



Synthetic, Characterization and Pesticidal Studies of Dibutyltin (IV) Derivatives of diphenylamine-2-amino-2'-Carboxylic acid

Pachouri Manoj Kumar and Mittal Pankaj*

*Department of Applied Sciences (Chemistry), Hindustan Institute of Technology and Management, Keetham, Agra, INDIA

Available online at: www.isca.in, www.isca.me

Received 23rd December 2014, revised 10th January 2015, accepted 16th January 2015

Abstract

Organotin (IV) derivatives of diphenylamines have synthesized by the reaction of dibutyltin diisopropoxide with diphenylamine-2-amino-2'-carboxylic acid (dpac) in 1:1, 1:2 and 2:1 molar ratios. These derivatives are characterized by elemental analyses, IR spectral analyses, PMR spectral analyses and molar conductance measurements. The products are screened for pesticidal activities against the pest 'Red Flour Beetle' (*Tribolium castaneum*). The derivatives so formed exhibited enhanced pesticidal activities compared to the ligand.

Keywords: Dibutyltin, diphenylamines, IR, PMR, pesticidal.

Introduction

The unique combination of physical, chemical and biological properties of tin/organotin compounds together with the versatility in their applications prompted a continued search of new class of tin/organotin derivatives during the past decades. The organotin compounds are of paramount importance from academic point of view as well as tin may form coordination complexes with suitable ligands displaying enhanced its coordination number. The organotin compounds have been used as biocidal¹⁻³ as well as pesticidal⁴⁻⁹. The present work deals with the synthesis, characterization and pesticidal studies of dibutyltin(IV) derivatives of diphenylamine-2-amino-2'-carboxylic acid.

Material and Methods

Experimental: Synthesis of dibutyltin diisopropoxide¹⁰ (DBTDIP): Isopropanol (3.1 ml, 0.04 M) in 10 ml dry benzene was mixed and stirred with sodium metal (0.92 g, 0.04 M) in a flask under anhydrous condition till the complete dissolution of sodium metal. Dibutyltin dichloride (6.1 g, 0.02 M) in 15 ml dry benzene was mixed drop-wise in the reaction mixture with continuous shaking by using dropping funnel, a white crystalline precipitate of sodium chloride separated which was filtered and the filtrate was refluxed for about 2.5 hours. The product so obtained was filtered and the filtrate was distilled under reduced pressure on a wax bath using water condenser. On distillation, a colourless liquid was obtained which changed to light brown upon standing.

Synthesis of Diphenylamine-2-amino-2'-carboxylic acid (dpac): 1.56 gm (0.01 M) o-chlorobenzoic acid and 1.08 gm (0.01 M) o-phenylenediamine were taken in 100 ml of distilled water in a flask. This mixture was made slightly alkaline with

potassium carbonate solution and a little copper oxide was mixed in the reaction mixture. The reaction mixture was refluxed on an oil bath for about 6 hours and cooled. 1.0 gram activated charcoal was added and boiled for about one hour to decolourise the product. It was filtered, concentrated and cooled. The obtained solution was acidified with dil. HCl in excess till the precipitation of the resultant product was complete. The obtained crude product was dissolved in ethyl alcohol for recrystallization and the recrystallized compound was dried over anhydrous calcium chloride in a desiccator to get light yellow solid.

Synthesis of Dibutyltin (IV) derivatives of Diphenylamine-2-amino-2'-carboxylic acid: Dibutyltin (IV) derivatives of Diphenylamine-2-amino-2'-carboxylic acid were synthesized by refluxing DBTDIP with dpac in dry toluene in 1:1, 1:2 and 2:1 molar ratios. A mixture of DBTDIP {0.7 ml (0.002 M)/ 0.7 ml (0.002 M)/ 1.4 ml (0.004 M)} and dpac {0.45 g (0.002 M)/ 0.92 g (0.004 M)/ 0.45 g (0.002 M)} was suspended in 30 ml dry toluene in a round bottom flask fitted with water condenser and a guard tube containing anhydrous CaCl₂. The solution was condensed for about 12-14 hrs on a wax bath. On cooling in a desiccator for overnight, the coloured solid was separated out which was filtered and washed with dry ether. The obtained product was recrystallized from DMSO and dried under reduced pressure over anhydrous CaCl₂ to get coloured crystalline solid.

Physical and Analytical Measurements: The purity of derivatives was determined by running their TLC for single spot on silica gel-G plate and by the repeated melting point determination of recrystallized samples taken in open capillary tube and thus uncorrected. These compounds were analyzed for elemental analysis on Carlo Erba Micro Analyser-1108 at the RSIC, CDRI, Lucknow. Tin (IV) metal was estimated by decomposing the compound with conc. HNO₃ followed by conc.

H₂SO₄ and then neutralized and precipitated by liq. NH₃ as tin oxide¹¹.

