

REFERENCES

- (1) Interim Report of the Subcommittee on the Nomenclature Phosphorus Compounds, Sept., 1963.
- (2) (a) "Definitive Rules for Nomenclature of Inorganic Chemistry. 1957 Report of the Commission of the Nomenclature of Inorganic Chemistry," *J. Am. Chem. Soc.*, **82**, 5523 (1960); (b) "Tentative Rules for Nomenclature of Organic Chemistry, 1961," Butterworths Scientific Publications, London, 1962, sect. C106.1; (c) ref. 2b, sect. C106.2.
- (3) W. M. Latimer, "Oxidation Potentials," 2nd Ed., Prentice-Hall, Inc., Englewood Cliffs, N. J., 1952, p. 66.
- (4) "Inorganic Syntheses," Vol. 1, McGraw-Hill Book Co., New York, N. Y., 1939, p. 172.
- (5) Ref. 2a, sect. 5.213.
- (6) "The Naming and Indexing of Chemical Compounds from *Chemical Abstracts*," Subject Index to *Chem. Abstr.*, **56**, IN-98N (Jan.-June, 1962).
- (7) N. V. Sidgwick, "The Chemical Elements and Their Compounds" Oxford University Press, 1950, p. 1238.
- (8) One or more of these is implied in ref. 7, pp. 1228-1229.
- (9) Ref. 7, p. 1228.
- (10) Ref. 2a, sect. 5.214.
- (11) Ref. 7, p. 1225.
- (12) Ref. 3, p. 64.
- (13) Ref. 7, p. 1222.
- (14) Ref. 2a, sect. 3.14.
- (15) A. A. Woolf and N. N. Greenwood, *J. Chem. Soc.*, 2200 (1950).
- (16) Ref. 2a, sect. 3.16.
- (17) Ref. 2a, sect. 3.17.
- (18) Ref. 6, sect. 399.
- (19) Ref. 2b, sect. 107.1.

Nomenclature Problems in Boron Chemistry*

By ROY M. ADAMS

Geneva College, Beaver Falls, Pennsylvania

Received January 20, 1964

In its position as the only electron-deficient nonmetal, boron is involved in structural and bonding problems which are in many respects unique. They also often parallel established and sometimes opposing viewpoints from metallic and nonmetallic chemistry and nomenclature. The more difficult problems in boron nomenclature arise from the conflicting demands of simplicity for boron chemistry and compatibility with general nomenclature of other elements.

Boron seems to be always found in nature bonded to oxygen.¹ Traditional nomenclature served reasonably well for this type of compound.

$B(OH)_3$ boric acid	$(HBO_2)_n$ metaboric acid
(ortho)	
BO_3^{4-} orthoborate ion	$(BO_2^-)_n$ metaborate ion
(nonexistent in aqueous systems)	[probably $B(OH)_4^-$ in aqueous systems] ²

Like other polyhydroxylic acids, boric acid condenses to form a number of complex anions. In minerals these seem to be of endless variety and states of hydration. However, they all appear to be derived from one of the three following ions by hydration and/or condensation.

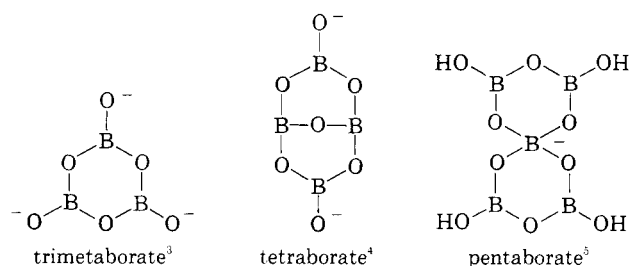


Figure 1.

In all these condensed anions the presence of the boroxin (B_3O_3) ring is noteworthy. Names completely describing these anions involve all the traditional problems of heterocyclic nomenclature, including fused and spiro ring systems as indicated above.

