RESEARCHES ON MODEL COMPOUNDS RELEVANT TO LINEAR BORON-NITROGEN POLYMERS.

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ABSTRACT

1. The following new organic boron-nitrogen compounds were synthesised:

\[ \text{o-phenylene t-butylaminoboronate} \]
\[ \text{o-phenylene ethylaminoboronate} \]
\[ \text{o-phenylene isopropylaminoboronate} \]
\[ \text{o-phenylene phenylaminoboronate} \]
\[ \text{o-phenylene dimethylaminoboronate} \]

The last four compounds were all obtained as hydrolytically stable dimers.

The problem of monomer = dimer, equilibrium and the influence thereon of substituents on the nitrogen atom has been studied qualitatively.

2. A preliminary study of the novel classes - acylamino- and sulphonylamino- boron compounds has been undertaken. Among the compounds characterised are

\[ \text{Bis(o-phenylenedioxyboron) sulphanide} \]

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## Researches on Model Compounds Relevant to Linear Boron-Nitrogen Polymers

The following new organic boron-nitrogen compounds were synthesised: 
- phenylene t-butylaminoboronate
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- o-phenylene isopropylaminoboronate
- phenylene phenylaminoboronate
- o-phenylene dimethylaminoboronate

The last four compounds were all obtained as hydrolytically stable dimers. The problem of monomer ↔ dimer, equilibrium and the influence thereon of substituents on the nitrogen atom has been studied qualitatively. Novel classes - acylamino- and sulphonylamino- boron compounds - have been undertaken. Among these, the sulphonylamino-boron compounds are characterised as Bis(~-phenylenedioxyboron)sulphamide.
and the amides Ph₂B·N(CH₃) and PhCOCH₃.

Stabilisation by chelation or autocomplexing is expected.

3. Oxygen-bridging is being investigated and model compounds

\[ \ce{X - O - Y} \]

are being examined.

4. Attempts to prepare organic boron sulphates were unsuccessful.

**DISCUSSION**

1. **BORON SULPHATES**

   The initial programme was concentrated on the organo-boron sulphates (II), which were (and are) unknown.

   \[ \ce{\text{II}} \]

   It was hoped that such compounds might be stabilized, particularly towards hydrolytic attack, by either intra-(chelation) or inter-molecular donation (\(\ce{O=\text{S}=O \rightarrow \ce{H^-}}\)). Such chelation has previously been demonstrated to occur in the acyloxy boron compounds.¹

   The synthetic routes so far investigated, all of which yielded negative results as far as boron sulphate formation was concerned, were (i) – (v).

   (i) The interaction of a boron halogen compound (α-phenylene chloro- or bromo-boronates, dibutyl chloroborornates or phenyl dichloroborane) with dry silver sulphate in the absence or presence of various solvents (benzene, ether, acetonitrile, methylene dichloride or chloroform) under reflux.

   (ii) Potassium sulphate with α-phenylene chloroboronate in the
presence of liquid sulphur dioxide, under reflux.

(iii) o-Phenylenecarboborane and dimethyl sulphate at 60° for 1 hr.

(iv) o-Phenylessethyl borate and sulphuryl chloride under reflux.

(v) o-Phenylenedicyanatothionate and mercuric sulphate in the presence of benzene under reflux.

A possible explanation for the lack of formation of organoboron sulphates may be due to the considerable electron attracting capacity of the sulphonyl group. Thus a sulphonyl group and a boron atom would in a boron sulphate be in competition for the electrons of the oxygen atom. In a recently published patent there is claimed the synthesis of organoboron sulphates, by refluxing dialkyl sulphates with dialkylboron chlorides, using an initial reflux temperature 100° - 150°. It was stated that these compounds are highly reactive and decompose above the upper reflux limit. It is proposed to repeat these experiments at a later date.

