

Unsymmetrical Boron Complexes of Schiff Bases Derived from S-Benzylthiocarbazate

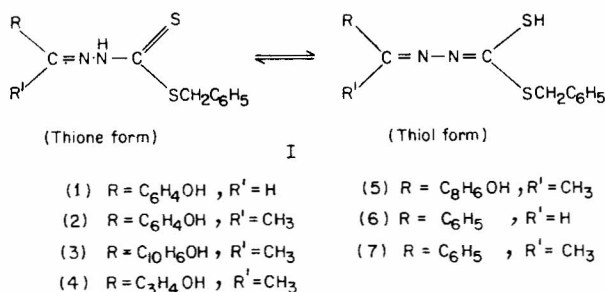
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Schiff base ligands derived from S-benzylthiocarbazate form unsymmetrical boron complexes viz. tri-coordinated $[\text{OC}_6\text{H}_4\text{OB}(\text{DTZ})]$ or $[\text{OC}_6\text{H}_4\text{OB}(\text{D'T'Z'H})]$ and tetra-coordinated, $[(\text{OC}_6\text{H}_4\text{OB})_2(\text{D'T'Z})]$. The complexes have been prepared by the reactions of 2-isopropoxy-1,3,2-benzodioxaborole with schiff bases in 1:1 (with monobasic bidentate DTZH) and 1:1 and 2:1 (with bibasic tridentate D'T'Z'H₂) molar ratios. The resulting complexes are yellow to brown coloured solids, having sharp melting points and soluble in THF, DMSO and CDCl_3 . The complexes have been characterised by IR, ^1H and ^{11}B NMR, and electronic spectral data.

Dithiocarbazate and its derivatives as well as their metal complexes are frequently used as anticancer¹, antitumour, antituberculosis² and antipyretic agents³. In view of this and in view of our interest in symmetrical and unsymmetrical complexes of boron, we report herein the reactions of 2-isopropoxy-1,3,2-benzodioxaborole with the schiff bases, (I; 1-7) obtained, respectively by the condensation of S-benzylthiocarbazate with 2-hydroxybenzaldehyde, 2-hydroxyacetophenone, 2-hydroxy-1-naphthaldehyde, 2,4-pentanedione, 1-phenyl-1,3-butanedione, benzaldehyde and methyl phenyl ketone. The complexes isolated have been characterised by elemental analyses and spectral data (IR, electronic, PMR & ^{11}B NMR). The ligands (I) are expected to exhibit tautomeric equilibrium between the thione and thiol form.



Materials and Methods

2-Isopropoxy-1,3,2-benzodioxaborole was prepared by refluxing triisopropoxyborane with catechol in dry benzene removing the liberated alcohol azeotropically⁴, and distilling the residue under reduced pressure (Found: B, 6.01; OPrⁱ, 32.88. Calc. B, 6.08; OPrⁱ, 33.10%).

IR spectra were recorded in KBr on a Perkin-Elmer 577 grating spectrophotometer, PMR spectra in

DMSO-*d*₆ on a Perkin-Elmer R-12B spectrometer, using TMS as an internal standard, electronic spectra in MeOH (200-600 nm) on a Toshniwal spectrophotometer using 1 cm quartz cell, ^{11}B NMR spectra on a Bruker WH 90 spectrometer operating at 64.21 MHz at 30°C using $\text{BF}_3 \cdot \text{Et}_2\text{O}$ as the external standard.

S-Benzylthiocarbazate was prepared by the literature method⁵. For the preparation of schiff bases (1-7) a weighed amount of S-benzylthiocarbazate was dissolved in ethanol and mixed with an equimolar amount of aldehyde or ketone (ethanolic solution). The reaction mixture was kept over a water-bath for about 10 min, left overnight, the crystalline solid filtered off and recrystallised from ethanol to afford schiff bases (1-7).

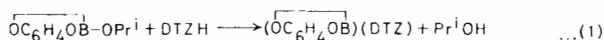
Boron schiff base complexes

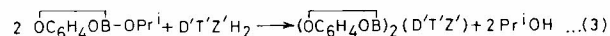
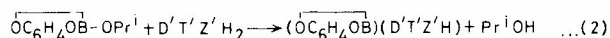
The complexes of boron with schiff bases (1-7) were prepared as follows:

A weighed amount of 2-isopropoxy-1,3,2-dioxaborole (1-2 g) was mixed with calculated amount of the schiff base (1.5-3.1 g) in dry benzene (75 ml). The reaction mixture was refluxed over a fractionating column and the isopropanol liberated collected azeotropically with benzene and estimated oxidimetrically. The completion of the reaction was ascertained by the estimation of isopropanol. After the completion of the reaction, the excess of the solvent was distilled off and the product dried *in vacuo*. Their analytical data are given in Table 1.

