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NOVEL BORON COMPLEXES DERIVED FROM CATECHOL AND ARYLAZONAPTHOLS

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ABSTRACT

The reaction of 2-isopropoxy-1,3,2-benzodioxaborole with arylazonapthols in molar ratio 1:1 in benzene gives mixed ligand boron spirochelates [o-OC_6H_4O] B[$OC_{10}H_6$:NN(Ar)] (where Ar = C_6H_5,o-$CH_3C_6H_5$, p-$CH_3C_6H_4$, p-$CH_3OC_6H_4$, p-BrC_6H_5, o-ClC_6H_4 and p-ClC_6H_5, p-FC_6H_5). The complexes are colored nonvolatile solids soluble in common organic solvents and have been characterized by elemental analysis, IR and NMR (^1H and ^{11}B) spectral studies. The physicochemical studies give evidence for the monofunctional bidentate behaviour of the arylazo ligands and tertra coordination around the central boron atom.

Keywords: Catechol; Arylazonapthols; Mixed boron heterocyclic; Tetracoordinated boron complexes.

INTRODUCTION

The chemistry of mixed boron complexes derived from diols and a variety of ligands particularly with O-O and N-O donors has been an area of interest for chemists. The structural studies of these derivatives show that the central boron atom is either tri or tetra coordinated[1-3,4] or may simultaneously exhibit both tri and tetra coordination as reported for glycolate boron arylsalicylaldimine derivatives[5]. Boron complexes containing catecol dianion and a bidentate chelating ligand are predominately tetrahedral but may also be tricoordinated.

In view of the above studies on the study of boron spirochelates containing N-O donor was undertaken. In this paper the synthesis and characterization of some boron complexes derived from catecol and arylazonapthol has been reported.

EXPERIMENTAL

All starting materials were purified by distillation/recrystallization prior to use. The use of dry solvents and reactants was made for all moisture sensitive reactions. IR spectra (4000-400cm^{-1}) were recorded on SHIMA-DZU FT-IR 8400 spectrophotometer (KBr) and nmr on a JEOL FX 300 FT NMR spectrometer ($CDCl_3$). Arylazo napthols were prepared by reported methods by coupling diazotizinum chloride of the respective amine with 2- napthol[16,17].

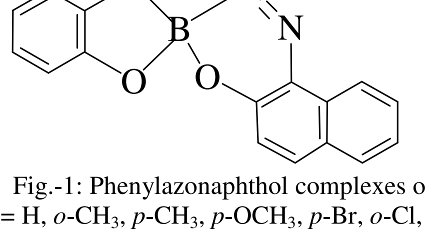

Fig.-1: Phenylazonaphthol complexes of boron
(X= H, *o*-CH_3, *p*-CH_3, *p*-OCH_3, *p*-Br, *o*-Cl, *p*-Cl, *p*-F).

Preparation of 2-arylazo-1,3,2-benzodioxaborole

The general procedure adopted for the synthesis of the 2-arylazo-1,3,2- benzodioxaboroles, $[OC_6H_4O]B$ (AAN) is discussed.A solution of 2-isopropoxy-1,3,2-benzodioxaborole and 1-arylazo-2-naphthol (1:1) in dry benzene was refluxed on a fractionating column for 10 hours. The course of the reaction was monitored by estimation of the liberated isopropanol. On completion of the reaction the excess solvent was removed under reduced pressure. The reddish products obtained were purified by recrystallization with benzene: n-hexane mixture (80:20) (yield 80-90%).

RESULTS AND DISCUSSION

Arylazonapthols display ketohydrazone-azoenol tatumerism and mainly exist in the azohydroxy tautomeric form. The hydrogen bonding in these derivatives is abnormally strong, they form intramolecular resonance assisted H-bonds and there tautomeric behavior is influenced by substents in the phenylazo moiety [6,7].

The mixed ligand 2-(1-arylazo-2-naphthol)-1,3.2-benzodioxaboroles derivatives were prepared by the reaction of 2-isopropxy-1,3,2-benzodioxaborole with 1-arylazo-2-naphthol in 1:1 molar ratio in benzene. The preparative and characterization data of the complexes is given in Table-1.

