

## 689. Coloured Boronium Salts.

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Diphenylbipyridylboronium salts are relatively resistant to hydrolysis and undergo metathetical reactions in aqueous solution. The colourless very sparingly soluble hydrated nitrate, as well as the perchlorate and the hydrogen sulphate are readily precipitated from aqueous solution. The colours of the iodides and some other salts of the  $[\text{Ph}_2 \text{ bipy B}]^+$ ,  $[\text{Ph}_2 \text{ phenan B}]^+$  and  $[\text{n-Bu}_2 \text{ bipy B}]^+$  cations are considered to be due to charge-transfer transitions. The yellow colour of bipyridylphenylenedioxyboronium perchlorate (I;  $\text{X} = \text{ClO}_4$ ) is attributed to intraionic charge transfer. A bisdimethylaminobipyridylboronium salt is also described.

SEVERAL boronium salts, exemplified by 2,2'-bipyridyldiphenylboronium chloride,  $[\text{Ph}_2 \text{ bipy B}]\text{Cl}$ , have been described,<sup>1</sup> this particular salt having been obtained from bipyridyl and chlorodiphenylborane in nitrobenzene under strictly anhydrous conditions. The stability to water of many of the boronium salts does not appear to have been generally realized, though the pyridine complex,  $[\text{Bu}_2 \text{ py}_2 \text{ B}]\text{Cl}$ , is described as water-soluble and the suggested boronium constitution<sup>2</sup> is almost certainly correct. The first-mentioned chloride can be prepared in quantitative yield from bipyridyl and chlorodiphenylborane in benzene, and is insoluble in this solvent; it can conveniently be crystallized from hot water, and no free bipyridyl could be detected in the aqueous solution even after the salt had been boiled with dilute hydrochloric acid. The chloride dissolves in concentrated sulphuric acid at room temperature with evolution of hydrogen chloride; the acid sulphate is the main product, though a little bipyridyl may be detected in the solution after dilution. Complete decomposition by sulphuric acid requires 15–20 minutes at 180°, and was the basis for the analytical determination of the bipyridyl content of many of the compounds studied.

The stability of the bipyridyldiphenylboronium ion to mild acid conditions is shown also by our preparation of the halides in 50–55% yields by boiling diphenylborinic acid or its ethanolamine ester with bipyridyl and 5*N*-hydrochloric acid for 2–3 hours.

The ion, like the pyridinium salts, is readily decomposed by alkali, no doubt on account of nucleophilic attack on the bipyridyl. Colourless aqueous or aqueous-alcoholic solutions of the hydroxide can be prepared from the chloride and silver oxide, and behave as solutions of strong bases on potentiometric titration with dilute acid. Attempts to isolate the hydroxide by evaporation of solvent at or below room temperature yielded dark tars, whose solutions in ethanol contained neither  $[\text{Ph}_2 \text{ bipy B}]^+$  ions nor free bipyridyl. Reaction between the *o*-phenanthroline analogue and silver oxide suspended in ethanol yielded deep purple-red solutions, from which no  $[\text{Ph}_2 \text{ phenan B}]^+\text{X}^-$  salts could be recovered, but colourless strongly alkaline solutions, from which dilute nitric or hydriodic acid precipitated the nitrate or iodide, could be prepared with water as solvent. Aqueous solutions of  $[\text{Ph}_2 \text{ phenan B}]\text{OH}$  became viscous after several hours at room temperature and were no longer alkaline.

*Metathetical Reactions.*—The yellow iodide,  $[\text{Ph}_2 \text{ bipy B}]\text{I}$ , is only sparingly soluble in water and is precipitated by potassium iodide added to an aqueous solution of the chloride. The colourless bromide is a little more soluble. The thiocyanate, azide, tetraphenylborate, and dimethyldithiophosphate are all formed as yellow precipitates in aqueous solution; the dimethylphosphinate, in contrast, is colourless and very soluble in water (it was prepared from the hydroxide and dimethylphosphinic acid and not purified). The colourless perchlorate<sup>1</sup> and nitrate are very sparingly soluble and are precipitated at once from aqueous solutions of the chloride: the solubility of the nitrate in water at 25°,  $3.6 \times 10^{-3}$  moles  $\text{l}^{-1}$ , was calculated from the conductance of its saturated solution. The conductance of  $[\text{Ph}_2 \text{ bipy B}]\text{Cl}$  in water at 25° was appropriate for a 1 : 1 salt; the molar

<sup>1</sup> Davidson and French, *J.*, 1958, 114; *Chem. and Ind.*, 1959, 750; *J.*, 1962, 3364.

