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SYNTHESIS AND CHARACTERIZATION OF SCHIFF BASE LIGAND AND THEIR ORGANOTIN (IV) COMPLEXES FROM 2,3-DIAMINOPHENAZINE AND SALICYALDEHYDE AND EVALUATION OF BIOLOGICAL ACTIVITIES

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ABSTRACT

The six coordinated diorganotin(IV) complexes of the kind R2Sn(L) [R = group, phenyl, methyl, ethyl) where Ligand = Schiff base prepared from the reaction of 2,3-diaminophenazine and salicyaldehyde are synthesized. The mode of bonding within the complexes has been prompt on the idea of analytical and chemical analysis techniques (IR, ^{1}H, ^{13}C and ^{119}Sn NMR spectra), wherever the ligand coordinate to the central tin metal through oxygen and nitrogen of carbonyl and azomethine cluster severally. The ligands and their organotin complexes are evaluated for antimicrobial activity against phytopathogenic fungi aspergillus niger , aspergillus flavus, at 37±1°C and bacterium bacillus subtilis, Escherichia coli and staphylococcus aureus at 37±1°C and gram positive bacterium bacillus cereus , staphylococcus aureus , gram negative bacterium Escherichia coli compared with fluconazole and ciprofloxacin as reference drugs. The complexes are found to be additional active than the ligand.

Keywords: Schiff bases, Organotin(IV) complexes, Biological Activities

I. INTRODUCTION

Schiff base ligands are recognized as ‘‘advantaged ligands’’ owing to easy preparation by the condensation of amines and aldehydes. Salens, is one of the class of Schiff base ligands, which have been prepared by the condensation of aldehyde and 2, 3-diamines [1-3]. There has been increasing interest within the synthesis and characterization of unsymmetrical Schiff base ligands and their organotin(IV) complexes are of biological interest. [4]. An oversized chemistry of organotin(IV) complexes of the Schiff base ligands are exteremely studied which have been prepared as a result of they need some characteristics properties like manifestations of thermal stability,novel structures, relevant biological properties, healthful utility and high synthesis flexibility. Tin and its compounds have variety of applications within the pharmaceutical trade[5]. These embrace established uses within the fields of odontology and medicine, and recently there are further developments in radiopharmacology and chemotherapy, though not used at the current time, certain organotin complexes have shown potential as antineoplastic medicine, that represents one amongst the foremost exciting areas of analysis in trendy medication. Organotin complexes with Schiff’s bases of 2,3-diaminophenazine have been widely studied though a much of interest has been paid to Schiff's bases and their organotin(IV) complexes, furthermore they're having broad application within the preparation of a large variety of biologically vital compounds[6-8]. In this paper, we focused on the synthesis of Schiff bases of 2,3-diaminophenazine and salicyaldehyde and their respective organotin complexes along with the screening of these complexes against gram +ve, gram –ve bacteria, and the pathogenic fungi.[9-12]

