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Stereochemical and Biochemical Aspects of Organoboron(III) Compounds of Hydrazonecarboxamides and Hydrazonecarbothioamides

Chitra Saxena and R. V. Singh*
Department of Chemistry, University of Rajasthan, Jaipur-302004, India

Hydrazonecarboxamides and hydrazonecarbothioamides and their derivatives have important pharmacodynamic significance. In the search for better fungicides and bactericides, organoboron(III) compounds derived from these ligands were screened for their antifungal and antibacterial activities. The heterocyclic aldimines were prepared by the condensation of (2-furanyl)methanal, (2-thienyl)methanal, (2-pyridinyl)methanal, (*1H*-indol-3-yl)methanal or 3-phenyl-2-propenal with hydrazinecarboxamide or hydrazinecarbothioamide. Unimolar and bimolar reactions between phenyldihydroxyborane and these ligands have produced PhB(OH)(NO), $PhB(NO)_2$, PhB(OH)(NS) and $PhB(NS)_2$ types of biologically active compounds. Structural assignment has been made through UV, IR and NMR (^1H, ^{11}B and ^{13}C) spectroscopy. TGA and XRD of a representative compound have also been carried out. The compounds were tested *in vitro* against a number of fungal and bacterial strains and were found to possess moderate to good toxicity.

Keywords: organoboron(III) compounds; hydrazonecarboxamides; hydrazonecarbothioamides; biocides; spectroscopy

INTRODUCTION

The preparation of organoboron(III) compounds of different imines[1,2] has evoked a good deal of interest. The last three decades have seen a wide variety of literature[3–6] dealing with organoboron compounds. The role of organoboron compounds in cancer treatment was mainly related to their use as neutron capture agents.[7,8] Aromatic organoboron compounds are excellent insecticides, though compounds in which the carbon is linked to boron via oxygen are ineffective.[9] Organoboron compounds, with few exceptions,[10] are only moderately toxic and the toxicity may well reflect, in part, the toxicity of the hydrocarbon moiety.

Hydrazonecarboxamides and hydrazonecarbothioamides are the most useful nitrogen and oxygen or sulphur donor ligands.[11,12] An abundance of literature references is available for their antiviral,[13] antimalarial,[14] antitumour[15] and anticonvulsant[16] activities. Organoboron compounds of these ligands have been found to possess conspicuous biocidal activity.[17] Biological activity is enhanced on undergoing chelation.[18] From these viewpoints, we have studied stereochemical and biochemical aspects of organoboron(III) compounds of ON and SN donor heterocyclic aldimines and the findings are presented in this paper.

The ligands used exist in the tautomeric forms[17] in the solution state at the top of the next page.

RESULTS AND DISCUSSION

Stereochemical aspects

The reactions of $PhB(OH)_2$ and the respective monobasic bidentate heterocyclic aldimines, i.e. L_1H, L_2H, L_3H, L_4H, L_5H, L_6H, L_7H, L_8H, L_9H or $L_{10}H$ (as defined in the Experimental section), in 1:1 and 1:2 stoichiometric proportions proceed in a facile manner resulting in the isolation of $PhB(OH)(L_n)$ and $PhB(L_n)_2$ types of complexes, respectively ($n = 1–10$). The progress of the reaction was ensured by the liberation of benzene–water azeotrope. The resulting complexes were isolated as creamy yellow to brown solids with sharp melting points. Molecular weight determinations revealed the monomeric nature of the complexes, and the low molar conductivities (9–14 $\Omega^{-1}\,cm^2\,mol^{-1}$) of these complexes indicated their non-electrolytic behaviour.

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* Author to whom correspondence should be addressed.