<sup>2</sup> Gerrard, Lappert, and Shafferman, *J.*, 1957, 3828.

conductance varied linearly with  $C^{\frac{1}{2}}$  over the range from  $2 \times 10^{-4}$  to 0.01 M, whence the conductance at zero concentration is 100.0 and the mobility of the bipyridyldiphenylboronium ion 23.7.

A sparingly soluble acid sulphate,  $[\text{Ph}_2 \text{ bipy B}]\text{HSO}_4 \cdot \text{H}_2\text{O}$  is precipitated when dilute sulphuric acid is added to an aqueous solution of the chloride. This was identified as an acid sulphate by potentiometric titration, and the water could be removed by heating at  $140^\circ/\sim 0.01$  mm. for 2 hours. The normal sulphate is evidently much more soluble, since no precipitate results when aqueous sodium sulphate is added to a neutral solution of the chloride, but addition of hydrochloric or sulphuric acid causes immediate precipitation of the hydrogen sulphate. It is surprising that not only the acid sulphate, but also the nitrate,  $[\text{Ph}_2 \text{ bipy B}]\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$ , and the chloride, bromide, and iodide crystallize from water as hydrates. The halides, also  $[\text{Ph}_2 \text{ phenan B}]\text{I} \cdot \text{H}_2\text{O}$ , crystallized as monohydrates, and all absorb in the infrared spectrum near  $3470 \text{ cm.}^{-1}$ . If the yellow iodide,  $[\text{Ph}_2 \text{ bipy B}]\text{I} \cdot \text{H}_2\text{O}$ , is kept at room temperature for several hours at a pressure of less than 0.01 mm., the colour changes to orange, and the absorption at  $3470 \text{ cm.}^{-1}$  of a Nujol mull prepared in a dry-box disappears. If a potassium iodide disc is prepared from this material in the usual way, the presence of water is then apparent from the spectrum (the sharp absorption near  $3470 \text{ cm.}^{-1}$  is quite different from the broad absorption that is shown by inadequately dried potassium iodide). The anhydrous orange iodide takes up water when exposed to the air, reverting to yellow, and the absorption at  $3470 \text{ cm.}^{-1}$  returns.

The yellow di-n-butyl iodide  $[\text{Bu}_2^n \text{ bipy B}]\text{I}$ , crystallizes from water in an anhydrous condition and prolonged evacuation of the crystals at less than 0.01 mm. results in no change. Of the salts prepared, only the perchlorate, thiocyanate, azide, dimethyldithiophosphinate, and tetraphenylborate crystallize in anhydrous form.

*Light Absorption.*—Since the coloured salts give colourless solutions in water (hot water in many instances), the colours are considered due to charge-transfer transitions from the anion to the  $\pi$ -electron system of the bipyridyl or phenanthroline. This behaviour is similar to that of the methiodides of several heterocyclic bases (*e.g.*, quinoline methiodide), and has been discussed by Kosower and Burbach,<sup>3</sup> who made a detailed study of methylpyridinium iodide and showed that the absorption at about  $300 \text{ m}\mu$  was greater in ethanol than in water. These authors were able to explain on this basis Hantzsch's observations<sup>4</sup> that the colour of ethylpyridinium iodide changes from colourless in water, in which the salt would be ionized and the ions well separated, to deep yellow in chloroform in which the salt would exist mainly in the form of ion-pairs or more complex aggregates. All the bipyridylboronium salts studied absorbed very strongly ( $\log E$  4.5—5.0) at about  $210 \text{ m}\mu$ , with a shoulder or subsidiary peak at 235—240  $\text{m}\mu$  and less intensely ( $\log E$  about 4) at about 300—310  $\text{m}\mu$ . Phenanthrolineboronium complexes have quite different spectra in this region, and the absorptions are no doubt due to  $\pi \rightarrow \pi^*$  transitions within the heterocyclic system. The absorptions at longer wavelength, causing visible colour, are shown in the Figure, which refers to  $10^{-3}\text{M}$ -solutions of bipyridyldiphenylboronium iodide in four solvents.