The IR spectra of the complexes shows the absence of the intramolecular H-bonded ν(N-H) or ν(O-H) band for the ketohydrozone and azoenol tautomeric forms present in the spectra of the free ligands at ~3100 cm^{-1}. The band at 1545-1540 cm^{-1} has been assigned to a $\nu(N\cdots N)$ vibration[8].

A medium intensity bands in the region 740-745 cm^{-1} and 1275-1300 cm^{-1} have been assigned to ν(B-N) and ν(C-O-B) stretching modes[9]. The IR spectra of the complexes show the absence of the intense bands in the region 1310-1380 cm^{-1} characteristic for tri-coordinated boron-oxygen compounds[10]. The important peaks observed for the complexes are given in Table-1.

Table-1: Preparative and spectral data of 2-(1-arylazo-2-naphthoxolate)-1,3,2-benzodioxaboroles.

S.No.	Reactants		M.P.(^0C) (% Yield)	Analysis		IR(cm^{-1})			NMR		
	Ligand Arylazo (g)	$[O-O]B(OPr^i)$ (g)		B% Found (Calcd.)	Pr^iOH(g) Found (Calcd.)	ν(N=N)	$\nu(B\leftarrow N)$	V(C-O-B)	^1H		^{11}B
									CH_3 or OCH_3	Ar-H	
1.	C_6H_5NN: (1.65)	1.18	178 (86)	2.91 (2.95)	0.36 (0.39)	1545	740	1275	-	6.83-8.08	7.32
2.	o-$CH_3C_6H_4NN$: (2.02)	1.37	192 (83)	2.81 (2.84)	0.41 (0.46)	1540	745	1280	2.33	6.91-8.10	7.29
3.	p-$CH_3C_6H_4NN$: (1.96)	1.33	186 (85)	2.79 (2.84)	0.42 (0.46)	1535	745	1285	2.34	6.92-8.08	7.36
4.	p-$OCH_3C_6H_4NN$: (1.97)	1.26	183 (81)	2.65 (2.72)	0.39 (0.42)	1540	745	1295	3.62	6.85-8.00	7.41
5.	p-BrC_6H_4NN: (1.30)	2.37	191 (86)	2.36 (2.42)	0.39 (0.43)	1540	750	1280	-	6.84-8.01	7.40
6.	o-ClC_6H_4NN: (2.38)	1.50	171 (84)	2.63 (2.69)	0.54 (0.50)	1545	750	1295	-	6.81-8.05	7.34
7.	p-ClC_6H_4NN: (1.84)	1.16	167 (87)	2.61 (2.69)	0.42 (0.38)	1540	740	1300	-	6.83-8.05	7.45
8.	. p-FC_6H_4NN: (1.73)	2.57	201 (88)	2.78 (2.81)	0.57 (0.86)	1535	745	1285	-	6.90-8.07	7.38

The spectra of the complexes were recorded in $CDCl_3$ using TMS as internal standard. The signals observed are summarized in Table-1. The ^1H nmr spectra of the organyloxy (phenylazonaphtholate) boranes show the absence of the N-H/O-H proton signal observed in the spectra of the free azo ligands[11]. The spectra show signals for the aryl protons at δ 6.8 - δ 8.10 ppm. In some complexes the CH_3- and –OCH_3 proton signals of the substituted methyl and methoxy group in the azophenyl moiety are observed at δ 2.3-2.4 and δ 3.7 ppm respectively[12].

The ^{11}B nmr spectra of the azo derivatives were recorded in $CDCl_3$ with reference to $BF_3(C_2H_5)_2O$. The ^{11}B chemical shift of the compounds (Table-1) are in the range δ 7.32-7.45 which is consistent with the tetra-coordination of the boron in the complexes as the ^{11}B signals for tetra coordinated boron atom in BNO_3 environment are observed in the range 2.0-14.0 ppm[13].

The physico-chemical and spectroscopic studies of the complexes suggest the formation of tetra-coordinate boron complexes with N-O bonding of the azo ligands and the following type of structure for the 2-(1-arylazo-2-naphtholate)-1,3,2-benzodioxaborole complexes can be proposed (Fig.1) :

CONCLUSION

The present investigation shows that 2-isopropxy-1,3,2-benzodioxaborole react with 1-arylazo-2-naphthol to give organyloxy(phenylazonaphtholate)-boranes with a spiroboron atom. The formation of the heterocyclic chelates has been confirmed by elemental and spectral studies.

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