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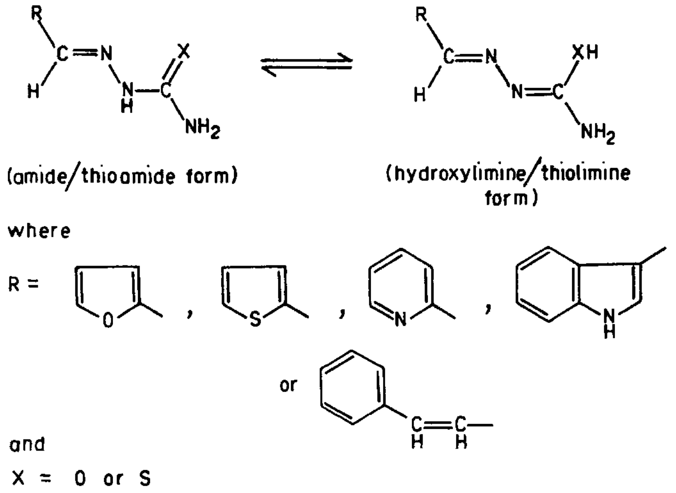

[1]

Quantitative data, spectral analyses comprising ultraviolet (UV), infrared (IR), NMR (^1H, ^{13}C and ^{11}B) spectra, TGA and XRD studies support the proposed structures of the compounds.

Ultraviolet spectra

The UV spectra of the ligands 2-(2-thienylmethylene)hydrazinecarbothioamide (L_4H) and 2-(2-pyridinylmethylene)hydrazinecarboxamide (L_5H) were recorded in methanol. The bands at *ca* 270 and 300 nm assignable to π–π^* electronic transitions within the benzene ring remain almost unchanged in the spectra of the compounds. Another band observed at around 350 nm in the spectra of the ligands is due to the n–π^* transition of the azomethine ($\rangle$C=N) moiety. However, in the spectra of compounds this band undergoes a hypsochromic shift[19] of 15–20 nm, due to the coordination of the azomethine nitrogen to the boron atom. This shift indicates the delocalization of the electronic charge within the chelate ring and thereby the stabilization of the resulting compound.

Infrared spectra

Bands due to ν(C=O) and ν(C=S) modes in the spectra of ligands are observed at $1700 \pm 10\ cm^{-1}$ and $1050 \pm 10\ cm^{-1}$, respectively. These bands disappeared in the spectra of organoboron compounds, suggesting the enolization of the ligands and their chelation through amido oxygen and thiolic sulphur, respectively.[20] This fact is further corroborated by the observation of the bands due to ν(C—O) and ν(C—S) modes at lower frequencies in the spectra of the boron compounds. The most significant band in the IR spectra of the ligands, in the region $1610–1590\ cm^{-1}$ assignable to the ν(C=N) group,[21] shifts slightly towards higher frequencies in the boron complexes, suggesting the bonding of the azomethine nitrogen to the boron atom. This is further supported by the presence of a band at $1550–1530\ cm^{-1}$ due to B←N, as reported earlier also.[22] However, a band at $\sim 1595\ cm^{-1}$ is assigned to an uncoordinated azomethine group in the case of 1:2 boron compounds. New bands at 1360–1335, 880–865 and *ca* $1260\ cm^{-1}$ are due to ν(B—O),[23] ν(B—S)[24] and ν(Ph—B)[25] vibrations, respectively. The medium-intensity bands exhibited in the $3250–3100\ cm^{-1}$ region are due to ν(NH)[26] of the free ligands. These bands, however, disappear from the spectra of the boron compounds, suggesting the possible loss of a proton from the α-nitrogen during complexation and subsequent formation of boron–oxygen/sulphur and boron–nitrogen bonds. There are no changes in the ν_{as} and ν_s modes of the NH_2 group[27] appearing at ~ 3430 and $3350\ cm^{-1}$, respectively, indicating the non-involvement of this amino group in chelation.

^1H nuclear magnetic resonance (NMR) spectra

^1H NMR spectral information is given in Table 1. The following structural inferences have been drawn by comparing the spectra of the ligands with those of the corresponding organoboron compounds. For convenience, the spectra of 2-(2-furanylmethylene)hydrazinecarbothioamide (L_2H) and its 1:1 and 1:2 boron derivatives are discussed in detail.

