

Boron complexes of sulphur containing Schiff bases derived by the condensation of S-methyl or S-benzyl dithiocarbazate with β -diketones

P K SINGH and J P TANDON*

Department of Chemistry, University of Rajasthan, Jaipur 302 004, India.

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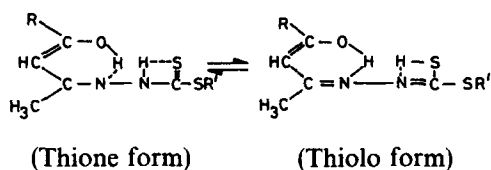
Abstract. Tetra-coordinated boron derivatives, $(EtO)B(DTZ)$ and $(DTZH)B(DTZ)$, (where DTZ^{--} and DTZ^- represent the anions of the Schiff base $DTZH_2$) have been synthesized by 1:1 and 1:2 molar reactions of triethoxyborane with bibasic tridentate Schiff bases, derived by the equimolar condensation of S-methyl or S-benzyl dithiocarbazate with acetyl acetone or benzoyl acetone. Further 1:1 derivatives have been shown to undergo replacement reactions with *t*-butyl alcohol, showing thereby the labile nature of the ethoxy group. Based on infrared and proton magnetic resonance spectral studies and monomeric nature, suitable structures have been assigned to these derivatives.

Keywords. Boron complexes; dithiocarbazate derivatives; Schiff bases; 1H NMR spectra; IR spectra.

1. Introduction

Extensive studies on the transition metal complexes of dithiocarbazate Schiff bases have been carried out and a review featuring their geometry and configurations has also appeared (Ali and Livingstone 1974). However, similar investigations concerning the non-transition element complexes are scanty (Pardhy *et al* 1980; Agarwal *et al* 1980). In earlier communications (Singh *et al* 1980; Singh and Tandon 1977) a variety of boron derivatives with nitrogen donor ligands have been reported and some of these have been found to possess considerable biological activity (Singh and Tandon (unpublished)). Recently, the physiological aspects of boron complexes have also been reviewed (Niedenzu 1979).

Some new boron derivatives having B–S bond, are synthesized by the reactions of triethoxyborane with the Schiff bases having the donor system HSNOH and which may be structurally represented as follows:



I, $R = -CH_3$, $R' = -CH_3$ (AcAcMTZH₂)

II, $R = -CH_3$, $R' = -CH_2C_6H_5$ (AcAcBTZH₂)

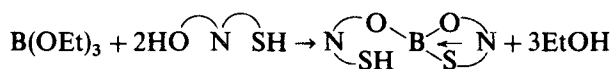
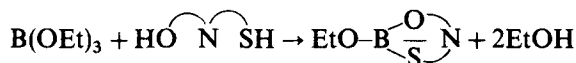
III, $R = -C_6H_5$, $R' = -CH_3$ (BzAcMTZH₂)

IV, $R = -C_6H_5$, $R' = -CH_2C_6H_5$ (BzAcBTZH₂)

* To whom all correspondence should be addressed.

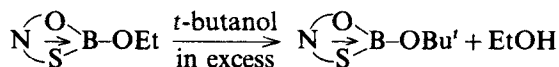
2. Discussion

The desired products are obtained by 1 : 1 and 1 : 2 molar reactions of triethoxyborane with the ligands AcAcMTzH₂, AcAcBTzH₂, BzAcMTzH₂, BzAcBTzH₂. However, a 2:3 molar reaction simply yielded a mixture of the products formed by 1:1 and 1:2 molar reactions. The 1:1 product could be isolated using a mixture of benzene and *p*-xylene. These reactions were quite facile due to the weaker B–OR bonding as well as the reactive nature of the dithiocarbazate Schiff bases (Ali and Livingstone 1974).



(where HO $\begin{array}{c} \curvearrowright \\ \text{N} \\ \curvearrowleft \\ \text{SH} \end{array}$ represents the donor system of bibasic tridentate Schiff base).

The 1:1 products further undergo replacement reactions with *t*-butyl alcohol as indicated below:



The resulting products are obtained as coloured, nonvolatile and highly viscous liquids or solids. These are soluble in common organic solvents, monomers and unstable in the open atmosphere probably due to the weaker B–S bond.

