P R E F A C E

"There are ..... agents in Nature able to make the particles of bodies stick together by very strong attractions," wrote Newton in 1718, "And it is the buisiness of experimental philosophy to find them out."[1]

How do these "agents" act within and between molecules has been a subject of vigorous research for the past hundred years or so. The vast field of molecular or association complexes has gradually developed through such research and many novel examples of molecular associations have been added to enrich this branch of Chemistry. Thus, many molecules which were never thought to be able to behave as electron donors or acceptors have since been proved to behave so.

In the present work, we would like to present examples of some novel donor - acceptor type of complexes formed by a group of organotin - ortho -(aryl azo) benzoates acting as extremely versatile donors. Complexes are formed with a very wide variety of molecules including well-known electron acceptors, unsaturated hydrocarbons and their derivatives, ethers, halo alkanes and even saturated hydrocarbons. In some cases, charge-transfer bands are also observed.

The formation of association complexes with saturated hydrocarbon molecules is extremely novel in as much as no spectroscopic evidence of such acceptor (or donor) properties of the saturated hydrocarbons was so far available. A number of thermodynamic and other evidences were however available which indicated

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1. I. Newton, "Optics", 4th Ed., Book 3, Part I, G. Bell and Sons Ltd., London, 1931, Qs. 31.

possibilities of molecular association involving saturated hydrocarbons.[2-4]

The work is divided into four chapters.

In the first chapter, a short review of association complexes has been given. This chapter includes classification of association complexes into several types depending on the bonding situations, different types of donor and acceptor molecules participating in bonding in such complexes and the methods generally used for their quantitative study.

In the second chapter, the electronic spectra of azo dyes and their metallic and organometallic derivatives have been discussed. Special emphasis has been laid on explaining the solvent effects on the absorption spectra of azo dyes and their organometallic derivatives.

In the third chapter, a detailed study of the absorption spectra of Triorganotin-ortho-(aryl azo) benzoates in different solvents has been presented to show formation of novel association complexes. Methods for computation of integrated band intensities, oscillator strengths and determination of association constants have been fully discussed. The magnitudes of the association constants suggests rather weak interaction with saturated hydrocarbons ($K \sim 10^{-2}$ litre/mole). The trend in the values, however, supports the hypothesis that the organotin

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2. J. Le Brumant, M.Selim and G. Martin, Chemical Abstracts, 78: 135128d (1973).
3. K. Shudo and T. Okamoto, Tetrahedron, 33(14), 1717(1977).
4. W. Woycicki and P. Rhensius, J. Chem. Thermodynamics, 11(2), 153 (1979)

molecules act as donor and the other partner as acceptor since magnitudes of the association constants increase with acceptor strength of the interacting molecule. For example, the association constant of the Chloranil-complex is about 10^3 litre/mole.

The fourth chapter deals with the effect of protic solvents on the association complexes formed by the triorganotin-o-(aryl azo) benzoates. A detailed study of these effects helps to understand more fully the donor - acceptor nature of the association complexes.

In the appendix, computational methods used for the determination of integrated band intensities have been discussed in details.