A Reinvestigation of the Existence of 1,3,2-Dioxaborinium(1+) Cations

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1,3,2-Dioxaborinium(1+) Salts, 2-Perchlorato-1-oxa-3-oxonia-2-borato-cyclohexadienes,
2-Triflato-1-oxa-3-oxonia-2-borato-cyclo-hexadienes

It is shown that the previously reported 1,3,2-dioxaborinium salts containing tri- 
cooridnated boron are in fact tetracoordinated coordination compounds. The same holds 
for the corresponding triflates.

Introduction

The chemistry of boron cations was a field long 
neglected [2]. Meanwhile, many cATIONS containing 
tetracoordinated boron have been reported [3] and 
their chemistry has been explored. In addition there 
exists scattered information relating to tri- [4-8] 
and dicoordinated [9, 10] boron cations. Unlike 
carbenium ion chemistry their role in boron chem-
istry is not yet well understood. This situation, 
however, will quickly change as their chemical 
behaviour is being studied.

Having evaluated some governing factors relating 
to the stability of dicoordinated cations of boron [9] 
we became interested in those of coordination 
number 3 because their stability should also depend 
on mesomeric effects. Such effects could prevail in 
tricoordinated 1,3,2-dioxa-borinium(1+) salts 1 
which were isolated as perchlorates and hexachloro-
antimonates [5-7]. One important argument for 
the presence of a tricoordinated boron atom in 
these compounds was an $^11B$ NMR signal at ~ 26 
ppm which is typical for a CBO$_2$ structural unit [11].

Results

Since the triflate group is an exceptionally good 
leaving group we turned our attention to the pre-
paration of the triflates 6a and 6b. However, these 
compounds (Table I) contain tetracoordinated 
boron by $^1B$ NMR evidence. Therefore we repeated 
the preparation of 5a and 5b. Although we could 
easily obtain these compounds [12], they exhibited, 
in our hands, $^11B$ NMR data for tetracoordinated 
boron in CH$_2$Cl$_2$ or benzene solution. Therefore 
they have to be described by formula 2 rather than 
by 1. Evidence for this structure rests also on the 
IR spectra which show well defined bands at 1010 
and 1145 cm$^{-1}$ typical for a monodentate ClO$_4$- 
species of local C$_3$V symmetry. In addition, a band 
of medium intensity is found at 918 
cm$^{-1}$, which is also indicative of coordinated ClO$_4^-$ of C$_3$V symmetry [14].
Table I. NMR data of 1,3,2-dioxa-bora-cyclohexadiene-compounds 5 and 6; δ-values in ppm.

<table>
<thead>
<tr>
<th>Compound</th>
<th>δ^{11}B</th>
<th>Solvent</th>
<th>δ^{19}F</th>
<th>Solvent</th>
<th>δ^{1}H</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>5.6</td>
<td>CH₃CN</td>
<td>8.1</td>
<td>CH₂Cl₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5b</td>
<td>5.5</td>
<td>CH₃CN</td>
<td>6.8</td>
<td>CH₂Cl₂</td>
<td></td>
<td></td>
</tr>
<tr>
<td>6a</td>
<td>8.6</td>
<td>CH₂Cl₂</td>
<td>-77.09</td>
<td>CDCl₃</td>
<td>2.3 (S, CH₃)</td>
<td>CDCl₃</td>
</tr>
<tr>
<td>6b</td>
<td>H₂O</td>
<td>CH₂Cl₂</td>
<td>7.26-7.98 (M, C₆H₅)</td>
<td>10.95 (S H₂O)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C₆H₃B(OH)₂</td>
<td>29.4</td>
<td>CH₂Cl₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound ratio</th>
<th>δ^{11}B</th>
<th>Intensity ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₃B(OH)₂ + BzacH</td>
<td>29.9</td>
<td>(2:1)</td>
</tr>
<tr>
<td>1:2</td>
<td>29.1</td>
<td>(1:1)</td>
</tr>
<tr>
<td>1:3</td>
<td>29.9</td>
<td>(1:1)</td>
</tr>
</tbody>
</table>

This signal disappears on addition of D₂O; BzacH = benzoylacetone; solvent CH₂Cl₂.

perchlorate (found: δ^{35}Cl = 1000 ppm, h(1/2) 65 Hz, literature [13]: δ^{35}Cl = 1000 ppm) [13]. Evidence for coordination of acetonitrile is obtained also from 1H NMR spectra of a 1:1 solution of 5a and CH₃CN in CDCl₃ which shows a 9 Hz downfield shift for the signal of acetonitrile although part of the perchlorate precipitates from the solution, and this may have changed the stoichiometry.