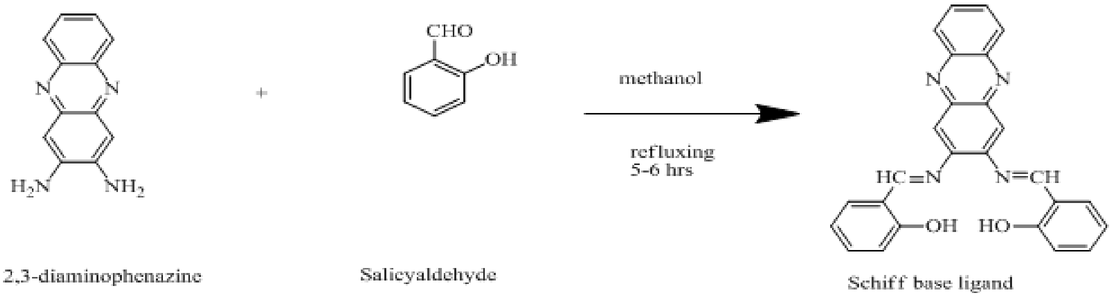
II. EXPERIMENTAL

All of the reactions were operated in an inert atmosphere using dry nitrogen. All the used reagents and solvents were dried, distilled and refined by their standard ways of purification and purity of ready compounds was checked frequently by thin layer chromatography (TLC). Tin content was estimated gravimetrically as SnO_2. Elemental analysis (C, H, and N) was carried out on Perkin-Elmer 2400 instrument (Waltham, Massachusetts) IR spectra were recorded on Shimadzu IR affinity-I 8000 FT-IR spectrometer using KBr pellets having wavelength range 400-4000 cm-1. nuclear magnetic resonance spectra were recorded in CDCl3 and d6-DMSO on Bruker Avance II 400 mhz NMR spectroscope and TMS was used as internal standard all chemical shifts were considered in parts per million (ppm).

2.1 Preparation of Ligand From 2,3-Diaminophenazine And Salicyaldehyde And Their Organotin(Iv) Complexes

2.1.1. Preparation of Schiff base Ligand

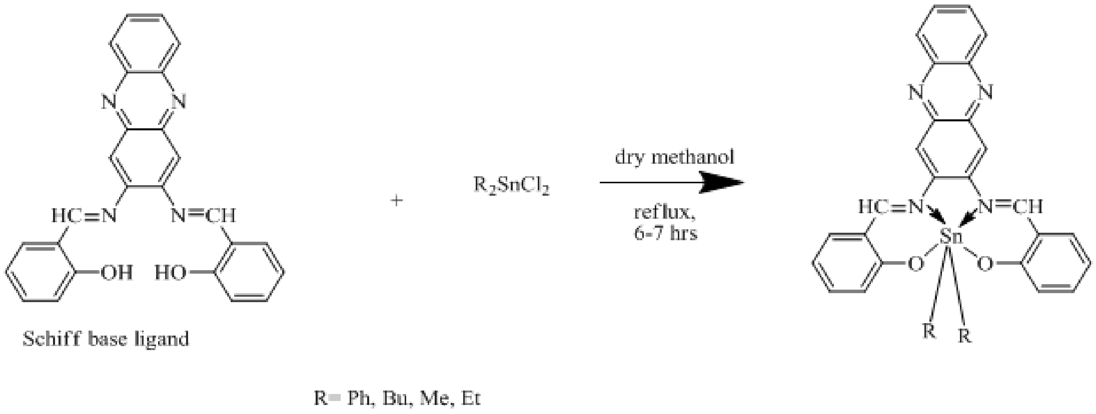
The Schiff base ligand was ready by the condensation of salicyaldehyde (2mmol,) and 2,3-diaminophenazine(1mmol) in minimum amount of dry methanol . The reaction mixture was stirred and refluxed for regarding 3-4 hrs. A brown colored solid product so obtained was checked by skinny layer action (TLC) and repeatedly washed with chloroform and petroleum ether to form bound the limpidness of the products and finally it had been dried beneath vacuum.



Scheme1. Synthesis of Schiff base Ligand

2.1.2. Preparation of Organotin(IV) complexes

The reaction of diorganodichlorotin (phenyl, butyl, methyl, ethyl) with the sodium salt of the Schiff base ligand in the 1:1 ratio in dry methanol which is prepared by dissolving sodium metal of the prepared Schiff base ligand in dry methanol and then refluxed for about 2-3 hrs. The starting material R_2SnCl_2 (where R= phenyl, butyl, methyl, ethyl) was added to the sodium salt of Schiff base ligand and then the mixture was further refluxed for about 5-6 hr and dark brown colored complexes were collected. The product obtained was finally dried over vaccum.



Scheme II. Synthesis of Organotin(IV) complexes

III. RESULTS & DISCUSSION

The reaction was carried out in 1:1 molar ratio of ligand and the organotin material in minimum amount of dry methanol as the solvent. The Organotin(IV) complexes obtained were sticky compounds, and all the complexes were dried over vacuum with a mixture of dry hexane and chloroform to remove the stickiness. All the complexes show solubility in DMSO.

