

## BORON TRIFLUORIDE-AMINE COMPLEXES

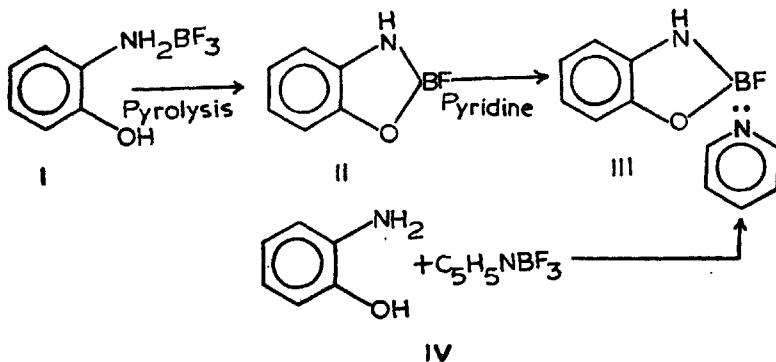
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The complexes of BF<sub>3</sub> (boron trifluoride) with various halo, hydroxy anilines have been prepared. The pyrolysis of hydroxy aniline BF<sub>3</sub> complex, its reaction with triethylamine and calcium hydroxide have been described. The U.V. spectra of benzene borole have been recorded. The antibacterial activity of halo, hydroxy aniline BF<sub>3</sub> complexes has also been evaluated.

Aromatic and aliphatic primary amines (Brown *et al.* 1954; Feichtinger & Puschho 1958; Gerrard & Mooney 1960; Kreutzberger & Ferris 1962; Gerrard & Russell 1967; and Satchell & Satchell 1965, 1967) and *o*-*m*-, and *p*-phenylene diamines formed (1:1) and (1:2) complexes respectively, when reacted with boron trifluoride at 0°C. Heating at high temperature, splitted off hydrogen fluoride, forming an insoluble and infusible polymers (Goldstein *et al.* 1963) in latter case. Phenol (Karlinskii & Buchking 1963) and anisole (Pencezek & Pencek 1963) have been reported to form (1:1) adduct with BF<sub>3</sub>. The use of Amine BF<sub>3</sub> complexes in pharmacology (Hazard *et al.* 1955), as a curing agents (Lidarik & Stary 1964; and Anchor chemicals 1965), Latent hardner (Nowak & Saure 1964; and Harrison 1969) for resins, insect chemosterilants (Settepani *et al.* 1970) and other industrial applications aroused our interest.

The boron trifluoride aniline complexes reported in (Table I) were obtained from halo hydroxy anilines and BF<sub>3</sub> in acetic acid. Pyrolysis of *o*-hydroxyaniline : BF<sub>3</sub> (I) gave 1:3-aza, oxo, 2-fluoro benzeneborole (II). This compound (II) forms adduct with pyridine (1:1) (III). The adduct (III) was also prepared by heating *o*-aminophenol and pyridineborontrifluoride (IV) complex.



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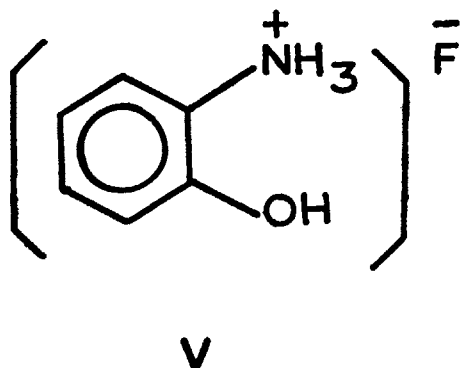
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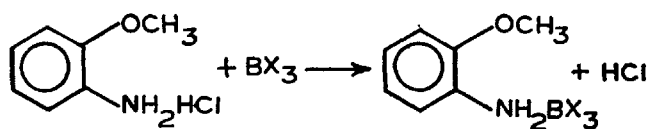
TABLE I  
Boron trifluoride aniline complexes

