The Tautomeric Structure of 1-Methyl-5-methylaminotetrazole and a Warning regarding Nuclear Magnetic Resonance Spectral Determinations in Deuteriated Dimethyl Sulphoxide

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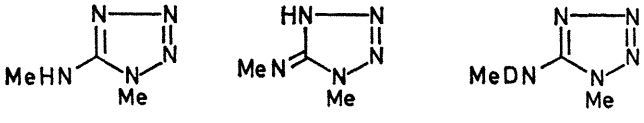
Summary 1-Methyl-5-methylaminotetrazole exists in the amino-form; conclusions to the contrary are shown to be due to deuterium oxide contamination in the $(CD_3)_2SO$ used.

RECENTLY, we drew attention[1] to what we believed to be the erroneous conclusion by Butler[2] that 1-methyl-5-methylaminotetrazole (**1**) exists in $(CD_3)_2SO$ to the extent of 35% in the imino-form (**2**). Butler has since disputed our work, and ascribed our result to the use of wet $(CD_3)_2SO$.[3] We have now repeated our earlier n.m.r. work, and again find that in dry (distilled from CaH_2)[4] $(CD_3)_2SO$, the n.m.r. of (**1**) shows the *N*-methyl protons as a doublet, *J* 5 Hz, unaffected by the addition of water, but collapsed to a singlet by irradiation at the NH-proton frequency, or by addition of D_2O. Butler's conclusions[2,3] were based on a three *N*–Me peak spectrum obtained in $(CD_3)_2SO$: we now present evidence which suggests that this was due to the solvent then used being contaminated with a small quantity of D_2O. The Figure shows the n.m.r. spectra (*N*-Me region) obtained for the solution in $(CD_3)_2SO$: addition of precise small quantities of D_2O caused the appearance and increase of the third peak [due to the species (**3**)], which can be caused to disappear again on the addition of H_2O which displaced the equilibrium [(**1**) ⇌ (**3**)] in favour of (**1**) again. The spectrum reported[2b] is very similar to that of (c) in the present Figure: Butler quotes[2b] τ 7·122 and *J* 5·1 Hz for NHMe and τ 7·135 for NMe; we find τ 7·115 and *J* 5·0 Hz for NHMe and τ 7·122 for NDMe; the small isotopic shift is not unexpected.

As Butler points out,[3] he is not the first to suggest imino-forms for secondary 5-aminotetrazoles: such conclusions made in 1954 are unacceptable on present knowledge (*cf.* ref. 5); as regards the work of Scott and Tobin,[6] quoted in ref. 3, a similar explanation probably applies to their three-peak n.m.r. spectrum, as these authors are aware.[6]



Contrary to an opposite opinion,[3] the tautomerism of NH_2- and NHMe-compounds is usually very similar, except where steric factors intervene: other substituted amino-groups, *e.g.* $NHSO_2R$-compounds, can by contrast show considerably different behaviour.[7]

Our previous[1] conclusions stand: in addition we caution on the use of commercial $(CD_3)_2SO$ which may contain appreciable quantities of D_2O.

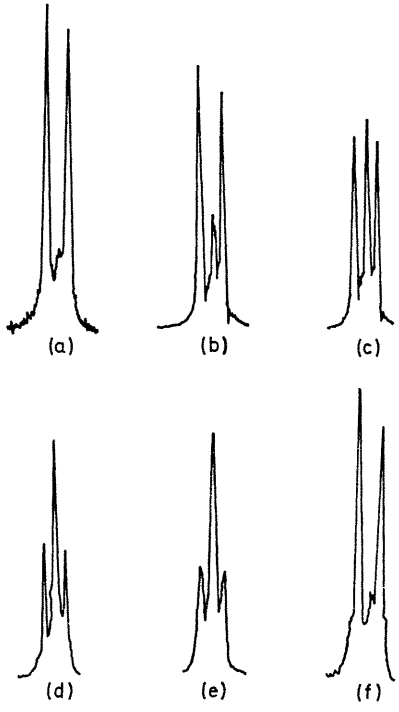


FIGURE. *Exocyclic* N-*methyl region of the n.m.r. spectrum of* 1-*methyl-5-methylaminotetrazole* (1 *mmol*) *in* $(CD_3)_2SO$ (*dried over* CaH_2): *initial spectrum* (a); *and spectra after the addition of* (b) 0·8 *mmol of* D_2O; (c) 1·2 *mmol* (*total*) *of* D_2O; (d) 1·6 *mmol of* D_2O; (e) 2·0 *mmol of* D_2O; (f) 2·0 *mmol of* D_2O *followed by* 5·5 *mmol* of H_2O.

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[2] (a) R. N. Butler, *Chem. Comm.*, 1969, 405; (b) *J. Chem. Soc.* (*B*), 1970, 138.
[3] R. N. Butler, *Chem. Comm.*, 1970, 1096.
[4] A. F. Cockerill, *J. Chem. Soc.* (*B*), 1967, 964.
[5] A. R. Katritzky and J. M. Lagowski, *Adv. Heterocyclic Chem.*, 1963, **2**, 75.
[6] F. L. Scott and J. C. Tobin, *J. Chem. Soc.* (*C*), 1971, 703.
[7] For review see A. R. Katritzky and J. M. Lagowski, *Adv. Heterocyclic Chem.*, 1963, **1** and **2**; A. R. Katritzky, *Chimia* (*Switz.*), 1970, **24**, 134.