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Monobutyltin (IV) Derivatives of Diphenylamine-2-amino-2'- carboxylic acid

Manoj Kumar Pachouri and Pankaj Mittal*
Applied Science Department, Anand Engineering College, Keetham, Agra, 282007, India
pankajmittal.bsa@gmail.com

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Abstract

A new series of organometallic compounds of tin(IV) have been synthesized by refluxing monobutyltin triisopropoxide with diphenylamine -2 -amino-2'- carboxylic acid in the 1:1, 1:2, 1:3 and 2:1 molar ratios. The products so obtained were analyzed for elemental composition, Infra-Red spectrum, ^1H Nuclear magnetic resonance spectrum as well as molar conductance measurements. They were also analyzed for their antipestal properties against the pest Tribolium castaneum. Monobutyltin (IV) derivatives have shown higher antipestal activities on comparison with their ligands.

Keywords: Monobutyltin, Refluxing, Conductance, Antipestal.

Introduction

Organotin compounds are well known for their importance in the form of biocidals[1-8] as well as pesticidals[9-13]. These compounds can be synthesized in the laboratory because tin has ability to form complexes with suitable ligands with coordination number greater than 4. This research work involves the preparation, structural analysis and antipestal studies of monobutyltin(IV) compounds of diphenylamine -2-amino -2'- carboxylic acid (dpac).

Materials and methods

Preparation of Monobutyltin triisopropoxide[14] (MBTTIP): Weighed 0.69g (0.03M) of Na piece and dissolved in some amount of dry benzene solvent in RB flask which consists of adapter having two connections, reflux condenser at one point and dropping funnel having calcium chloride guard tube at another point. Now, 2.4ml (0.03M) isopropyl alcohol in benzene was mixed slowly into the reaction mixture through dropping funnel with continuous stirring which was refluxed till the sodium pieces got completely dissolved. Now, 2.8ml (0.01M) of monobutyltintrichloride suspended in benzene was poured slowly in to the flask with constant shaking; a white ppt of NaCl was separated. The content was again allowed to reflux for 3.5 hrs. The compound so formed undergone vacuum distillation on a wax bath. The product so obtained was colourless liquid which converts to light-brown after sometime.

Preparation of Diphenylamine -2 - amino -2'- carboxylic acid (dpac): 3.12g (0.01M) ortho - chloro benzoic acid and 2.16 g (0.01M) ortho-phenylene diamine in 200ml distill water were taken into RB flask. Some amount of K_2CO_3 solution and copper oxide were added in the above reaction mixture to make it slightly alkaline which was refluxed for six hrs on an oil bath then allowed it to cool for some time. Activated charcoal (1.0g) was added in the reaction content and boiled for about 1 hour for decolorisation. The precipitate so obtained was filtered, concentrated and allowed to cool. An excess amount of dil. HCl was added in the solution for acidification till the formation of product which was dissolved in methanol to recrystallize it. The product was dried in a desiccator over anhydrous $CaCl_2$ to obtain a light-yellow solid.

Preparation of Monobutyltin (IV) derivatives of Diphenylamine – 2 – amino -2' -carboxylic acid: A combination of monobutyltin triisopropoxide {0.75ml (0.002 M) / 0.75ml (0.002M) / 0.75ml (0.002M)/1.4ml (0.004M)} and diphenylamine-2-amino-2'-carboxylic acid{0.45g (0.002M)/ 0.90g (0.004M) / 1.35g (0.006M)/0.45g (0.002M)} dissolved in 60 ml benzene was taken in R.B. flask having reflux condenser at one end and a guard tube with anhyd. $CaCl_2$ at the other end. The solution was refluxed for about ten to fourteen hours on a wax bath. After cooling, filter the coloured solid so obtained through suction and washed with little amount of dry ether. Recrystallize it with DMF and allow it to dry under reduced pressure then coloured crystals were obtained.

Physical and Analytical Measurements: A technique of chromatography (TLC) and repeated melting point determination has been used to check the purity of compounds. The elements present in the compounds were analyzed by an instrument CEMA-1108 at the RSIC, Central Drug Research Institute, Lucknow.

The estimation of Sn (IV) was done by decomposing the derivatives of tin with conc. HNO_3 and conc. H_2SO_4 then liq. NH_3 was used for their neutralization and precipitation as tin oxide[15].

Perkin Elmer RX-1 spectrometer was used to record IR spectrum and PMR Brucker AC 300 MHz spectrometer was used to record ^1H NMR spectrum at RSIC, Central Drug Research Institute, Lucknow. The value of molar conductance

of these derivatives was taken through Systronics-conductivity meter-306.