In the solid state, however, the structure of 5a and 5b is best represented by 4. The compounds hydrolyse fairly readily in CH₂Cl₂ solution. Thus the 11B NMR signals reported previously for 5a and 5b are most likely due to phenylboronic acid [13].

The triflates 6a and 6b, prepared in analogy to the perchlorates, are sharp melting, powdery solids and are more soluble in dichloromethane than the corresponding perchlorates. They show 11B chemical shifts (Table I) typical for tetracoordinated boron. All NMR data for 6a are in accord with a structure containing a coordinated triflate group in analogy to 4. Therefore, the comparison of the perchlorates and triflates very strongly point to the conclusion that none of these compounds is truly ionic, i.e. are salts of a 1,3,2-dioxaborinium(1+) cation. However, the electronegative group X = ClO₄ or SO₂CF₃ may be readily replaced by a suitable base, the compounds thus acting as a tricoordinate boron cationic species with a loosely coordinated anion. This situation thus resembles the highly reactive compounds CpM(CO)₂BF₄ (M = Mo, W) [16].

The formation of compounds 5 and 6 seems to occur in two steps. 11B NMR signals in an approximately 1:1 ratio are recorded on addition of the diketone to a solution of phenylboronic acid (see Table I), one at δ^{11}B=27, the other at 6.8 ppm. Since this intensity ratio changes in favour of the high field signal at higher diketone ratios an equilibrium situation (1) is indicated. The addition of either HClO₄ or HOSO₂CF₃ then produces the 11B NMR signal of 5a and 6a respectively, according to (2a, b).

In contrast, 6b could only be isolated as a hydrate, and we assume that this compound has the constitution of the intermediate 7 [15].

FORMULAE II

FORMULAE II

\[ (\text{a}) + \text{HX} \Rightarrow \]

\[ \text{R}^2\text{R}^1\text{C} = \text{O} + \text{H}_2\text{O} \Rightarrow \]
Experimental

All manipulations were carried out under rigorously dry conditions in a nitrogen atmosphere using standard high vacuum or Schlenk tube techniques. Solvents were carefully dried and stored under di-nitrogen. Most of the starting materials are commercially available and were used as such. Anhydrous perchloric acid was prepared by extracting a mixture of oleum and 70% perchloric acid in dichloromethane [17]. The solution obtained was standardized by base titration.

IR-spectra: Perkin-Elmer 325, Nujol/hostaflon mulls; NMR: Jeol FX 90 and Bruker WP200; standards for $^1$H: tetramethylsilane; $^1$B: F$_3$B·O(C$_2$H$_5$)$_2$ ext.; $^{35}$Cl: 1 M NaClO$_4$ solution, ext.

General method: A two necked, round bottomed flask (100 ml) fitted with a dropping funnel and reflux condenser was charged with dibenzoylmethane, phenylboronic acid and 25 ml CH$_2$Cl$_2$. This flask was immersed in an ice-salt bath and the mixture stirred magnetically. A solution of triflic acid (or HClO$_4$) in CH$_2$Cl$_2$ was added dropwise, and a yellow powder starts separating after addition of ~1/5 of the acid. Having completed the addition stirring was continued for another 2 h, the solid filtered, washed with 20 ml of CH$_2$Cl$_2$ and dried in vacuo.

Results are summarized in Table II.

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Table II. Preparative and analytical results for the perchlorates and triflates, 5 and 6.

