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CHEMICAL SHIFTS IN BORON 1s BINDING ENERGIES OF SOME GASEOUS COMPOUNDS

Patricia Finn and William L. Jolly*

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Abstract: Chemical shifts in boron 1s electron binding energies for gaseous BF_3 , BCl_3 , $B(OCH_3)_3$, B_2H_6 , $B(CH_3)_3$, BH_3CO , and $H_3BN(CH_3)_3$ are shown to be linearly related to boron atom charges estimated by Pauling, CNDO, and extended Hückel methods. The best correlation is found with the extended Hückel charges, with inclusion of the interatomic "Madelung potential" (average deviation from straight-line relation, ± 0.83 eV). By application of the thermodynamic method (based on the approximation that $\Delta E = 0$ for the interchange of a pair of equally-charged atomic cores between two different chemical species), the chemical shifts are estimated with an average error of ± 0.57 eV. There is no obvious correlation between the 1s binding energy chemical shifts and published ^{11}B nmr chemical shifts.

Recently we reported¹ the nitrogen 1s electron binding energies for a series of gaseous nitrogen compounds and correlated the experimental values with calculated atomic charges and thermodynamic data. In this study we have measured the boron 1s electron binding energies of a series of gaseous boron compounds in order to provide data for further tests of the correlation of binding energies with atomic charges and thermodynamic data. We have also compared the boron 1s binding energies with boron-11 nuclear magnetic resonance chemical shifts.

Experimental

Magnesium K_{α} X-radiation was used for photoionization. Kinetic energies of the photoelectrons were measured with an iron-free, double-focusing magnetic spectrometer.² Each compound was first studied alone to determine the approximate magnitude of the photoelectron kinetic energy. Then an approximately 1:1 mixture of the compound and a reference compound, usually boron trifluoride, was studied. Because absolute binding energies were not determined, all the reported binding energies are relative. The width of each channel was 0.3 eV; the counting times were such that approximately 1000 counts were recorded in the channel nearest the signal peak. Signal-to-noise ratios were 2.0-4.0, and the widths of the photoelectron lines at half-height were 1.2-1.8 eV. Most samples were run twice; no peak position changed more than 0.1 eV.

Trimethyl borate was obtained from Alfa Inorganics, Inc., trimethylamine borane from Callery Chemical Co., and boron trifluoride and boron trichloride from the Matheson Co. Borane carbonyl,³ diborane,⁴ and boron trimethyl⁵ were prepared by literature procedures. The purity of the samples was checked by mass spectroscopy and by infrared spectroscopy.⁶⁻¹²

Results and Discussion

The measured boron 1s electron binding energies, relative to that of boron trifluoride, are listed in Table I.

Atomic Charge Method.- Pauling, CNDO, and extended Hückel methods were used for calculating boron atomic charges to permit a comparison of their correlations with experimental binding energies.

The Pauling method is based on a relation between the ionic character of a bond and the difference in the electronegativities of the atoms.¹³ Using Pauling's technique¹⁴ for estimating the electronegativities of charged atoms, the calculations were iterated until consistent sets of charges and electronegativities were obtained. The calculated charges are listed in column 4 of Table I. The least squares fitted straight line relation between binding energy and Pauling charge, $E_B = 5.16q - 4.07$, fits the data with an average error of ± 1.50 eV. A similar poor correlation with Pauling charges was found previously¹ for nitrogen compounds.

Using a Fortran IV program, the CNDO molecular orbital charge calculations¹⁵ were made with a CDC 6400 computer, using Cartesian coordinates obtained from program PROXYZ¹⁶ coupled with literature values for the molecular parameters.¹⁷ The calculated CNDO atomic charges are listed in column 5 of Table I. The least squares fitted straight line relation between binding energy and CNDO charge, $E_B = 7.58q - 6.37$, fits the points with an average error of ± 1.45 eV (only slightly better than in the Pauling charge correlation).