2. SULPHAMIDES OF BORON

Due to the possibility that the electron-acceptor strength of the sulphonyl group prevents sulphate formation, it was thought that if a stronger electron-donor group was attached to the sulphur, it would be possible to effect bridging of two boron atoms by a substituent containing a sulphonyl group. As sulphamic acid had previously been tried, but without success, it was decided to attempt to synthesise boron-substituted-sulphamides. In sulphamide, the diacid of sulphuric acid, it was considered that the nitrogen atoms would satisfy the requirements, and this lead to two approaches to the synthesis of boron sulphanamides.

(i) By direct metathesis of chloroboranes with sulphamide or substituted-sulphamides; thus on refluxing o-phenylene chloroborane with sulphamide in benzene, hydrogen chloride was evolved, leaving a white benzene-insoluble solid, which analysed as the H,N,N′,N′-bis(o-phenylenedioxyboron) sulphamides (III)

\[ \text{SO}_2(\text{NH}_2)_2 + 2\text{C}_6\text{H}_4\text{O}_{2}\text{BCL} \rightarrow \]

(III)

Compound (III) was not very stable to hydrolysis.
(11) The second approach was to react alkylaminoboronates with sulphuryl chloride.

\[ 2 \text{R}_2\text{RNHR} + \text{SO}_2\text{Cl}_2 \rightarrow \text{R}_2\text{B-N-S-N-BR}_2 \cdot \text{R'OH} \]

This second approach has not up to the present time been investigated, since synthesis of the \( \gamma \)-phenylene alkylaminoboronates, which are the required precursors has lead to other interesting chemistry (see Section 3).

3. \( \gamma \)-PHENYLENE ALKYL- OR ARYL- AMINOBORONATES

Investigation of \( \gamma \)-phenylene alkylaminoboronates was undertaken partly in order to provide starting materials for borophosphates and partly as a means of producing new boron compounds with boron-nitrogen-boron linkages. The latter problem was envisaged as involving the following alternative reaction sequences.

(i) By analogy with the pyrolysis of tria(alkylamino)boranes, which eliminate amine to produce boron-nitrogen-boron linkages; thus, it was intended to pyrolyse the \( \gamma \)-phenylene alkylaminoboronates to give the required compounds.

\[ 2 \text{C}_6\text{H}_4\text{O}_2\text{RNHR} \rightarrow \text{C}_6\text{H}_4\text{O}_2\text{B-N(R)} \cdot \text{SO}_2\text{H}_4\text{O} + \text{RNH}_2 \]

(ii) By direct metathesis between \( \gamma \)-phenylene alkylaminoboronates and \( \gamma \)-phenylene chloroboronates.

\[ \text{C}_6\text{H}_4\text{O}_2\text{BCl} + \text{RHNBO}_2\text{C}_6\text{H}_4 \rightarrow \text{C}_6\text{H}_4\text{O}_2\text{B-N(R)} \cdot \text{SO}_2\text{H}_4\text{C}_5 \]

A number of \( \gamma \)-phenylene alkylaminoboronates were synthesised, and two methods of preparation were used. The first method was by the reaction of \( \gamma \)-phenylene chloroboronate and the appropriate amine in the presence of benzene or light petroleum, and subsequent removal by filtration of the amine hydrochloride.

\[ \text{C}_6\text{H}_4\text{O}_2\text{BCl} + 2 \text{RNH}_2 \rightarrow \text{C}_6\text{H}_4\text{O}_2\text{RNHR} + \text{RNH}_3^+\text{Cl}^- \]

The second method of synthesis was by transaminating \( \gamma \)-phenylene diethylenaminoboronate, by the use of the appropriate amine in the presence of light petroleum. This method was preferred due to the speed and efficiency of reaction. The \( \gamma \)-phenylene phenyl-, isopropyl-, ethyl-, and t-butyl-aminoboronates were prepared by the methods outlined. Some of the properties of the above aminoboronates are summarised in Table 1.

