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Studies of Boranes. XLVI.[1] Nuclear Magnetic Resonance Studies of Octaborane(14) and Isononaborane(15)

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The low-temperature ^1H and line-narrowed ^{11}B NMR spectra of B_8H_{14} and i-B_9H_{15} have been obtained. The data obtained from these spectra suggest that B_8H_{14} contains four "unique terminals" and two bridging hydrogens around the open face of the B_8 cage, while i-B_9H_{15} has six asymmetric bridging hydrogens around the open face of a B_9 cage of C_{3v} symmetry. Attempts at growing crystals of B_8H_{14} proved futile, as the compound glasses near its melting point.

Introduction

Of the isolated neutral boranes containing less than ten borons, the structures of only three have not been confirmed by X-ray crystallography: hexaborane(12), octaborane(14), and isononaborane(15). Crystallographic structural data for B_6H_{12} have not been forthcoming due to the tendency of the compound to form a glass near its melting point. A similar phenomenon has also been observed for B_8H_{14}, while i-B_9H_{15} decomposes before melting. A recent ^{11}B NMR study utilizing the exponential line-narrowing technique has, however, established the 4212 topological formulation as the most likely structure for B_6H_{12}.[2] The success of this technique in the ^{11}B NMR studies of B_6H_{12} and other boron hydrides has suggested its application to the extremely unstable hydrides B_8H_{14} and i-B_9H_{15}. The structures of these compounds have been uncertain since early ^{11}B NMR studies suggested that they both contain six bridging hydrogens.[3-5] These proposed structures fail to reconcile the expected nonbonded H–H interactions associated with placing six bridging hydrogens around the open face of a B_8 or B_9 cage.

In this work we report the high-field ^1H and ^{11}B NMR studies of B_8H_{14} and i-B_9H_{15} and the structural implications that are suggested.

Experimental Section

Apparatus and Materials. Standard high-vacuum techniques were used throughout this investigation. All solvents were reagent grade and dried prior to use. Methylene-d_2 chloride (99.5% D) was obtained from Stohler Isotope Chemicals. The 70.6-MHz ^{11}B NMR spectra were recorded at −45° on a Varian Associates HR-220 spectrometer equipped with a "home-built" pulse apparatus. On each of the compounds studied 4K scans were collected with a pulse rate of 0.11 sec. Line-narrowing was performed in the manner previously described[2] using standard Nicolet software and a Nicolet 1080 computer. Continuous-wave ^1H NMR spectra at −45° were recorded at 220 MHz on the same spectrometer. Pulsed ^1H NMR spectra at temperatures lower than −45° were recorded at 100 MHz on a Varian Associates XL-100-15 spectrometer.

Octaborane(14) was prepared by the method of Dobson and Schaeffer;[3] however, the reaction vessel shown in Figure 1 was used instead of the one described in the original report of the synthesis. Stopcocks A, B, and C are 10-mm greaseless stopcocks, and the greaseless joints depicted are Fischer-Porter Solvent Seals. The solid salt from the reaction of B_8H_{12} with NaH was prepared and converted to the tetramethylammonium salt in the same manner as reported by Dobson and Schaeffer[3] except that only 3–4-mmol scale was used here. The salt was loaded in the air into the tube located directly under stopcock A. The vessel was attached to the vacuum line and evacuated through A. Anhydrous HCl (1 ml) was condensed on top of the solid at −196° and allowed to react for 30 min at −78°. The excess HCl was slowly removed at −78° through A, taking care not to splatter the product as the HCl was being removed. When HCl could no longer be detected pumping from the vessel (~3 hr), stopcock A was closed, and the vessel was attached to the line at the joint above stopcock C. The −45 and −196° baths were placed as shown in Figure 1, and stopcocks B and C were opened. The B_8H_{14} was pumped through stopcock B and collected in the U trap at −196°. Collection of the B_8H_{14} generally required 4 hr, during which time the liquid N_2 level in the −196° dewar had to be maintained within 0.5 in. of the top and the temperature of the other bath kept between −40 and −45°. After the B_8H_{14} was collected, stopcocks B and C were closed. The B_8H_{14} was moved into the NMR tube at the bottom of the U trap by slowly lowering the liquid nitrogen level. Solvent was then added through stopcock C and the NMR tube was sealed.

