Direct Detection of the Aminotetrazole–Iminotetrazoline Tautomerism by Proton Magnetic Resonance Spectroscopy

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Summary Aminotetrazole–iminotetrazoline tautomerism has been directly observed in 1-methyl-5-methyl aminotetrazole by ^{1}H n.m.r.

THE concept of the aminotetrazole–iminotetrazoline tautomerism has been widely used in explanations of the reactions of aminotetrazoles. Indications of this phenomenon have been obtained from the u.v. spectrum of 2-methyl-5-methylaminotetrazole.[1] and from the presence of a band assignable to an imino-group in the i.r. spectra of some 5-aminotetrazoles,[2] but no clear observation or assessment of the tautomerism has been achieved. ^{1}H n.m.r. spectroscopy has now shown clearly this tautomerism for 1-methyl-5-methylaminotetrazole.

The ^{1}H n.m.r. spectrum of this material in $(CD_3)_2SO$ solution shows a broad NH signal (τ 3·28), a sharp 1-NMe signal (6·32) and a 5-NMe signal which consists of three peaks, a singlet (7·08) assigned to the 5-NMe protons of the tautomeric form (II) and a doublet (7·15; J 2Hz) assigned to the 5-NMe protons of form (I) showing the spin–spin splitting with the NH proton. In this solution a slow tautomerism obtains. Addition of water increases the rate of the tautomerism sufficiently to collapse the 5-NMe doublet of form (I) to a singlet but the exchange is still relatively slow and the NH signal and the two separate 5-NMe signals remain. Further addition of a small concentration of hydroxide ions causes a large increase in the proton-exchange rate. This results in the disappearance of the NH signal and the collapse of the two separate 5-NMe resonances to a sharp, single peak midway between them. This represents the normal 5-NMe signal, similar to that of the 1-NMe protons.

The relative areas of the 5-NMe signals from the pure $(CD_3)_2SO$ solution indicate a tautomeric ratio (I) : (II) of *ca.* 65 : 35. In the aqueous $(CD_3)_2SO$ solution this becomes *ca.* 1 : 1. The linewidths indicate limiting lifetimes for the species of $\geq$ 1 sec. in the $(CD_3)_2SO$ solution and *ca.* 0·5 sec in the aqueous $(CD_3)_2SO$ solution.

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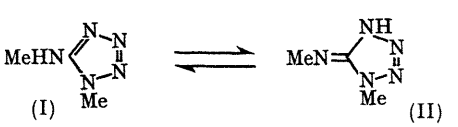

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[1] R. A. Henry, W. G. Finnegan, and E. Lieber, *J. Amer. Chem. Soc.*, 1954, **76**, 2894.
[2] D. B. Murphy and J. P. Picard, *J. Org. Chem.*, 1954, **19**, 1807.