Results and discussion

Table-1 represents data related to physical characteristics and percentage analysis of elements of monobutyltin triisopropoxide and Diphenylamine – 2 – amino -2'- carboxylic acid (dpac)/ (L) derivatives. All such compounds were stable at room temperature. They were hygroscopic. These compounds were found soluble in dimethylformamide as well as dimethylsulphoxide solvents however these were insoluble in water. 0.001M solution of these derivatives possesses low values of molar conductance (3.8 – 4.8ohm^{-1}cm^{2}mol^{-1}) which exhibit their behavour as non-electrolytes[16].

Infra-red spectral analysis: For Monobutyltin triisopropoxide, bands/peaks obtained at – i. 2920cm^{-1} and 2860cm^{-1} (w) due to C-H of υ –CH_2- and υ –CH_3 stretching vibrations of the butyl group[17,18], ii. 1385cm^{-1} (s) owing to υC-H bending vibration of geminal-dimethyl moiety of the isopropoxy group[19], iii. 1160cm^{-1} (w) owing to υC-O present in the isopropoxy group[19], iv. 650cm^{-1} (m) and 615cm^{-1} (w) due to υ Sn-C[20], v. 545cm^{-1} (w) and 475cm^{-1} (s) due to υ Sn-O[21].

For diphenylamine-2-amino-2'-carboxylic acid, bands/peaks obtained at: i. 3290 cm^{-1} (m) owing to υN-H str. vibrations of pri. aryl –NH_2 group and 2640cm^{-1} owing to υO-H str. vibration of carboxlic acid group, ii. 1695cm^{-1} (s) due to υ –CO str. vibration of carboxylic group.

For monobutyltin(IV) derivatives of diphenylamine – 2 – amino -2'- carboxylic acid, bands/peaks obtained at: i. 3280 cm^{-1} (m) owing to υN-H str. vibrations of pri. aryl –NH_2 group and at 3060cm^{-1} owing to υ C-H of the aromatic ring[17,19], ii. 2945cm^{-1} and 2860 cm^{-1} (w) owing to υC-H of –CH_2- and –CH_3 stretching vibrations of the butyl group[17,19], iii. 1430cm^{-1} (s) corresponds to υ_sCOO stretching vibrations, 1630cm^{-1} (s) due to υ_{as}COO stretching vibrations[22], iv. ΔυCOO value of 200 cm^{-1} indicates bridging –COO$^-$ group[25], 1360cm^{-1} (m) owing to υC-H bending vibration of the geminal-dimethyl moiety of isopropoxy group[19] in the 2:1 derivative, vi. 635cm^{-1} (m) and 610cm^{-1} (w) due to υ Sn-C[20], 545 cm^{-1} (w) and 460 cm^{-1} (s) due to υ Sn-O[21] and 440cm^{-1} (s) due to υ Sn-N in 1:1 and 2:1 derivatives, vii. No peak around 3250cm^{-1} in 1:1 and 2:1 derivatives suggested that free–NH_2 group was absent and it also indicates the bonding of –NH_2 group to tin, whereas it was shown in 1:2 and 1:3 molar ratio compounds at 3290 cm^{-1}.

^{1}H NMR spectral analyses: ^{1}H NMR spectra of monobutyltin triisopropoxide exhibited multiplet having the value of chemical shift of 1.30 - 1.80ppm for butyl group[24] linked with Sn. Multiplet of 0.50 - 1.20ppm was appeared for isopropoxy group.

In the NMR spectrum of diphenylamine-2-amino-2'-carboxylic acid, a multiplet showing between 7.10 – 8.15ppm was due to aromatic ring protons. Singlets obtained at 11.50ppm, 3.80ppm and 3.30ppm correspond to protons of – COOH, - NH_2 and –NH- groups respectively.

In the NMR spectrum of monobutyltin(IV) compounds of diphenylamine-2-amino-2'-carboxylic acid, a multiplet was appeared between 7.10 – 8.15ppm due to presence of aromatic ring protons. A peak between 0.50 – 1.30ppm may be caused by –C_4H_9 group[24] protons linked with Sn. A singlet at 3.80ppm was obtained in 1:2 and 1:3 molar ratio compounds correspond to –NH_2 group proton which was not found in 1:1 and 2:1 molar ratio compounds. –NH- proton has shown a singlet at 3.40ppm.

Table-1: Physical characteristics and elemental analytical data of synthesized compounds.

