The Tautomeric Structure of Secondary Amino-azoles

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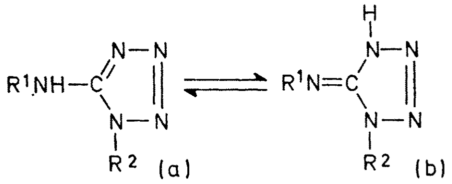
Summary Secondary amino-azoles, in certain instances, may exist in an imino-form.

IN a recent paper Fletcher and Katritzky[1] report that the ^{1}H n.m.r. spectrum of 1-methyl-5-methylaminotetrazole (I) in perdeuteriodimethyl sulphoxide indicates that the compound exists in the amino-form (Ia), in contrast to my results. These workers report a signal for the 5-*N*-methyl protons which consists of a doublet (J 5 Hz) and such a spectrum, of course, is consistent with their interpretation. However, my spectrum[2] for this system showed, as well as this doublet, a third peak due to the form (Ib). Addition of water produced a spectrum similar to that reported by Fletcher and Katritzky.[1] Dimethyl sulphoxide is a highly hygroscopic solvent and only a small quantity of water was required to produce this change. Addition of further water produces no further significant change. My experimental results for the system (I) have been fully confirmed for a series of the system (II) by Scott and Tobin[3] who have recently observed the expected three peaks for the 5-*N*-benzyl CH_2 protons using dimethyl sulphoxide and dimethyl and diethyl sulphoxide mixtures as solvent. Addition of water changed the spectrum to a doublet.



(I) R^1 = Me; R^2 = Me
(II) R^1 = p-X—C_6H_4—CH_2; R^2 = H
X = H, Me, Cl, Br

Although Fletcher and Katritzky[1] claim that amino-derivatives of azoles always exist in amino-forms, a rather sweeping claim, this is by no means the first time that an imino-form has been suggested for secondary 5-aminotetrazoles. Henry, Finnegan, and Lieber[4] quote reasonable u.v. evidence for an imino-form for 2-methyl-5-methylaminotetrazole. Murphy and Picard[5] quote i.r. evidence for the presence of an imino-form for compound (I) in the solid state. Indeed, the presence of an imino-form for such systems is not unexpected because of the stabilising effect of the alkyl substituent on the incipient imino double bond. Primary amino-groups are, of course, a different system and the arguments concerning compound (IV) in the previous paper[1] are of minor relevance to this discussion.

In strong hydrogen-bonding aprotic dipolar solvents, *e.g.* dimethyl sulphoxide,[6,7] rapid exchange of N–H protons can be reduced to give separate resonances.

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[6] R. N. Butler, *J. Chem. Soc.* (*B*), 1969, 680.
[7] R. F. Stockel, *J. Chem. Educ.*, 1969, **46**, 391.