SYNTHESIS AND PROPERTIES OF A TAUTOMERIZABLE HETEROMACROCYCLIC COMPOUND

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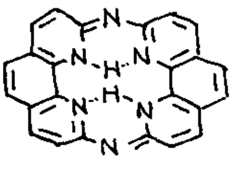
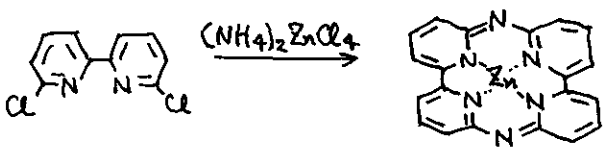
In the course of our search for azamacrocyclic compounds, it was shown that thermolysis of 2,9-diamino-1,10-phenanthroline gave a cyclic dimer, which existed in the fully conjugated tautomer (1). We now report the synthesis and prototropic tautomerism of a novel macrocyclic compound containing 2,2'-bipyridine moieties.

Thermolisis of a mixture of 6,6'-dichloro-2,2'-bipyridine and ammonium tetrachlorozincate at 320°C for 6 hrs gave a zinc complex (2), together with 6,6'-diamino-2,2'-bipyridine. Dissolving the zinc complex in conc. H_2SO_4 followed by HCl bubbling through the solution gave the metal-free macrocycle (3). On spectroscopic investigation, it has been found that the compound forms 3a ⇌ 3b tautomeric system. The tautomerism is depending upon the solvent; 3a (yellow) form is preferred in nonpolar solvents such as chloroform and benzene, and 3b (almost colourless) form in polar solvents such as methanol and water.

The macrocycle 3 is protonated in an acid solution. The equilibrium was studied spectrophotometrically. Visible and ultraviolet absorption spectra of the solutions in hydrochloric acid of various concentrations show isosbestic points. The equilibrium involves free base and diprotonated species. The macrocycle also acts as an acid in sodium hydroxide solutions. Deprotonated species may be mono- or di-anion.



1



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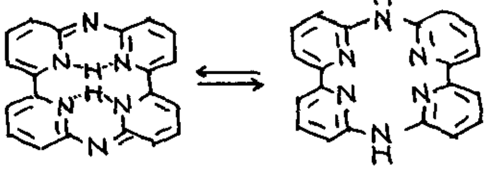

3a

3b