Compound/Derivative (Mol. Formula) Ratio	Colour	m.p./b.p. (±2°C)	% Analysis found/ (calculated)			
			C	H	N	Sn
MBTTIP ($C_{13}H_{30}O_3Sn$)	Light brown liquid	94 at 0.03 mm	45.05 (44.23)	9.00 (8.51)	---	32.40 (33.65)
dpac ($C_{13}H_{12}O_2N_2$)	Light yellow solid	140	67.12 (66.42)	5.10 (5.26)	12.00 (12.28)	--
BuSn(L)(OPr^i) ($C_{20}H_{26}O_3N_2Sn$) 1:1	Reddish-brown solid	110	52.33 (52.06)	5.98 (5.64)	6.54 (6.07)	26.14 (25.81)
BuSn(LH)$_2$(OPr^i) ($C_{33}H_{38}O_5N_4Sn$) 1:2	Pinkish- brown solid	105	57.98 (57.48)	6.12 (5.52)	8.74 (8.13)	17.88 (17.27)
BuSn(LH)$_3$ ($C_{43}H_{42}O_6N_6Sn$) 1:3	Greyish-white solid	120	60.10 (60.21)	4.37 (4.90)	9.17 (9.80)	14.05 (13.89)
(BuSn)$_2$L(OPr^i)$_4$ ($C_{33}H_{56}O_6N_2Sn_2$) 2:1	Dark brown sticky solid	--	49.92 (48.65)	7.15 (6.88)	3.68 (3.44)	29.61 (29.24)

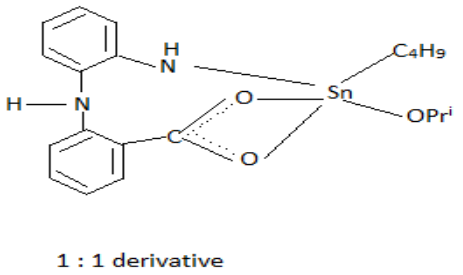
Probable Structures of Monobutyltin(IV) Derivatives: On the basis of IR and 1H NMR spectral data, probable structures of derivatives of monobutyltin(IV) with diphenylamine- 2-amino - 2'-carboxylic acid are given as below:

Antipestal activity: The derivatives so obtained were analyzed for their antipestal properties against a pest i.e. Red Flour Beetle (*Tribolium castaneum*) using bio-assay method[25].

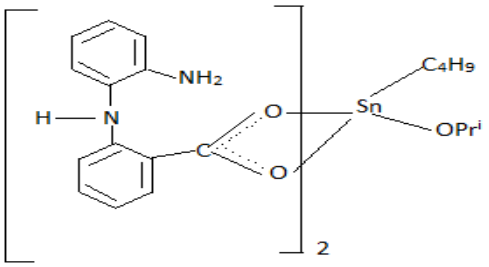
On comparison of % pest mortality data of MBTTIP and its compounds of Diphenylamine -2 - amino - 2'- carboxylic acid (dpac) / (L) (Table-2) indicates that the derivatives were exhibited higher antipestal activities as compared to ligand.

Conclusion

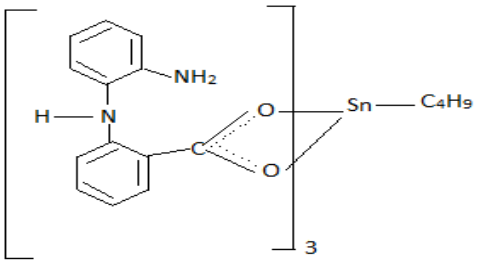
In view of above said analysis done, it has been analyzed that the at room temperature the compounds so formed are stable. The derivatives of Monobutyltin(IV) with diphenylamine–2–amino-2'-carboxylic acid exhibited greater antipestal characteristics than ligands.



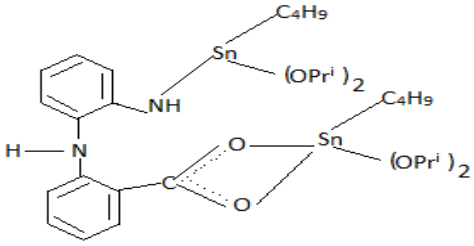
1 : 1 derivative



1 : 2 derivative



1 : 3 derivative



2 : 1 derivative

Table-2: Percentage mortality data of Synthesized Compounds.

Compound (Molecular Formula) Ratio	% mortality data at different concentrations		
	0.08 % (w/v)	0.06 % (w/v)	0.03 % (w/v)
MBTTIP ($C_{13}H_{30}O_3Sn$)	33	30	17
dpac ($C_{13}H_{12}O_2N_2$)	18	15	10
$BuSn(L)(OPr^i)$ ($C_{20}H_{26}O_3N_2Sn$) 1:1	43	37	28
$BuSn(LH)_2(OPr^i)$ ($C_{33}H_{38}O_5N_4Sn$) 1:2	40	33	32
$BuSn(LH)_3$ ($C_{43}H_{42}O_6N_6Sn$) 1:3	42	37	30
$(BuSn)_2L(OPr^i)_4$ ($C_{33}H_{56}O_6N_2Sn_2$) 2:1	47	42	33

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