No.	2-hydroxy, aniline BF <sub>3</sub> complex	m.p. °c	Yield %	Properties	Formula	N%		B%	
						Found	Required	Found	Required
1.	" "	206-7	83.0	an amorphous light brown powder	C <sub>6</sub> H <sub>7</sub> ON BF <sub>3</sub>	7.68	7.90	5.87	6.21
2.	5-amino,-	>295	67.5	Greyish needles	C <sub>6</sub> H <sub>8</sub> ON <sub>2</sub> BF <sub>3</sub>	14.12	14.58	5.36	5.73
3.	5-Bromo,-	205-7	70.0	light brown powder	C <sub>6</sub> H <sub>6</sub> ON Br BF <sub>3</sub>	4.98	5.49	4.17	4.31
4.	3,5-Dibromo,-	230-31	75.0	light reddish powder	C <sub>6</sub> H <sub>4</sub> ON Br <sub>2</sub> BF <sub>3</sub>	4.15	4.17	3.12	3.28
5.	3-Carboxy,-	>302	80.0	diamond grey globules	C <sub>7</sub> H <sub>7</sub> O <sub>3</sub> N BF <sub>3</sub>	5.84	6.33	4.59	4.97
6.	5-Amino, 3-chloro	>295	62.2	greenish (light) amorphous powder	C <sub>6</sub> H <sub>7</sub> ON <sub>2</sub> Cl BF <sub>3</sub>	12.16	12.39	4.51	4.86
7.	5-Chloro,-	>300	74.8	dark greenish yellow powder	C <sub>6</sub> H <sub>6</sub> ON Cl BF <sub>3</sub>	6.41	6.63	5.16	5.23
8.	8-Amino, quinoline	119-20	62.5	brownish red needles	C <sub>9</sub> H <sub>8</sub> N <sub>2</sub> BF <sub>3</sub>	12.86	13.21	5.08	5.18
9.	8-Hydroxy, quinoline	94-96	51.9	Lemon yellow needles	C <sub>9</sub> H <sub>7</sub> ON BF <sub>3</sub>	6.18	6.57	5.01	5.16

The U.V. spectra of benzen-1-aza, 3-oxa, 2-fluoro borole (II) showed high intensity compared with aniline  $\text{BF}_3$  complex (I), supports the formation of borole ring (II). It did not show ionic structure (V) in alcohol (95 per cent).



*o*-Hydroxy, aniline hydrochloride when treated with  $\text{BF}_3$  etherate splits off hydrogen chloride forming adduct (I), similar to *o*-anisidine hydrochloride (Kinney & Mahoney 1943).



Aniline adduct formed easily and found more stable compared with ether complexes (Katalnikov & Paramonov 1966). 8-Aminoquinoline yielded adduct with  $\text{BF}_3$  through tertiary nitrogen.

#### EXPERIMENTAL

2-nitro, 4-bromo (Meldola & Streatfeild 1898) (30 per cent, m. p. 86–87°C), 2-nitro, 4,6-dibromo (Dandegaonkar & Shastri 1965) (38 per cent, m. p. 114–15°C), 2-nitro, 4-chloro (Faust & Saame 1873) (82 per cent, m.p. 85°C), 2,4-dinitro 6-chloro (Faust & Saame 1873) (75 per cent, m. p. 113–14°C) phenols and 3-nitro salicylic acid (Hubner *et al.*, 1879) (58 per cent, m.p. 139°C) were obtained as reported. The reduction of these halo nitro phenols to corresponding amino derivatives was achieved using Schlieper's procedure (1893). The compounds obtained were 2-amino, 4-bromo (80.6 per cent, m.p. 126–7°C); 2-amino, 4, 6-dibromo (62.6 per cent, m.p. 90–91°C); 2-amino, 4-chloro (58 per cent, m.p. 74°C); 2,4-diamino, 6-chloro (61 per cent, m.p. 300°C) phenols and 3-amino salicylic acid (21 per cent, m. p. 235°C). 8-Amino, quinoline (Price & Gutbrie 1946) (50 per cent, m.p. 63°C) was obtained by reduction of 8-nitroquinoline with iron and acetic acid.

*Preparation of Aniline BF<sub>3</sub> Complexes*—A solution of BF<sub>3</sub>O(C<sub>2</sub>H<sub>5</sub>)<sub>2</sub> (4.62 g; 0.04 mole) in dry chloroform (20 ml) was added dropwise to the well stirred solution of (2-hydroxy; 2-hydroxy, 5-amino; 2-hydroxy, 5-bromo; 2-hydroxy, 3,5-dibromo; 2-hydroxy, 3-carboxy; 2-hydroxy, 5-amino, 3-chloro; 2-hydroxy, 5-chloro; anilines and quinolines of 8-amino, 8-Hydroxy compounds) in equimolar ratio, dissolved in chloroform (650 ml) at room temperature. After the complete addition, the reaction mixture was refluxed for 4 hours. The solid thus separated was filtered off, washed with dry ether and dried in vacuum.

