

Gmelin Handbuch
der Anorganischen Chemie

Gmelin Handbuch der Anorganischen Chemie

Achte völlig neu bearbeitete Auflage
8th Edition

B Boron Compounds

1st Supplement Volume 1

Boron and Rare Gases, Hydrogen, and Oxygen

With 68 illustrations

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Springer-Verlag
Berlin · Heidelberg · New York 1980

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LITERATURE COVERAGE: THROUGH 1977

Die vierte bis siebente Auflage dieses Werkes erschien im Verlag von
Carl Winter's Universitätsbuchhandlung in Heidelberg

Library of Congress Catalog Card Number: Agr 25-1383

ISBN 3-540-93417-0 Springer-Verlag, Berlin · Heidelberg · New York
ISBN 0-387-93417-0 Springer-Verlag, New York · Heidelberg · Berlin

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LN-Druck Lübeck

Preface and Introduction

The present first supplement volume complements the 20 volumes on boron compounds (Borverbindungen) that have been published within the New Supplement Series (Erg.-Werk) of the eighth edition of the Gmelin Handbook by uniformly updating the literature to the end of 1977. However, the description in this supplement volume follows largely the Gmelin principle of the last position. The systems boron-hydrogen and boron-oxygen are presented in the first part; the remaining systems will be discussed in subsequent parts of the first supplement volume.

Many examples of organic derivatives and carbon-containing compounds are included in the presentation, particularly in those cases where the basic carbon-free species are not known. However, the carboranes will be discussed in detail in a subsequent part.

As was the case in the volumes of the New Supplement Series, many chapters are already presented in the English language.

The IUPAC nomenclature is adhered to as much as possible; any deviations are clearly indicated. Unless otherwise noted, a positive sign for the chemical shifts of the nuclear magnetic resonance signals indicates downfield from the references $(\text{CH}_3)_4\text{Si}$ for $\delta^1\text{H}$ and $\delta^{13}\text{C}$, $(\text{C}_2\text{H}_5)_2\text{O} \cdot \text{BF}_3$ for $\delta^{11}\text{B}$, aqueous NaNO_3 for $\delta^{14}\text{N}$, and 85% H_3PO_4 for $\delta^{31}\text{P}$.

Frankfurt am Main
Lexington, Kentucky (USA)
May 1980

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Kurt Niedenzu

Boron and Boron Compounds in the Gmelin Handbook

"Bor" (Main Volume Syst.-No. 13)	Historical. Occurrence. The Element. Compounds of B with H, O, N, the Halogens, S, Se, and Te. Literature closing date: end of 1925.
"Bor" (Supplement Volume Syst.-No. 13)	Occurrence. The Element. Compounds of B with H, O, N, the Halogens, S, and C. Literature closing date: end of 1949.
"Borverbindungen" 1 (New Supplement Series Vol. 13)	Boron Nitride. B-N-C Heterocycles. Polymeric B-N Compounds. Literature coverage from 1950 up to 1972.
"Borverbindungen" 2 (New Supplement Series Vol. 15)	Carboranes, Part 1. Nomenclature and Types of Carboranes. Carboranes (without Hetero- and Metallocarboranes, and Higher Carboranes). Literature coverage from 1950 up to 1973 or 1970, respectively.
"Borverbindungen" 3 (New Supplement Series Vol. 19)	Compounds of B Containing Bonds to S, Se, Te, P, As, Sb, Si, and Metals. Literature coverage from 1950 to the end of 1973.
"Borverbindungen" 4 (New Supplement Series Vol. 22)	Compounds with Isolated Trigonal Boron Atoms and Covalent Boron-Nitrogen Bonding (Aminoboranes and B-N Heterocycles). Literature coverage from 1950 to the end of 1973.
"Borverbindungen" 5 (New Supplement Series Vol. 23)	Boron-Pyrazole Derivatives and Spectroscopic Studies on Trigonal B-N Compounds. Literature coverage from 1950 to the end of 1973.
"Borverbindungen" 6 (New Supplement Series Vol. 27)	Carboranes, Part 2. Hetero- and Metallocarboranes. Polymeric Carborane Derivatives. Electronic Properties. Literature coverage from 1950 up to 1974 or 1971, respectively.
"Borverbindungen" 7 (New Supplement Series Vol. 28)	Boron Oxides. Boric Acids. Borates. Literature coverage from 1950 to the end of 1973.
"Borverbindungen" 8 (New Supplement Series Vol. 33)	The Tetrahydroborate Ion and Its Derivatives. Literature coverage from 1950 to the end of 1974.
"Borverbindungen" 9 (New Supplement Series Vol. 34)	Boron-Halogen Compounds, Part 1. Literature coverage from 1950 to the end of 1974.
"Borverbindungen" 10 (New Supplement Series Vol. 37)	Boron Compounds with Coordination Number 4. Literature coverage from 1950 to the end of 1975.
"Borverbindungen" 11 (New Supplement Series Vol. 42)	Carboranes, Part 3. Dicarba- <i>c</i> - <i>oso</i> -dodecaboranes. Literature coverage from 1950 to the end of 1975.