2.1 IR spectra

The IR spectra of the Schiff bases in solid form display strong bands at 1500 and 1050 cm⁻¹ assignable to $\nu_{\text{C-N}}$ and $\nu_{\text{C=S}}$ respectively Sahni and Kapoor (1979). These bands support the presence of the thione form; however, in solution spectra in ethanol, both these bands disappear and a sharp band at ~ 2570 cm⁻¹ is observed due to SH which is indicative of the thiol form. These studies probably indicate that the –NH–C=S group exists mainly in the solid form, whereas in solution an equilibrium exists between the two tautomeric forms.

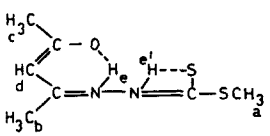
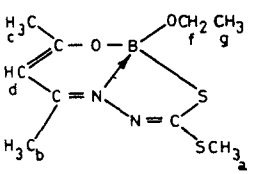
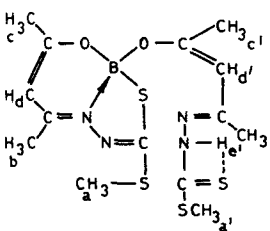
A strong band appears in the region, 3200–3125 cm⁻¹ due to the hydrogen bonded $\nu_{\text{OH}}/\nu_{\text{NH}}$ which is not observed in the 1 : 1 boron derivatives, due to the deprotonation of OH/NH group and the chelation of oxygen to boron. However, in the spectra of the 1 : 2 derivatives the characteristic band of NH is observed indicating that one of the functional groups of at least one Schiff base does not undergo deprotonation.

The shifting of the frequency due to azomethine stretch $\nu_{\text{C=N}}$ to the higher side, (~ 1600 cm⁻¹–1630 cm⁻¹) in the boron derivatives is probably due to an increase in the C=N bond order after the formation of N → B bond (Samuel *et al* 1970). All these derivatives show a strong band at ~ 1540 cm⁻¹ which may be due to the $\nu_{\text{B-N}}$ as reported earlier (Wang *et al* 1970). The $\nu_{\text{B-O}}$ (asym) appears at ~ 1310 cm⁻¹ in all the boron derivatives (Singh *et al* 1980).

2.2 NMR spectra

The proton magnetic resonance spectra of AcAcMTZH₂ and its 1:1 and 1:2 boron derivatives have been recorded in carbon tetrachloride. The chemical shift values in

Table 1. ^1H NMR data for the Schiff base (AcAcMTZH_2) and its boron complexes in δ ppm.

Compound	a (a')	b (b')	c (c')	d (d')	e (e')	f	g
	2.10	2.40	2.56	5.83	10.75	—	—
	2.21	2.94	2.61	6.28	—	3.53	1.13
	2.38 (2.18)	2.92 (2.43)	2.57 (2.64)	6.13 (5.78)	10.52 (4.26)	—	—

(δ) ppm for the various protons are listed in table 1 and the following points appear to be significant from the structural point of view: (i) In 1 : 1 derivative, the disappearance of hydroxyl (δ 10.75 ppm) and thio proton signal (δ 4.45 ppm) shows chelation of boron through both oxygen and sulphur atoms, whereas in 1 : 2 derivative the appearance of the thio proton signal at δ 4.25 ppm, clearly indicates that at least in one of the ligand moieties one functional group remains unbonded. (ii) In 1 : 1 derivative, the methine proton and one of the methyl proton (labelled d and b respectively in table 1) signals show downfield shifting leaving behind two methyl proton (labelled a and c table 1) signals almost unchanged. This may be due to the boron acquiring a tetracoordinated state after accepting a lone pair of electrons from the azomethine nitrogen. (iii) In 1 : 2 derivative, however, two sets of proton signals are observed for every proton. One set remains at almost the same position as in the ligand, thereby showing that one of the ligands is acting as tridentate and another one as unidentate as shown in table 1.

3. Experimental

A glass apparatus fitted with quickfit interchangeable joints was used and the reactions were carried out under strictly anhydrous conditions. The fractionations were made on a column packed with Reschig rings and fitted to a ratiohead with a condenser.