The broad signal due to the NH proton at

Table 1 ^1H NMR spectral data (δ, ppm) of ligands and their organoboron(III) compounds

Compound[a]	—NH (bs)[b]	$—NH_2$ (bs)	$H-\overset{\vert}{C}=N$ (s)	Aromatic (m)	—OH (s)	$C_6H_5—B$ (m*)
L_1H	10.68	2.55	7.94	7.89–6.32	—	—
$PhB(OH)(L_1)$	—	2.56	8.08	7.92–6.86	4.04	6.48
$PhB(L_1)_2$	—	2.52	8.12	7.96–6.84	—	6.56
L_2H	11.40	3.00	8.00	7.68–6.60	—	—
$PhB(OH)(L_2)$	—	2.96	8.16	7.82–6.72	4.10	6.24
$PhB(L_2)_2$	—	3.04	8.22	7.86–6.80	—	6.44
L_3H	10.48	2.50	8.56	8.14–6.85	—	—
$PhB(OH)(L_3)$	—	2.48	8.68	8.20–7.08	4.08	6.46
$PhB(L_3)_2$	—	2.52	8.70	8.32–7.16	—	6.52
L_4H	10.63	2.93	8.65	8.44–7.18	—	—
$PhB(OH)(L_4)$	—	2.94	8.88	8.52–7.26	4.12	6.42
$PhB(L_4)_2$	—	2.96	8.96	8.58–7.32	—	6.58
L_5H	10.88	2.44	8.12	7.48–6.20	—	—
$PhB(OH)(L_5)$	—	2.44	8.24	7.64–6.48	4.02	6.16
$PhB(L_5)_2$	—	2.46	8.26	7.68–6.44	—	6.18
L_6H	11.76	2.84	8.64	8.32–7.32	—	—
$PhB(OH)(L_6)$	—	2.86	8.92	8.64–7.48	4.12	6.32
$PhB(L_6)_2$	—	2.84	8.96	8.68–7.56	—	6.54

[a] Liquid identifications and abbreviations (L_1H, etc.) are given in the Experimental section.

[b] Abbreviations: bs, broad singlet; s, singlet; m, multiplet; m*, central point of multiplet.

δ 11.40 ppm in the ligand disappears in the case of the boron complexes, indicating deprotonation with simultaneous covalent bond formation between the thiolic sulphur and the boron atom. The azomethine proton signal ($H-\overset{|}{C}=N$) at δ 8.00 ppm undergoes deshielding (δ 8.16 ppm in the 1 : 1 complex and δ 8.22 ppm in the 1 : 2 complex), which confirms the coordination of the azomethine nitrogen to the boron atom. The new complex multiplets centred at δ 6.24 ppm and δ 6.44 ppm in the 1 : 1 and 1 : 2 boron derivatives are due to the phenyl protons of the Ph—B moiety. The OH proton signal in the 1 : 1 complex is observed at δ 4.10 pm.

^{13}C NMR spectra

The ^{13}C NMR spectra of 2-(2-thienylmethylene)hydrazinecarbothioamide (L_4H), 2-(2-pyridinylmethylene)hydrazinecarboxamide (L_5H) and their organoboron compounds show low-

Table 2 ^{13}C NMR spectral data (δ, ppm) of ligands and their organoboron(III) compounds

Compound	Chemical shift					
	C—O/C—S	$\rangle C=N$	Aromatic			
L_4H	178.19	152.76	139.32	126.45	125.37	134.60
$PhB(OH)(L_4)$	171.16	146.42	140.28	126.52	125.44	134.79
$PhB(L_4)_2$	172.49	148.15	140.44	127.16	125.42	134.66
L_5H	177.63	153.14	145.56 123.14	128.84	126.24	125.68
$PhB(OH)(L_5)$	170.64	145.86	145.44 123.36	128.72	126.33	125.69
$PhB(L_5)_2$	173.28	147.54	145.52 123.34	128.66	126.38	125.76