The absorptions in methanol (curve A) and ethanol (B) are the long-wavelength tail of the 300—310  $\text{m}\mu$  band already mentioned, but in butanol (dielectric constant 17 at  $25^\circ$ , curve C) an inflection due to the charge-transfer is apparent and in chloroform (dielectric constant 4.8, curve D) the broad charge-transfer band extends to about 500  $\text{m}\mu$ . Spectra in methylene dichloride and ethylene dichloride (dielectric constants 9.1 and 10.4) are similar to curve D. Rather broad absorption bands, attributed also to charge-transfer transitions, are observed also in the spectra of the neutral bipyridyl complexes  $\text{Me}_2 \text{ bipy Be}$  and  $\text{Et}_2 \text{ bipy Be}$ .<sup>5</sup>

The spectrum of bipyridyldiphenylboronium dimethyldithiophosphinate closely

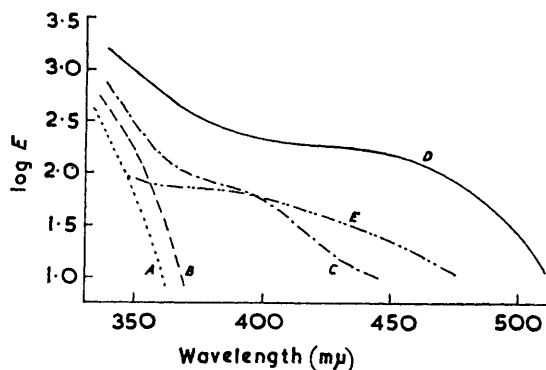
<sup>3</sup> Kosower and Burbach, *J. Amer. Chem. Soc.*, 1956, **78**, 5838.

<sup>4</sup> Hantzsch, *Ber.*, 1919, **52**, 1544.

<sup>5</sup> Coates and Green, *J.*, 1962, 3340.

resembles that of the iodide, but above 360  $m\mu$  the extinction coefficient is a little greater (*e.g.*, 2.55 and 2.35, respectively, at 400  $m\mu$ ). That of the azide is similar but displays a broad maximum at about 420  $m\mu$  instead of an inflection. That of the thiocyanate differs markedly in that the charge-transfer band (maximum at 390—400  $m\mu$ ) is much narrower, and the extinction coefficient falls rapidly above 410  $m\mu$ , whereas those of the other salts just mentioned do not drop significantly until about 480—500  $m\mu$ .

If the colours of these salts in the solid state or in solvents of relatively low dielectric constant are due to charge-transfer between anion and cation, then it should be possible to prepare coloured bipyridylboronium salts that retain their colour even in polar

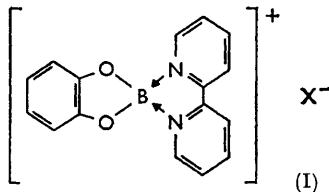


Absorption spectra of  $[\text{Ph}_2 \text{bipy B}]\text{I}$  ( $10^{-3}\text{M}$ ) in methanol (A), ethanol (B), n-butanol (C), and chloroform (D), and of bipyridyl-*o*-phenylenedioxyboronium iodide ( $10^{-3}\text{M}$ ) in methanol (E).

solvents if the charge-transfer takes place within the cation. This could occur if the boron were bound to nitrogen or oxygen atoms instead of to carbon (as in the dibutyl- and diphenyl-boronium salts already discussed), since there may be electron transfer from the "lone-pairs" of the nitrogen or oxygen into the  $\pi$ -electron system of the bipyridyl.

Addition of 2,2-bipyridyl to *o*-phenylene chloroboronate<sup>6</sup> in benzene resulted in the formation of a red precipitate, but much yellow material was also formed after a very small

proportion of the bipyridyl had been added. Inverse addition resulted in a yellow precipitate at first, but again the final product was an orange mixture, which was not separated, though the red material was found to be a little more soluble in methylene chloride. We believe the yellow material was the chloride (I;  $\text{X} = \text{Cl}$ ) since a yellow aqueous solution of the mixture, filtered from a small residue of insoluble red material (not necessarily the same as that mentioned above),



yielded the orange tetrahydrate of (I;  $\text{X} = \text{I}$ ), which lost water giving the orange anhydrous salt when evacuated at less than 0.01 mm. at room temperature. The colour of the (anhydrous) iodide was similar in water, ethanol, and chloroform, but charge-transfer could take place both from oxygen and from the iodide anion. Intra-ionic charge-transfer occurs in the yellow perchlorate (I;  $\text{X} = \text{ClO}_4$ ). These salts are stable to warm water, but are rapidly hydrolysed when their aqueous solutions are heated to boiling.

