Nitrogen Inversion in Tetrahydro-1,2-oxazines and 1,2-Oxazolidines

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THE n.m.r. spectrum† of neat *N*-methyltetrahydro-1,2-oxazine (I) at 55° shows the following four principal resonances: *ca.* τ 8·4 a complex multiplet (4-H, 5-H), at 7·54 a relatively sharp singlet (*N*-methyl protons), *ca.* 7·4 a broad triplet (methylene group adjacent to nitrogen), and *ca.* 6·2 another triplet (methylene group adjacent to oxygen). The spectrum is clearly consistent with rapid inversion of both the ring and the nitrogen atom.

On lowering the temperature (Figure) all resonances except that due to the *N*-methyl group undergo changes. The most striking change occurs in the CH_2–N resonance which shows that at low temperatures the two protons are no longer magnetically equivalent. The coalescence temperature for these protons is +5 ± 5° leading to an estimated free energy of activation $\Delta G_c^‡ = 13{\cdot}7 \pm 0{\cdot}5$ kcal./mole. The spectral changes in *N*-methyl-1,2-oxazolidine (II) are somewhat less complex; a chloroform solution shows coalescences at about 42°, ($\Delta G_c^‡ = 15{\cdot}6 \pm 0{\cdot}5$ kcal./mole) for the N-CH_2 protons.

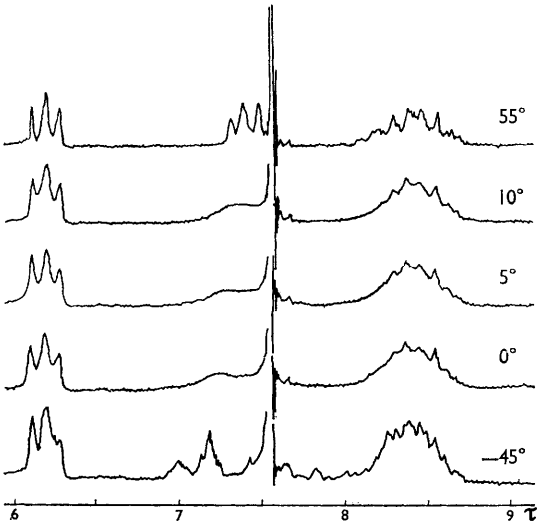
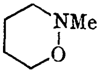
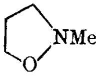


FIGURE. *Temperature dependence of the n.m.r. spectrum of* N-*methyltetrahydro-*1,2-*oxazine*



(I)



(II)

For both compounds in strongly hydrogen-bonding solvents there is a marked increase in the coalescence temperature of *ca.* 20°, equivalent to a barrier increase of *ca.* 1·3 kcal./mole (see Table). In other solvents there is little change. This result indicates that nitrogen inversion is the observed process, not only for the five-membered ring, but also for the six-membered ring. During nitrogen inversion a hydrogen bond must be broken. This is not necessarily the case for ring inversion.[1]

The barrier to nitrogen inversion in (I) does not seem to depend markedly on the dielectric constant of the solvent as was observed by Griffith and Roberts for an open-chain hydroxylamine.[2] Furthermore, it would seem that an α-oxygen atom leads to a much more pronounced decrease in the rate of nitrogen inversion than a neighbouring nitrogen atom, for, in a derivative of (II), where oxygen is replaced by NMe a $\Delta G_c^‡$ value of 11·1 kcal./mole has been measured at −45°.[3]

Compound	Solvent	$T_c(\pm 5°)$	$\Delta G_c^‡(\pm$ 0·5 kcal. mole)
(I)	None	5	13·7
(I)	Hexane	3	13·7
(I)	CH_2Cl_2	5	13·7
(I)	D_2O–CD_3OD (4 : 1)	33	15·0
(II)	$CDCl_3$	42	15·6
(II)	D_2O	62	16·9

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† The spectra were measured on a Perkin-Elmer R10 spectrometer in Stirling and a Varian A60 spectrometer in Strasbourg.

[1] J. M. Lehn, F. G. Riddell, B. J. Price, and I. O. Sutherland *J. Chem. Soc.* (*B*), 1967, 387.
[2] D. L. Griffith and J. D. Roberts, *J. Amer. Chem. Soc.*, 1965, **87**, 4089.
[3] B. Dietrich, J. M. Lehn, and P. Linscheid, to be published.