

Early birds: the chiral boranes

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Abstract. The state of the art in the field of chiral compounds with boron cages is discussed. The synthesis of chiral decaborane derivatives is described.

Chiral compounds with borane frameworks still remain the early birds of boron chemistry despite of the 26 year long history beginning with the pioneering paper¹ by W.R.Hertler in 1964. So far, only ten papers¹⁻¹⁰ dealing explicitly with optically active boron cage species have been published, concerning approximately twenty individual compounds.

The absolute configuration has been disclosed in a single case by an X-ray diffraction study⁹ and determined in five other cases by correlation, while it remains obscure with other compounds.

The following list of bona fide all optically active species with boron cages itself reflects the unsatisfactory state of affairs in the stereochemistry of borane derivatives. Such listing of all chiral organic species would not be possible already hundred years ago.

This report is aimed at awaking the boron community and provoking new experimentation in this area of stereochemistry. Being aware of the impact of the investigation of chiral organic compounds on the development and understanding of organic chemistry we expect the same effect of such research in boron chemistry as well.

Hertler¹ resolved the species 1 and converted (+)1 to 2 in order to decide between two possible positional isomers^{1,2}. Zakharkin and coworkers³ were first to partially resolve the first dicarba-*nido*-undecaborate anion (-)3, and to obtain the first chiral *nido*-dicarbaborane 6 and *closo*-dicarbaborane 7. Hawthorne et al⁶ extended the experiments of the latter authors and proved the nonfluxionality of the pentagonal "open face" in the dicarba-*nido*-undecaborate ions.

Our work afforded the first optically active species with a decaborane framework (9-11). Their absolute configurations became known, long after the actual synthesis, by correlation to the species (+)11 whose absolute configuration was disclosed by X-ray diffraction (Fig. 1) as the first one with boron cage species⁹.

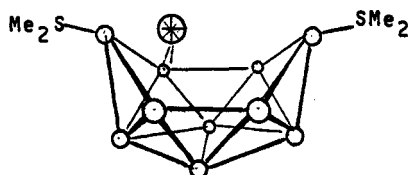


Fig. 1
 σ -(+)-5-Br-6,9-(Me₂S)₂-B₁₀H₁₁

List of all so far reported optically active species
with borane frameworks

Code number	Compound	$[\alpha]_D^{20}$	Absolute config. ^{a)}	References
1	2-Me ₃ N-7-CO-B ₁₀ H ₈	+22° -14°	-----	1,2 1,2
2	2,7-(Me ₃ N) ₂ -B ₁₀ H ₈	+13°	-----	1,2
3	7-Ph-7,8-C ₂ B ₉ H ₁₁	-10.0° + 9.8°	-----	3,4 4
4	7-Ph-8-Me-7,8-C ₂ B ₉ H ₁₀ ⁻	+28.0°	-----	4
5	7-Ph-7,9-C ₂ B ₉ H ₁₁	+14.6°	-----	4
6	7-Ph-7,8-C ₂ B ₉ H ₁₂	-10.2°	-----	3
7	1-Ph-3-p-Tol-1,2-C ₂ B ₁₀ H ₁₀	+18.0°	-----	3
8	4-Br-1,2-C ₂ B ₁₀ H ₁₁	+12.5°	ρ^b)	6
9	5-Br-6,9-(THC) ₂ -B ₁₀ H ₁₁ ^{d)}	-49.5° +16.5°	ρ^b) σ^b)	5 5
10	5-Br-6--THC-9-Me ₂ S-B ₁₀ H ₁₁	+39.6°	σ^b)	5
11	5-Br-6,9-(Me ₂ S) ₂ -B ₁₀ H ₁₁	-72.7° +70.0°	ρ^b) σ^c)	5 5,9
12	i-B ₁₈ H ₂₂ ^{e)}	+2250°	-----	7
13	5,6-C ₂ B ₈ H ₁₂	-920°	-----	8

a) σ and ρ indicate the direction of deployment of the numbering spiral⁵.

b) By correlation to the species (+)11.

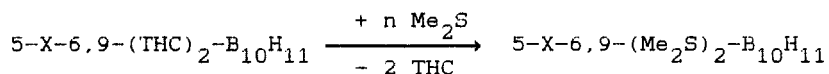
c) Absolute configuration determined by X-ray⁶.

d) (+)Thiahomocamphane¹², m.p. 198°C, $[\alpha]_D^{20}$ +28.8°.

e) Along with the relevant α - and l -anions.

To obtain the optically active species 9-11 it was necessary to develop first a method of the peripheral substitution of decaborane¹¹ and to synthesize the hitherto unknown (+)thiahomocamphane [THC]¹². Specific nomenclature convention has been modified in order to simplify and precise the communication on chiral borane derivatives⁵.

Enormous effect of sterical hindrance and of the inductive effect of bromine on the rates of ligand displacement reactions were observed⁵:



X	H	(-)Br	(+)Br
Relat. rate	500	25	1
Half time	9h	>1 week	>1/2 year

The dramatic difference between both diastereoisomers is due to a very subtle sterical hindrance which could not be detected with a nonchiral auxiliary base instead of THC.

The insertion of acetylene into (-)9 led to the chiral species 8, the first known 4-substituted *ortho*-carborane⁶.

Methanolysis of (-)11 afforded unexpectedly a symmetric species $4\text{-Me}_2\text{S-7-MeO-B}_9\text{H}_{12}$ ^{10,19} due to unique type of "vicinal substitution".

Resolution of the first and still sole binary borane to enantiomers 12 has been carried out on $i\text{-B}_{18}\text{H}_{12}$. The enantiomers excel in extreme values of specific rotation, and their ORD curves show a unique twofold Cotton effect⁷.

The attempted resolution of the $d,l\text{-5,6-C}_2\text{B}_8\text{H}_{12}$ led unexpectedly to the first asymmetric synthesis with complete conversion of the racemate to a single enantiomer 13 due to the unique fluxionality of the intermediate $[\text{C}_2\text{B}_8\text{H}_{11}]^-$ ion⁸.

Some tasks for the future: Contrive general methods for unequivocal determination of absolute configurations. Adept the effective resolution methods of organic chemistry for protochiral boron cage species. Chiralize other basic frameworks. Exploit the chiral species for elucidation of reaction pathways and for kinetic studies, etc.

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