₁₂, 19469-16-0.

Supplementary Material Available: Table VI, a listing of angles involving hydrogen atoms, and Table VII, listing of structure factor amplitudes (12 pages). Ordering information is given on any current masthead page.

- (25) (a) J. C. Huffman, L. G. Sneddon, and R. Schaffer, *J. Chem. Soc., Chem. Commun.*, **8**, 474-475 (1972) (B₁₀H₁₃⁺); (b) M. R. Churchill and B. G. Deboer, *Inorg. Chem.*, **12**, 2674 (1973).
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Contribution from the Department of Chemistry, Indiana University, Bloomington, Indiana 47401

Studies of Boranes. 48.¹ Reactions of Hexaborane(10) with Lewis Acids to Yield Acid-Base Complexes and Synthesis of Halogenated Hexaborane(10) Derivatives via Halogen-Transfer Reactions²

PATRICK J. DOLAN, DAVID C. MOODY, and RILEY SCHAEFFER*

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Hexaborane(10) has been shown to complex with a variety of Lewis acids including BCl₃, B₂Cl₄, BBr₃, BI₃, Al(CH₃)₃, Al(C₂H₅)₃, and Al(*i*-C₄H₉)₃ and remains uncomplexed in the presence of (CH₃)₃B, (C₂H₅)₃B, and BF₃. The BBr₃ and BI₃ complexes undergo halogen exchange with B₆H₁₀ and its derivatives to form BrB₆H₉, IB₆H₉, I₂B₆H₈, and other halogenated species. The reaction of excess B₆H₁₀ with BI₃ has also been found to produce B₁₃H₁₉ in up to 40% yields. Chlorine gas reacts with KB₆H₉ to form ClB₆H₉.

Introduction

The pyrolysis of diborane has traditionally been the method of synthesis of various boranes. One of the unusual features of this reaction is the fact that hydrides containing six to nine boron atoms are almost entirely missing among the pyrolysis products. The Bronsted basicity of hexaborane(10) suggested by Lipscomb and the general Lewis basicity implied by work of Davison and of Shore may play a role in the pyrolysis reaction.³ Recent investigations in this laboratory provide some support for this suggestion in that it has been shown that

hexaborane(10) can be used for the synthesis of *n*-B₉H₁₅ and the preparation of the new hydrides B₁₄H₂₂ and B₁₅H₂₃, although at much lower temperature than used in diborane pyrolysis.⁴ Furthermore, the basicity of hexaborane(10) is important in the formation of B₁₃H₁₉.⁵ The present study was undertaken to explore more fully the characteristics of hexaborane(10) as a Lewis base. Several hexaborane derivatives were made and reacted with a range of Lewis acids to accomplish this task.

Experimental Section

Apparatus and Materials. Standard high-vacuum techniques were used throughout this investigation. Mass spectra were measured on an AEI MS-9 mass spectrometer at 70 eV, and ¹¹B nuclear magnetic resonance spectra were recorded on a Varian Associates HR-220

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