# ACETOXYBORON DERIVATIVES OF N-SUBSTITUTED SALICYLALDIMINES

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Abstract—Tetra-coordinated Schiff base complexes of boron of the general type  $(OAc)_2B(SB)$  (where  $SB^-$  is the anion of the monofunctional bidentate Schiff base, SBH) have been synthesized by the reaction between boric acid and the Schiff base in acetic anhydride medium. In whatever molar ratio the reactants are taken, complexes of 1:1 stoichiometry are only obtained. These have been characterized by elemental analysis, IR and <sup>1</sup>H NMR spectra and found to be monomeric in refluxing benzene and non-electrolytes in DMF.

### INTRODUCTION

A survey of the literature revealed that much attention has been paid to the  $\beta$ -diketone chelates of boron[1-3]. The literature also records extensive work on boronnitrogen compounds, but references to Schiff base derivatives are scanty[4,5].

Complexes containing a boron-nitrogen dative bond have been found to be useful biologically [6,7] and industrially [8]. Further, thermochemical calculations show larger back bonding from nitrogen to boron than oxygen [9].

In view of this, it was considered of interest to synthesize some new boron derivatives of monofunctional bidentate Schiff bases.

The resulting derivatives can be structurally represented as follows, provided the nitrogen of the azomethine group also coordinates:



## EXPERIMENTAL

Materials. Schiff bases were obtained by the usual condensation method of salicylaldehyde with amines and then either distilled under reduced pressure or recrystallized from alcohol. They were analyzed for carbon, hydrogen and nitrogen and the results of analyses alongwith their physical properties are recorded in Table 1. Boric acid (A.R.) was used as such without any further purification.

Synthesis of boron Schiff base derivatives. 1 to 1.5 g of boric acid was dissolved in 50 ml of acetic anhydride by heating gently and the solution was cooled to room temperature. To this, an equimolar quantity of aldimine was added and the colour immediately turned reddish. These reactions are exothermic and appear to be complete even in the cold. The resulting compounds were recrystallized from acetic anhydride and analyzed for acetoxy group, boron and nitrogen.

Analytical methods. For the estimation of boron and acetoxy group, a weighed quantity of the compound was dissolved in distilled alcohol. The resulting solution was first titrated for the acetoxy group with phenolpthalein as indicator and after the end point was reached, 2 gm of mannitol was added and the solution was again titrated for the estimation of the boron content. Nitrogen was estimated by Kjeldahl's method.

Physical measurements. Molecular weights were determined

ebullioscopically with the help of a Gallenkamp ebulliometer. Conductivities were measured with a conductivity bridge type 235 (ANU VIDYUT ROORKEE).

IR spectra were scanned as Nujol mulls and in the form of KBr pellets in the range of 4000-400 cm<sup>-1</sup> with the help of a Perkin-Elmer 337 Grating IR spectrophotometer.

The <sup>1</sup>H NMR spectra were recorded in the 0-10  $\delta$  ppm and 10  $\delta$  ppm offset region by a Perkin-Elmer RB-12 spectrometer in carbon tetrachloride or deutrochloroform and TMS was used as internal reference.

#### DISCUSSION

Boric acid when first dissolved in acetic anhydride yields the tetraacyl pyroborate[10]:

This has now been found to react immediately with the monofunctional bidentate Schiff base in the presence of acetic anhydride with the formation of the boron Schiff base derivatives as follows:



However, further replacement of the acetoxy group could not be achieved even after long hours of refluxing. This may be due to the stable tetra-coordinated state of boron Schiff base derivatives. All the resulting compounds were coloured having high m.p. and appear to be stable when exposed to the atmosphere.

*IR spectra*. The IR spectra of the Schiff bases as well as the corresponding boron derivatives have been scanned and some important features may be summarized as given below:

In the case of the monobasic bidentate Schiff bases,

		Physical Properties		А	nalysis (%)			
S.No		State Colour	B.P. (mm/°C)	M.P. (°C)	Carbon Found (Calcd)	Hydrogen Found (Calcd)	Nitrogen Found (Calcd)	ν C=N (cm⁻¹)
1.	N-Methylsalicylideneamine	Yellow	4/92-94	_	70.46	6.58	10.32	1640
	C <sub>8</sub> H <sub>9</sub> ON	liquid			(71.02)	(6.70)	(10.40)	
2.	N-Ethylsalicylideneamine	Yellow	4-4.5/88-91	—	72.02	7.93	9.38	1630
	C <sub>9</sub> H <sub>11</sub> ON	liquid			(72.44)	(8.14)	(9.42)	
3.	N-Isopropylsalicylideneamine	Yellow	1/52-55	_	73.69	7.66	8.78	1628
	$C_{10}H_{13}ON$	liquid			(73.53)	(7.81)	(8.65)	
4.	N-n-Butylsalicylideneamine	Yellow	5/125-28	_	74.21	8.41	8.08	1635
	C <sub>11</sub> H <sub>15</sub> ON	liquid			(74.49)	(8.52)	(7.93)	
5.	N-Isobutylsalicylideneamine	Yellow	2.5/102-05	_	73.88	8.38	7.87	1627
	C <sub>11</sub> H <sub>15</sub> ON	liquid			(74.49)	(8.52)	(7.93)	
6.	N-Tertiarybutylsalicylideneamine	Yellow	2-2.5/92-96	_	74.65	8.26	7.95	1615
	C <sub>11</sub> H <sub>15</sub> ON	liquid			(74.49)	(8.52)	(7.93)	
7.	N-Phenylsalicylideneamine	Yellow	1.8-2/148-51	50	78.70	5.55	7.08	1615
	C <sub>13</sub> H <sub>11</sub> ON	solid			(79.12)	(5.62)	(7.12)	
8.	N-o-Tolylsalicylideneamine	Yellow	0.7/147	53	78.72	6.11	6.54	1610
	C14H13ON	solid			(79.64)	(6.20)	(6.66)	
9.	N-m-Tolylsalicylideneamine	Yellow	3/162-64	_	78.57	6.02	6.58	1620
	C <sub>14</sub> H <sub>13</sub> ON	brown liquid	,		(79.64)	(6.20)	(6.66)	
10.	N-p-Tolylsalicylideneamine	Orange	_	94	79.53	6.25	6.71	1625
	C <sub>14</sub> H <sub>13</sub> ON	needles			(79.64)	(6.20)	(6.66)	

Table 1. Characteristics and analyses of Schiff bases

Table 2. Physical properties and analyses of boron Schiff base complexes

					Analysis (%)	_	ν C=N (cm <sup>-1</sup> )	
S.No	Molecular formula and characteristics		M.P.°C	Acetoxy Found (Calcd)	Boron Found (Calçd)	Nitrogen Found (Calcd)		Mol. Wt. Found (Calcd)
1.	XNMe	light pale yellow	201	42.52	4.03	5.25	274	1650
		crystalline solid		(44.86)	(4.11)	(5.32)	(263)	
2.	XNEt,	Pinkish white	170	41.37	3.96	4.95	285	1635
		solid		(42.60)	(3.91)	(5.05)	(277)	
3.	$X N Pr^{i-}$ ,	white solid	167	38.87	3.66	4.65	273	1635
				(40.55)	(3.72)	(4.81)	(291)	
4.	XNBu <sup>n-</sup> ,	white solid	141	37.12	3.49	4.52	316	1645
				(38.69)	(3.55)	(4.59)	(305)	
5.	XNBu <sup>i−</sup> ,	light brown solid	126	36.38	3.47	4.48	307	1635
				(38.69)	(3.55)	(4.59)	(305)	
6.	XNBu'-,	light pinkish	199	37.32	3.51	4.64	297	1622
		violet solid		(38.69)	(3.55)	(4.59)	(305)	
7.	XNPh,	yellow solid	125	35.47	3.28	4.26	318	1624
				(36.42)	(3.34)	(4.32)	(324)	
8.	XNMePh-O,	yellow solid	150	33.81	3.12	4.12	358	1625
				(34.70)	(3.18)	(4.12)	(340)	
9.	XNMePh-m,	pinkish yellow	155	33.21	3.08	4.15	338	1628
		crystalline solid		(34.70)	(3.18)	(4.12)	(340)	
10.	XNMePh-p,	crystalline	194	34.05	3.21	4.04	305	1630
		yeilow solid		(34.70)	(3.18)	(4.12)	(340)	

where  $X = (AcO)_2 BOC_6 H_4 C(H)$ :, n = normal, i = iso, t = tertiary.

the OH stretching frequency is not observed possibly because of both types of hydrogen bonding, intermolecular (O-H....O) as well as intramolecular (O-H....N). The frequency of the hydrogen bonded OH is lowered considerably and it overlaps with the  $\nu$  C-H vibrations.

A strong band at ~1615 cm<sup>-1</sup> is observed in the Schiff bases, which may be assigned to  $\nu$  C=N. This, however, shows a shift towards higher frequencies in the resulting boron derivatives. Similar behaviour of  $\nu$ C=N has been observed in the case of BF<sub>3</sub> imine adducts and this has been explained as due to a fractional increase in C=N bond order on coordination[11].