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<table>
<thead>
<tr>
<th>Compound</th>
<th>Ref. No.</th>
<th>B.P. (°C/mm.)</th>
<th>$M_r$</th>
<th>Normal state of Aggregation</th>
<th>Miscellaneous</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_6H_4O_2BNHMe$</td>
<td>IV</td>
<td>68/0.3</td>
<td></td>
<td>Monomer</td>
<td>Readily attacked by moist air</td>
</tr>
<tr>
<td>$C_6H_4O_2BNHP$</td>
<td>V</td>
<td>54/0.2</td>
<td></td>
<td>Monomer = Dimer</td>
<td>Slowly attacked by moist air</td>
</tr>
<tr>
<td>$C_6H_4O_2BNHet$</td>
<td>VI</td>
<td>265-75</td>
<td></td>
<td>Dimer</td>
<td>Stable but slowly attacked by cold water</td>
</tr>
<tr>
<td>$C_6H_4O_2BNPh$</td>
<td>VII</td>
<td>266-8</td>
<td></td>
<td>Dimer</td>
<td>Stable and very slowly attacked by cold water</td>
</tr>
</tbody>
</table>

Structurally, compounds (V) – (VII) are considered to be dimers (VIII), due to their low reactivity, molecular weights, infrared spectra (see below) and steric requirements.

![Chemical structure]

(VIII)

Compound (IV) is considered to be monomeric from similar evidence. Infrared spectra of compounds (V) – (VII) show broad bands attributed to BN stretching frequencies at 920-100 cm$^{-1}$ which is in accord with previous observations for the BN stretching frequencies of the other similar dimer (Me$_2$NBCl$_2$)$_2$. The monomeric o-phenylene t-butyl aminoborocane has a BN stretching frequency at 1350-2 cm$^{-1}$, which is in agreement with BN stretching frequencies in other boracenes, (including monomeric Me$_2$NBCl$_2$).

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The spectra of all of the dimeric compounds show rather low NH stretching frequencies at 3225 – 3125 cm⁻¹, this may be compared with the NH stretching frequency of the monomeric \( \text{O-phenylene} \)
\( \text{t-butylaminoborionate} \) located at 3472 \( \pm \) 2 cm⁻¹.

Compound (V), when freshly prepared and prior to distillation, was a fluid and had the NH stretching frequency at 3472 \( \pm \) 2 cm⁻¹ and the NH frequency at 3472 \( \pm \) 2 cm⁻¹. After distillation it solidified and although both these peaks still persisted to a small degree in a spectrum of the solid, the dimer peaks were very much more predominant. There thus appears to be an equilibrium between the monomeric and dimeric states for compound (V). The significant spectroscopic data are summarised in Table 2.

<table>
<thead>
<tr>
<th>R in ( \text{C}_6\text{H}_4\text{O}_2\text{BHR} )</th>
<th>Bu⁺</th>
<th>Et⁺</th>
<th>Fr⁺</th>
<th>Fr⁺</th>
<th>Ph⁺</th>
</tr>
</thead>
<tbody>
<tr>
<td>NH (cm⁻¹)</td>
<td>3472±2</td>
<td>3174±2</td>
<td>3425±2</td>
<td>3195±2</td>
<td>3125±2</td>
</tr>
<tr>
<td>BN (cm⁻¹)</td>
<td>2535±2</td>
<td>915±10</td>
<td>1543±2</td>
<td>922±10</td>
<td>918±10</td>
</tr>
</tbody>
</table>

* monomers

The reason for dimerisation is clearly due to the thermodynamic preference for existence in this state, but may be prevented if the steric effects of the substituent groups introduce a high entropy term. The low steric requirement of the \( \text{O-phenylene} \) dioxyboron ring enables the thermodynamic factor for dimerisation to be greatly enhanced. This is instanced by the fact that even \( \text{O-phenylene isopropylaminoboronic acid} \) is dimeric, despite the presence of the bulky isopropyl group.