Extended Hückel calculations were made with a CDC 6600 computer using a Fortran IV program.¹⁸ The Slater exponents used were 1.2, 2.6,

Table I

Boron 1s Chemical Shifts, Estimated Boron Charges, ^{11}B nmr Chemical Shifts, and

Thermochemically Estimated Chemical Shifts

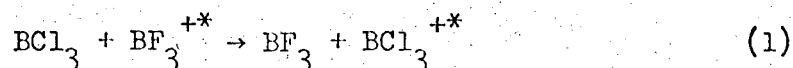
<u>Compound Number</u>	<u>Compound</u>	<u>Relative Binding Energy, eV</u>	<u>Pauling Charge</u>	<u>CNDO Charge</u>	<u>Extended Hückel Charge</u>	<u>^{11}B nmr Chemical Shifts, ppm</u>	<u>Thermochemical Energy, eV</u>
1	BF_3	0	0.60	0.70	1.65	6.6	0
2	BCl_3	-2.3	-0.22	0.25	0.81	-29.2	-2.42
3	$\text{B}(\text{OCH}_3)_3$	-4.4	0.14	0.49	1.13	0.0	-3.02
4	B_2H_6	-6.3	0.01	-0.03	-0.01	0.5	-5.42
5	$\text{B}(\text{CH}_3)_3$	-6.4	-0.62	0.13	0.31	-68.2	-6.86
6	BH_3CO	-7.6	-0.78	-0.43	0.15	-----	-8.03
7	$\text{BH}_3\text{N}(\text{CH}_3)_3$	-9.1	-0.60	-0.08	-0.19	24.9	-9.46

3.25, 3.9, 4.55, 5.2, and 4.5 for H, B, C, N, O, F, and Cl, respectively. Coulomb integrals were obtained from valence orbital ionization potentials.¹⁹ The calculated charges are listed in column 6 of Table I. The least squares fitted straight line relation, $E_B = 4.34q - 7.54$, provides the best fit of the three atomic charge methods with an average error ± 1.04 eV. For nitrogen compounds the extended Hückel method also gives the best fit.²⁰

By inclusion of the interatomic "Madelung potential", M ,²¹ the linear relationships between binding energy and atomic charge are improved. The improvement is negligible for the Pauling charges, yielding an average error ± 1.49 eV for the least squares fitted straight line $E_B - M = 5.77q - 3.98$. The average errors for the CNDO least squares fitted straight line $E_B - M = 8.29q - 6.04$, and the extended Hückel straight line $E_B - M = 5.15q - 7.48$, are significantly reduced, to ± 1.21 and ± 0.83 eV, respectively.

NMR Chemical Shifts.- The ^{11}B nmr chemical shifts reported by Phillips, Miller and Muettterties²² relative to methyl borate are listed in column 7 of Table I. There seems to be no correlation whatsoever between these data and the relative binding energies, even when considering the planar molecules alone.

Thermodynamic Method.- The difference in the boron 1s electron binding energies of boron trichloride and boron trifluoride is the energy of reaction 1. (An asterisk denotes removal of a core electron).



The basis of the thermodynamic method is the approximation that $\Delta E = 0$

tetramethylammonium ion. Médard

and Thomas²⁶ have determined ΔH_6° to be -80.8 kcal/mol. The value of ΔH_7° (117.2 kcal/mol) was estimated by the formula of Kapustinsky, which, for salts of univalent anions, is²⁷