The absorption spectrum of the iodide in methanol is shown in the Figure (curve E). Comparison with the spectrum of  $[\text{Ph}_2 \text{bipy B}]\text{I}$  in the same solvent (curve A) indicates the absorption due to intra-ionic charge-transfer in (I;  $\text{X} = \text{I}$ ).

Reaction between 2,2-bipyridyl and chlorobisdimethylaminoborane gave an orange-yellow product, which was quickly hydrolysed on exposure to air liberating dimethylamine and bipyridyl and becoming dark red. However, the tetraphenylborate,  $[(\text{Me}_2\text{N})_2 \text{bipy B}]^+ [\text{Ph}_4\text{B}]^-$ , was obtained in the form of ruby red rhombic crystals. The deep colour of this is probably mainly due to intra-ionic charge-transfer, but is not

<sup>6</sup> Gerrard, Lappert, and Mountfield, *J.*, 1959, 1529.

necessarily so, since the tetraphenylborate ion could act as an electron source,  $[\text{Ph}_2 \text{ bipy B}]^+[\text{Ph}_4\text{B}]^-$  being yellow like the iodide.

## EXPERIMENTAL

Spectra were recorded with an Optica  $\text{CF}_4$  recording grating spectrophotometer.

*Boron Analysis.*—Compounds were decomposed by the oxygen-flask technique, and boric acid determined by titration against standard alkali with Bromo-thymol Blue as indicator.

*Bipyridyl and o-Phenanthroline Analysis.*—Both bases were determined colorimetrically, after decomposition with sulphuric acid at  $180^\circ$  for 15–20 min., followed by dilution and the addition of ferrous sulphate and ammonium citrate to aliquots parts.

Bipyridyl-*o*-phenylenedioxyboronium salts were decomposed with sulphuric acid, but it was necessary to remove phenolic compounds by alkaline extraction before the determination of bipyridyl.

*2,2'-Bipyridyldiphenylboronium Chloride Monohydrate.*—Bipyridyl (6.2 g.) in benzene solution was added to a stirred solution containing chlorodiphenylborane (8 g., 1 mol.) in benzene under a nitrogen atmosphere. A yellow viscous liquid formed, but after being stirred for a few minutes was replaced by a fine white precipitate. This was collected and pumped dry to give bipyridyldiphenylboronium chloride (14 g., 100%), m. p.  $333^\circ$  (decomp.) (lit.,  $329^\circ$ ). The *monohydrate* was obtained by crystallizing the chloride from boiling water, and collected as fine needles (Found: B, 3.0; bipy, 41.2; Cl, 9.4.  $\text{C}_{22}\text{H}_{20}\text{BClN}_2\text{O}$  requires B, 2.9; bipy, 41.7; Cl, 9.5%).

*2,2'-Bipyridyldiphenylboronium Perchlorate.*—The addition of an aqueous solution of sodium perchlorate to an aqueous solution containing the chloride (1 g.) precipitated the perchlorate, which crystallized from ethanol-water as fine white needles (0.6 g., 50%), m. p.  $320^\circ$  (decomp.) (Found: bipy, 36.5. Calc. for  $\text{C}_{22}\text{H}_{18}\text{BClN}_2\text{O}_4$ : bipy, 37.1%).