Table 3 ^{11}B NMR spectral data (δ ppm) of organoboron(III) compounds

1:1 1:2	$PhB(OH)(L_1)$ $PhB(L_1)_2$	$PhB(OH)(L_2)$ $PhB(L_2)_2$	$PhB(OH)(L_3)$ $PhB(L_3)_2$	$PhB(OH)(L_4)$ $PhB(L_4)_2$	$PhB(OH)(L_5)$ $PhB(L_5)_2$	$PhB(OH)(L_6)$ $PhB(L_6)_2$
1:1	5.24	2.04	3.02	9.44	2.28	2.16
1:2	6.28	2.28	2.46	10.54	2.42	2.18

wavelength chemical shifts for carbons attached to the azomethine nitrogen and thiolo sulphur/amido oxygen in the compounds as compared with the ligands (Table 2).

^{11}B NMR spectra

The ^{11}B nuclear resonance is observed in the region δ 2.04–10.54 ppm (Table 3). This suggests a tetracoordinated environment[28] around the boron atom and the presence of a ($B \leftarrow N$) coordinate bond. The driving force for the formation of this coordinate bond is the ability of $PhB(OH)_2$ to accept a share of electrons from a suitable donor atom (nitrogen in the present case). This confirms the conclusions drawn on the basis of the UV, IR, ^1H and ^{13}C NMR spectra, regarding the coordination of azomethine nitrogen to the boron atom.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis of $PhB(OH)(L_3)$ has also been carried out to evaluate its thermal stability at a heating rate of 15 °C min^{-1}. The spectrum shows that the compound is thermally stable up to 126 °C and thereafter a continuous loss in weight occurs, resulting in the formation of B_2O_3 at 527 °C. Aromatic units are more stable than aliphatic ones and this is confirmed in the present case (Table 4).

X-ray powder diffraction (XRD)

The possible geometry of the product, $PhB(OH)(L_3)$ has been deduced on the basis of X-ray powder diffraction studies. The results show that the compound belongs to the orthorhombic crystal system, having unit cell parameters $a = 9.8448$ Å, $b = 18.2272$ Å, $c = 27.3299$ Å and $\alpha = \beta = \gamma = \sim 90°$. The interplanar spacing values (d in Å), $h\,k\,l$ values and 2θ angles are reported in Table 5.

On the basis of the above spectral evidence, tetracoordinated structures can be proposed for the 1:1 (Fig. 1) and 1:2 (Fig. 2) organoboron compounds with 2-(2-pyridinylmethylene)hydrazinecarbothioamide (L_6H) as the ligand molecule.

Biochemical aspects

Antifungal and antibacterial activities of nitrogen and oxygen or sulphur donor heterocyclic aldimines and their corresponding organoboron(III) compounds are recorded in Tables 6 and 7. The results show that biological activity increases on undergoing chelation. The toxicity also increased as the concentration increased.

Mode of action

Degradative enzymes produced by microorganisms are important in host infection, food deterioration and breakdown of organic matter.[29] Enzyme production is here intended to mean both synthesis of the enzyme by the microorganism and activity of the enzyme in the medium after it is produced. Since the organoboron(III) compounds inhibit the growth of microorganisms, it is assumed that production of the enzymes is being affected and that the microorganism is unable to utilize food for itself or intake of nutrients decreases and consequently growth ceases. At lower concentrations, growth of microorganisms is arrested, whilst higher concentrations prove fatal. Higher concentrations destroy enzyme mechanism by blocking metabolic pathways (i.e. lipid, carbohydrate, amino acid etc.)

