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July 1992

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Sunwoo Lee
Syracuse University

Peter A. Dowben
University of Nebraska-Lincoln, pdowben@unl.edu

A.T. Wen
McMaster University

A.P. Hitchcock
McMaster University

John A. Glass Jr.
Syracuse University

See next page for additional authors

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Lee, Sunwoo; Dowben, Peter A.; Wen, A.T.; Hitchcock, A.P.; Glass, John A. Jr.; and Spencer, James T., "Structures of selected boranes and carboranes" (1992). *Peter Dowben Publications*. 140.
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Authors

Sunwoo Lee, Peter A. Dowben, A.T. Wen, A.P. Hitchcock, John A. Glass Jr., and James T. Spencer

Structures of selected boranes and carboranes

Sunwoo Lee and P. A. Dowben

Department of Physics, Syracuse University, Syracuse, New York 13244-1130

A. T. Wen and A. P. Hitchcock

Department of Chemistry, McMaster University, Hamilton, Ontario L8S 4M1, Canada

John A. Glass, Jr. and James T. Spencer

Department of Chemistry, Syracuse University, Syracuse, New York 13244-4100

(Received 23 October 1991; accepted 16 December 1991)

Nido-pentaborane(9) (B_5H_9), **1**, *nido*-2,3-diethyl-2,3-dicarbahexaborane(8) [$(C_2H_5)_2C_2B_4H_6$], **2**, *nido*-decaborane(14) ($B_{10}H_{14}$), **3**, *closo*-1,2-dicarbododecaborane(12) ($H_2C_2B_{10}H_{10}$), **4**, can be used as possible source compounds for boron and boron carbide thin film deposition. Inner shell electron energy-loss spectroscopy (ISEELS) studies of the boron 1s and carbon 1s core excitations of gas phase species have been undertaken so as to characterize these molecular precursors at solid surfaces. The near edge structure of ISEELS provides a good "fingerprint" for the identification of these molecular species. A comparison is made between calculated [modified neglect of differential overlap (MNDO)] bond lengths for molecular clusters and the x-ray or electron diffraction bond lengths, bond lengths determined from extended energy-loss fine structure.

I. INTRODUCTION

Selective area deposition of boron and boron carbide thin films from *nido*-decaborane(14) and *nido*-diethyl-2,3-dicarbahexaborane(8) on Si(111) has recently been explored using broadband synchrotron radiation.¹⁻³ The initial adsorption of *nido*-decaborane(14) and *nido*-2,3-diethyl-2,3-dicarbahexaborane(8) on Si(111) is mainly molecular as determined by photoemission spectroscopy (PES).²⁻⁴ It is therefore important to characterize those molecular precursor states to the selective area deposition of boron and boron carbide films with particular emphases on adsorbed precursor states. Modeling of molecular precursor states in the film growth process in chemical vapor deposition (CVD) is particularly valuable in developing a clear picture of the CVD process and in identifying suitable CVD source compounds.⁴ In this paper, we suggest that the local atomic geometry of the selected adsorbed boranes and carboranes can be characterized through near edge and extended fine structure features of inner-shell excitation spectra recorded by photons [near edge x-ray absorption fine structure (NEXAFS), extended x-ray absorption fine structure (EXAFS)] or electrons [extended energy-loss fine structure (EXELFS), inner shell electron energy-loss spectroscopy (ISEELS)], as this study of the inner-shell spectra of related gas species demonstrates.⁵⁻⁷ Theoretical MNDO (modified neglect of differential overlap) semiempirical molecular orbital calculations were carried out in order to gain a deeper understanding of the experimental results. In addition, we demonstrate the MNDO calculations provide an accurate picture of these adsorbed borane and carborane species.