The nonoxygenated chemistry of boron has stemmed largely from the work of Stock on the boron hydrides during the early part of this century.³ The elucidation of the structures during the past decade and the evidently unusual bonding involved have contributed continuing new nomenclature demands. Chemists have in general followed Stock's lead and named the boron hydrides similarly to the silicon hydrides, *i.e.*, with a Greek prefix to indicate the number of boron atoms and the suffix *ane* to indicate a covalent hydride, *e.g.*

 B_2H_6 diborane $B_{10}H_{12}$ tetraborane

Due to interest in the high heats of combustion of these materials, an intensive government-sponsored research effort was begun in about 1950 into the chemistry of these substances.^{7a} In 1952 a group met under the prime contractors' sponsorship and the chairmanship of the late Dr. George W. Schaeffer to attempt to establish a recommended nomenclature for the burgeoning chemistry. A paper on "The Nomenclature of Boron Compounds" presented by Dr. Schaeffer and Dr. Thomas Wartik before the Division of Chemical Literature at the 125th meeting of the American Chemical Society, March 25, 1954, in Kansas City was subsequently reviewed in

* Adapted from the paper presented before the Divisions of Inorganic Chemistry and Chemical Literature, 136th National Meeting of the American Chemical Society, Atlantic City, N. J., September 18, 1959.

some detail.^{7b} This work was developed further by an Advisory Subcommittee on the Nomenclature of Organic Boron Compounds (Dr. Kurt L. Loening of *Chemical Abstracts* Service, chairman) under the Nomenclature Committee of the Division of Organic Chemistry (Dr. John Fletcher, chairman). A summary report was presented to the parent committee in 1958 and referred back to the subcommittee for further study. After the establishment of the Division of Inorganic Chemistry and in 1958 of its Committee on Nomenclature (Dr. Schaeffer, chairman), the boron nomenclature subcommittee, still under the chairmanship of Dr. Loening, became a subcommittee of this committee. Although the premature death of Dr. Schaeffer in 1959 has delayed completion of definitive work, the recommendations of the boron subcommittee have been followed by most workers in the field^{7c} and in part by *Chemical Abstracts*^{7d} as the basis for their nomenclature and are reviewed and referred to here as the "boron report."

The report recommended the use of an Arabic numeral in parentheses at the end of the name to indicate the number of hydrogen atoms in a borane, where necessary for identification. This has been widely accepted, e.g.

Compound	B ₅ H ₉	B ₅ H ₁₁
boron report	pentaborane(9)	pentaborane(11)
earlier names	stable pentaborane pentaborane	unstable pentaborane dihydropentaborane

The simplest of the boranes, borane(3) or just borane = BH₃ (formerly called borine), then becomes a basis for the naming of trivalent boron compounds; thus BF₃ can be called trifluoroborane as well as boron (tri)fluoride. This use of borane as a parent compound was at first thought to be the most controversial part of the report, but it has received surprisingly wide acceptance, even in preference to well-established names, e.g., trimethoxyborane for methyl borate. Other systems which have been used include organometallic-type nomenclature and variations of an organic phosphorus-type nomenclature^{8a}; e.g., the compound ClB(OCH₃)₂ has been called:

dimethoxychloroborane	(boron report)
dimethoxyboron chloride	(organometallic system)
dimethoxychloroborine	(phosphorus-type nomenclature)
dimethyl chloroboronate	
dimethyl borochloridate	

Perhaps the major argument against the use of the phosphorus-type nomenclature has been the confusion as to details of its application to such boron compounds. There are also many who would prefer to limit the -ine suffix for hydrides to those which have an unshared electron pair on the central atom.

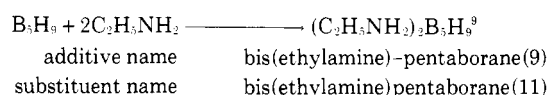
The borane system helps to correlate the chemical fact that all these compounds tend to behave similarly as Lewis acids. The adducts of these compounds with Lewis bases can then be given simple additive names.

H ₃ N:B(OCH ₃) ₃	(CH ₃) ₃ P:BH ₃
ammonia-trimethoxyborane	trimethylphosphine-borane

There have been suggestions that names for neutral adducts of this type should use the total liganacy of the boron skeleton for the numerical suffix and refer to the neutral ligands as substituents.^{8b}

	(CH ₃) ₃ NBH ₃	(CH ₃ CN) ₂ B ₁₀ H ₁₂
additive name	trimethylamine-borane(3)	bis(acetonitrile)-decaborane(12)
substituent name	(trimethylamine)-borane(4)	bis(acetonitrile)-decaborane(14)

The latter suggestion presents advantages if coupled with a boranate system for ionic boron compounds, in conversion from the neutral to ionic species of similar structure (see below); i.e., (trimethylamine)borane(4) is more similar to boran(4)ate than is trimethylamine-borane to tetrahydroborate. There are the disadvantages that in some cases such adducts may appear to be derivatives of a different hydride of the same number of boron atoms, e.g.



and incompatibility with established additive names for most other "Lewis salts," e.g., acetone-aluminum chloride and trimethylamine-gallane.¹⁰

The positional designation suggested by the boron subcommittee has received wide acceptance. The system is based on a "Ring Index" type numbering¹¹ of a planar projection of the simpler hydrides.