Table 4 Thermogravimetric analysis of $PhB(OH)(L_4)$

Initial decomposition temp. (°C)	Weight loss (%)					Decomposition temp. (°C)
	100 °C	200 °C	300 °C	400 °C	500 °C	
126	1.00	4.78	6.83	79.54	96.36	527

Table 5 X-ray powder diffraction data of $PhB(OH)(L_4)$

Peak no.	2θ (deg.) obs.	calcd.	Change in ϑ, $\Delta\theta$ (deg.)	h	k	l	d-spacing (obs.) (Å)
1	16.20	16.18	0.02	0	2	4	5.467
2	16.20	16.17	0.03	0	0	5	5.467
3	18.70	18.68	0.02	2	1	0	4.741
4	23.20	23.25	−0.05	2	3	0	3.831
5	23.20	23.24	−0.04	0	1	7	3.831
6	26.00	26.04	−0.04	1	5	0	3.424
7	26.00	26.02	−0.02	1	3	6	3.424
8	26.00	26.01	−0.01	0	0	8	3.424
9	30.80	30.77	0.03	1	6	0	2.901
10	30.80	30.80	0.00	1	5	5	2.901
11	30.80	30.78	0.02	2	2	7	2.901
12	34.70	34.67	0.03	2	6	0	2.583
13	34.70	34.70	0.00	2	5	5	2.583

Refined values of: $a = 9.8448$ (Orthorhombic system)
$b = 18.2272$
$c = 27.3299$

and due to lack of availability of nutrients the organism dies. Enzymes which require free sulphydryl groups (—SH) for activity appear to be especially susceptible to inactivation by the complexes. Due to greater lipoid solubility, the complexes facilitate their diffusion through membrane to the site of action and ultimately kill them by combining with (—SH) groups of cell enzymes.[30]

The organoboron(III) complexes are quite stable and are sparingly soluble in water. As regards the mechanism of biological activity, in general, it seems that compounds which are amides or esters tend to hydrolyse in the presence of water and form compounds which are either inert or have modified activity spectra.[31] Fungal and bacterial cells accumulate the water-soluble complex, which later dissociates to give the free central atom or its complex ion. It is thought that the central atoms inactivate these catalysts (enzymes). However, not all enzymes are equally inactivated by low concentrations of these complexes. Variation in the effectiveness of different biocidal agents against different organisms[32] depends on the impermeability of the cell.

Increased bioactivity of the complexes may also be due to interference with biosynthesis. The toxicity of organoboron(III) compounds can well be understood on the basis of chelation theory. Chelation reduces the polarity of the central ion mainly because of partial sharing of its positive charge with the donor groups and possible π-electron delocalization over the whole chelate ring. Such chelation increases the lipophilic character of the central atom, which subsequently favors its permeation through the lipoid layer of the membrane.[33]

In antibacterial activity, the complexes were more toxic towards Gram(+) stains than to Gram(−) stains. The reason is the difference in

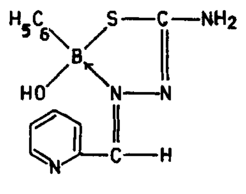

Figure 1

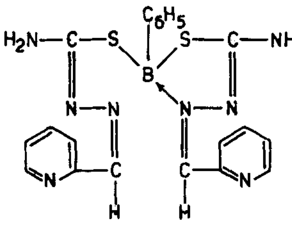

Figure 2

the structures of the cell walls. The walls of Gram(−) cells are more complex than those of Gram(+) cells (lipopolysaccharides form an outer lipid membrane and contribute to the antigenic properties of Gram(−) cells).

The sulphur compounds have greater bioactivity.

It is evident from the data of Tables 6 and 7 that under identical experimental conditions the boron complexes are more toxic than the parent ligands against the same microorganism. However, none of the ligands or boron compounds possessed better inhibitory action than the conventional fungicide 2-(methoxycarbomoyl)benzimidazide which was used for comparing the results. On the other hand, some boron compounds are more active against Gram(−)-stain bactria than the bactericide streptomycin. Overall, the boron compounds are superior to the parent ligands.

EXPERIMENTAL

Care was taken to keep the organoboron(III) compounds, other chemicals and glass apparatus free from moisture. Clean and well-dried glass apparatus fitted with Quickfit ground joints was used throughout the experimental work. All the chemicals and solvents used were dried and purified by standard methods.

