Scope of the Thesis

The field of electronic spectroscopy is seeing such fierce development that any knowledge gained becomes outdated before it is fully comprehended. However, it is necessary to recall that the basic need for the emergence of this discipline is for the characterization of chromophores and to study their interaction with the surroundings or other molecules. New organic molecules are regularly being synthesized and it is a routine to perform spectroscopic investigations for better understanding of the properties of these molecules, and to divulge their possible uses. Such studies are exceedingly important in the viewpoint of biochemical and biophysical processes. Solvent sensitive small molecules as fluorophores are precious owing to their capability to probe micro-environments which can decipher bulk information in the study of molecular biology, drug discovery, material science, tissue diagnostics, environmental indicators, enzyme substrates and cellular staining agents. Sometimes, spectroscopy is also used as a probing tool to study the occurrence of different molecular phenomenon.

The objective of the thesis is to sightsee various facets of electronic spectroscopy with the photophysical exploration of some well-known, as well as newly synthesized molecules in solution phase, and also their interactions with other small molecules and biological macromolecules. Such studies have the potential to endeavor better understanding on the properties of those molecules and may also divulge newer applications. Newer principles get established owing to such investigations which may be used to improve the scientific research, for example to design drugs with better biological prominence. The selection of the fluorophores studied in this thesis work is based on the following reasons.

1-Keto-1,2,3,4-tetrahydrocabazole (KTHC) derivatives

1-Keto-1,2,3,4-tetrahydrocabazole (KTHC) derivatives are important intermediates for obtaining naturally occurring carbazole alkaloids and carbazoloquinones. Carbazole alkaloids are well recognized for their pharmacological activities, especially after the isolation and synthesis of carbazomycins, the first antibiotics having carbazole framework, from *Streptoverticillium species*. In addition there is a number of 1,2,3,4-tetrahydrocabazoles which also have several therapeutic applications. Furthermore 1-keto-1,2,3,4-tetrahydrocabazoles [figure 2.1],
obtained via the Japp-Klingemann approach, are the important synthetic precursors towards the synthesis of carbazole derivatives which include carbazoloquinones and other natural products having carbazole moiety like Murrayanine, Murrayaquinone A, Pyrayaquinones A and B, Koenigine-quinone A and B and 4-Deoxycarbazomycin B. The compound 4-Deoxycarbazomycin B is known to have promising antimicrobial activity against both gram positive and gram negative bacteria.

KTHC-derivatives are also structurally related to indole alkaloids. Many of the indole alkaloids possess significant physiological activity and some of them are used in medicine. It is worth mentioning that tryptophan having indole moiety, an amino acid, is the biochemical precursor of indole alkaloids.

Figure 2.1. Representative structure of 1-keto-1,2,3,4-tetrahydrocabazole

The extended delocalization of the π-framework over the rigid 2-ketoindole moiety makes the KTHC molecules interesting candidates for spectroscopic investigation. Saha et al. synthesized some fluorescent methoxy and methylenedioxy derivatives of 1-keto-1,2,3,4-tetrahydrocarbazole. It has been our goal to investigate the photophysical properties of these new fluorescent derivatives, and also to study their photoinduced interactions with small molecules as well as biological macromolecules. In this thesis we have reported studies on the following six derivatives: 1-keto-6,7-dimethoxy-1,2,3,4-tetrahydrocarbazole [KTHC-67], 2-(7-methoxy-1-oxo-2,3,4,9-tetrahydro-1H-carbazol-6-yloxy)acetic acid [MOTHCA], 6,7-dimethoxy-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-one [DMTCO], 5-methyl-8,9-dihydro-5H-[1,3]dioxolo[4,5-b]carbazol-6(7H)-one [MDDCO] and 5,6,7,9-Tetrahydro-[1,3]dioxolo[4,5-h]carbazol-8-one [TDCO] as shown in figure 2.2.

Photophysical properties of DMTCO, MDDCO and TDCO have been examined in various pure and mixed solvents, and also their photoinduced interaction with aromatic amines N,N-dimethylaniline (DMA) and N,N-diethylaniline (DEA) have been investigated. The emissive
properties of these molecules depend on solvent nature, especially to the hydrogen bonding ability of the solvents. The molecules also participate in photoinduced electron transfer with DMA and DEA. The KTHC-67 and MOTHCA fluorophores form weak inclusion complexes with β-cyclodextrin, exclusively in the excited state.

