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OPAS TOJIRA: PHOTOISOMERIZATION STUDIES OF SOME HYDRAZONE COMPOUNDS. THESIS ADVISORS: PRAPIN WILAIRAT, Ph.D., SAUVAROP LIMCHAROEN, Dr.rer.nat., ORAPIN RANGSIMAN, Dr.rer.nat., 187 p. ISBN 974-664-103-4.

The photosensitive imine compound, pyridoxal isonicotinoyl hydrazone (PIH), and structural analogues, pyridoxal benzoyl hydrazone (PBH), pyridoxal salicyloyl hydrazone (PSH), benzaldehyde isonicotinoyl hydrazone (BIH), benzaldehyde benzoyl hydrazone (BBH), benzaldehyde salicyloyl hydrazone (BSH), salicylaldehyde isonicotinoyl hydrazone (SIH), salicylaldehyde benzoyl hydrazone (SBH) and salicylaldehyde salicyloyl hydrazone (SSH) were synthesized and characterized using electronic absorption, fluorescence excitation and emission, and infrared absorption spectroscopic techniques.

The existence of tautomeric forms of PIH in the solid state was investigated and confirmed using recrystallization, infrared spectroscopy and X-ray diffraction. There is formation of the zwitterionic form of the pyridoxal due to the transfer of the phenolic proton to the pyridoxal nitrogen when PIH crystallizes in the hydrated structure (1:1 PIH-to-water). UV-Visible and fluorescence spectral data indicate that the Schiff-base/pyridinium phenolate tautomeric forms only occur in the solid state. In solution state, the compound is readily converted to the normal Schiff-base (non-dipolar) form.

The configurational change of the two diastereomers associated with the carbon-nitrogen double bond of PIH and analogues has been observed via the change in electronic absorption spectra when their methanolic solutions are exposed to light. Upon keeping in the dark, the spectra slowly convert to the initial state at ambient temperature. In solid state, this behaviour does not occur to any significant extent.

The kinetics of the thermal cis-trans isomerization reactions of all the hydrazones in methanolic solutions have been investigated at four temperatures: 25.0, 30.0, 35.0 and 40.0 °C using UV-visible spectrophotometry. The results show that these reactions are first order, with the activation energies of 10–19 kcal mol<sup>-1</sup> (42–80 kJ mol<sup>-1</sup>) and logarithm of preexponential factors of 3–10. The temperature dependence of the first-order rate constant has also been analyzed using the Activated Complex Theory of reaction rate.

The activation energies and the preexponential factors are related to the *cis*-molecular structures of the hydrazones. It is difficult to directly compare the rates of the thermal cis-trans isomerizations of the various hydrazones. However, with hydrazones having the same value of the preexponential factors, their rates of reactions can be compared.