For example, Fig. 2 shows the widely accepted skeletal numberings for pentaborane(9) and decaborane(14). Since

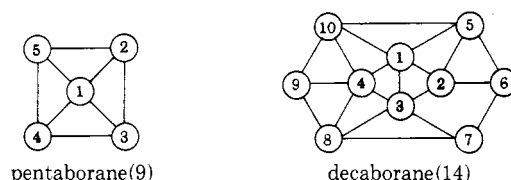


Fig. 2.—Skeletal numbering by planar projection.

such structures were first defined by X-ray diffraction techniques, the earlier workers tended to use numbering systems based on reflection symmetries.¹² Others have suggested that all numberings should be based on an icosahedral numbering system (Fig. 3) since this skeletal arrangement seems to be the basis for most of the boranes.

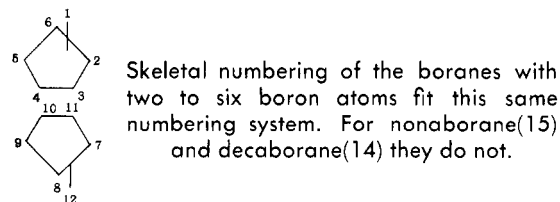


Fig. 3.—Icosahedral numbering system.

Since much of the chemistry of the higher boranes has developed from decaborane(14), still other workers have wanted to extend its numbering system to all the boranes and their ions in the B₈ to B₁₂ region.

The attached groups may be referred to as terminal (τ) or bridging (μ). Indications that the most stable ligands to boron in many derivatives involve π -bonding

leads to a nomenclature problem since organometallic nomenclature has rather extensively used π - to refer to μ -bonding (Fig. 4).

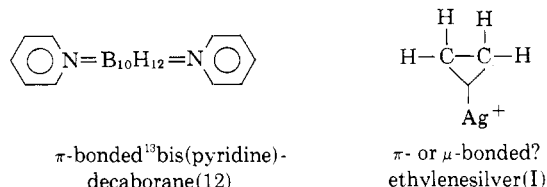


Fig. 4.—A question of bonding nomenclature.

For the closed polyhedral hydrides, one apex is numbered first followed by belt atoms, followed by the opposite apex (Fig. 3). "Clovo" may be used to describe such structures.¹⁵ The recently discovered isomers¹⁶ of octadecaborane(24) together with the asymmetry of the second isomer simultaneously raise the problems of isomerism, possible optical activity, and new positional numbering problems (Fig. 5).

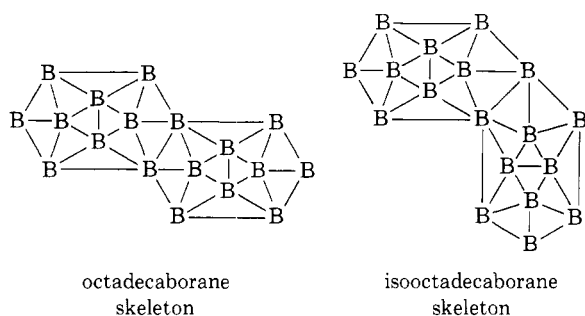


Fig. 5.—Isomerism in the boranes.

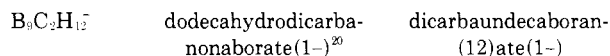
The recently reported icosaborane(16)¹⁷ also cannot be handled by previously described numbering systems. The lability of bonds in the boranes apparently makes isomerism a relatively rare problem, so that terms such as symmetrical and asymmetrical or normal and iso may handle the situation.

In hydrides or ions in which hydrogen in BH_2 groups is substituted, the designation of which hydrogen is replaced can apparently be handled by prefixes such as *exo* or *endo*; e.g., the compound in Fig. 4 may be called *exo*-bis(pyridine) decaborane(12).