A thin-walled Pyrex capillary (~0.5-mm diameter) was successfully loaded with B_8H_{14} by using a slightly modified form of the vessel shown in Figure 1. The U trap and collection tube between B and C were replaced with a "pump-through" capillary. A small amount of B_8H_{14} was similarly prepared and pumped into the capillary at −196°. The capillary was subsequently sealed at both ends while keeping the B_8H_{14} cold with a swab dipped in liquid nitrogen. The B_8H_{14} sample was transferred cold to the X-ray diffractometer and mounted over a gaseous nitrogen cold stream (−150°). Although the sample was successfully mounted without noticeable decomposition, no crystals could be obtained as the compound glasses near its melting point. Attempts to shock the B_8H_{14} into a crystalline form by rapid warming and cooling also yielded only a glass.

Isononaborane(15) was prepared by a previously reported procedure.[4]

Results and Discussion

Octaborane(14). This compound was initially reported by Dobson and Schaeffer[3] in 1968, but no subsequent studies have appeared, probably owing to the difficulty encountered in preparing this extremely unstable compound. The 6230 "resonance hybrid" structure was proposed on the basis of a low-field ^{11}B NMR spectrum which, due to the absence of triplet resonances, suggested a structure with six bridging hydrogens. In an attempt to reconcile the structure with the expected nonbonded H–H interactions involved in crowding six bridges around the open face of the B_8 cage, we undertook this study.

Attempts at growing crystals of B_8H_{14} in a glass capillary proved futile since the material only glassed. Our structural studies were then limited to the ^1H and ^{11}B NMR studies. The data obtained from the normal and line-narrowed 70.6-MHz ^{11}B NMR spectra of B_8H_{14} are presented in Table I.[6] The B(4,5,7,8) resonance was assigned on the basis of a relative intensity of 4 while the assignments of the two area 2 resonances are in doubt. The upfield resonance is tentatively assigned to B(1,2); however, this assignment is based solely on the general trend that apical environments correspond to high-field resonances.[3] The triplet-like fine structure of the B(4,5,7,8) resonance in the line-narrowed spectrum was interpreted as a doublet (J = 60 Hz) of doublets (J = 40 Hz). The 40-Hz coupling is an average value for a boron–bridge hydrogen coupling ($J_{^{11}B-H_\mu}$), while the 60-Hz value is reminiscent of the "unique terminals" found in B_5H_{11} ($J_{^{11}B-H_\mu*}$ = 51 Hz)[2,7] and $B_9H_{13}CO$ ($J_{^{11}B-H_\mu*}$ = 55 Hz).[8] These data suggest the structure shown in Figure 2a; normal bridging hydrogens between B(4)–B(5) and B(7)–B(8) and "unique terminals" on B(4), B(5), B(7), and B(8). The 220-MHz ^1H NMR spectrum (Figure 3) is consistent with a structure containing only two bridging hydrogens; the measured ratio of terminals to bridges is 6.2:1 (calcd 6:1). The assignment

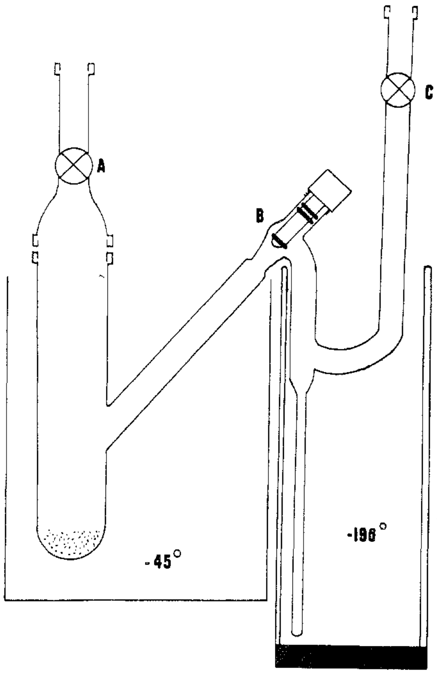

Figure 1. Vessel for the preparation of B_8H_{14}.