4. \( \text{O-phenylene Diallylamino boronates} \)

In the light of the discovery of the dimeric \( \text{O-phenylene} \) dioxyborons described in Section 3, it was decided to investigate the dialkylamino series also. The \( \text{O-phenylene diethyl-} \) and \( \text{di-n-butyl-aminoboronic acid} \) had previously been prepared and were monomeric high boiling liquids, which were very susceptible to hydrolytic attack. Therefore any possibility of isolating a dimer in this series, was only likely with the lowest homologue, namely \( \text{O-phenylene dimethylaminoboronic acid} \). This compound was synthesised by direct transamination of \( \text{O-phenylene diethylaminoboronic acid} \) with dimethylamine, using light petroleum as solvent. Distillation afforded a crystalline solid, which from molecular weight, its hydrolytic stability and molecular model consideration was assigned.
the dimeric structure (IX).

\[ \text{Infrared data also indicated the dimeric structure, since the } \text{CH}_{2} \text{ stretching frequency was considered to be at 946±10 cm}^{-1} \text{ (broad), which is much lower than the 1354±2 cm}^{-1} \text{ assigned to the CH stretching in the other } \text{2-phenylene dialkylaminoborates.}^{7} \]

Isolation of dimeric 2-phenylene dimethylaminoborurate was of further interest, since it provides the first example of a dimeric tetra-substituted borazen,\(^8\) thus also confirming our view regarding the low steric requirements of the planar fused 2-phenylendioxyboron ring.

5. AMIDOBORON COMPOUNDS

These compounds have the functional group (X).

\[ \text{(X)} \]

The idealised synthetic routes (i) to (v) have been explored.

(1) \[ \text{B-dR}_{2} + \text{H}_2\text{NCH}_3 \rightarrow \text{B-NHCOCH}_3 + \text{R}_2\text{NH} \]

\( R = \text{Et, Pr}^{i} \)

(2) \[ \text{B-Cl + PhNHOCH}_3 \rightarrow \text{B-NHOCH}_3 + \text{HCl} \]

\( \text{Ph} \)

(3) \[ \text{B-Cl + [PhNOCOCH}_3]^{-}\text{Na}^{+} \rightarrow (\text{II}) + \text{NaCl} \]

\[ \text{(II)} \]
6. OXYGEN-BRIDGING

A major purpose of our research is the synthesis of model compounds for polymers, having two boron atoms attached through an oxygen group. In the present case, bridging through an oxygen atom was explored.

Compounds of the type \( \text{R} \cdot \text{O} \cdot \text{X} \cdot \text{X} \) although known are very limited in number. Examples are where \( \text{R} = \text{AcO}, \text{Bu}, \text{Ph} \) and \( \text{X} = \text{AcO}, \text{Bu}, \text{Ph} \) or halogen. A survey of the literature of these compounds was carried out in order to find methods to extend the series. It is proposed also to use these compounds to attempt the preparation of novel ring systems, e.g. tetrameric boroxoles.

The synthesis of \( [\text{Ph(BuO)}_3]_2 \text{O} \), (XIII), from \( n \)-butoxychlorophenylborane was attempted.

Two reaction schemes were carried out (see below), but in neither case was (XIII) isolated. It may have been an unstable intermediate, however, in reactions (5) and (7).

\[
(6) \quad 2 \text{BuO} \cdot \text{B} \cdot \text{Cl} + \text{HgO} \rightarrow \frac{2}{3} (\text{PhRO})_3 + \text{Ph} \cdot \text{B} \cdot (\text{OBu})_2 + \text{HgCl}_2
\]
\[ 2 \text{PhBr} + \text{[(CH}_3\text{)}_3\text{S}]_2\text{O} \rightarrow \frac{1}{3}\text{PhBrO}_3 + \text{PhBr(OH)}_2 + 2\text{[(CH}_3\text{)}_3\text{S}]_2\text{Cl}. \]

**BIBLIOGRAPHY**

7. Lappert and Majumdar, unpublished observations.

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