Preparation of ligands

The ligands were prepared by the procedure reported previously.[34] The abbreviations used for the ligands are given below:

2-(2-Furanylmethylene)hydrazinecarboxamide L_1H
2-(2-Furanylmethylene)hydrazinecarbothioamide L_2H
2-(2-Thienylmethylene)hydrazinecarboxamide L_3H

Table 6 Antifungal screening data of ligands and their organoboron(III) compounds

	Average percentage inhibition after 96 h (concn in ppm)								
	Helminthosporium gramineum			*Fusarium oxysporum*			*Macrophomina phaseolina*		
Compound	50	100	200	50	100	200	50	100	200
L_1H	16	22	35	20	32	41	18	27	40
$PhB(OH)(L_1)$	24	38	57	29	55	64	32	47	58
$PhB(L_1)_2$	32	48	65	37	69	72	40	56	68
L_2H	24	34	52	31	44	58	23	34	51
$PhB(OH)(L_2)$	36	51	68	35	60	74	35	48	62
$PhB(L_2)_2$	42	63	80	41	68	76	40	62	71
L_3H	31	44	60	35	42	62	28	46	62
$PhB(OH)(L_3)$	48	59	72	40	64	88	46	62	80
$PhB(L_3)_2$	53	68	84	41	67	90	43	68	81
L_4H	36	52	63	41	48	62	43	56	64
$PhB(OH)(L_4)$	47	70	79	64	76	82	56	68	81
$PhB(L_4)_2$	60	81	86	76	84	92	62	75	82
L_7H	32	44	58	30	41	64	23	47	56
$PhB(OH)(L_7)$	41	56	70	41	60	74	32	56	68
$PhB(L_7)_2$	53	69	83	50	69	82	40	68	75
L_8H	36	49	62	32	40	69	27	52	58
$PhB(OH)(L_8)$	46	63	74	52	64	76	35	62	68
$PhB(L_8)_2$	58	76	90	64	74	82	43	71	79
2-(Methoxy carbomoyl) benzimidazide	81	100	100	86	100	100	82	100	100

Table 7 Antibacterial screening data of ligands and their organoboron(III) compounds

	Diameter of inhibition zone (mm) after 24 h (concn in ppm)							
	Staphylococcus aureus (+)		*Pseudomonas cepacicola* (−)		*Escherichia coli*(−)		*Klebsiella aerogenous* (−)	
Compound	500	1000	500	1000	500	1000	500	1000
L_1H	4	6	3	5	3	5	3	4
$PhB(OH)(L_1)$	6	8	4	6	5	8	5	7
$PhB(L_1)_2$	7	9	5	7	7	10	8	10
L_2H	5	7	4	8	3	7	5	7
$PhB(OH)(L_2)$	6	9	5	9	5	9	7	10
$PhB(L_2)_2$	8	11	6	11	7	12	10	12
L_3H	5	7	3	6	4	6	3	5
$PhB(OH)(L_3)$	7	10	4	8	5	8	5	7
$PhB(L_3)_2$	9	12	6	10	8	12	8	11
L_4H	6	8	3	7	5	7	3	6
$PhB(OH)(L_4)$	7	10	5	9	7	9	5	8
$PhB(L_4)_2$	9	13	8	12	10	13	8	12
L_7H	5	7	4	5	4	6	5	7
$PhB(OH)(L_7)$	8	10	5	7	7	9	7	10
$PhB(L_7)_2$	10	12	7	9	9	13	8	12
L_8H	6	9	4	6	6	7	6	8
$PhB(OH)(L_8)$	9	11	5	8	8	9	7	11
$PhB(L_8)_2$	11	15	7	10	9	11	9	12
Streptomycin	15	17	2	3	17	18	3	5