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| <p>"Borverbindungen" 12
(New Supplement
Series Vol. 43)</p> | <p>Carboranes, Part 4. Dicarba-<i>closo</i>-dodecaboranes.
Literature coverage from 1950 to the end of 1975.</p> |
| <p>"Borverbindungen" 13
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Literature coverage from 1950 to the end of 1975.</p> |
| <p>"Borverbindungen" 14
(New Supplement
Series Vol. 45)</p> | <p>Boron-Hydrogen Compounds, Part 1.
Literature coverage from 1950 to the end of 1975.</p> |
| <p>"Borverbindungen" 15
(New Supplement
Series Vol. 46)</p> | <p>Amine-boranes.
Literature coverage from 1950 to the end of 1975.</p> |
| <p>"Borverbindungen" 16
(New Supplement
Series Vol. 48)</p> | <p>Boron-Oxygen Compounds, Part 2.
Literature coverage from 1950 to the end of 1975.</p> |
| <p>"Borverbindungen" 17
(New Supplement
Series Vol. 51)</p> | <p>Borazine and Its Derivatives.
Literature coverage from 1950 to the end of 1976.</p> |
| <p>"Borverbindungen" 18
(New Supplement
Series Vol. 52)</p> | <p>Boron-Hydrogen Compounds, Part 2.
Literature coverage from 1950 to the end of 1976.</p> |
| <p>"Borverbindungen" 19
(New Supplement
Series Vol. 53)</p> | <p>Boron-Halogen Compounds, Part 2.
Literature coverage from 1950 to the end of 1976.</p> |
| <p>"Borverbindungen" 20
(New Supplement
Series Vol. 54)</p> | <p>Boron-Hydrogen Compounds, Part 3.
Literature coverage from 1950 to the end of 1976.</p> |
| <p>"Boron Compounds"</p> | <p>Formula Index
(for all the preceding volumes)</p> |
| <p>"Boron Compounds"
1st Suppl. Vol. 1</p> | <p>Boron and Rare Gases. Boron and Hydrogen.
Boron and Oxygen.
Literature coverage through 1977.</p> |

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1 Das System Bor-Edelgase

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Binäre Verbindungen von Bor mit Edelgasen sind nicht bekannt, doch liegen einige theoretische Überlegungen hierzu vor. Experimentelle Untersuchungen bestätigen die Existenz ternärer Verbindungen. Für die entsprechende Literatur bis 1972 s. Erg.-Werk, Bd. 37 „Borverbindungen“ 10, S. 270/2; die neueren Daten sind im folgenden zusammengefaßt.

Neon. Nach ab initio-SCF-Rechnungen unter Verwendung von Gauß-Orbital-Basisätzen ergibt sich aus Berechnungen der elektronischen Energien und der Bildungswärmen, daß Komplexe von Borverbindungen mit Neon nicht beständig sind, da der berechnete Ladungsaustausch nicht zur Komplexbildung ausreicht [1].

Argon. BF_3 bildet mit Ar ein schwach polares van der Waalssches Molekül, wie massenspektrometrische und Untersuchungen mit Radiofrequenzen bei Gasen (147 K) zeigen. Bei einem 90% Ar und 10% BF_3 enthaltenden Gasgemisch können mehrere Radiofrequenzresonanzen beobachtet werden (s. Fig. bei [2]), die sich linear mit dem elektrischen Feld ändern. Dies steht in Übereinstimmung mit einer symmetrischen Anordnung und einer dreizähligen Symmetrieachse. Ein elektrisches Dipolmoment von etwa 0.2 D beruht vermutlich mehr auf einer Verzerrung am BF_3 -Teilmolekül als auf einem Ladungsaustausch. Im Massenspektrum wird ArBF_2^+ beobachtet [2]. Nach ab initio-SCF-MO-Rechnungen unter Verwendung von erweiterten Gauß-Basisätzen ergeben Energieberechnungen und Bildungswärmen, daß ein im Vergleich zum Ne (durch niedrigeres Ionisationspotential) etwas größerer Ladungsaustausch nicht zur Komplexbildung ausreicht [1].