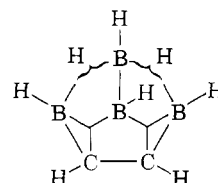
The use of systematic nomenclature^{18a} for the hydroboron ions has been rather widely accepted. Since the

oxidation numbers of the boron atoms are often fractional in the polyboron ions, the boron report recommends the use of ionic charge numbers^{18b} rather than Stock numbers as a suffix. Other names have persisted more strongly in this area than in perhaps any other area or inorganic boron nomenclature. The disadvantages of extending the borohydride-type name to substituted and polyboron ions are obvious. The boranate nomenclature used by the Wiberg school and most German workers,¹⁹ has advantages if a majority of these ions have hydrogen as the most abundant ligand, as appears to be the case. The systematic and boranate-type names are compared in Table I.

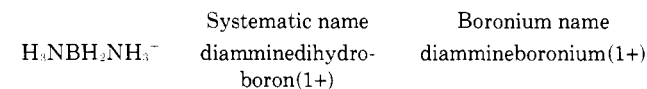
The nomenclature of polyboron ions containing heteroskeletal atoms also needs definition. Logical extension of the two types of names would apparently lead to:



For neutral compounds containing skeletal heteroatoms, the "a" system normally uses as a suffix the total number of skeletal atoms. Some have wondered whether in noncarbon-based skeletons this is necessary. However, it appears to be for locators, e.g.



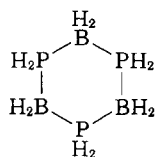
2,3-dicarbahehexaborane(8) not 2,3-dicarbatettraborane(8).²¹ For cations some have used the stem boronium.



The nomenclature of rings and chains containing alternating nonmetal atoms appears to be swinging toward a siloxane²²-type system.

Table I

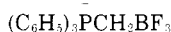
	Systematic name	Boranate name
BF_4^-	Tetrafluoroborate(1-)	Tetrafluoroboranate(1-)
permissible abbreviation	Fluoroborate	Tetrafluoroboranate
BH_4^-	Tetrahydromonoborate(1-)	Monoboran(4)ate(1-)
	or tetrahydridoborate(1-)	
permissible abbreviation	Hydroborate	Boranate
$\text{BH}(\text{OCH}_3)_3^-$	Trimethoxyhydroborate(1-)	Trimethoxyboran(4)ate(1-)
$\text{B}_{10}\text{H}_{13}^-$	Tridecahydrodecaborate(1-)	Decaboran(13)ate(1-)
$\text{C}_5\text{H}_5\text{NB}_{10}\text{H}_{13}^-$	Pyridine-tridecahydrodecaborate(1-)	Pyridine-decaborane(13 or 14?)ate(1-)
$\text{B}_{12}\text{Cl}_{12}^{2-}$	Dodecachlorododecaborate(2-)	Dodecachlorododecaboran(12)ate(2-)
Advantages	Consistency with nomenclature of other inorganic ions	More similar to the names of related neutral hydrides
	Simpler names if most of the ligands are not hydrogen	Simpler names if most of the ligands are hydrogen
	Does not introduce another number in the name when numbers are already needed for positional locators and charge suffixes	



cyclotriborphosphane (siloxane-type name)

An unsettled problem is the assumed ligancy for nitrogen and boron when such names are used; *i.e.*, should it be 3 or 4? In these names the order of precedence of elements in the name is just reversed from that in the "a" system, *i.e.*, B, Si, C, P, N, S, O. The trivial names borazine (for $B_3N_3H_6$) and boroxin for $H_3B_3O_3$ have been generally accepted although some workers still use the German "ole" suffix, which implies a five-membered heterocycle in English nomenclature.¹² In other cases "Ring Index"¹² nomenclature is recommended.

The many possibilities for zwitterions in compounds containing boron and a group-V element have generally been handled as follows:

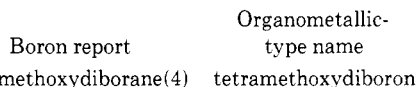


triphenylphosphinemethylene-trifluoroborane

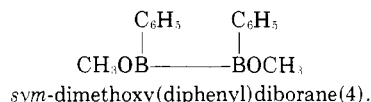
The Commission on the Nomenclature of Organic Chemistry of the IUPAC²³ has tentatively recommended names of the type triphenylphosphonio(trifluoroborato)-methane.

For the metal borides stoichiometric names have generally been used: CaB_6 , calcium hexaboride; AlB_{12} aluminum dodecaboride.