3.1 IR Spectra

The IR spectra of the Schiff base ligand and its corresponding organotin(IV) complexes is shown in table1. While comparing the IR spectra of the ligand with their corresponding organotin(IV) complexes, the coordination site of the donor atoms has been predicted. The prepared Schiff base ligand showed a wide spectra in the range 3240 cm^{-1} indicated the presence of OH group of the aldehyde which in complexes which shifted to the lower frequency indicating the deprotonation of the OH group. The range from 1615-1620 cm^{-1} corresponding to the presence of azomethine group in the ligand which on complexation shift to lower frequency indicating the donation of electrons from nitrogen to the central tin metal. The presence of the medium peak at 628-701cm^{-1} due to Sn-C, 533-551cm^{-1} due to Sn-O, 426-446 cm^{-1} due to Sn-N respectively supported the coordination of carbon, oxygen, nitrogen to the central tin metal. [11]

Table1. FT-IR spectra of Schiff base Ligand and their Organotin(IV) complexes

S.No.	Compounds	υ (C=N)	υ(O-H)	υ(Sn-N)	υ(Sn-O)	υ(Sn-C)
1	**H_2L**	1610	3240	-----	------	-----
2	**Ph_2SnL**	1588	3010	446	551	701
3	**Bu_2SnL**	1592	3023	431	548	694
4	**Et_2SnL**	1585	3044	426	541	628
5	**Me_2SnL**	1580	3011	430	533	638

3.2 ^{1}H NMR Spectra

The ^{1}H NMR spectra of the ligand and its corresponding organotin(IV) complexes is shown in table 2. The Schiff base ligand shows a sharp single peak at 13.54 ppm and 12.91 ppm indicating the presence of OH group in the ligand, which disappeared on complexation which showed deprotonation in complexes. The azomethine hydrogen appeared as singlet in the range 8.50 ppm showing the formation of Schiff base ligand which shifted to deshielded region in complexes. The aromatic hydrogen appeared in the range 6.92- 8.22 ppm which shifted to the deshielded region in complexes. A multiplet of 10 protons was appeared in 7.31-7.39 ppm for the phenyl group, in butyl, ethyl, methyl complexes, there appeared protons in the aliphatic regions showing coordination to the central tin metal. [4]

Table2. ^{1}H NMR of Schiff base Ligand and their Organotin (IV) complexes

S.no.	Compounds	Phenolic H	CH=N	Aromatic H	R
1.	**H_2L**	13.54,s,(1H), 12.91,s, (1H)	8.50,s, (2H)	6.92-7.01,m,(2H),7.09-7.14,m,(2H),7.34-7.36,m,(2H) 7.50-7.52,m,(2H),7.65-7.67,m,(2H),7.86-7.88,m,(2H),8.21-8.22,m,(2H)	-----
2.	**Ph_2SnL**	------	8.89,s,(2H)	7.01-7.07,m,(2H),7.16-7.20,m,(2H),7.41-7.43,m,(2H)7.63-7.65,m,(2H),7.85-7.87,m,(2H), 8.01-8.03,m,(2H), 8.54-8.56,m,(2H)	7.31-7.39, m, (10H)
3.	**Bu_2SnL**	------	8.91,s,(2H)	7.02-7.09,m,(2H),7.18-7.24,m,(2H),7.43-7.45,m,(2H)7.64-7.66,m,(2H),7.87-7.89,m,(2H),8.04-8.06,m,(2H), 8.55-8.57,m,(2H)	0.73-0.76,t ,(6H),1.15-1.19,m ,(4H) ,1.81-1.82,m (4H),1.92-1.94,t,(4H)
4.	**Et_2SnL**	------	8.98,s,(2H)	7.01-7.08,m,(2H),7.16-7.22,m, (2H), 7.42-7.44,m,(2H) 7.65-7.67,m,(2H), 7.85-7.87,m,(2H), 8.03-8.05,m,(2H), 8.54-8.56,m,(2H)	0.93,t,(6H) 1.65,q,(4H)

5.	**Me_2SnL**	------	8.93,s,(2H)	7.03-7.09,m,(2H),7.15-7.19,m, (2H), 7.40-7.42,m,(2H) 7.61-7.63,m,(2H), 7.81-7.83,m, (2H), 7.99-8.01,m,(2H), 8.52-8.54,m,(2H)	0.84,s,(6H)

