

Complexes of Unsymmetrical Boranes with Bidentate Schiff Bases: Proton, Carbon-13 & Boron-11 Nuclear Magnetic Resonance Spectra of Complexes Containing B—N Bonds

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Reactions of 2-isopropoxybenzo-1,3-dioxo-2-borole with halogen substituted schiff bases yield tetra-coordinated, stable complexes of boron. The resulting complexes have been characterised by elemental analyses and molecular weight determinations. The mode of bonding of the schiff base ligands to boron atom has been deduced on the basis of IR, ^1H , ^{13}C and ^{11}B NMR spectra. A few of these complexes have also been screened for their biocidal activity.

Compounds containing B—N bonds have found wide applications in biology^{1,2}, industry³ and agriculture³. As a part of our endeavour in this area^{4,5}, the synthesis of some new boron complexes with nitrogen donor ligands, particularly with bidentate schiff bases derived from halogen substituted anilines, is reported in this paper.

Materials and Methods

All the experiments were carried out under anhydrous conditions.

The unsymmetrical borane, 2-isopropoxybenzo-1,3-dioxo-2-borole (I) was prepared by the procedure reported in the literature⁶ (Found: B, 6.01; OPrⁱ, 32.88. Reqd: B, 6.01; OPrⁱ, 33.15%).

The schiff bases (1-6; Table 1) used were prepared by the condensation of appropriate aldehyde/ketone with substituted anilines⁷ and fully characterised by elemental analyses and spectral data.

Synthesis of borane-schiff base complexes (7-12; Table 2)

A mixture containing unsymmetrical borane(I) and schiff base in equimolar quantity in dry benzene was refluxed for 10-15 hr using a fractionating column. The isopropanol liberated was fractionated off azeotropically with benzene and estimated to ensure the completion of reaction. The excess of the solvent was distilled off and the product crystallised from dry *n*-hexane, it was finally dried at 50-68°/0.2 mm. The characterisation data of the products are given in Table 2. These complexes were obtained in around 80% yield.

Analyses and spectral measurements

The complexes were analysed by the previously reported methods^{8,9}. Molecular weights were determined by the Rast camphor method. IR spectra were scanned in nujol on a Perkin-Elmer 577 grating

Table 1—Physical Characteristics and Analyses of Schiff Bases of *p*-Fluoro-, *p*-Chloro and *p*-Bromo-anilines

Schiff base	Colour and state	m.p. (°C)	Found (Calc.), %		
			C	H	N
N-Salicylaldimine- <i>p</i> -fluoroaniline $\text{HOC}_6\text{H}_4\text{CH:NC}_6\text{H}_4\text{F-}p$ (1)	Yellow crystalline	72	71.32 72.55	3.92 4.65	6.05 6.54
N-2-Hydroxy-1-naphthaldimine- <i>p</i> -fluoroaniline $\text{HOC}_{10}\text{H}_6\text{CH:NC}_6\text{H}_4\text{F-}p$ (2)	Yellow solid	117	76.10 76.98	4.16 4.52	5.10 5.28
N-Salicylaldimine- <i>p</i> -chloroaniline $\text{HOC}_6\text{H}_4\text{CH:NC}_6\text{H}_4\text{Cl-}p$ (3)	Yellow solid	101	67.40 67.50	5.10 5.19	6.00 6.06
N-2-Hydroxy-1-naphthaldimine- <i>p</i> -chloroaniline $\text{HOC}_{10}\text{H}_6\text{CH:NC}_6\text{H}_4\text{Cl-}p$ (4)	Yellow solid	78	72.40 72.54	4.10 4.27	4.90 4.98
N-Salicylaldimine- <i>p</i> -bromoaniline $\text{HOC}_6\text{H}_4\text{CH:NC}_6\text{H}_4\text{Br-}p$ (5)	Orange yellow crystalline solid	105	56.40 56.52	3.50 3.62	4.98 5.07
N-2-Hydroxy-1-naphthaldimine- <i>p</i> -bromoaniline $\text{HOC}_{10}\text{H}_6\text{CH:NC}_6\text{H}_4\text{Br-}p$ (6)	Yellow solid	160	62.40 62.57	3.60 3.68	4.15 4.29

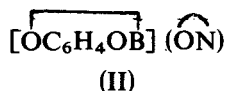
Table 2—Reactions of 2-Isopropoxybenzo-1,3-dioxo-2-borole (I) with Halogen Substituted Schiff Bases in 1:1 Molar Ratio