2-(2-Thienylmethylene)hydrazinecarbothioamide L_4H
2-(2-Pyridinylmethylene)hydrazinecarboxamide L_5H
2-(2-Pyridinylmethylene)hydrazinecarbothioamide L_6H
2-(1*H*-Indol-3-ylmethylene)hydrazinecarboxamide L_7H
2-(1*H*-Indol-3-ylmethylene)hydrazinecarbothioamide L_8H
2-(3-Phenyl-2-propenylidene)hydrazinecarboxamide L_9H
2-(3-Phenyl-2-propenylidene)hydrazinecarbothioamide $L_{10}H$

Synthesis of organoboron(III) compounds

A calculated amount (0.46–1.59 g) of $PhB(OH)_2$ was taken in dry benzene (50 ml) in a 100-ml round-bottomed flask and an equimolar (1.03–2.68 g) or bimolar (1.36–2.90 g) amount of the heterocyclic aldimine, i.e. L_1H, L_2H, L_3H, L_4H, L_5H, L_6H, L_7H, L_8H, L_9H or $L_{10}H$, was added. The progress and completion of the reaction was ascertained by observing the liberated water in the form of a water–benzene binary azeotrope, which remained immiscible with pure benzene. The excess of the solvent was first distilled off and then removed through a vacuum pump. The resulting product was repeatedly washed with dry cyclohexane and finally dried under vacuum for about 4 h. The details of these reactions and the analyses of the resulting products are recorded in Table 8.

Analytical methods and physical measurements

The analytical procedures adopted for the nitrogen donor ligands and their organoboron(III) compounds are outlined below.

Electronic spectra were recorded on a Pye–Unicam SP-8-100 ultraviolet spectrophotometer in the range 200–500 nm. IR spectra were recorded on a Perkin-Elmer 577 grating spectrophotometer using KBr pellets. ^1H, ^{13}C and ^{11}B NMR spectra were recorded on a JEOL FX90Q spectrometer. ^1H and ^{11}B NMR spectra were recorded DMSO-d_6 and ^{13}C NMR spectra in dry DMSO (dimethyl sulphoxide). Tetramethylsilane (TMS) was used as the internal reference for ^1H and ^{13}C NMR spectra and

$BF_3 \cdot Et_2O$ as the external reference for ^{11}B NMR spectra. TGA was carried out on a Stanton Red Croft G750/770 instrument. The X-ray powder diffractogram was obtained on a Philips PW 1130/00 automatic diffractometer using a Cu-Kα target with a nickel filter. Molecular weights were determined by the Rast camphor method. Conductance was measured at 24 ± 1 °C using a Systronics conductivity bridge (Model 305). Nitrogen and sulphur were estimated by Kjedahl's and Messenger's methods, respectively. Boron was estimated as boric acid in the presence of mannitol using phenolphthalein as an indicator.

Table 8 Quantitative analyses and physical properties of organoboron(III) compounds