Table 2. Reactions of $B(OEt)_3$ with the ligands in 1:1 and 1:2 molar ratios.

$B(OEt)_3$ (g)	Ligand (g)	Molar ratio	Compound, yield (g) and state	Ethanol in azeotrop (g)	Analysis %	Molecular wt.
1.57	2.19	1:1	(EtO)B(AcAcMTZ), 2.70 Yellow oil	0.96 (0.98)	4.21 (4.19)	25.10 (24.82)
0.88	2.48	1:2	(AcAcMTZH)B(AcAcMTZ) 2.38, Orange yellow oil.	0.41 (0.42)	2.60 (2.59)	— (32.29)
1.66	3.20	1:1	(EtO)B(AcAcBTZ), 3.28 Light greenish yellow solid	1.00 (1.04)	3.20 (3.23)	— (19.18)
0.53	2.03	1:2	(AcAcBTZH)B(AcAcBTZ), 2.00, Light greenish yellow solid	0.50 (0.50)	1.82 (1.88)	568 (593)
0.83	1.52	1:1	(EtO)B(BzAcMTZ), 1.70, Yellow oil	0.50 (0.52)	3.45 (3.38)	320 (331)
0.65	2.38	1:2	(BzAcMTZH)B(BzAcMTZ), 2.32, Yellow oil	0.60 (0.61)	2.20 (2.03)	— (26.03)
1.07	2.51	1:1	(EtO)B(BzAcMTZ), 2.80, yellow semisolid	0.65 (0.67)	3.00 (2.80)	— (18.32)
0.43	2.04	1:2	(BzAcBTZH)B(BzAcBTZ), 2.00, Yellow semisolid	0.40 (0.41)	1.53 (1.46)	684 (702)

Figures in parenthesis gives the calculated values.

3.1 Materials

Triethoxyborane was prepared by refluxing boric acid (S. Merck) with absolute ethanol in dry benzene (BDH) and removing water azeotropically (Lippincott). It was distilled before use and analysed: Found: B, 7.44; OC_2H_5 , 91.97%. Calcd. for $\text{B}(\text{OEt})_3$: B, 7.41; OC_2H_5 , 92.59%.

S-methyldithiocarbamate and S-benzylthiocarbamate were prepared as reported earlier (Ali *et al* 1971; Ali and Bose 1977). To prepare the Schiff bases, a weighed amount of S-methyl- or S-benzyl dithiocarbamate was dissolved in ethanol and mixed with an equimolar amount of β -diketone (ethanolic solution). The reaction mixture was kept over a water bath for about 10 min and left overnight at room temperature. The crystals which separated out were filtered off and recrystallized from the same solvent.

3.2 Analytical methods and physical measurements

Boron was estimated as reported earlier (Singh and Tandon 1977). Nitrogen was determined by the Kjeldahl's method and the sulphur was analysed by the literature method (Saraswat *et al* 1977). Carbon and hydrogen were analysed by the carbon hydrogen analyzer (Coleman-5602). Ethanol liberated in the reactions was estimated oxidimetrically (Bradley *et al* 1950). Molecular weight was determined ebullioscopically in boiling benzene using thermistor sensing.

IR spectra were recorded in Nujol mulls on a Perkin Elmer 577 grating infrared spectrophotometer and PMR spectra were scanned in carbon tetrachloride (using TMS as internal standard) on a Perkin-Elmer RB-12 spectrometer.

3.3 Synthesis of boron Schiff base complexes

A weighed amount of triethoxyborane was mixed with the calculated amount of Schiff base in dry benzene (~ 75 ml). The reaction mixture was refluxed over a fractionating column and the ethanol liberated was collected azeotropically with benzene. The completion of the reaction was ascertained by the ethanol estimation. After its complete removal, the excess of the solvent was distilled off and the products dried under reduced pressure (2 mm) for 2 hr. Further details are listed in table 2.

3.4 Exchange reactions of boron Schiff base derivatives

t-Butanol in excess was mixed with dry benzene solution of ethoxyboron Schiff base derivatives and the reaction mixture was refluxed over a ratio head. The ethanol was collected azeotropically with benzene and the rest of the procedure was the same as described in § 3.3.

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