II. EXPERIMENTAL/THEORETICAL CALCULATIONS

A. Experimental

ISEELS of *nido*-decaborane(14), *nido*-pentaborane(9), *nido*-2,3-diethyl-2,3-dicarbahexaborane(8) (diethylcarborane) and *closo*-1,2-dicarbododecaborane(12) (orthocarborane) and EXELFS spectroscopy of *nido*-pentaborane(9) and *closo*-1,2-dicarbododecaborane(12) were carried out on a McMaster inner shell electron energy-loss spectrometer equipped with a hemispherical electron energy analyzer. *Nido*-2,3-diethyl-2,3-dicarbahexaborane(8) was synthesized by literature methods at Syracuse University.⁸ *Nido*-pentaborane(9) was from our laboratory stock. *Nido*-decaborane(14) and *closo*-1,2-dicarbododecaborane(12) were commercially available from Callery and Aldrich, respectively, and vacuum sublimed and stored *in vacuo* prior to use. The identity and purity of all molecular compounds were determined by nuclear magnetic resonance (NMR), Fourier transform infrared spectroscopy (FTIR), and mass spectral measurements.

The ISEELS and EXELFS spectra recorded the number of electrons inelastically scattered in single collisions with the target molecules as a function of energy loss under electric dipole transition conditions (large impact energy $E=2.5$ keV plus the energy loss; small scattering angle, $<2^\circ$). The resolution available with this system was 0.6 eV full width at half-maximum (FWHM). The molecular compounds were admitted to the collision chamber through a standard leak valve. The sample cell, vapor inlet and the collision chamber were heated for low vapor pressure compounds ($P < 10^{-4}$ Torr) to get an efficient spectral acquisition.

B. Theoretical calculations

In order to evaluate the bond lengths of selected boranes and carboranes determined from the EXELFS data, MNDO semiempirical molecular orbital calculations were undertaken. The experimental literature values from either x-ray or electron diffraction were also compared with our values. The calculations were performed using either versions 4.01 or 5.02 of MOPAC^{9,10} on either a Hewlett-Packard Series 800 computer system in the Center for Molecular Electronics at Syracuse University or a VAX 8820 system of the Syracuse University Academic Computing Services. All calculations were freely varied and run with the PRECISE option¹¹ employed except where noted. To find the MNDO optimized minimum energy geometries on the potential energy surface for the molecular compounds, the procedure utilized several steps.^{12,13} The starting input geometry of the compounds was approximated based on appropriate substitutions of a parent cluster structure. The structures were optimized without symmetry restrictions in most cases. In cases where the initial geometry did not lead to an optimized structure, the final MNDO output geometry was reinput and the calculations were run until a MNDO optimization was achieved. In most cases, this was realized in fewer than five of these cycles. The MNDO calculated minimum energy structures for boranes and carboranes molecular clusters are shown in Fig. 1, with the bond lengths summarized in Table I.

III. RESULTS

A. Inner shell electron energy-loss spectroscopy of boranes and carboranes

Boron 1s ISEELS of *nido*-pentaborane(9), **1**, *nido*-2,3-diethyl-2,3-dicarbahexaborane(8), **2**, *closo*-1,2-dicarbadoecaborane(12), **3**, and *nido*-decaborane(14), **4**, were measured. There are a number of distinct boron 1s ionization potentials (IPs) of **1** and **4**, depending on the local environment of the boron atom in the cluster: [*nido*-pentaborane(9): apical boron—194.2 eV, basal borons—196.1 eV; *closo*-1,2-dicarbadoecaborane(12): 9,12 borons—194.5 eV, 8,10 borons—195.0 eV, 4,5,7,11 borons—195.6 eV, 3,6 borons—196.3 eV; see Fig. 1 for atom numbering].¹⁴ Boron 1s ionization potentials for **2** and **3** were estimated from pentaborane and carborane IPs based on similarity of local structure. The estimated IPs for **2** are 195.2 eV for the 4,6-basal borons, 195.7 eV for the 5-basal boron atom and 196.0 eV for apical (1) boron atom. The estimated IPs for **3** are 194.2 eV for 1,4,5,7 borons, 194.5 eV for 3,6,8,10 borons, and 195.5 eV for 2,9 borons. The differences in the boron 1s ionization potentials of 1 to 2 eV can be related to the local charge at the boron atoms. The observed boron inner shell electron energy-loss spectra of *closo*-1,2-dicarbadoecaborane(12) and *nido*-pentaborane(9) are shown in Fig. 2.

