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CYCLIC AMIDINES AS CONVENIENT MODELS FOR THE STUDIES OF PROTON TRANSFER REACTIONS

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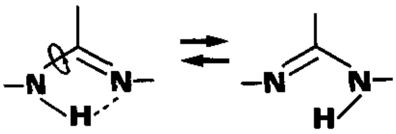
Proton transfer is an elementary chemical reaction of undeniable importance. From our investigations on proton migrations in cyclic amidines, particularly in cyclic azines such as dihydropyrimidines (DHP), dihydroquinazolines, dihydro-s-triazines and tetrahydropyrimidines, we can conclude, on the basis of the concentration dependence of the rate of proton exchange, that this transfer is an intermolecular process, in contrast to the migration in acyclic amidines, where the proton shift is usually intramolecular. In spite of the widely accepted opinions that the H-transfer between electronegative atoms, such as N or O, is a very fast process and that the presence of individual tautomers cannot therefore be detected in the NMR time scale, we have been able to reduce this equilibration rate by carefully controlling the reaction conditions. The successful observation of this phenomena in a series of DHP's may be explained in terms of an appealing hypothesis (Kresge, 1975), which postulates that the delocalization of the lone pair of electrons on nitrogen might be the reason for slowing down the rate of protonation of this atom. By suitable modification of the substituents or the ring system itself, it was possible to increase or decrease the extent of electron delocalization with a concomitant increase of decrease in the rate of proton exchange.

A



B

A detailed discussion of the mechanisms of intermolecular (A) and intramolecular (B) H-migration will be presented and substantiated by molecular models, theoretical calculations and H-bonding theory.