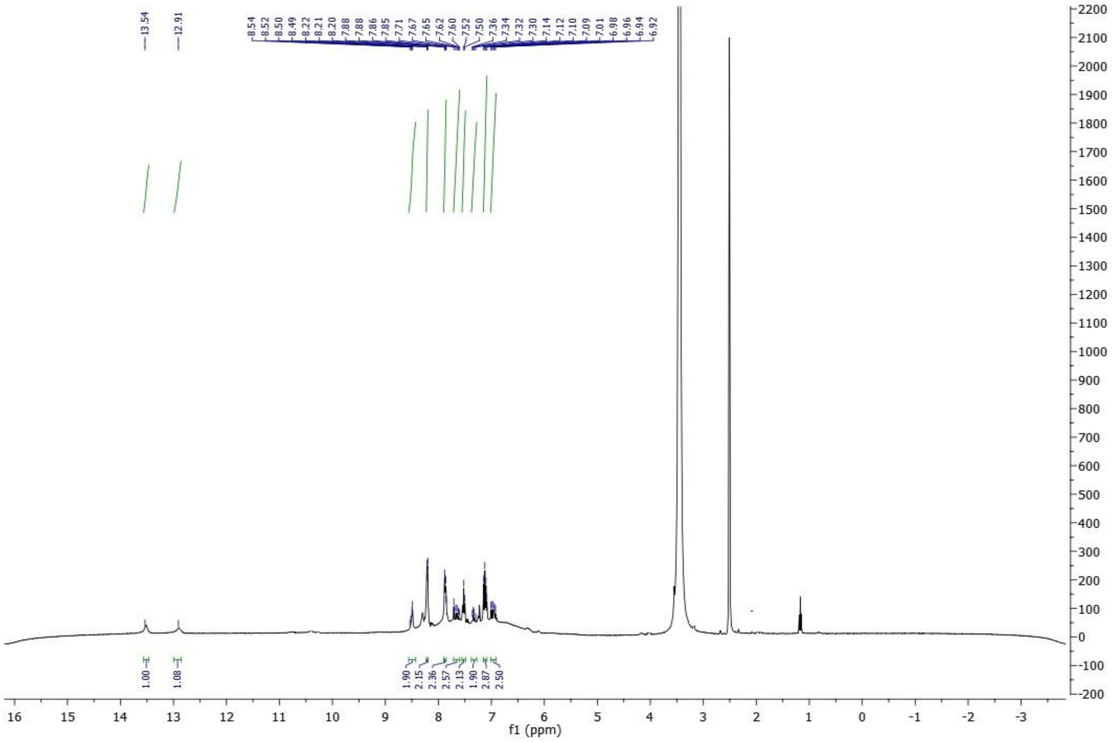


Fig1. ^1H NMR spectra of Schiff base ligand

3.3 ^{13}C NMR Spectra

The ^{13}C NMR spectra of the ligand and its corresponding organotin(IV) complexes is shown in table 3. The Schiff base ligand shows peak at 165.93 ppm which is due to phenolic carbon which get shifted to lower value. The aromatic carbon lied in the range 122.98 ppm to 148.99 ppm. The azomethine carbon lied in the 156.50 which shifted to lower range in the complexes.

Table2. ^{13}C NMR Spectra of Schiff base Ligand and their Organotin(IV) complexes

S.No.	Compounds	Phenolic C	C=N	Aromatic C	R
1	**H_2L**	165.93	156.50	148.99,143.03,139.51,131.51, 128.91,128.40,128.05,124.00, 123.86, 122.98, 94.73	------
2	**Ph_2SnL**	161.21	150.01	148.95,143.01,139.48,131.52, 128.93,128.44,128.01,124.05, 123.81, 122.99, 94.79	128.37(m), 130.72(p), 135.22(o), 138.79(i)

3	**Bu_2SnL**	162,56	150.21	148.91,143.10,139.47,131.54, 128.95,128.42,128.03,124.07, 123.83, 122.94, 94.74	13.79, 26.29, 37.22,39.11
4	**Et_2SnL**	161.98	150.28	148.93,143.05,139.53,131.49, 128.88,128.39,128.04,124.01, 123.82, 122.95, 94.71	8.15, 14.79
5	**Me_2SnL**	160.89	150.36	148.92,143.09,139.54,131.48, 128.92,128.44,128.06,124.08, 123.89, 122.91, 94.72	8.11