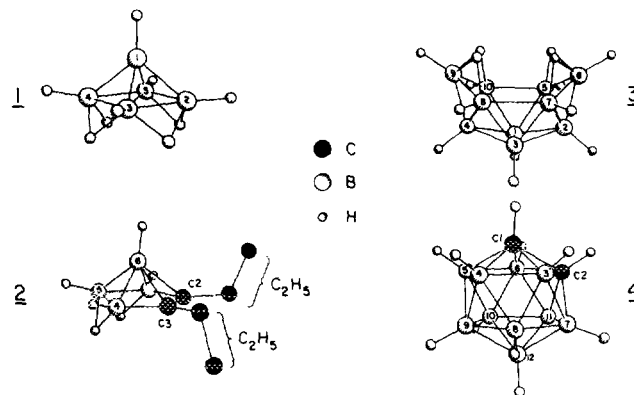


FIG. 1. MNDO calculated minimum energy geometry for the borane and carborane clusters 1-4. The protons on the ethyl groups of $(C_2H_5)_2C_2B_4H_6$ have been omitted for clarity.

B. Comparison of EXELFS with MNDO calculations of *nido*-pentaborane(9) and *closo*-1,2-dicarbadoecaborane(12)

The EXELFS in the inner shell electron energy-loss spectra of *nido*-penta-borane(9) and *closo*-1,2-dicarbadoecaborane(12) were analyzed by standard EXAFS techniques.¹⁵ The energy-space EXELFS and Fourier transform (FT) of the k^1 -weighted EXELFS are shown in Fig. 3. The procedures utilized in the spectral analysis are described elsewhere.¹⁶ The EXELFS signals of **1** and **4** were isolated by 2-section quadratic spline background subtractions. The magnitude of the Fourier transforms [Fig. 3(b)] give the distributions of the neighbor atoms as a function of phase-shifted radial distance. The average nearest neighbor B-B bond length for *nido*-pentaborane(9) were derived from the Fourier filtered first shell signal using spherical wave calculated phases.¹⁷ It agrees with the bond lengths obtained from the MNDO calculations and the known experimental values obtained from x-ray and electron diffraction data.¹⁸ The EXELFS value for the B-B length of *closo*-1,2-dicarbadoecaborane(12) was, however, somewhat different from those obtained by conventional diffraction and MNDO. The structural data from the MNDO calculations and the crystallographically determined data for compounds 1-4 are summarized in Table I. Table II presents the nearest neighbor B-B bond lengths determined from the EXELFS spectra, the MNDO calculations and the x-ray diffraction and electron diffraction data, respectively. In general, the experimental and calculated bond distance values are in good agreement.

IV. DISCUSSION

The *closo*-borane cage neutral species are, in general, more thermally stable and far less reactive than the related open framework boron hydrides of comparable molecular weight. This is an important factor for the cluster to serve as a good molecular precursor for the selective area deposition. Many boron hydride molecular precursors are unsuitable in the selective area deposition¹⁹ since they tend to be unstable with respect to decomposition. This is due to their positive free energy formation values.²⁰ There are,

TABLE I. Experimental (x-ray or electron diffraction) and calculated (MNDO) bond lengths for borane clusters 1-4.^a