<table>
<thead>
<tr>
<th>Reactants (g (mmol))</th>
<th>PhB(OH)$_2$ Diketone</th>
<th>Acid</th>
<th>CH$_2$Cl$_2$ yield</th>
<th>m.p. [°C]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Perchlorato-2,4,6-triphenyl-1-oxa-3-oxonia-2-borata-cyclohexadien(3,5) (5a)</td>
<td>(5.00)</td>
<td>(4.96)</td>
<td>(4.96)</td>
<td>111$^a$</td>
</tr>
<tr>
<td>2-Perchlorato-2,4-diphenyl-6-methyl-1-oxa-3-oxonia-2-borata-cyclohexadien(3,5) (5b)</td>
<td>(5.00)</td>
<td>(4.96)</td>
<td>(4.96)</td>
<td>114$^b$</td>
</tr>
<tr>
<td>2-Triflato-2,4,6-triphenyl-1-oxa-3-oxonia-2-borata-cyclohexadien(3,5) (6a)</td>
<td>(5.80)</td>
<td>(5.66)</td>
<td>(5.67)</td>
<td>94 dec.</td>
</tr>
<tr>
<td>2-Aquo-2,4-diphenyl-6-methyl-1-oxa-3-oxonia-2-borata-cyclohexadienyl(3,5)-trifluorsulfonat (6b)</td>
<td>(5.75)</td>
<td>(5.76)</td>
<td>(5.67)</td>
<td>74</td>
</tr>
</tbody>
</table>

Analysis (caeled (found))

<table>
<thead>
<tr>
<th>Formula</th>
<th>mol. weight</th>
<th>C [18]</th>
<th>H</th>
<th>B</th>
<th>S</th>
<th>Cl</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>C$<em>{32}$H$</em>{26}$ClO$_6$</td>
<td>410.6</td>
<td>61.43</td>
<td>3.93</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(48.29)</td>
<td>(4.11)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>5b</td>
<td>C$<em>{16}$H$</em>{16}$ClO$_6$</td>
<td>348.5</td>
<td>55.14</td>
<td>4.05</td>
<td>3.10</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(49.19)</td>
<td>(4.01)</td>
<td>2.83</td>
<td>-</td>
<td>(10.2)</td>
</tr>
<tr>
<td>6a</td>
<td>C$<em>{22}$H$</em>{18}$BF$_3$O$_5$S</td>
<td>460.2</td>
<td>57.42</td>
<td>3.50</td>
<td>2.35</td>
<td>6.97</td>
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<tr>
<td></td>
<td></td>
<td>(40.78)</td>
<td>(3.63)</td>
<td>2.04</td>
<td>8.23</td>
<td>-</td>
</tr>
<tr>
<td>6b</td>
<td>C$<em>{17}$H$</em>{16}$BF$_3$O$_5$S</td>
<td>398.1</td>
<td>49.06</td>
<td>3.88</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(48.44)</td>
<td>(4.21)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>


[12] Attempts to obtain single crystals for X-ray structure determinations have so far been unsuccessful.


[14] The chemical shift reported for $5\text{a}$ in CH$_3$CN was $\delta^{11}\text{B} = 26$ ppm. This value is close to $\delta^{11}\text{B} = 28.4$ reported for phenylboronic acid in ethanol (M. J. S. Dewar and J. R. Jones, J. Am. Chem. Soc. 89, 2408 (1964); ibid. 89, 4251 (1967)), the product of hydrolysis of $5\text{a}$. $\delta^{11}\text{B}$ values for $p$-substituted phenyl boronic acids are found in the $\delta$-range 31–25.8 (H. C. Beachall and D. W. Beistel, Inorg. Chem. 3, 1028 (1964)). We observed $\delta^{11}\text{B} = 26.8$ ppm for phenylboronic acid in CH$_2$Cl$_2$.

[15] During crystallisation of compounds of type $5$ phenylboronic acid slightly contaminated by the $\beta$-diketone could have been obtained [5].


[18] Carbon analysis gave consistently low figures even in the presence of V$_2$O$_5$ or WO$_3$. This corresponds to reported results [5–7].