Infra-red spectrum of compounds was recorded by Perkin Elmer RX-1 spectrometer and ¹H NMR spectrum was recorded by PMR Bruker AC 300 MHz spectrometer at RSIC, CDRI, Lucknow. The molar conductance was determined by using Systronics conductivity meter 306.

Results and Discussion

The physical and analytical data of dibutyltin diisopropoxide and its derivatives are given in table-1. All the synthesized derivatives were found stable and hygroscopic at room temperature. They are soluble in DMF and DMSO and insoluble in water. The low values of molar conductance of these derivatives (4.1 – 4.7 ohm⁻¹cm²mol⁻¹) indicate their behaviour as non-electrolytes¹².

Infra-red spectral analysis: In the IR spectrum of DBTDIP, the weak peaks around 2910 cm⁻¹ and 2865 cm⁻¹ indicate ν C-H of ν -CH₂- and ν -CH₃ of the butyl group^{13,14}. The strong peak at 1370 cm⁻¹ occurs due to ν C-H bending vibration of geminal dimethyl structure of the isopropoxy group¹⁵. A weak peak at 1145 cm⁻¹ occurs due to ν C-O present in isopropoxy group¹⁵. The medium peak around 645 cm⁻¹ and a weak peak around 620 cm⁻¹ may be due to ν Sn-C¹⁶. The weak peak around 535 cm⁻¹ and a strong peak around 460 cm⁻¹ may be due to ν Sn-O¹⁷.

In the IR spectrum of dpac, a medium peak around 3280 cm⁻¹ may be due to ν N-H stretching vibration of primary aromatic amino group and 2650 cm⁻¹ due to ν O-H stretching of -COOH group. The sharp peak at 1690 cm⁻¹ takes place for ν -CO stretching vibration of carboxylic group.

In the IR spectra of dibutyltin(IV) derivatives of dpac, a medium band at 3285 cm⁻¹ indicates ν N-H stretching vibration of primary aromatic amino group and at 3030 cm⁻¹ may be due to ν C-H of the aromatic ring^{13,15}. The weak peaks at 2940 cm⁻¹ and 2855 cm⁻¹ indicate ν C-H of -CH₂- and -CH₃ of the butyl group^{13,14}. The weak peak in the region 1175 cm⁻¹ corresponds for ν C-O of the isopropoxy group in 2:1 derivative¹⁵. A strong peak around 1435 cm⁻¹ corresponds to ν_sCOO stretching vibrations while a strong peak around 1635 cm⁻¹ may be due to ν_{as}COO stretching vibrations¹⁸. The separation value, ΔνCOO of about 200 cm⁻¹ suggested the presence of bridged carboxylate group¹⁹.

A medium peak around 1370 cm⁻¹ occurs due to ν C-H bending vibrations of the gem dimethyl structure of the isopropoxy group¹⁵ in 2:1 derivative. The medium peak around 640 cm⁻¹ and weak peak around 605 cm⁻¹ occur due to ν Sn-C¹⁶, while weak peak around 540 cm⁻¹ and strong peak around 465 cm⁻¹ occurs due to ν Sn-O¹⁷.

The absence of free amino (-NH₂) peak in the region 3300-3240 cm⁻¹ in 1:1 and 2:1 derivatives suggests possible bonding of amino group to tin, while this band is appeared in 1:2 derivative at 3285 cm⁻¹.

PMR spectral analysis: In the pmr spectrum of DBTDIP, a multiplet between 1.20 – 1.60 ppm may be due to protons of butyl group²⁰ attached with tin. A multiplet between 0.70 – 1.20 ppm may be due to protons of isopropoxy group.

Table-1
Physical, Analytical and Pesticidal Data of DBTDIP and its derivatives with dpac

S. No.	Compound (Molecular Formula) Ratio	Colour	m.p./ b.p. (±2°C)	% Analysis Found/ (Calcd.)				% mortality data at different concentrations		
				C	H	N	Sn	0.08% (w/v)	0.06% (w/v)	0.03% (w/v)
1	DBTDIP (C ₁₄ H ₃₂ O ₂ Sn)	Light brown liquid	130.5 at 10 mm	48.40 (47.90)	9.80 (9.12)	nil	32.95 (33.84)	40	33	18
2	dpac (C ₁₃ H ₁₂ O ₂ N ₂)	Light yellow solid	140	67.12 (66.42)	5.10 (5.26)	12.00 (12.28)	nil	18	15	10
3	Bu ₂ Sn(L) (C ₂₁ H ₂₈ O ₂ N ₂ Sn) 1:1	Reddish black solid	125	55.26 (54.90)	6.75 (6.10)	6.28 (6.10)	25.90 (25.93)	52	42	32
4	Bu ₂ Sn(LH) ₂ (C ₃₄ H ₄₀ O ₄ N ₄ Sn) 1:2	Blackish brown solid	118	60.15 (59.39)	6.55 (5.82)	8.78 (8.15)	17.54 (17.32)	42	33	27
5	(Bu ₂ Sn) ₂ L(OPr ^t) ₂ (C ₃₅ H ₆₀ O ₄ N ₂ Sn ₂) 2:1	Brownish red solid	115	52.62 (51.85)	7.92 (7.41)	3.46 (3.40)	29.22 (29.38)	57	47	37

In the pmr spectrum of dpbc, a multiplet is shown between 7.10 – 8.15 ppm, which corresponds for aromatic protons. A singlet at 11.55 ppm, 3.85 ppm and 3.35 ppm corresponds to –COOH, –NH₂ and –NH- protons respectively.