Table I

^{11}B NMR Spectrum of Octaborane(14) in *n*-Pentane Solution at −45°

	δ,[a] ppm	J, Hz: ^{11}B-H_t	J, Hz: ^{11}B-$H_{\mu}*$	J, Hz: ^{11}B-H_{μ}	Intens
B(*3,6* or 1,2)	−24.9	160			2
B(4,5,7,8)	+20.7	155	60	40	4
B(*1,2* or 3,6)	+38.2	160			2

^1H NMR Spectrum of Octaborane(14) in CS_2 Solution at −45°

	δ,[b] ppm	J, Hz	Intens
H_t-B(*3,6* or 1,2)	−4.76 (−4.8)[c]	158	2
H_t-B(4,5,7,8)	−2.02 (−2.1)	153	4
$H_{\mu}*$	−0.83 (−0.99)	60	4
H_t-B(*1,2* or 3,6)	−0.44 (−0.59)	155	2
H_{μ}	+3.20 (+3.2)	~40	2

[a] Relative to external $BF_3 \cdot OEt_2$. [b] Relative to TMS (negative when below TMS). [c] Values in parentheses represent chemical shifts taken from the 100-MHz spectrum at −81° in CS_2 solvent.

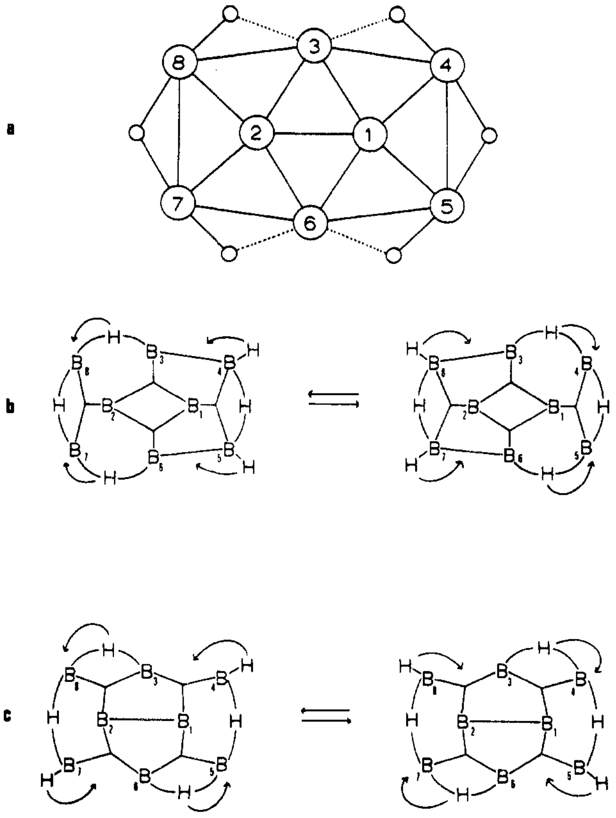

Figure 2. (a) Proposed structure (terminal hydrogens omitted) for B_8H_{14}. (b, c) Previously proposed 4412 structures for B_8H_{14} with hydrogen tautomerism.

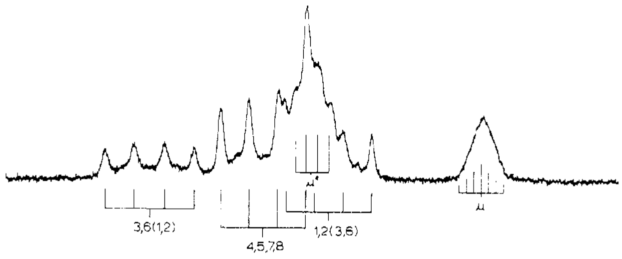

Figure 3. The 220-MHz ^1H NMR spectrum of B_8H_{14} in CS_2 at −45°.