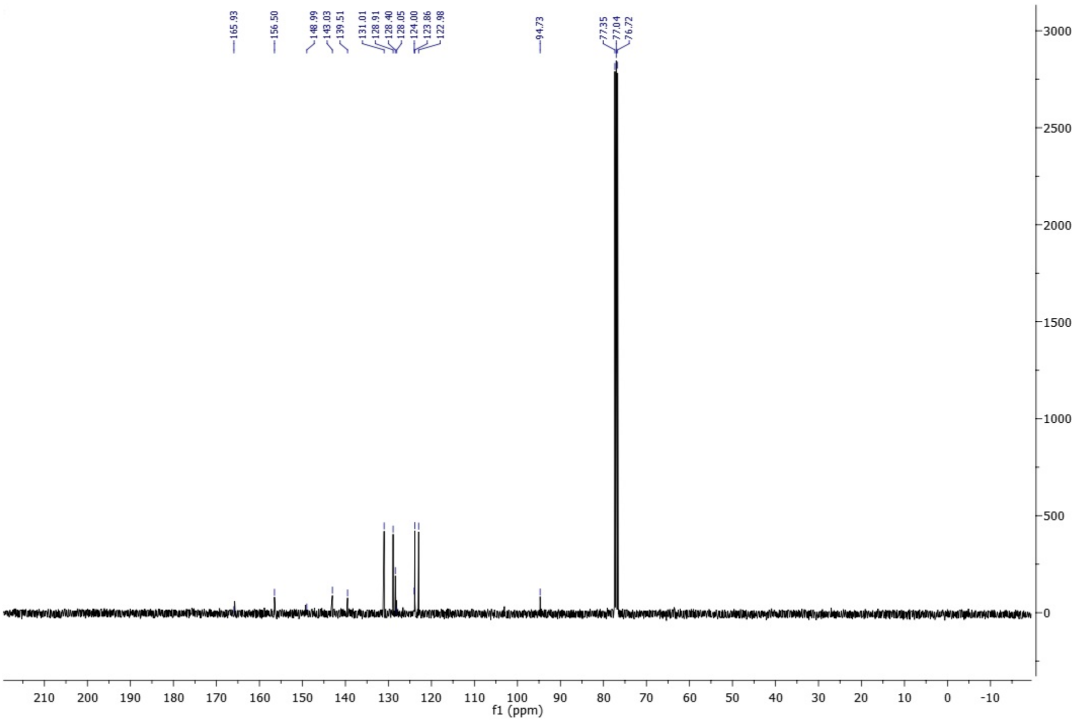


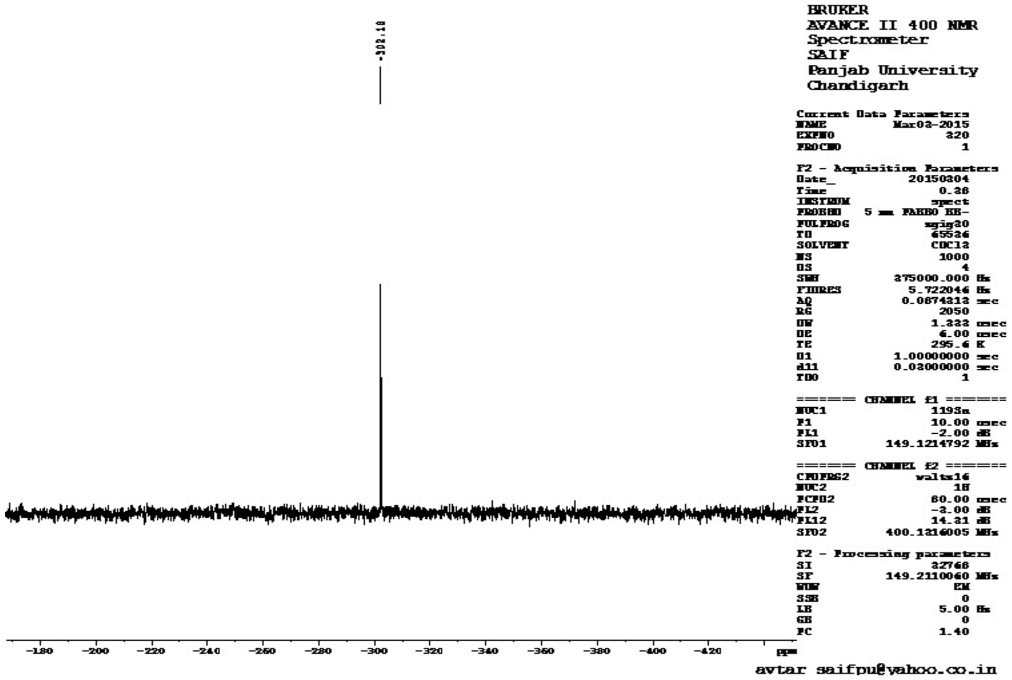
Fig.2 ^{13}C NMR spectra of Schiff Base Ligand