In the pmr spectra of synthesized dibutyltin (IV) derivatives of dpac, a multiplet is obtained between 7.10 – 8.20 ppm, which corresponds to aromatic protons. The multiplet between 1.05 – 1.40 ppm in 1:1 and 1:2 derivatives and 0.40 – 1.30 ppm in 2:1 derivative may be due to protons of butyl group¹⁹ attached with tin. A singlet at 3.55 ppm is obtained in 1:2 derivative which corresponds to –NH₂ group proton which is absent in 1:1 and 2:1 derivatives. A singlet is obtained in the region 3.50 – 3.60 ppm corresponds to –NH- proton.

Pesticidal activity: All the synthesized derivatives were screened for their pesticidal activities on a Red Flour Beetle (*Tribolium castaneum*), a storage food grain pest adopting bio-assay technique²¹. A comparative study of % pest mortality (Table-1) indicates the enhancement of pesticidal activity of derivatives as compared to ligand.

Conclusion

From the above structural and pesticidal analysis, it has been found that all the synthesized derivatives are stable at room temperature. The dibutyltin(IV) derivatives of diphenylamine 2-amino-2'-carboxylic acid show higher pesticidal activities as compared to ligand fragments.

References

1. Arakawa Y., *Main Group Metal Chem.*, **12**, 1 (1989)
2. Saxena A.K., *Appl. Organometal. Chem.*, **1**, 39 (1987)
3. Dey K. and Mukhopadhyay S., *J. Indian Chem. Soc.*, **78**, 73 (2001)
4. Gupta P.R., Mishra R.C. and Dogra G.S., *Indian J. Agric. Sci.*, **51**, 514 (1981)
5. Mittal P., Pachouri M.K. and Sharma R.C., Studies on monobutyltin (IV) derivatives of 3-hydroxy-2-naphthoic acid, *Asian J. of Chemistry*, **18**(1), 737-739 (2006)
6. Mittal P., Pachouri M.K. and Sharma R.C., Pesticidal behavior of monobutyltin (IV) derivatives of salicylic acid against Red Flour Beetle, *J. Ind. Council Chem.*, **23**(2), 23-26 (2006)
7. Mittal P. and Pachouri M. K., Characterization and Pesticidal studies of some new Dibutyltin (IV) derivatives of 1-hydroxy-2-naphthoic acid, *Res. J. Chem. Sci.*, **2**(4), 61-63 (2012)
8. Mittal P., Pachouri M. K. and Singh N. P., Synthetic, Characterization and Pesticidal studies of Dibutyltin (IV) derivatives of salicylic acid, *Res. J. Chem. Sci.*, **3**(3), 79-81 (2013)
9. Pachouri M.K. and Mittal P., Characterization and Pesticidal studies of Dibutyltin (IV) derivatives of diphenylamine-2-hydroxy-2'-carboxylic acid, *Res. J. Chem. Sci.*, **4**(1), 75-77 (2014)
10. Gaur D.P., Srivastava G. and Mehrotra R.C., *J. Organometal. Chem.*, **63**, 221 (1973)
11. Vogel A.I., Quantitative Inorganic Analysis, *Longmans, London*, (1975)
12. Kettle S.F.A., Coordination Compounds, *Thomas Nelson and Sons*, 168 (1975)
13. Bellamy L.J., *The Infra-red Spectra of Complex Molecules*, *Methuen, London*, (1962)
14. Nakanishi K. and Solomon P.H., *Infra-red Absorption Spectroscopy 2nd Ed.*, *Holden-Day, London*, (1962)
15. Silverstein R.M., Bassler G.C. and Morrill T.C., *Spectrometric Identification of Organic Compounds*, *John Wiley, New York*, (1981)
16. Brown M.P., Okawara R. and Rochow E.G., *Spectrochim. Acta*, **16**, 595 (1960)
17. Pardhy S.A., Gopinathan S. and Gopinathan C., *Synth. React. Inorg. Met. Org. Chem.*, **13**, 305 (1983)
18. Peruzzo V., Plazzogna G. and Tagliavini G., *Organometal. Chem.*, **24**, 347 (1970)
19. Srivastava, T.N. and Singh, J.D., *Indian J. Chem.*, **24A**, 489 (1985)
20. Asahi Research Centre Co. Ltd. Tokyo, *Hand Book of Proton NMR Spectra and Data*, Vol. 2nd & 4th, *Academic Press, Japan*, (1985)
21. U.S. Environmental Protection Agency, *Report of DDT Advisory Committee* (1975)