Compound	M. p. (decomp.)	Found (%)	Molecular formula	Required (%)
$[\text{Ph}_2\text{B bipy}]\text{Br}\cdot\text{H}_2\text{O}$ .....	$370^\circ$	B, 2.6; bipy, 37.3	$\text{C}_{22}\text{H}_{20}\text{BBrN}_2\text{O}$	B, 2.6; bipy, 37.3
$[\text{Ph}_2\text{B bipy}]\text{I}\cdot\text{H}_2\text{O}$ .....	345	B, 2.5; bipy, 34.0	$\text{C}_{22}\text{H}_{20}\text{BIN}_2\text{O}$	B, 2.3; bipy, 33.6
$[\text{Ph}_2\text{B bipy}]\text{CNS}$ .....	273	B, 3.0; bipy, 41.1	$\text{C}_{23}\text{H}_{18}\text{BN}_3\text{S}$	B, 2.9; bipy, 41.2
$[\text{Ph}_2\text{B bipy}]\text{N}_3$ .....	217	B, 3.0; bipy, 43.1	$\text{C}_{22}\text{H}_{18}\text{BN}_5$	B, 3.0; bipy, 43.0
$[\text{Ph}_2\text{B bipy}]\text{SSPMe}_2$ .....	228	— bipy, 35.5	$\text{C}_{24}\text{H}_{24}\text{BN}_2\text{PS}_2$	— bipy, 35.1
$[\text{Ph}_2\text{B bipy}]\text{BPh}_4$ .....	204	B, 3.4; bipy, 25.0	$\text{C}_{46}\text{H}_{38}\text{B}_2\text{N}_2$	B, 3.4; bipy, 24.5
$[\text{Ph}_2\text{B bipy}]\text{NO}_3\cdot\frac{1}{2}\text{H}_2\text{O}$ .....	263	B, 2.8; bipy, 40.2	$\text{C}_{22}\text{H}_{19}\text{BN}_3\text{O}_{3.5}$	B, 2.8; bipy, 39.9
$[\text{Ph}_2\text{B bipy}]\text{HSO}_4\cdot\text{H}_2\text{O}$ .....	275	B, 2.7; bipy, 35.3	$\text{C}_{22}\text{H}_{21}\text{BN}_3\text{O}_5\text{S}$	B, 2.5; bipy, 35.9
$[\text{Ph}_2\text{B phenan}]\text{Cl}\cdot\text{H}_2\text{O}$ .....	275	B, 2.7; phenan, 46.0	$\text{C}_{24}\text{H}_{20}\text{BClN}_2\text{O}$	B, 2.7; phenan, 45.3
$[\text{Ph}_2\text{B phenan}]\text{I}\cdot\text{H}_2\text{O}$ .....	330	B, 2.3; phenan, 37.3	$\text{C}_{24}\text{H}_{20}\text{BIN}_2\text{O}$	B, 2.2; phenan, 36.9
$[\text{Ph}_2\text{B phenan}]\text{NO}_3\cdot\frac{1}{2}\text{H}_2\text{O}$ ...	209	B, 2.7; phenan, 43.7	$\text{C}_{24}\text{H}_{19}\text{BN}_3\text{O}_{3.5}$	B, 2.6; phenan, 43.3

Several other salts were prepared by this method, and are listed in the Table above together with three *o*-phenanthroline compounds. The large majority of the compounds described decompose at or below their melting points.

*2,2'-Bipyridyldibutylboronium Iodide.*—Impure *bipyridyldibutylboronium chloride* was prepared from chlorodibutylborane and bipyridyl in benzene solution. The chloride was dissolved in water, and to the solution was added an aqueous solution of potassium iodide. The yellow *iodide* was precipitated and recrystallized from water; it had m. p.  $226^\circ$  (decomp.) (Found: B, 2.7; bipy 37.5.  $\text{C}_{18}\text{H}_{26}\text{BIN}_2$  requires B, 2.7; bipy, 38.3%).

*Bipyridyl-*o*-phenylenedioxyboronium Iodide Tetrahydrate.*—The reaction between *o*-phenylene chloroborate and bipyridyl in benzene solution gave a coloured product consisting of a yellow and a red solid. The mixture was dissolved in water, and the solution filtered from a small amount of a red residue. Addition of potassium iodide solution caused *bipyridyl-*o*-phenylenedioxyboronium iodide tetrahydrate* to separate slowly as orange needles. The salt is rapidly hydrolysed by boiling water, and decomposes when heated (Found: B, 2.3; bipy, 33.0; I, 26.6.  $\text{C}_{16}\text{H}_{20}\text{BIN}_2\text{O}_4$  requires B, 2.3; bipy, 33.0; I, 26.8%).

The corresponding *perchlorate* was obtained as yellow needles from aqueous solutions of the iodide and sodium perchlorate (Found: bipy, 41.1.  $\text{C}_{16}\text{H}_{12}\text{BClN}_2\text{O}_6$  requires bipy, 41.8%).

*Bipyridylbisdimethylaminoboronium Tetraphenylborate.*—The reaction between chlorobisdimethylaminoborane and bipyridyl in benzene gave an orange product which was rapidly

hydrolysed on exposure to air. Propan-2-ol solutions of the product and sodium tetraphenylborate gave an orange precipitate. Red, rhombic crystals of the *tetraphenylborate* were separated from dimethylammonium tetraphenylborate (also formed) by repeated crystallization from chloroform-ether (Found: C, 78.8; H, 7.5; B, 3.6; bipy, 26.9.  $C_{38}H_{40}B_2N_4$  requires C, 79.4; H, 7.0; B, 3.8; bipy, 27.2%).

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