

# PHENYLPYRIDINES AS pH DEPENDENT FLUORESCENCE PROBES IN A NONPOLAR SOLVENT

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In contrast to the excited state proton transfer required for the isomeric phenylpyridines to fluoresce in water, the 2,6-derivative has an unexpectedly low  $pK_a = 3.7$  that prevents this process from occurring. Using deuterium isotope effects we confirmed that excited state protonation occurs in the mono-phenyl derivatives. A reverse isotope effect can, however, occur if the triplet yield is large, since intersystem crossing is accompanied by deprotonation.

As an extension of our interest in hydrogen bonding induced fluorescence we have initiated a fluorescence study of four molecules: 2-, 3-, 4-phenyl and 2,6-diphenylpyridine in a low dielectric constant, hydrocarbon solvent, where proton transfer is unfavorable. The major difference between a protonated and a hydrogen bonded species in these systems is that the N-H distance is predicted to be  $\sim 1.0 \text{ \AA}$  in the former and  $\sim 2.5 \text{ \AA}$  in the latter. Semi-empirical AM1 calculations will be presented to support the distinction between the two processes. Since the first three molecules in water are effective proton scavengers in the excited state we have been interested in perturbing their fluorescence with H-bond/proton donors. By forming 1:1 complexes with trifluoroacetic acid we have been able to significantly perturb the excited state behavior of these molecules. The formation constants for the H-bonded complexes have been determined (see Table I below) and correlate well with the basicities of these molecules.

The fluorescence of phenylpyridines induced by complexation with an acid is due to an excited state hydrogen bond transfer, i.e., from the configuration  $(N \cdots H - O)^*$  to  $(N - H \cdots O)^*$ , consistent with the increased basicity of an azine in the excited singlet state, and the diagram shown in Fig. 1.

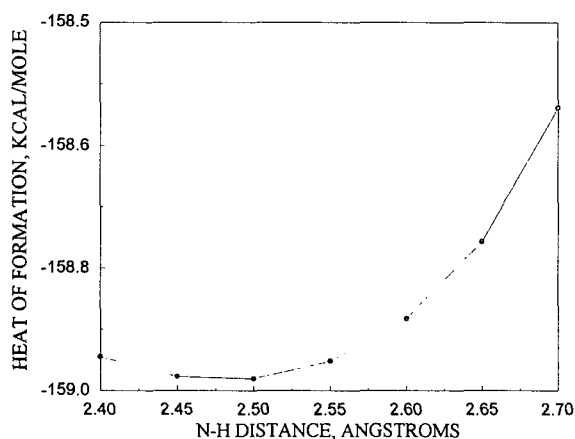


Fig. 1. - Interaction between 2,6-diphenylpyridine and trifluoroacetic acid.

The results of these studies provide a basis for the fluorescence sensing of trace amounts of acid in a nonpolar solvent by forming 1:1 H-bonded complexes with phenylpyridines. In the case of 2,6-diphenylpyridine interacting with trifluoroacetic acid the ground state stabilization energy is predicted to be  $\sim 3.6 \text{ Kcal/mol}$ , with an N-H separation of  $2.51 \text{ \AA}$ . Such an interaction gives rise to a  $>40$ -fold increase in emission. Fluorescence quantum yields and spectroscopic data, complemented with semi-empirical AM1 calculations, will be presented to illustrate the emission behavior of these molecules and the geometrical changes, determined by time re-