For other binary compounds binary names also suffice; *e.g.*, B_2Cl_4 , diboron tetrachloride. Some have extended this type of name to potential derivatives:



However, substitutive-type nomenclature would be more consistent with established nomenclature, particularly when the groups are different, *e.g.*



In summary, a number of current problems in boron nomenclature have been listed. Nomenclature groups on both the national and international levels are seeking the best solutions. It is human to prefer standardization for others and individual freedom for one's self. As chemistry grows, so must nomenclature standards to prevent chaos in communication. The boron subcommittee

welcomes constructive criticisms and suggestions in any area with which it is or should be concerned.

REFERENCES

- (1) W. A. Gale, "Advances in Chemistry Series No. 32," American Chemical Society, Washington, D. C., 1961, pp. 13-19.
- (2) J. V. Edwards, G. C. Morrison, V. F. Ross, and J. W. Schultz, *J. Am. Chem. Soc.*, **77**, 266 (1955).
- (3) C. L. Christ and J. R. Clark, *Acta Cryst.*, **9**, 830 (1956); *ibid.*, **16**, 975 (1963).
- (4) N. Morimoto, *Mineral J. (Sapporo)*, **2**, 1 (1956); *Chem. Abstr.*, **52**, 12,687 (1958).
- (5) W. H. Zachariasen, *Z. Krist.*, **98**, 266 (1937).
- (6) A. Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, N. Y., 1933.
- (7) (a) D. R. Martin, ref. 1, pp. 1-4; (b) *Chem. Eng. News*, **32**, 1441 (1954); **34**, 560 (1956); (c) S. H. Bauer, "Boron Hydrides and Related Compounds" in "Encyclopedia of Chemical Technology," 1st Suppl. Vol., 1957, pp. 103-104; (d) "The Naming and Indexing of Chemical Compounds," reprint of the introduction to the Subject Index of *Chemical Abstracts*, Vol. 56, 1962, paragraphs 287-292.
- (8) (a) *Chem. Eng. News*, **30**, 4515 (1952); (b) W. Knoth, *J. Am. Chem. Soc.*, **86**, 115 (1964).
- (9) A. F. Zhigach, E. B. Kazakova, and I. S. Antonov, *J. Gen. Chem. USSR*, **27**, 1725 (1957).
- (10) D. F. Shriver and C. E. Nordam, *Inorg. Chem.*, **2**, 1298 (1963).
- (11) A. M. Patterson, L. T. Capell, and D. F. Walker, "The Ring Index," 2nd Ed., American Chemical Society, Washington, D. C., 1960.
- (12) J. S. Kaspar, C. M. Lucht, and D. Harker, *J. Am. Chem. Soc.*, **70**, 881 (1948).
- (13) B. M. Graybill and M. F. Hawthorne, *ibid.*, **83**, 2673 (1961).
- (14) S. Winstein and H. J. Lucas, *ibid.*, **60**, 836 (1938).
- (15) R. M. Adams, *Inorg. Chem.*, **2**, 1087 (1963).
- (16) R. P. Simpson, K. Folting, and W. N. Lipscomb, *J. Am. Chem. Soc.*, **85**, 1879 (1963).
- (17) L. B. Friedman, R. B. Dobrott, and W. N. Lipscomb, *ibid.*, **85**, 3505 (1963); N. E. Miller and E. L. Muetterties, *ibid.*, **85**, 3506 (1963).
- (18) (a) Report of the IUPAC Commission on Inorganic Nomenclature, *ibid.*, **82**, 5523 (1960); (b) R. V. B. Ewens and H. Bassett, *Chem. Ind. (London)*, 131 (1949).
- (19) H. Nöth, *Angew. Chem.*, **73**, 37 (1961).
- (20) D. Grafstein and J. Dvorak, *Inorg. Chem.*, **2**, 1128 (1963).
- (21) T. P. Onak, R. E. Williams, and H. G. Weiss, *J. Am. Chem. Soc.*, **84**, 2830 (1962).
- (22) *Chem. Eng. News*, **30**, 4517 (1952).
- (23) IUPAC, "Tentative Rules for Nomenclature of Organic Chemistry, 1961" Butterworth & Co. (Publishers) Ltd., London, 1962, section C, rule C-87.
- (24) R. J. Brotherton, A. L. McCloskey, L. L. Petterson, and H. Steinberg, *J. Am. Chem. Soc.*, **82**, 6242 (1960).