	1	2	3	4	5	6	7	8	9	10	11	12
1, 1		1.69 (1.71)	1.69 (1.71)	1.69 (1.71)	1.69 (1.71)							
2		1.76 (1.84)	1.76 (1.83)	1.77 (1.81)	1.71 (1.70)	1.77 (1.81)						
3		1.80 (1.80)	1.71 (1.80)	1.78 (1.79)	1.78 (1.79)	(2.93)	(2.96)	(2.96)	(2.93)	1.77 (1.78)		
4		1.67 (1.74)	1.72 (1.74)	1.72 (1.74)	1.72 (1.74)	1.72 (1.74)	(2.87)	(2.83)	(2.83)	(2.83)	(2.87)	(3.33)
2, 1	1.69 (1.71)		1.80 (1.86)	(2.63)	1.80 (1.86)							
2	1.76 (1.84)		1.43 (1.46)	(2.54)	(2.67)	1.52 (1.53)						
3	1.80 (1.80)		1.78 (1.79)	(2.97)	1.76 (1.87)	1.72 (1.69)	1.80 (1.87)	(3.03)	(2.97)	(3.03)		
4	1.67 (1.74)		1.71 (1.74)	(2.87)	(2.87)	1.71 (1.74)	1.71 (1.74)	(2.82)	(3.33)	(2.82)	1.71 (1.74)	(2.82)
3, 1	1.69 (1.71)	1.80 (1.86)		1.80 (1.86)	(2.63)							
2	1.76 (1.83)	1.43 (1.46)		1.52 (1.53)	(2.67)	(2.53)						
3	1.71 (1.86)	1.78 (1.79)		1.80 (1.79)	(2.96)	(2.93)	1.77 (1.78)	1.78 (1.79)	(2.93)	(2.96)		
4	1.72 (1.74)	1.71 (1.74)		1.77 (1.83)	(2.94)	(2.90)	1.77 (1.83)	1.77 (1.80)	(2.94)	(3.45)	(2.94)	(2.94)
4, 1	1.69 (1.71)	(2.63)	1.80 (1.86)		1.80 (1.86)							
2	1.77 (1.81)	(2.54)	1.52 (1.53)		1.78 (1.81)	(2.77)						
3	1.78 (1.79)	(2.97)	1.80 (1.79)		(3.03)	(3.75)	(3.03)	1.76 (1.87)	1.72 (1.69)	1.80 (1.87)		
4	1.72 (1.74)	(2.87)	1.77 (1.83)		1.77 (1.81)	(2.94)	(2.97)	1.77 (1.82)	1.77 (1.82)	(2.95)	(3.48)	(2.94)
5, 1	1.69 (1.71)	1.80 (1.86)	(2.63)	1.80 (1.86)								
2	1.71 (1.70)	(2.67)	(2.67)	1.78 (1.81)		1.78 (1.81)						
3	1.78 (1.79)	1.76 (1.87)	(2.96)	(3.03)		1.77 (1.86)	(2.98)	(3.53)	(3.03)	2.01 (1.90)		
4	1.72 (1.74)	(2.87)	(2.94)	1.77 (1.81)		1.77 (1.83)	(3.48)	(2.95)	1.77 (1.82)	1.77 (1.82)	(2.97)	(2.95)
6, 2	1.77 (1.81)	1.52 (1.53)	(2.53)	(2.77)	1.78 (1.81)							
3	(2.93)	1.72 (1.69)	(2.93)	(3.75)	1.77 (1.86)		1.77 (1.86)	(3.27)	(3.78)	(3.27)		
4	1.72 (1.74)	1.71 (1.74)	(2.91)	(2.94)	1.77 (1.83)		(2.94)	(3.45)	(2.94)	1.77 (1.80)	1.77 (1.83)	(2.94)
7, 3	(2.96)	1.80 (1.87)	1.77 (1.78)	(3.03)	(2.98)	1.77 (1.86)		2.01 (1.90)	(3.27)	(3.53)		
4	(2.86)	1.71 (1.74)	1.77 (1.83)	(2.97)	(3.48)	(2.94)		1.77 (1.82)	(2.94)	(2.96)	1.77 (1.81)	1.77 (1.82)
8, 3	(2.96)	(3.03)	1.78 (1.79)	1.76 (1.87)	(3.53)	(3.27)	2.01 (1.90)		1.77 (1.86)	(2.98)		
4	(2.82)	(2.82)	1.77 (1.80)	1.77 (1.82)	(2.96)	(3.46)	1.77 (1.82)		1.77 (1.84)	(2.98)	(2.96)	1.77 (1.84)
9, 3	(2.93)	(3.75)	(2.93)	1.72 (1.69)	(3.27)	(3.78)	(3.27)	1.77 (1.86)		1.77 (1.86)		
4	(2.82)	(3.34)	(2.94)	1.77 (1.82)	1.77 (1.82)	(2.94)	(2.94)	1.77 (1.84)		1.77 (1.84)	(2.94)	1.77 (1.80)
10, 3	1.77 (1.78)	(3.03)	(2.96)	1.80 (1.87)	2.01 (1.90)	(3.27)	(3.53)	(2.98)	1.77 (1.86)			
4	(2.82)	(2.82)	(3.46)	(2.95)	1.77 (1.82)	1.77 (1.80)	(2.95)	(2.99)	1.77 (1.84)		1.77 (1.82)	1.77 (1.84)
11, 4	(2.87)	1.71 (1.74)	(2.94)	(3.48)	(2.97)	1.77 (1.83)	1.77 (1.81)	(2.96)	(2.94)	1.77 (1.82)		1.77 (1.82)
12, 4	(3.33)	(2.82)	(2.94)	(2.94)	(2.95)	(2.94)	1.77 (1.82)	1.77 (1.84)	1.77 (1.80)	1.77 (1.84)	1.77 (1.82)	