The strong absorption bands in complexes appear at ~1700 and ~1355 cm<sup>-1</sup> and these may be assigned to  $\nu$  C=O of the acetoxy group and  $\nu$  C=O coupled with  $\nu$  B=O asym. respectively. In the beryllium and boron chelates reported earlier [12-14], these have been shown

			Azomethine proton	Aromatic protons				
	Compound		-C=N   H		Alkyl protons			Acetoxy
					CH <sub>3</sub> CH <sub>2</sub>		СН	protons
1.	(a) (b)	C <sub>8</sub> H <sub>9</sub> ON (AcO) <sub>2</sub> B(C <sub>8</sub> H <sub>8</sub> ON)	8.08 8.30	6.82 7.12	3.20 3.43			2.10
2.	(a) (b)	C9H11ON (AcO)2B(C9H10ON)	8.20 8.35	<b>6.88</b> 7.10	1.30 1.44	3.50 3.77	_	2.10
3.	(a) (b)	$C_{10}H_{13}ON$ (AcO) <sub>2</sub> B( $C_{10}H_{12}ON$ )	8.28 8.45	7.00 7.13	1.15 3.36	_	3.36 4.30	2.10
4.	(a)	C <sub>11</sub> H <sub>15</sub> ON″	8.05	6.96	0.75	3.30A 1.48B		
	(b)	$(AcO)_2B(C_{11}H_{14}ON)$	8.22	7.12	1.09	3.93A 1.62B		2.08
5.	(a) (b)	C <sub>11</sub> H <sub>15</sub> ON <sup>i-</sup> (AcO) <sub>2</sub> B(C <sub>11</sub> H <sub>14</sub> ON)	8.10 8.25	7.0 7.10	0.87 1.0	3.20 3.50	1.70 1.75	2.08
6.	(a) (b)	$C_{11}H_{15}ON^{t-1}$ (AcO) <sub>2</sub> B( $C_{11}H_{14}ON$ )	8.14 8.60	6.93 7.36	1.10 1.60	-	_	2.12
7.	(a) (b)	$C_{13}H_{11}ON$ (AcO) <sub>2</sub> B(C <sub>13</sub> H <sub>10</sub> ON)	8.30 8.45	7.06 7.42	_	-		2.00
8.	(a) (b)	$C_{14}H_{13}ON-o$ (AcO) <sub>2</sub> B( $C_{14}H_{12}ON$ )	8.35 8.35	7.02 7.38	2.25 2.35			2.02
9.	(a) (b)	$C_{14}H_{13}ON-m$ (AcO) <sub>2</sub> B(C <sub>14</sub> H <sub>12</sub> ON)	8.23 8.45	6.80 7.40	2.10 2.40		_	2.07
10.	(a) (b)	C <sub>14</sub> H <sub>13</sub> ON- <i>p</i> (AcO) <sub>2</sub> B(C <sub>14</sub> H <sub>12</sub> ON)	8.52 8.52	7.12 7.32	2.28 2.45		_	2.02

Table 3. 'H NMR spectral data of Schiff bases and their boron complexes in ppm

to appear at  $1701 \pm 10$  and  $1375 \pm 10$  cm<sup>-1</sup>. The decrease in the latter case may be attributed to the coordination of boron to nitrogen as reported by Lappert *et al.*[15].

<sup>1</sup>HNMR spectra. The <sup>1</sup>H NMR spectra of the Schiff bases and the corresponding derivatives were recorded. A comparison of these spectra reveals the following aspects:

The disappearance of phenolic -OH resonance peak from the region  $12.5 \pm 0.2 \delta$  ppm in the boron Schiff base derivatives provides strong evidence for complexation through the phenolic OH group. This is further supported by the appearance of a resonance peak in the region  $2.1 \pm 0.1 \delta$  ppm attributed to a methyl group flanked by a

# C=O group.

A comparison of the azomethine proton resonance in the Schiff bases  $(8.2 \pm 0.2 \delta \text{ ppm})$  with that of the resulting complexes  $(8.4 \pm 0.2 \delta \text{ ppm})$  shows a shift downfield, which may be attributed to the deshielding caused by the coordination through nitrogen of the azomethine group to boron. However, little or no shift in the case of the complexes derived from the Schiff bases of the toluidines may be explained by the electron donating property of the coplanar methyl substituted phenyl ring through mesomerism.

A considerable shift in the position of the aromatic protons as well as the alkyl protons attached either to nitrogen or to phenyl ring further substantiates the chelation of boron to the nitrogen of the azomethine group.

Conductance. Conductance measurements have shown the nonelectrolytic nature of the boron Schiff

base derivatives in dimethylformamide due to the stable tetracoordinated structure of these complexes.

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