Product (nature)	m.p. (°C)	Found (Calc.), %		Mol. wt.
		B	N	
(C ₆ H ₄ O ₂ B)C ₁₃ H ₉ NOF Yellow solid (7)	130	3.20(3.30)	4.10(4.20)	325 333
C ₆ H ₄ O ₂ B(C ₁₇ H ₁₁ NOF) Orange solid (8)	139	2.82(2.87)	3.60(3.65)	375 383
C ₆ H ₄ O ₂ B(C ₁₃ H ₉ NOCl) Yellow solid (9)	186	3.10(3.15)	4.00(4.01)	340 349
C ₆ H ₄ O ₂ B(C ₁₇ H ₁₁ NOCl) Yellow solid (10)	189	2.70(2.75)	3.40(3.50)	390 399
C ₆ H ₄ O ₂ B(C ₁₇ H ₁₁ NOBr) Yellow solid (11)	210	2.45(2.47)	3.10(3.15)	435 444
C ₆ H ₄ O ₂ B(C ₁₃ H ₉ NOBr) Yellow solid (12)	156	2.70(2.79)	3.50(3.55)	380 394

spectrophotometer. PMR spectra were recorded on a Perkin-Elmer RB-12 spectrometer (60 MHz) in DMSO-*d*₆ using TMS as the internal standard. Boron-11 spectra were scanned on a Bruker WH-90 spectrometer operating at 64.21 MHz at 31°C using BF₃·Et₂O as the external standard. Carbon-13 spectra were recorded on a Bruker WH 90 spectrometer operating at 25.15 MHz. Chemical shifts are accurate up to ±0.1 ppm.

Results and Discussion

The reactions of 2-isopropoxybenzo-1,3-dioxo-2-borole(I) and the schiff bases (1-6) in equimolar proportions in refluxing benzene yield isopropanol and the derivatives of type (II)



where $\widehat{\text{ON}}$ represents the donor system of the schiff base. The resulting complexes are coloured solids, having sharp melting points, monomeric and non-electrolytic in nature.

IR spectra

In the IR spectra of ligands a sharp and strong band in the region 3250-3100 cm⁻¹, assignable to νOH, disappears in the spectra of the complexes indicating deprotonation of OH group and the chelation of oxygen to the boron atom. This is further supported by the shift in νC—O modes (1300-1275 cm⁻¹) of the free ligands to higher frequency region in the spectra of the complexes. The νC=N modes of the free ligands around 1600 ± 5 cm⁻¹ are also shifted (Δν = 10 cm⁻¹) to higher wavenumbers in the complexes and appear at 1610 ± 5 cm⁻¹, suggesting the coordination of

azomethine nitrogen¹⁰ and thus resulting in a stable tetracoordinated environment around boron.

Some new and sharp bands observed only in complexes in the regions, 1300-1350 and 1520-1555 cm⁻¹ are due to the νB—O and νB←N modes¹¹ respectively.

PMR spectra

The PMR spectra of the ligands and a few representative complexes (7, 10, 12; Table 2) have been recorded. The ligand, salicylaldimine-*p*-fluoroaniline (1) exhibits a signal at δ 12.10 assignable to OH proton. This signal completely disappears in the spectrum of the complex (7) showing deprotonation as well as the ligation of phenolic oxygen to the boron atom. The azomethine proton signal observed at δ 8.50 in the ligand shows marked downfield shift (δ 8.80) in the complex (7). This is due to the coordination of azomethine nitrogen to the boron atom¹². A complex multiplet observed at δ 7.40-6.80 in the ligands remains unchanged in the complexes showing the non-involvement of aromatic protons in complexation.

Boron-11 NMR spectra

The ¹¹B NMR spectra of the complexes (9 and 10) exhibit sharp and strong singlets at δ 7.49 and 7.40 respectively, which are in good agreement with the values reported earlier in the literature for the tetracoordinated boron¹¹.

Carbon-13 NMR spectra

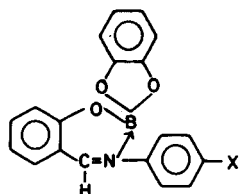
The ¹³C NMR spectra of the complex (8) and the corresponding ligand, 2-hydroxy-1-naphthaldimine-*p*-

Table 3—¹³C NMR Data of Ligand (2) and Complex (8)

Carbon	¹³ C (ppm)	
	Ligand	Complex
1	162.1	158.4
2	116.5	116.4
3	113.4	129.8
4	120.3	120.6
5	124.0	125.8
6	118.1	119.0
7	150.4	141.6
8	134.3	120.6
9	118.4	109.5
10	123.4	116.2
11	163.5	162.1
12	116.8	116.0
13	112.0	112.5
14	—	107.5
15	—	116.5
16	—	149.5

fluoroaniline (2) have been recorded as typical examples. Carbon-13 chemical shifts are recorded in Table 3. Considerable shifts observed in the positions of the signals of carbons carrying a phenolic oxygen and an azomethine nitrogen support the coordination of the ligand to the boron atom in a manner arrived at by a study of the IR and PMR spectra of the complexes.

On the basis of above spectral evidences, tentative structure (III) can be proposed for the complexes derived from salicylaldehyde and *p*-haloanilines.



(where X = F, Cl or Br)

Biocidal activity

The biological screening of a few representative complexes against some gram +ve and gram -ve bacteria and some saprophytic or pathogenic fungi shows that the complexes are quite active against bacteria and fungi even at very low concentrations. Comparatively, the fluoro complexes are much more active than the corresponding chloro and bromo com-

plexes. This may be attributed to the higher electron withdrawing capacity of fluorine atom¹².

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