^aThe experimental values are given first with the calculated (MNDO) values in parentheses. The numbering scheme for each compound is given in Fig. 1. The calculated structural data given for 2 are for $(C_2H_5)_2C_2B_4H_6$ and the experimental structural data given are for $C_2B_4H_4$.

however, indications that molecular precursor states to complete dissociation exist on solid surfaces and the activation barrier to dissociative adsorption has been determined in previous studies.^{2,3} The adsorption of *nido*-2,3-diethyl-2,3-dicarbaheborane on boron covered Si(111) occurs with the initial loss of exopolyhedral organic units.⁴ This reactivity has a thermodynamic origin in that the cage boron atoms (which in this case includes substrate boron atoms) appear to be a thermodynamic sink.²¹

The near edge structure spectra of gaseous and condensed *nido*-decaborane(14) on Si(111) resemble each other (Fig. 4). This implies that the adsorbed *nido*-decaborane(14) at 100 K apparently does not react with the surface. Spectral features occur with similar positions and relative intensities, indicating that there is little relaxation of the molecules on the surface. The similarity between the photoexcited near edge structure spectrum for the condensed species and the ISEELS spectrum of 4 indicates

that the B 1s spectra serve as good "fingerprint" data for the identification of molecular precursor states. In general, we have found that the ISEELS spectra of gaseous species (as shown in Fig. 2) have considerably better signal to noise ratios than found for the photoexcited NEXAFS spectra of very thin condensed films. We believe that the fine structure observed in ISEELS is of such quality that the ISEELS data will have to be taken with degraded resolution, or computationally broadened to be made comparable to condensed molecular films, as has been done for Fig. 4. Such problems in comparing spectra of gas phase species and condensed molecular species have also been observed in valence band photoemission.²

As seen in Fig. 3, the radial distribution function for orthocarborane ($H_2C_2B_{10}H_{10}$) and pentaborane (B_5H_9) have been calculated from ISEELS data. Although extended x-ray absorption fine structure (EXAFS) is a well known technique for the characterization of the local

