SPECTROSCOPY OF MOLECULAR INTERACTIONS

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CERTIFICATE

This is to certify that the thesis entitled "Spectroscopy of Molecular Interactions" being submitted by A. Ram Reddy to the Indian Institute of Technology, Delhi, for the award of the degree of Doctor of Philosophy in Chemistry, is a record of bonafide research work carried out by him. Mr. A. Ram Reddy has worked under my guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard .

The results contained in this dissertation have not been submitted, in part or in full to any University or Institute for the award of any degree or diploma.

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ABSTRACT

2,4-dinitrophenol (DNP) and p-nitrophenol (PNP) undergo proton transfer in presence of strong electron donors. The proton transfer equilibria of DNP and PNP with a variety of electron donor have been examined by electronic absorption spectroscopy. The role of solvents of varying polarity on the extent of proton transfer has been thoroughly examined. The nature of the interaction between DNP with several π and n donors and of PNP with n donors has been quantitatively investigated in detail since the strength of the electron donor-acceptor interaction is one of the important factors to determine the extent of proton transfer.

The enolimine-ketoamine equilibria in Schiff bases may be considered as a special case of proton transfer (proton tautomerism). The equilibrium has been studied in a series of alkyl and aryl-salicylaldimines in non-polar and polar solvents. The special role of polar, hydrogen bond forming solvents (e.g. alcohols) has been evaluated. The effect of substituents on the alcohol and on aryl-salicylaldimines in determining the extent of tautomeric equilibrium has been examined.

Near infrared spectroscopy (NIR) has not been extensively employed for a quantitative study of donor-acceptor equilibria, as compared to other spectroscopic methods. The utility of this technique to determine hydrogen bonding equilibria between phenol and

a few heterocyclic systems in a non-polar solvent has been demonstrated. NIR is a valuable technique for studying the anharmonicity effects as first overtone vibrational frequencies occur in this region. Hydrogen bond formation is known to affect the mechanical anharmonicity constants of A-H stretching vibrations. This aspect has been investigated for the hydrogen bonding interaction of methanol with a series of ketones, phenol with a series of ketones and of methylethylketone with a series of alcohols.

In contrast to many reports in the literature on hydrogen bonding of molecules with closed shell ground states, very little is known on the interaction of those which have unpaired spin in the electronic ground state. In order to understand the energetics of this interaction and its role in hydrogen abstraction reactions, the hydrogen bonding interaction of a stable free radical,1,1-diphenyl-2-picrylhydrazyl (DPPH) with chloroform, bromoform, dichloromethane and 1,2-dichloroethane in carbontetrachloride has been investigated by electronic absorption spectroscopy.

N,N'-dimethylaniline and tetrachloro-p-benzoquinone (chloranil) react to yield a product, crystal violet cation. The reaction is considered to go through an initial formation of a donor-acceptor charge transfer complex and of radical ions. This reaction has been investigated, in detail, in solvents of varying polarity. The dependence of rate constants and activation energies of the reaction on the nature of the solvent has been examined. The effect of substituents para to

the $N(CH_3)_2$ group on the aniline ring in altering the progress of the reaction has been examined.

Every attempt has been made to acknowledge the findings of other investigators relevant to the work described in this thesis. The author apologizes for any omission or mistake due to oversight.

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