Results and Discussion

The formation of the various complexes, listed in Table 1, occurs by the reactions (1-3).





(where DTZH and D'T'Z'H₂ represent the monobasic bidentate and bibasic tridentate ligands, respectively).

IR spectra

The presence of strong bands around 1500 and 1050 cm⁻¹, assignable to νC=N and νC=S respectively⁶, in the IR spectra of the schiff bases (1-7) indicates that the ligands exist mainly in the thione form in the solid state. However, in the solution spectra both these bands disappear and a sharp band appears around 2570 cm⁻¹ assignable to νSH. This indicates that the schiff bases exist in thiol form in solution. Strong bands appearing in the region 3200-3150 cm⁻¹ in the spectra of ligands have been assigned to H-bonded νOH/νNH. This is observed at the same position in the complexes of 1:1 stoichiometry, i.e. with bibasic tridentate ligands, indicating the non-involvement of νOH/νNH group on complexation.

However, in the spectra of the 2:1 complexes, the bands in the region 3200-3150 cm⁻¹ disappear completely, showing the deprotonation of OH/NH followed by chelation of the boron atom through oxygen/nitrogen of the functional group. The formation of B-O band⁷ in the spectra of the complexes is also supported by the appearance of a new band around 1350 cm⁻¹.

The free ligand bands in the region 1050 cm⁻¹ assignable to νC=S undergo shift to lower wavenumbers in the spectra of complexes. This lowering can be attributed to the coordination of ligands through the thiole sulphur atom, which is also supported by the presence of a sharp band in the region 870-910 cm⁻¹ due to νB-S.

The shift in νC=N (azomethine) modes of the free ligands to higher wavenumbers only in 2:1 complexes is due to the coordination of azomethine nitrogen to the boron atom after donation of lone pair of electrons from N→B⁸. This is further supported by the presence of a strong band around 1540 cm⁻¹ due to νB←N as reported earlier⁹.

Table 1—Analytical Data of Boron Schiff Base Complexes

Sl. No.	Product	Yield (%)	m.p. (°C)	Found (%) (Calc.)				
				C	H	N	B	S
Schiff base (1)								
1	($\overline{\text{OC}_6\text{H}_4\text{OB}}$)(C ₁₅ H ₁₃ N ₂ S ₂ O)	78	135	61.40 (61.61)	4.00 (4.15)	6.45 (6.84)	2.60 (2.68)	15.00 (15.64)
2	($\overline{\text{OC}_6\text{H}_4\text{OB}}$) ₂ (C ₁₅ H ₁₂ N ₂ S ₂ O)	82	115	60.00 (60.22)	3.72 (3.71)	5.01 (5.20)	3.98 (4.08)	11.00 (11.89)
Schiff base (2)								
3	($\overline{\text{OC}_6\text{H}_4\text{OB}}$)(C ₁₆ H ₁₅ N ₂ S ₂ O)	79	200	60.61 (60.82)	4.40 (4.37)	6.60 (6.45)	2.25 (2.35)	14.01 (14.74)
4	($\overline{\text{OC}_6\text{H}_4\text{OB}}$) ₂ (C ₁₆ H ₁₄ N ₂ S ₂ O)	83	178	63.20 (63.39)	4.00 (4.15)	5.10 (5.28)	4.00 (4.15)	11.95 (12.07)
Schiff base (3)								
5	($\overline{\text{OC}_6\text{H}_4\text{OB}}$)(C ₁₉ H ₁₇ N ₂ S ₂ O)	79	230	63.08 (63.29)	4.78 (4.85)	5.65 (5.90)	2.40 (2.32)	13.01 (13.50)
6	($\overline{\text{OC}_6\text{H}_4\text{OB}}$) ₂ (C ₁₉ H ₁₆ N ₂ S ₂ O)	81	165	64.04 (64.24)	4.00 (4.14)	4.60 (4.83)	3.60 (3.79)	10.90 (11.05)
Schiff base (4)								
7	($\overline{\text{OC}_6\text{H}_4\text{OB}}$)(C ₁₃ H ₁₄ N ₂ S ₂ O)	80	160	60.01 (60.31)	4.98 (5.02)	7.14 (7.40)	2.80 (2.91)	16.69 (16.93)
8	($\overline{\text{OC}_6\text{H}_4\text{OB}}$) ₂ (C ₁₃ H ₁₃ N ₂ S ₂ O)	82	120	58.00 (58.13)	4.06 (4.26)	5.10 (5.42)	4.00 (4.26)	12.04 (12.40)
Schiff base (5)								
9	($\overline{\text{OC}_6\text{H}_4\text{OB}}$)(C ₁₈ H ₁₇ N ₂ S ₂ O)	83	80	62.03 (62.33)	4.67 (4.97)	6.00 (6.06)	2.16 (2.38)	13.43 (13.85)
10	($\overline{\text{OC}_6\text{H}_4\text{OB}}$) ₂ (C ₁₈ H ₁₆ N ₂ S ₂ O)	78	95	62.00 (62.28)	4.00 (4.15)	4.72 (4.84)	3.65 (3.80)	10.80 (11.07)
Schiff base (6)								
11	($\overline{\text{OC}_6\text{H}_4\text{OB}}$)(C ₁₅ H ₁₃ N ₂ S ₂ O)	80	165	61.40 (62.37)	4.00 (4.20)	6.85 (6.93)	2.60 (2.72)	15.02 (15.84)
Schiff base (7)								
12	($\overline{\text{OC}_6\text{H}_4\text{OB}}$)(C ₁₆ H ₁₅ N ₂ S ₂ O)	81	138	63.44 (63.46)	4.38 (4.56)	6.70 (6.73)	2.56 (2.64)	15.08 (15.38)