Krypton. Kr bildet mit BF_3 (ebenso wie Ar) polare van der Waalssche Moleküle, wie massenspektroskopische und Radiofrequenzuntersuchungen im Gaszustand bei 147 K zeigen. Im Massenspektrum wird KrBF_3^+ beobachtet [2].

Literatur zu 1:
[1] R. M. Archibald, D. R. Armstrong, P. G. Perkins (J. Chem. Soc. Faraday Trans. II **69** [1973] 1793/800). — [2] S. E. Novick, P. B. Davies, T. P. Dyke, W. Klemperer (J. Am. Chem. Soc. **95** [1973] 8547/50).

Excitation Energy	Excitation Wavelength	Excitation Frequency	Excitation Wavenumber
0.00000	∞	0.00000	0.00000
0.00171	17520.5	0.00171	17520.5
0.00899	13348.2	0.00899	13348.2
0.01410	10638.3	0.01410	10638.3
0.02038	9322.4	0.02038	9322.4
0.03100	6129.7	0.03100	6129.7
0.04482	4462.3	0.04482	4462.3

2 The System Boron-Hydrogen

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2.1 Monoboron Species

2.1.1 The BH Molecule

For the literature through 1975, see Erg.-Werk (New Supplement Series), Vol. 45 "Borverbindungen" 14, p. 1/18.

The BH species is identified as an intermediate during the reduction of BCl_3 with H_2 in a glow discharge tube by the $^1\Pi \rightarrow ^1\Sigma$ electronic transition [1]. The BH molecule is also proposed as an intermediate formed in an initiation step of the reaction of $(\text{OC})\text{BH}_3$ with O_2 according to $1/2 \text{O}_2 + (\text{OC})\text{BH}_3 \rightarrow \text{BH} + \text{H}_2\text{O} + \text{CO}$, with an estimated $\Delta H_{298}^\circ = -12$ kcal/mole and in a reaction of an intermediate BH_2 molecule with oxygen atoms according to $\text{O} + \text{BH}_2 \rightarrow \text{BH} + \text{OH}$, having an estimated $\Delta H_{298}^\circ = +7$ kcal/mole [2].

Excitation energies and oscillator strengths, presented in table 2/1, and static polarizabilities, $\alpha_{\parallel} = 20.58$ a.u.³, $\alpha_{\perp} = 22.15$ a.u.³, for the BH molecule have been calculated from time-dependent Hartree-Fock equations employing an internuclear distance of 2.3299 a.u. [3]. Utilizing Roothan-Hartree-Fock equations and gauge-invariant Gaussian basis functions magnetic susceptibilities of BH were calculated at a fixed internuclear distance of 2.329 a.u. with the basis combined from the 4s2p set for the B nucleus and the 1s contraction of four primitive functions for H. This gives a molecular energy of -24.918815 a.u., and calculated zero-order and second-order magnetic susceptibilities are $\chi_{\perp}^{(0)} = 36.76 \cdot 10^{-6}$ erg · gauss⁻² · mole⁻¹, $\chi_{\parallel}^{(2)} = -5040 \cdot 10^{-25}$ erg · gauss⁻⁴ · mole⁻¹, $\chi_{\parallel}^{(0)} = -10.70 \cdot 10^{-6}$ erg · gauss⁻² · mole⁻¹, $\chi_{\perp}^{(2)} = 1.07 \cdot 10^{-25}$ erg · gauss⁻⁴ · mole⁻¹ [4, 5]. By using a basis set, A, of 3s2p for boron and 2s for hydrogen an energy of -25.107784 a.u. is obtained and zero-order magnetic susceptibilities are $\chi_{\perp} = 43.77 \cdot 10^{-6}$ erg · gauss⁻² · mole⁻¹ and $\chi_{\parallel} = -11.57 \cdot 10^{-6}$ erg · gauss⁻² · mole⁻¹; and with a minimal basis set, B, of Slater type gauge invariant orbitals an energy of -24.985273 a.u. is derived and $\chi_{\perp} = 35.02 \cdot 10^{-6}$ erg · gauss⁻² · mole⁻¹ and $\chi_{\parallel} = -8.77$ erg · gauss⁻² · mole⁻¹. Proton and hydrogen magnetic shieldings from the calculations using basis sets A and B are given in table 2/2, p. 3 [5].