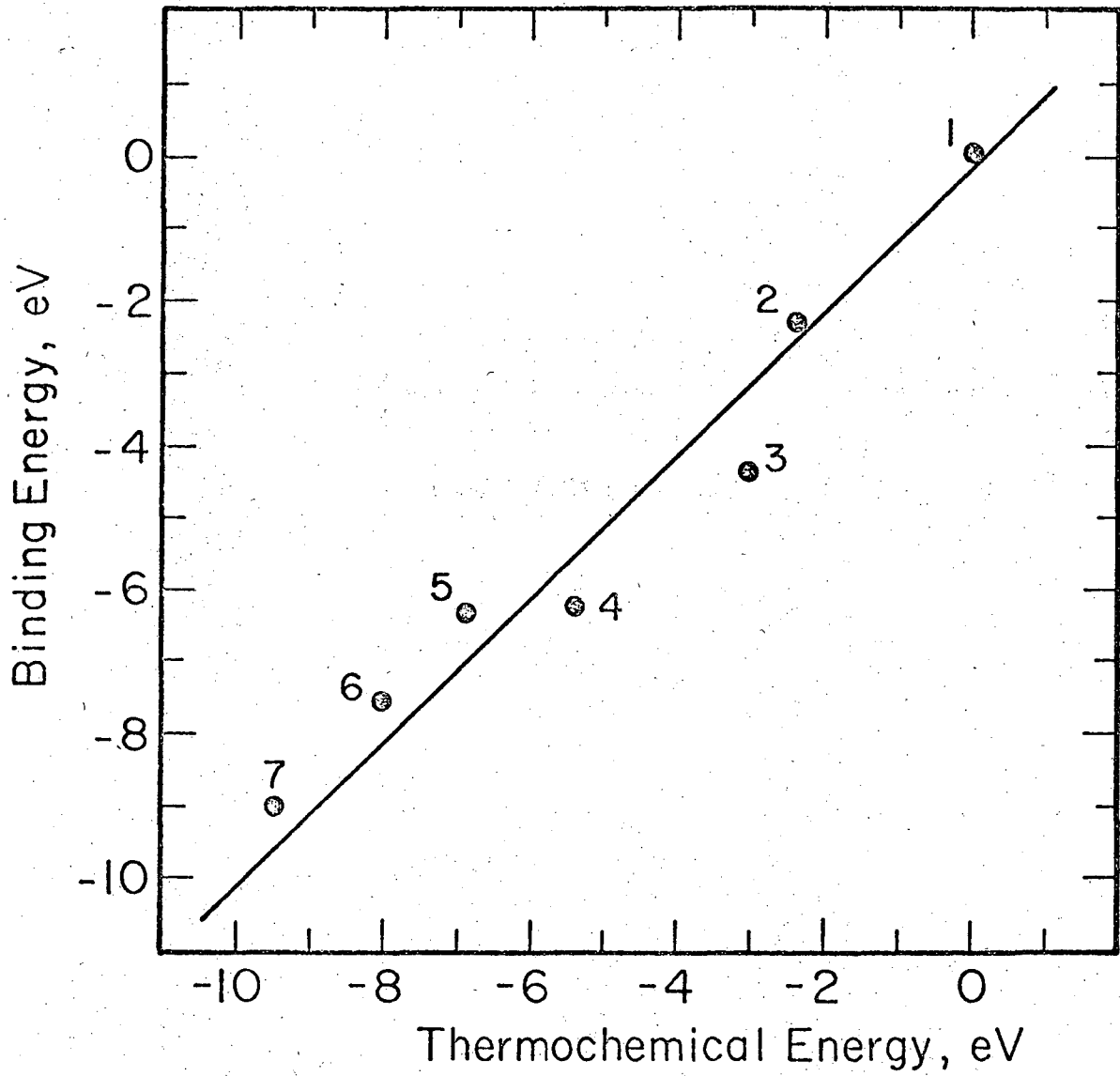
$$U = 287.2 \left[\frac{n(n+1)}{(r_+ + r_-)} \right] \left[1 - \frac{0.345}{(r_+ + r_-)} \right]$$

where n is the charge on the cation and r_+ and r_- are the cationic and anionic radii. The radius of the tetramethylammonium ion (2.43 Å) was calculated from the lattice constants for the chloride, bromide, and iodide salts^{28,29} and the halide ionic radii,³⁰ and the nitrate ion radius was taken as 2.10 Å.²⁷ A previously calculated value of ΔH_8° (89.0 kcal/mol²⁷) was used. The resulting value for the heat of formation of $(\text{CH}_3)_4\text{N}^+(\text{g})$ is 125.4 kcal/mol.

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Fig. 1 Plot of boron $1s$ binding energies vs thermodynamically estimated binding energies.

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