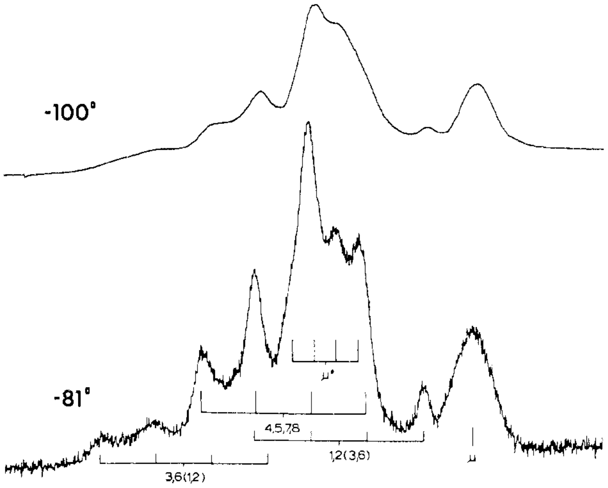

Figure 4. The 100-MHz ^1H NMR spectra of B_8H_{14} in CS_2 at −81 and −100°.

of the H(4,5,7,8) resonance is based on its intensity of 4 while the assignments of the two area 2 quartets, H(3,6) and H(1,2), are uncertain. The area 4 quartet $\mu*$ with a coupling constant of approximately 60 Hz is assigned to "unique terminals". The chemical shifts and coupling constants for the ^1H spectrum are also tabulated in Table I. The chemical shift of $\mu*$ falls between the two previously determined values for "unique terminals" (−2.09 and −0.23 ppm)[7,8] and is well separated from the normal chemical shift range for bridging hydrogens (+1–+3 ppm).

Neither of the previously proposed[3,9] 4412 structures for B_8H_{14} fits the data obtained in this work; however, rapid hydrogen tautomerism as shown in Figure 2(b and c) would equilibrate B(4), B(5), B(7), and B(8). The boron environments would also experience a weighted average of a terminal and a bridging hydrogen, and a coupling of 60–80 Hz would be expected. At much lower temperatures, however, this tautomerism should not be fast and the ^1H NMR spectrum of a static structure should contain resonances due to $-BH_2$ groups and two more bridging hydrogens. The ratio of terminals to bridges would change from 6:1 to 5:2. Since the low-temperature limit for the HR-220 spectrometer is −45 to −50°, we obtained the −81 and −100° ^1H NMR spectra at 100 MHz. These spectra are shown in Figure 4. Thermal

Table II

^{11}B NMR Spectrum of Isononaborane(15) in Dichloromethane Solution at −45°

	δ,[a] ppm	J, Hz		Intens
		^{11}B-H$_t$	^{11}B-H$_\mu$	
B(5,7,9)	−4.39	150		3
B(1,2,3)	+32.9	155		3
B(4,6,8)	+44.8	155	50	3

^{1}H NMR Spectrum of Isononaborane(15) in CD$_2$Cl$_2$ at −45°

	δ,[b] ppm	J, Hz	Intens
H$_t$	−3.02	150	~3
H$_t$	−0.75	150	~6
H$_\mu$	2.02		6

[a] Relative to BF$_3$·OEt$_2$. [b] Relative to TMS (negative when below TMS).

decoupling of borons does not appear to be a serious problem in these spectra; however, the −100° spectrum is broadened due to sample precipitation at this temperature. No new resonances were observed and the integrated terminal to bridging hydrogen ratio was found to be 6.0:1. We cannot be certain that −100° is low enough to stop this type of tautomerism. In the slightly similar B_6H_{10} system, bridge hydrogen tautomerism is relatively slow between −80 and −95° and is essentially stopped below −130°.[10] By comparison we suggest that the −100° ^{1}H NMR spectrum of a tautomerizing B_8H_{14} system should at least show effects of a slowed exchange.