Table 2/1

Calculated Excitation Energies and Oscillator Strengths (both in atomic units) in BH for Low-Lying Transitions and for Excitations from the 1σ Shell [3].

Low-lying Transitions			Excitations from the 1σ Shell		
Designation	Excitation Energy	Oscillator Strength	Designation	Excitation Energy	Oscillator Strength
$1^1\Sigma^+ - 2^1\Sigma^+$	0.2191	0.0543	$X^1\Sigma^+ - 1^1\Sigma^+$	7.2953	0.00862
$-3^1\Sigma^+$	0.2586	0.0192	$-2^1\Sigma^+$	7.5441	0.00171
$-4^1\Sigma^+$	0.2778	0.0582	$-3^1\Sigma^+$	7.6071	0.00846
$-5^1\Sigma^+$	0.2839	3.09×10^{-5}	$-4^1\Sigma^+$	7.6267	8.034×10^{-5}
$-6^1\Sigma^+$	0.3054	0.000928	$-5^1\Sigma^+$	7.6376	0.00336
$-7^1\Sigma^+$	0.3338	0.232	$-6^1\Sigma^+$	7.6561	4.310×10^{-5}
			$-7^1\Sigma^+$	7.6584	0.00492

Table 2/1 (continued)

Low-Lying Transitions			Excitations from the 1 σ Shell		
Designation	Excitation Energy	Oscillator Strength	Designation	Excitation Energy	Oscillator Strength
1' $\Sigma^+ - 1' \Pi$	0.08923	0.0483	X' $\Sigma^+ - 1' \Pi$	7.1742	0.194
- 2' Π	0.2576	0.0120	- 2' Π	7.5879	8.67×10^{-4}
- 3' Π	0.2783	0.0466	- 3' Π	7.6276	2.52×10^{-4}
- 4' Π	0.2954	0.00421	- 4' Π	7.6402	0.00163
			- 5' Π	7.6722	0.0103

Table 2/2

Calculated Proton and Boron Magnetic Shieldings, σ (in parts per million); $\sigma_{\text{iso}} = 1/3(2\sigma_{\text{I}} + \sigma_{\text{II}})$, $\Delta\sigma = \sigma_{\text{II}} - \sigma_{\text{I}}$ [5].

Nucleus	Basis Set	σ_{I}	σ_{II}	σ_{iso}	$\Delta\sigma$
Boron	A	-595.6	199.1	-330.7	794.7
	B	-669.5	203.0	-378.6	872.5
Hydrogen	A	1.2	33.5	12.0	32.3
	B	14.3	35.2	21.3	20.9

Employing the Hartree-Fock-Roothan method with an estimation of the integrals, force constants for the BH molecule are found to be (a) 0.337 atomic units without variation of the Slater parameter, (b) 0.2215 a.u. with the variation of the Slater parameter (1s), and (c) 0.2247 a.u. with the variation of the Slater parameter (2p). In a related approach in which all the one-electron one- and two-center integrals and two-electron one-center and two-center Coulomb and hybrid integrals were calculated exactly a force constant of 0.259 a.u. was found [6]. A force constant of 10.6 mdyne/Å is calculated for BH using a mathematical formalism which justifies the existence of maximum overlap methods [19]. Restricted basis sets of Gaussian functions within the framework of the one-configuration Hartree-Fock-Roothan approach were employed to calculate the potential curve for BH; the results were used to derive the spectroscopic constants $\omega_e = 2831$, $\alpha_e = 0.1087$, and $\omega_e x_e = 15.80 \text{ cm}^{-1}$ [7]. Application of a half-projected Hartree-Fock (SCF) method yields at the equilibrium internuclear distance of 1.273 Å a total energy of -25.1405 atomic units and a dissociation energy of 3.09 eV for the BH species [8]. The adiabatic ionization energy, in eV, of BH is calculated to be variously 8.44 (from potential curves of ion and neutral molecule, and using SCF approach), 9.63 (from potential curves of ion and neutral molecule, and using CEPA, coupled electron pair approach), 9.23 (from the relationship: ionization energy (BH) = dissociation energy (BH) + ionization energy (H) - proton affinity (B); and using SCF method), 9.70 (from the relationship: ionization energy (BH) = dissociation energy (BH) + ionization energy (H) - proton affinity (B); and using CEPA) [9]. Physical properties obtained from the application of a floating spherical Gaussian orbital method to the BH molecule are listed in table 2/3, p. 4 [10]. Nuclear spin coupling constants, in Hz, calculated for ^1BH are -56 (when $\alpha = 1.0$), -49 ($\alpha = 0.85$), -44 ($\alpha = 0.70$) using an LCAO-SCF- X_α method [11].