![Representative structures of 1-keto-6,7-dimethoxy-1,2,3,4-tetrahydrocarbazole [KTHC-67]

**Figure 2.2.** Representative structures of 1-keto-6,7-dimethoxy-1,2,3,4-tetrahydrocarbazole [KTHC-67] A, 2-(7-methoxy-1-oxo-2,3,4,9-tetrahydro-1H-carbazol-6-yloxy)acetic acid [MOTHCA] B, 6,7-dimethoxy-9-methyl-2,3,4,9-tetrahydro-1H-carbazol-1-one [DMTCO] C, 5-methyl-8,9-dihydro-5H-[1,3]dioxolo[4,5-b]carbazol-6(7H)-one [MDDCO] D, 5,6,7,9-Tetrahydro-[1,3]dioxolo[4,5-h]carbazol-8-one [TDCO] E.

### 1,8-Naphthalic anhydride

1,8-Naphthalic anhydride (NAN) is well-known for decades mostly as an intermediate for the preparation of different derivatives of 1,8-naphthalimide [figure 2.3]. 1,8-Naphthalimide derivatives have good photo-stability and high fluorescence quantum yield, and are used in variety of applications. They have been proposed as potential fluorescent probes of hypoxic cells as has been suggested in the works of Middleton et. al. 84, 85 and recently it is being used in the
preparation of efficient solar cells \(86-89\). Pardo \(et.al\). have investigated some of such derivatives with a view to laser activity \(90, 91\). The 1,8-naphthalimide-based anion sensors, being either fluorescent and/or colorimetric, are also in widespread use \(92\). Similar chromophores chemically doped onto the polymer backbones can be used as efficient light-emitting diodes \(93-100\). Some other derivatives of 1,8-Naphthalic anhydride also find use as fluorescent brightening agents for polymeric materials, as has observed in the works of Grabtchev \(et.al\.). \(101, 102\). 1,8-Naphthalic anhydride itself acts as a safener for the various herbicides \(103-107\).

![Figure 2.3. Representative structure of 1,8-naphthalic anhydride.](image)

The main disadvantage of using 1,8-naphthalic anhydride is that it hydrolyzes in water or in any protic solvents \(108\), although it is stable in aprotic medium and has some very interesting properties. It was our aim to explore the photophysical properties of NAN in different aprotic solvents of varying polarity and also its photoinduced interaction with aliphatic amines, in order to bring out its further usefulness. The excited state spectroscopic behavior of NAN was found to be solvent dependent. Besides, it works as a good photoinduced electron acceptor with the aliphatic amines triethylamine (TEA), tri-N-butylamine (TBA) and diisopropylethylamine (DIEA).

**1,1′-Binaphthyl-2,2′-diol enantiomers**

Molecules, which exist as non-superimposable mirror images of each other, are said to be chiral and are called as enantiomers having identical physical and chemical properties, unless placed in a chiral environment \(109-111\). Enantiomers have significance in biology particularly because biological systems and the biomacromolecules are themselves chiral. Thus we can see that there are several examples in the field of biology which display enantioselective behavior, that is, different chiral molecules can be distinguished not only in the field of human biology but also in the vast field of nature and natural products \(109-116\). In fact, enantiomers have a fundamental role
to play in molecular recognition and are the basis of drug designing and triggering of the responses of different organisms to different stimuli.

While numerous spectroscopic investigations have been performed for chiral recognition in fluorescence involving small molecules, lesser such studies were carried out with biological macromolecules. The enantiomeric atropoisomers of 1,1’-binaphthyl-2,2’-diol (BINOL) are among the most widely used ligands for both stoichiometric and catalytic asymmetric reactions, and are suitable candidates for studying the chiral recognition studies [figure 2.4] 117.

![Figure 2.4. Three dimensional structures of R-Binol A and S-Binol B](image)

Interactions of R- and S-BINOL with a model transport protein, human serum albumin (HSA) have been investigated to find the difference in binding type and associated phenomenon resulting from opposite handedness of the two compounds. HSA is asymmetric owing to the presence of chiral residues constituting its primary structure as well as to the presence of secondary and tertiary structure 118-120. The BINOL enantiomers have the propensity to lose a proton if suitable proton acceptors are present. The S- isomer has been found to affect HSA fluorescence and its secondary structure, through the formation of stronger hydrogen bonds with nearby residues, compared to R-BINOL.