Therefore we conclude that the tautomerizing 4412 structures are unlikely and that the data support the structure shown in Figure 2a. The reasons that "unique terminals" exist in the structures of some boron hydrides have not been established. Examination of a molecular model suggests that nonbonded H–H interaction may be a major contributing factor in the case of octaborane(14).

Isononaborane(15). The chemistry of i-B_9H_{15}[11] has been studied much more extensively than that of B_8H_{14}; however, structural data on this compound have also been limited to low-field ^{11}B NMR spectral studies.[4,5] A structure containing six bridging hydrogens and possessing C_{3v} symmetry has been suggested on the basis of these data, and an assignment of the three boron resonances in the 19.3-MHz ^{11}B NMR spectrum has been obtained by an extensive deuterium-labeling study.[5] Although a 6330 topological structure can be drawn, it violates the rules regarding hydrogen placement.[12] The steric problems associated with placing bridging hydrogens around the open face of a B_9 cage have also been the subject of a recent discussion by Huffman.[13] In the absence of X-ray crystallographic data, the structural influence of these proposed nonbonded H–H interactions was probed by high-field ^{11}B and ^{1}H NMR studies.

The proposed C_{3v} structure and the 70.6-MHz ^{11}B NMR spectra of i-B_9H_{15} are shown in Figure 5, along with the 220-MHz ^{1}H NMR spectrum. A tabulation of chemical shifts and coupling constants appears in Table II. The proton spectrum is consistent with a structure containing six bridging hydrogens. The measured terminal to bridging hydrogen ratio of 1.7:1 is in fair agreement with the calculated value of 1.5:1, and the chemical shift of the bridge resonance falls in the range for a normal bridging hydrogen. Although not as well resolved, the 100-MHz ^{1}H spectrum in CD_2Cl_2 at −81° yields a ratio of terminals to bridges of 1.6:1 and also a chemical shift of approximately +2.0 ppm for H$_\mu$. The assignments of the terminal hydrogen resonances in the proton spectra are uncertain. The line-narrowed ^{11}B spectrum (Figure 5a) reveals triplet fine structure for the B(4,6,8) resonance. The magnitude of this coupling is 50 Hz and is interpreted as resulting from coupling to two equivalent bridging hydrogens ($J_{^{11}\text{B-H}\mu}$ = 50 Hz). The coupling constant is rather large for a normal bridging hydrogen and is approaching that of "unique terminals" (50–60 Hz). From the proton spectrum (Figure 5c), however, it is evident that the environment of these protons is that of a bridge hydrogen. Not only is the chemical shift of the H$_\mu$ resonance consistent with a bridge (H$_\mu$, $\simeq$2.0 ppm; H$_{\mu*}$, $\simeq$−1.0 ppm) but its width and shape suggest that there are hidden couplings present, probably to B(5,7,9), in addition to the $J_{^{11}\text{B}(4,6,8)\text{-H}\mu}$ of 50 Hz. In fact, the B(5,7,9) resonance in the line-narrowed ^{11}B NMR spectrum is broadened as if unresolved fine structure were present. Although the width of the H$_\mu$ resonance suggests a ^{11}B(5,7,9)–H$_\mu$ coupling of 25–35 Hz, thermal decoupling could easily distort the coupling pattern and this value should be used as only a crude approximation of the coupling constant.[14] The rather large $J_{^{11}\text{B}(4,6,8)\text{-H}\mu}$ coupling thus appears not to be the result of "unique terminal" environment around B(4), B(6), and B(8) but does suggest slight terminal character to the bridges. Previous labeling studies[5] have established that bridge–terminal hydrogen exchange does occur at −50° for B(4,6,8) but does not occur at temperatures below −68°. The proton spectrum at −81°, however, does not indicate a change in the number of bridging hydrogens nor does it reveal any new resonances due to −BH$_2$ groups or "unique terminals". The bridge–terminal exchange involving only B(4,6,8) and the rather large coupling to H$_\mu$ may simply be the result of a slight asymmetry of the bridges toward this environment and away from B(5,7,9), in an attempt to alleviate H–H repulsions. We cannot completely discount an extremely rapid hydrogen