In the computation of potential curves for some BH Σ^+ ground states a cumulative selection procedure has been developed for the balanced selection of important configuration functions generated by a configuration interaction technique [12].

Table 2/3

Equilibrium Bond Length, R_e , and Related Spectroscopic Constants (B_e is the rotational constant; α_e measures the strength of interaction between vibrational and rotational ground states; k_e is the force constant; ω is the vibrational frequency; $\omega_e x_e$ is the anharmonicity. The values are calculated by using the floating spherical orbital method. The basis set used in the calculations of each of the last three columns consists of Concentric Double Gaussian (CDG), Single Gaussian (SG), Non-concentric Double Gaussian (NCDG), Triple Gaussian Difference Orbital (TG-DIFF), Triple Gaussian, Two Floating Lobes (TG-2 FL) wavefunctions for the lone pair/inner shell of the boron atom/bonding orbital. Figures in brackets refer to percent error with respect to experimental values) [10].

Property/Units	SG/SG/SG	CDG/CDG/NCDG	TG-DIFF/CDG/TF-2 FL
R_e/a_0	2.4774 (6.4)	2.1992 (-5.6)	2.4391 (4.1)
B_e/cm^{-1}	10.638 (-11.5)	13.499 (12.3)	10.974 (-8.7)
α_e/cm^{-1}	0.283 (-31.3)	0.4958 (20.3)	0.1723 (-58.0)
$k_e/\text{mdyn } \text{\AA}^{-1}$	3.613 (18.5)	4.761 (56.2)	2.6801 (-12.1)
ω_e/cm^{-1}	2579.37 (9.0)	2960.81 (25.1)	2221.33 (-6.1)
$\omega_e x_e/\text{cm}^{-1}$	86.00 (74.1)	138.99 (181.4)	48.19 (-2.4)

From a modified neglect of differential overlap approach for the BH molecule and an internuclear distance of 1.178 Å a calculated heat of formation of 72.1 kcal · mole⁻¹ is obtained [13]. Electron density contours and localizability in BH are discussed during the course of applying three partitioning methods of minimum fluctuations, intersections of isodensity contours for localized molecular orbitals, and the virial partitioning method to LCAO-MO-SCF calculations [14]. Both self-consistent field and configuration interaction wave functions for BH have been compared with respect to electron distributions and electron moments [15]. Application of a self-consistent electron pairs theory to ab initio electronic structure calculations on the BH molecule has given, using an internuclear distance of 2.32 atomic units, the following energy values (in a.u.): E (correlation) = -0.094796, E (SCF) = -25.107545, E (total) = -25.202341 [16]. Ab initio Hartree-Fock-Roothan calculations using double- ζ -basis Cartesian Gaussian functions, configuration 3 σ^2 , X¹ Σ , equilibrium distance 1.23 Å, give a dipole moment of 1.651 D [20].

Theoretical values for a series of molecular properties of BH, table 2/4, p. 5, have been calculated using wave functions derived from the spin-coupled theory [17]. The relations $\alpha^n + \beta^n / \langle p^n \rangle = f_1(S, S', \dots)$, and $(\alpha + \beta)^n / \langle p^n \rangle = f_2(S, S', \dots)$, where p is the electron momentum, α and β the Slater-type effective parameters, and $S, S', \dots$ the overlap integrals, between average functions, $\langle p^n \rangle$, were calculated; and values of $\langle p^{-1} \rangle / 2$ and $\langle p^2 \rangle / 2$ (the kinetic energy) were compared to those obtained by SCF Hartree-Fock wavefunctions [18]. The size of the lone pair LMO of BH has been calculated to be larger than the bond pair LMO using a double-zeta basis set SCF method [21]. Application of the effective pair correlation energy method suggests that the pair correlation energies involving core electrons are transferable whereas other pair energies depend on the localization [22]. Wavefunctions of BH have been calculated by the Hartree-Fock-Roothan method in frozen core AO approximation of the valence theory by using sp-lobed Gaussian-type basis functions [23].

It is suggested that the BH molecule can be decomposed by the reaction $\text{O} + \text{BH} \rightarrow \text{BO} + \text{H}$, with a calculated $\Delta H_{298}^\circ = -113 \text{ kcal} \cdot \text{mole}^{-1}$ [2].