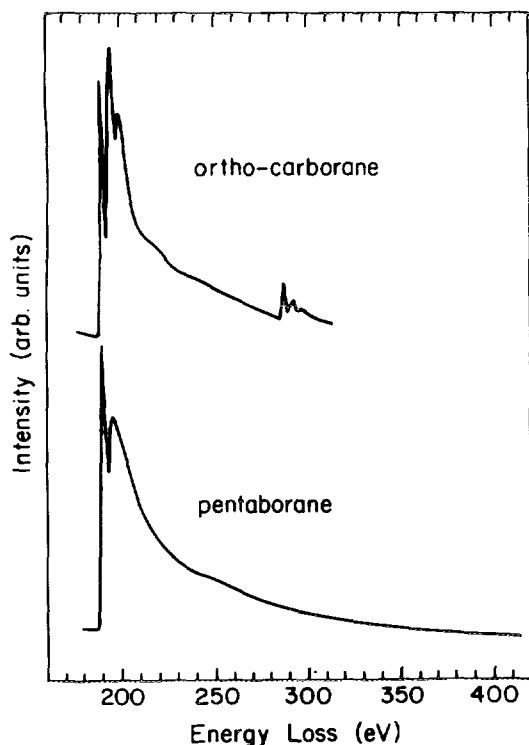


FIG. 2. As recorded electron energy-loss spectra for boron of gaseous *closo*-1,2-dicarbododecaborane(12) (denoted as orthocarborane) and *nido*-pentaborane(9) (denoted as pentaborane). The impact energy was 2.5 keV. The scattering angle was 2° and the resolution was 0.6 eV FWHM. The extended fine structure (EXELFS) is clearly visible in the B 1s continuum.

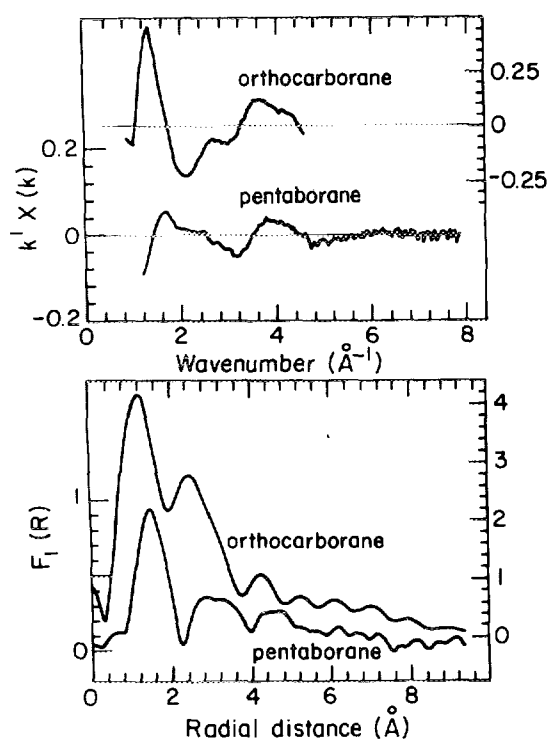


FIG. 3. k^1 -weighted EXELFS isolated from the raw B 1s data of 1 (B_5H_9) and 4 ($H_2C_2B_{10}H_{10}$) using a 2-section quadratic polynomial spline for background subtraction (top). The magnitude of the Fourier transforms of the EXELFS of 1 and 4 are shown at bottom.

TABLE II. Bond lengths from EXELFS, x-ray/electron diffraction and MNDO calculations.

Molecules	B-B bond lengths (Å)		
	EXELFS	X ray/electron	MNDO
B_5H_9	1.74	1.69	1.71
$B_{10}H_{10}C_2H_2$	1.62	1.76	1.82

atomic geometry of molecules, extended energy-loss fine structure EXELFS has also been demonstrated to be a comparably useful technique.^{22,23} It is, however, difficult to analyze extended fine structure associated with low energy core edges since the results are extremely sensitive to details of the background subtraction, particularly when polynomial spline functions are used.

