CHAPTER 4

TRIOGANOTIN(IV) COMPLEXES OF 4-[(E)-(3-FORMYL-4-HYDROXYPHENYL)-DIAZENYL]- AND 4-[(E)-4-HYDROXY-3-[(E)-4-(ARYL)IMINOMETHYHY]PHENYL- DIAZENYL]-BENZOIC ACIDS: SYNTHESSES, CHARACTERIZATION AND STRUCTURES

4.1 Introduction
4.2 Synthesis of triorganotin(IV) complexes
4.3 Spectroscopic characterization of triorganotin(IV) complexes

of L^6-10 H^+ (^6^Bu^3 SnL^6-10 H) and (Ph^3 SnL^6-7 H)
4.4 X-ray crystallography
4.5 Experimental
4.5.1 Synthesis of Ligands
4.5.2 Synthesis of triorganotin(IV) complexes
4.5.3 Chemical used for the preparations
4.5.4 Physical measurements
4.5.5 X-ray crystallography
References
4.1 Introduction

Organotin(IV) complexes of 2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid [1-5] and 2-[(E)-4-hydroxy-3-[(E)-4-(aryl)iminomethyl]phenyl diazenyl]benzoic acids [3,5-8] have been studied in great detail which are discussed in Chapter 3 due to their various structural motifs (Scheme 4.1 (I-III)) as well as for their important role in understanding Sn(IV) coordination chemistry in solution as well as in the solid state. In addition, this class of compounds has shown promise as larvicides against various species of mosquito (see Chapter 6). For example, n-butyltin(IV) azo carboxylates, viz., tri-n-butyltin(IV) 5-[(E)-2-(aryl)-1-diazenyl]-2-hydroxybenzoates and tri-n-butyltin(IV) 2-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoate have been investigated for their toxicities against both the Aedes aegypti (Ae. aegypti) and Anopheles stephensi (An. stephensi) mosquito larvae. The results indicated that these compounds have shown moderate [9] to good [3] activities, respectively. The latter compounds were further condensed with primary aromatic amines to obtain the tri-n-butyltin(IV) 2-[(E)-4-hydroxy-3-[(E)-4-(aryl)iminomethyl]phenyl diazenyl]benzoates (Chapter 3). The activities for these compounds were found to be lower and correlated with the size of the molecules (Chapter 6) [6].

In view of this, and in search of better candidates for the control of various mosquito larvae, the present study details the synthesis and characterization of the pre-ligand i.e. 4-[(E)-2-(3-formyl-4-hydroxyphenyl)-1-diazenyl]benzoic acid (L₄HH⁺, Fig. 4.1a) and the triorganotin(IV) complexes of the corresponding condensed ligands, i.e. 4-[(E)-4-hydroxy-3-[(E)-4-(aryl)iminomethyl]phenyl diazenyl]benzoic acids (L⁴⁻HH⁺, Fig. 4.1b). The generic structures of each of the ligands are shown in Chapter 2.

![Fig. 4.1 Generic structure of the ligand. Abbreviations: (a) LHH⁺ (pre-ligand) (b) L¹HH⁺: X = -CH₃; L²HH⁺: X = -Br, L³HH⁺: X = -Cl, L⁴HH⁺: X = -OCH₃ (condensed ligands), where H and H' represent hydroxy and carboxylic acid H atoms, respectively.](image-url)