The *o*-hydroxy aniline BF<sub>3</sub> complex (m. p. 206–7°C) (Found : C, 40.63; H, 3.736; N, 7.68 per cent C<sub>6</sub> H<sub>5</sub> ONH<sub>2</sub> BF<sub>3</sub> requires : C, 40.67; H, 3.950; N, 7.90 per cent) was highly soluble in water, ethanol and acetone, but insoluble in ether, benzene and CCl<sub>4</sub>. The complexes prepared are reported in Table I.

*The Reactions of o-hydroxy Aniline BF<sub>3</sub> Complex :*

1. *Pyrolysis*—On pyrolysis of *o*-hydroxy aniline BF<sub>3</sub> complex (1.5 g) at 180–190°C for 6 hours a bluish black sticky mass, soluble in water and alcohol was obtained. On sublimation at 180°C 12mm, a product (10 per cent) giving green fluorescence with chloroform was collected. The adduct (1:1) (m.p. 189°C decomp.) (Found : B 4.548 per cent C<sub>11</sub> H<sub>10</sub> O N<sub>2</sub> BF requires : B 5.09 per cent) was formed when heated with pyridine at 130–35°C for 4 hours and washed with ether.

2. *Reaction with Triethyl Amine*—The aniline BF<sub>3</sub> complex (1.2 g) was taken with triethylamine (2.0 g), heated under reflux at 170–80°C, cooled and washed with chloroform. The chloroform insoluble product (0.816 g) was identified as *o*-amino phenol (m. p. 174°C) which did not depress the m.p. of an authentic sample.

3. *Reaction of Complex with Calcium Hydroxide*—The complex (1.77 g) taken with calcium hydroxide (0.74 g) and heated at 140–45°C for 6 hours, cooled and extracted with alcohol. The alcoholic filtrates combined and concentrated, which afforded cyclic derivative (0.94 g) (69 per cent m.p. 160°C decomposed, Found : N, 10.10; B, 7.74 per cent C<sub>6</sub> H<sub>5</sub>OM : BF requires : N, 10.22; B, 8.03 per cent) Pyrolyzed product (0.343 g) on heating with pyridine (0.226 g) at 135°C for 4 hours formed a complex (1:1) with pyridine (m.p. 189–91°C decomposed) (Found : B, 4.73 per cent C<sub>11</sub> H<sub>10</sub> ON<sub>2</sub> BF requires : B, 5.09 per cent).

4. *Reaction of Pyridine BF<sub>3</sub> complex with o-Amino phenol*—Pyridine : BF<sub>3</sub> semi solid complex (1.59 g) and *o*-amino phenol (1.09g) (1:1) heated at 140–145°C for 5 hours, cooled washed with ether several times; gave the adduct (1.48 g, 72.81 per cent m. p. decomposed at 189–191°C) (Found : B, 4.83 per cent C<sub>11</sub> H<sub>10</sub> ON<sub>2</sub> BF requires : B, 5.09 per cent).

The U. V. absorption values observed for 2-fluoro, 1-aza, 3-oxa, benzenborole [ $\lambda$  max. 241 (4.86), 276.5 (4.69)] and boron trifluoride *o*-aminophenol  $\lambda$  max. 241 (1.37), 276 (1.16) and 279 (1.19)] agree with those of similar compounds [2-*n*-propyl, 1-aza, 3-oxa, benzenborole (Nyilas & Soloway 1959) and *o*-aminophenol (Morton & Stubbs 1940)]. The bathochromic shift and hyperchromic effect support the formation of five membered heterocyclic ring.

The pure cultures of the organisms received from Haffkine Institute, Bombay for antibacterial tests and the complexes were tested for their antibacterial activity by

following the method of Gould and Bowie (1952). Each concentration of antibacterial solutions was 1 mg/ml of acetone, of which 0.05 ml was used for each disc.

Antibacterial tests showed as anticipated, bromine compounds being more active than chlorine analogues and the activity is enhanced with increase in number of bromine atoms (Table II). Amino group has no effect while chelation improves activity to certain extent.

TABLE II  
*Antibacterial action of aniline BF<sub>3</sub> complex*

S. No.	Aniline BF <sub>3</sub> complex	Staphaureous mm.	E. coli mm.	E. coli HFR <sub>12</sub> mm.
1.	2-Hydroxy, 3-chloro, 5-amino: BF <sub>3</sub>	12	13	13
2.	2-Hydroxy, 3-carboxy,	15	15	16
3.	2-Hydroxy, 5-bromo-	21	14	15
4.	2-Hydroxy, 3, 5-dibromo-	23	15	16

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