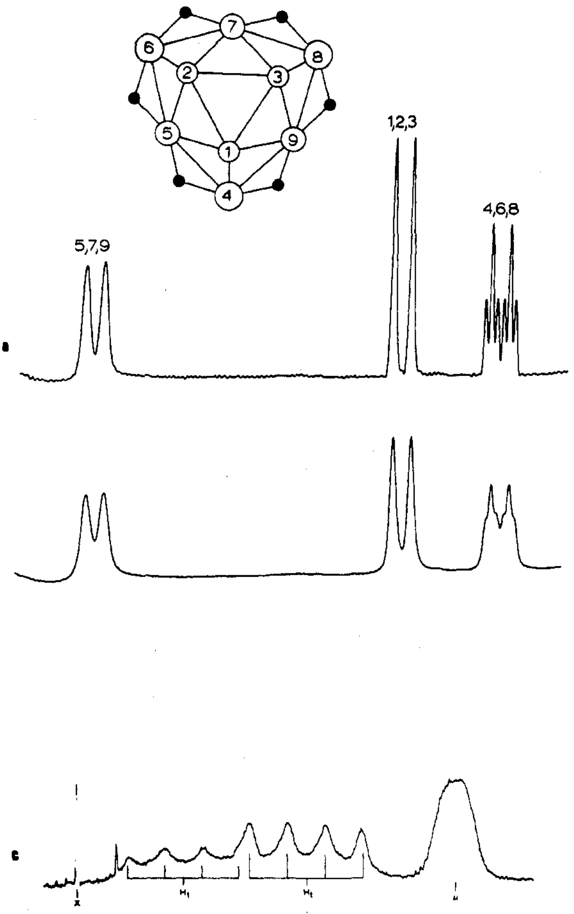

Figure 5. Proposed C_{3v} structure for i-B_9H_{15} (terminal hydrogens omitted) and (a) 70.6-MHz ^{11}B NMR spectrum line narrowed with TC = 10, (b) normal 70.6-MHz ^{11}B NMR spectrum and (c) 220-MHz ^{1}H NMR spectrum in CD_2Cl_2 at −45° (X signifies residual CH_2Cl_2).

tautomerism, but the data obtained thus far suggest that the open face of the i-B_9H_{15} cage is surrounded by bridging hydrogens and not by interconverting terminals and bridges. Rather long boron–boron distances around the periphery of the open face along with a slight asymmetry of B–H–B distances are proposed to account for a reduction in the severe nonbonded H–H interactions which would be expected in such a structure.

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Registry No. B_8H_{14}, 12008-46-7; i-B_9H_{15}, 12447-79-9.

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(14) No attempt was made to determine the spin–lattice relaxation time (T_1) for B(5,7,9) owing to the instability of the sample over the period of time required for such an experiment.

Notes

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Electronic Structure of Tungsten and Some of Its Borides, Carbides, Nitrides, and Oxides by X-Ray Electron Spectroscopy[1]

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Results of an x-ray electron spectroscopic investigation of the core and valence electronic energy levels of tungsten and some of its borides, carbides, nitrides, and oxides are presented in this communication. This investigation stems from some of the recent interest in this laboratory dealing with studies of substoichiometric amorphous thin films of some transition metal oxides[2a] and of the catalytic behavior of tungsten carbide.[2b] It was concluded in the WC investigation[2b] that electron density shifts from W to C. In addition, we found it interesting to observe the shifts in electron density upon addition of nonmetal substituents (varying in the number of *p* electrons) to the tungsten matrix. We have just this situation in the series of compounds W, WB, WC, WN, WO_2, and WO_3.