Radial distances derived from boron *K*-shell EXELFS for *closo*-1,2-dicarbododecaborane(12) are slightly different from those provided by MNDO and diffraction data, although bond lengths for *nido*-pentaborane(9) are in relatively good agreement with these other measurements and calculations (shown in Table II). This may be explained by either an inappropriate background subtraction or by the insufficient EXELFS data range which is limited by the onset of C 1s excitation. The shorter data range is the reason for the broader peak in the Fourier transform of the EXELFS of *closo*-1,2-dicarbododecaborane(12). An addi-

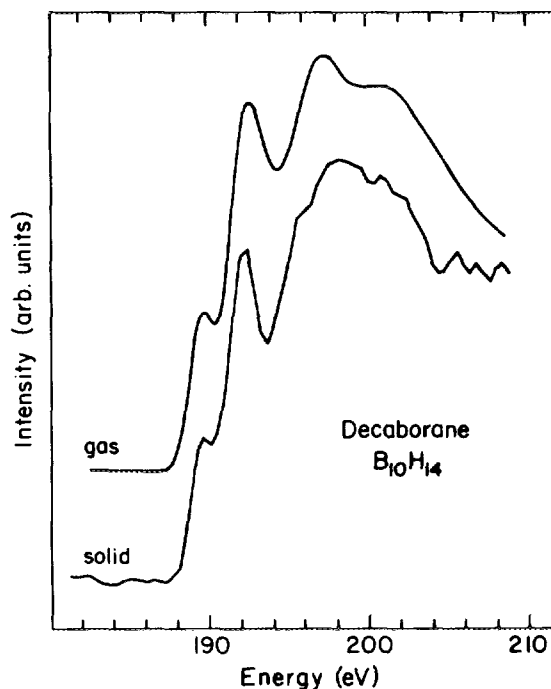


FIG. 4. Comparison of boron 1s energy-loss spectrum of gas phase decaborane(14) with the synchrotron x-ray absorption spectrum of a thin film of solid decaborane(14) condensed onto Si(111). Total electron yield detection was used in the latter case. A smooth background has been subtracted from each spectrum. The synchrotron data have been rigidly shifted (in energy) to obtain agreement with the gas phase data. This rigid shift represents the calibration problems associated with the synchrotron monochromator.

tional possibility is that our data analysis for *closo*-1,2-dicarbadoecaborane includes multiple scattering effect from the near edge structure. For classical EXAFS theory to be valid, the electron must be only weakly scattered.²⁴ Phase shift correction may also be a critical factor in obtaining an accurate value since the derived distance depends upon whether the curved-wave approximation¹⁷ or the plane-wave phase shift²⁵ approximation is used. It has been reported that plane-wave phase shift leads to shorter bond lengths especially between adsorbates and substrates^{26,27} at low energies. For *nido*-pentaborane(9) these complications are substantially reduced.

The calculated minimum energy structures for boranes and carboranes, as shown in Fig. 1, appear to be in good agreement with experiment as outlined in Tables I and II. The utility of using MNDO to calculate the structures of boranes and carboranes can be considered on the basis of this and other work (Ref. 12 and the references therein), to be well established.

V. CONCLUSIONS

Possible molecular precursor states relevant to selective area deposition of boron and boron carbide thin films from boranes and carboranes have been characterized through experiment and theory. The calculated and observed bond length values are in relatively good agreement although there is some discrepancy for *closo*-1,2-dicarbadoecaborane(12).

The MNDO calculations have demonstrated that they provide a very good description of the structure of gaseous boranes and carboranes, consistent with the molecular structures as determined by diffraction and with EXELFS results. The agreement between MNDO calculations and photoemission has already been demonstrated for *nido*-decaborane(14),^{25,28} *nido*-pentaborane(9),²⁹ *closo*-1,2-dicarbadoecaborane(12),³⁰ and *nido*-2,3-diethyl-dicarbadohexaborane(8).⁴

ACKNOWLEDGMENTS

This work was supported by the National Science Foundation (Grant No. DMR-8820779 and MSS-89-09793) and the National Science and Engineering Research Council of Canada and the Industrial Affiliates Program of the Center for Molecular Electronics at Syracuse University. The authors would like to acknowledge R. A. Rosenberg and S. P. Frigo for their assistance and guidance in obtaining the near edge structure spectrum of *nido*-decaborane(14).

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