3.4 ^{119} Sn NMR Spectra

The ^{119} Sn NMR of the complexes is shown in table 3. The ^{119} Sn NMR spectra of the prepared organotin complexes show a sharp singlet peak at -302.10 ppm for phenyl complex, -220.13 ppm for butyl complex, -190.32 ppm for ethyl complex and -180.47 ppm for methyl complex. This sharp singlet revealed the hexacoordinated structure of the complexes. [12]

Table3. ^{119} Sn NMR Spectra of Organotin(IV) complexes

S.No.	Compound	^{119} Sn Shift
1	Ph_2SnL	-302.10
2	Bu_2SnL	-220.13
3	Et_2SnL	-190.32
4	Me_2SnL	-180.47



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BRUKER
AVANCE II 400 NMR
Spectrometer
SAIF
Panjab University
Chandigarh

Current Data Parameters
NAME           Mar03-2015
EXPNO                 320
PROCNO                  1

F2 - Acquisition Parameters
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DS                      4
SWH           375000.000 Hz
FIDRES          5.722046 Hz
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RG                   2050
DW                  1.333 usec
DE                   6.00 usec
TE                  295.6 K
D1             1.00000000 sec
d11            0.03000000 sec
TD0                     1

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P1                  10.00 usec
PL1                 -2.00 dB
SFO1          149.1214792 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2               80.00 usec
PL2                 -3.00 dB
PL12                14.31 dB
SFO2          400.1316005 MHz

F2 - Processing parameters
SI                  32768
SF            149.2110060 MHz
WDW                    EM
SSB                     0
LB                   5.00 Hz
GB                      0
PC                   1.40

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Fig2. ^{119} Sn NMR of phenyl Organotin Complex

IV. BIOLOGICAL ACTIVITIES

The Schiff base ligands and their corresponding Organotin complexes were evaluated against in vitro antibacterial and antifungal activities against *bacillus subtilis, Escherichia coli, staphylococcus aureus, Aspergillus niger, Aspergillus flavus.* The biological activities were done by Serial dilution method under standard temp conditions. Ciprofloxacin and fluconazole were used as reference drungs against antibacterial and antifungal activities respectively. Nutrient broth and sabouraud dextrose agar were used as culture medium for bacterial and fungal strains respectively, and DMSO was used as solvent control for the biological activity. The incubation time was 24 hrs for bacterial strains and 7 days for fungal strains.

The Organotin(IV) complexes were additional active than the ligand. Among all the complexes, phenyl complexes showed additional efficiency altogether the complexes as toxicity depends upon the alkyl group hooked up to the central metal atom attributable to lipophilicity and ability to unleash electrons that increase the delocalization of electrons. It will additional be explained by the chelation theory that may be a results of coordination through central metal.

V. ACKNOWLEDGEMENT

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VI. CONCLUSION

The organotin complexes of Schiff base of 2,3-diaminophenazine were synthesized and characterized by FT-IR and NMR spectroscopy. All the compounds were evaluated against antimicrobial activities and were found to be potent against all the strains.

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