Product formed and colour	Molar ratio	M.p. (°C)	Yield (%)	Analysis (%)			Mol. wt Found (Calcd.)
				N Found (Calcd.)	S Found (Calcd.)	B Found (Calcd.)	
PhB(OH)(L_1)	1:1	198	65	16.28	—	4.17	236
Light brown				(16.34)		(4.20)	(257)
PhB(L_1)$_2$	1:2	183	82	21.39	—	2.72	368
Brown				(21.43)		(2.76)	(392)
PhB(OH)(L_2)	1:1	168	72	15.42	11.71	3.91	299
Brown				(15.38)	(11.74)	(3.96)	(273)
PhB(L_2)$_2$	1:2	152	75	19.72)	15.21	2.53	396
Brown				(19.81)	(15.11)	(2.55)	(424)
PhB(OH)(L_3)	1:1	192	68	15.32	11.63	3.99	327
Off-white				(15.38)	(11.74)	(3.96)	(273)
PhB(L_3)$_2$	1:2	96	77	19.87	15.22	2.61	456
Grey				(19.80)	(15.11)	(2.55)	(424)
PhB(OH)(L_4)	1:1	158	84	14.48	22.13	3.75	318
Light yellow				(14.53)	(22.18)	(3.74)	(289)
PhB(L_4)$_2$	1:2	147	60	18.36	28.03	2.41	484
Yellow				(18.41)	(28.10)	(2.37)	(456)
PhB(OH)(L_5)	1:1	214	76	21.08	—	4.13	305
Yellow				(20.90)		(4.03)	(268)
PhB(L_5)$_2$	1:2	207	70	27.12	—	2.75	444
Brown				(27.05)		(2.61)	(414)
PhB(OH)(L_6)	1:1	184	63	19.79	11.19	3.87	316
Yellow				(19.72)	(11.28)	(3.80)	(284)
PhB(L_6)$_2$	1:2	196	86	24.97	14.45	2.35	404
Brown				(25.10)	(14.37)	(2.42)	(446)
PhB(OH)(L_7)	1:1	188	74	18.44	—	3.64	320
Dark yellow				(18.30)		(3.53)	(306)
PhB(L_7)$_2$	1:2	172	85	23.01	—	2.29	515
Brown				(22.85)		(2.20)	(490)
PhB(OH)(L_8)	1:1	194	66	17.44	9.87	3.41	365
Brown				(17.39)	(9.95)	(3.36)	(322)
PhB(L_8)$_2$	1:2	206d	64	21.53	12.18	2.00	553
Dark brown				(21.45)	(12.27)	(2.07)	(522)
PhB(OH)(L_9)	1:1	191	79	14.48	—	3.78	321
Light yellow				(14.33)		(3.69)	(293)
PhB(L_9)$_2$	1:2	184d	75	17.97	—	2.22	421
Yellow				(18.10)		(2.33)	(464)
PhB(OH)(L_{10})	1:1	140	84	13.48	10.43	3.48	274
Yellow				(13.59)	(10.37)	(3.50)	(309)
PhB(L_{10})$_2$	1:2	172	90	16.92	12.88	2.09	521
Dark yellow				(16.93)	(12.92)	(2.18)	(496)

Biological screening

The ligands and their organoboron(III) compounds were tested for *in vitro* growth inhibitory activity against pathogenic fungi, namely *Helminthosporium gramineum*, *Fusarium oxysporum* and *Macrophomina phaseolina*, and bacteria, i.e. *Staphylococcus aureus*, *Pseudomonas cepacicola*, *Escherichia coli* and *Klebsiella aerogenous*. A culture of test fungus was grown on PDA (potato dextrose agar–agar) for seven days at the optimum temperature for growth. All the glassware used was sterilized in an autoclave before use.

The radial-growth method and inhibition zone technique were employed to evaluate the antifungal and antibacterial activities, respectively.[35]

Antifungal activity

Fungi were grown in PDA medium (glucose 20 g, starch 20 g, agar-agar 20 g, and 1000 ml of distilled water) at 25 ± 2 °C and the compounds, after being dissolved in 50, 100 and 200 ppm concentrations, were mixed in the medium. The medium was then poured into Petri dishes and a small disc (0.7 cm) of the fungus culture was cut with a sterile cork borer and transferred aseptically to the centre of a Petri dish containing the medium with and the compound. Checks were kept, in which the culture discs were grown under the same conditions on PDA without the compound. These Petri dishes were wrapped in polythene bags and were placed in an incubator operating at the same temperature. The linear growth of the fungus was obtained by measuring the diameter of the colony in the Petri dishes after four days (96 h) and percentage inhibition was calculated as $100(C-T)/C$, where C and T are the diameters of the fungus colony in control and test dishes respectively.

Antibacterial activity

The nutrient agar medium (peptone 5 g, beef extract 5 g, NaCl 5 g, agar-agar 20 g, and 1000 ml of distilled water) prepared at 28 ± 2 °C and 5 mm diameter paper discs of Whatman No. 1 were used. The compounds were dissolved in dry methanol in 500 and 1000 ppm concentrations. Filter paper discs were soaked in different solutions of the compounds, dried and then placed in the Petri dishes previously seeded with the test organism. The plates were incubated for 24–30 h at the same temperature and the inhibition around each disc was measured in millimeters.

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