Electronic spectra

The electronic spectrum of the schiff base (I) in anhydrous methanol exhibits three maxima at 210, 318 and 346 nm. The maximum at 210 nm, assignable to 1B band of the phenyl ring, slightly shifts to the higher wavelength on complexation and is observed at 216 and 214 nm in 1:1 and 2:1 complexes, respectively. The bands at 318 and 346 nm in the spectrum of I are due to the $n \rightarrow \sigma^*$ and $n \rightarrow \pi^*$ transitions, respectively, within the C=N chromophores. These two bands undergo hypsochromic shifts in the spectra of complexes probably due to the formation of a dative B←N bond on complexation¹⁰.

PMR spectra

The PMR spectra of 2:1 derivatives do not display the free ligand signals due to H-bonded OH (δ 13.08), NH (δ 10.20) and SH (δ 4.94 ppm), indicating deprotonation of these functional groups and the chelation of boron atom through oxygen, nitrogen and sulphur atoms of the ligand moiety, respectively.

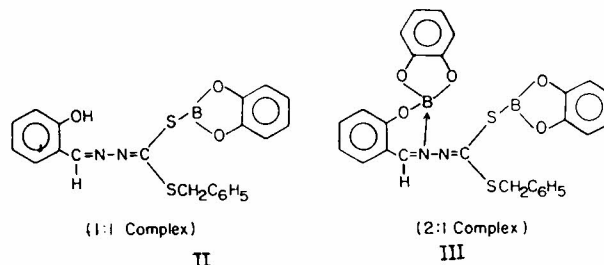
In 1:1 boron derivative, the appearance of signal due to OH proton at nearly same position (δ 13.00) as in the free ligand clearly indicates that OH group of the ligand moiety remains free and the boron atom gets bonded only through SH.

The bonding of the azomethine nitrogen of the ligand moiety in the 2:1 boron complexes is substantiated by the downfield shift (δ 8.88 ppm) of the azomethine ($-\text{HC}=\text{N}$) proton, which is observed at (δ 8.42 ppm) in the ligand.

¹¹B NMR spectra

In the ¹¹B NMR spectrum of 1:1 boron complex of the schiff base (I) a sharp signal appears at δ 20.08, indicating tri-coordinated state of boron in this 1:1 complex. On the other hand in the case of 2:1 boron

complex of the schiff base (I) two sharp signals at δ 21.05 and 7.35 are observed. This clearly points to the presence of tri- and tetra-coordinated boron atoms, respectively, in 2:1 complexes. Thus on the basis of the foregoing discussion, the 1:1 and 2:1 complexes can be represented by the typical structures (II) or (III) respectively.



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