Experimental Section

The samples studied in this investigation were W foil and WB, WC, W_2N + WN (mixture), WO_2, and WO_3 powders pressed into pellets. The tungsten oxides were obtained from RESEARCH Organic/Inorganic Chemical Corp. and the remaining samples from Ventron Corp., Alfa Inorganics. The W foil had a listed metallic purity of 99.95% and the WB and W_2N + WN (mixture) powders both had a listed purity of 99.5%. The purity of the WC powder was not reported. The WO_2 and WO_3 powders had a listed purity of 99 and 99.5%, respectively. X-ray diffraction patterns of WC, WO_2, and WO_3 showed that the samples were single phased with no detectable impurities. WB was found to actually exist as W_2B + WB (mixture) and W_2N + WN (mixture) was initially amorphous. In all cases, the photoelectron measurements revealed some oxide and carbon contamination.

Photoelectron spectra were recorded with a Hewlett-Packard 5950A ESCA spectrometer using monochromatized Al Kα (1486.6 eV) radiation. The instrumental resolution was ~0.55 eV measured as fwhm of the C 1s line of graphite. Samples were maintained at a temperature of 300°K and a vacuum of below 2×10^{-9} Torr during analysis. Charging effects were controlled by flooding the sample surface with a low flux (~0.4 mA) of zero kinetic energy electrons during analysis. Calibration was performed by vacuum evaporation of gold onto the sample surface and referencing the sample spectrum to the Au $4f_{7/2}$ peak at 83.8 eV.[3] The oxide impurity on the surface of the W foil was removed mechanically by a specially constructed grinding mechanism[4] designed to clean sample surfaces inside the high vacuum (below 2×10^{-8} Torr) sample preparation chamber. The W_2B + WB (mixture), WC, and W_2N + WN (mixture) samples were subjected to a "soft ion sputtering" procedure[5] utilizing 500 V Ar ions. Reduction of WO_2 to W was evident with the above procedure.[5] The WO_3 sample required no cleaning.

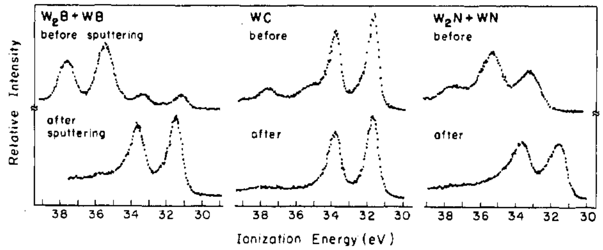

Figure 1. Photoelectron spectra of W_2B + WB, WC, and W_2N + WN 4*f* levels before and after sputtering with 500 V Ar ions.

Results and Discussion

Data from the photoelectron measurements made in this laboratory on some core levels of W, W_2B + WB, WC, W_2N + WN, WO_2, and WO_3 are presented in Table I. They are grossly consistent with some of those previously reported by several authors.[6-12] Table I lists the energies for the W $4f_{7/2}$ and $4f_{5/2}$ levels plus their respective splitting (ΔW 4*f*) for each of the samples studied. Reproducibility of the W 4*f* binding energies is between ±0.1 and 0.2 eV and that for the observed splitting is ±0.05 eV. In addition, energies for the nonmetal 1s line are given and where applicable the energy for the contaminant line is also given. The reproducibility of these lines is ±0.2 eV. For the cases where two sets of data are given for one sample, the set labeled "NS" represents data taken on a sample that has not been Ar ion sputtered as opposed to those labeled "S" representing samples that have been Ar ion sputtered. Figure 1 shows the W 4*f* levels of these samples before and after Ar ion sputtering. Note the shift in binding energy for all cases and the disappearance of the high-binding-energy peaks after sputtering. These higher-energy peaks are due to tungsten oxide contamination of the surface. The tungsten boride spectrum shows that the surface is composed primarily of tungsten oxide before sputtering; this oxide is effectively removed by sputtering. These shifts clearly

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