Retarded Rate of Inversion in Aziridines

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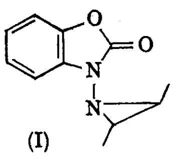
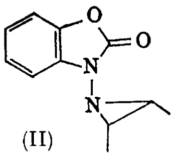
EARLY work by Bottini and Roberts using n.m.r. demonstrated that the normal inversion rate of trialkyl-substituted nitrogen is considerably retarded in the case of aziridines.[1] The effect of various *N*-substituents upon the rate of inversion has been studied; substituents able to delocalise the electron pair on nitrogen have an enhancing effect upon this rate.[2] Severe steric interactions also accelerate the inversion process as in the case of *N*-t-butylaziridine.[3]

Recently it has been shown that inversion in *N*-halogeno-aziridines is slow enough to permit separation of the two invertomers in the cases of *N*-chloro-2-methylaziridine[4] and 7-chloro-7-azabicyclo[4,1,0]heptane.[5] Actual observation of coalescence temperatures (T_c) in the n.m.r. spectra of the *N*-halogeno-aziridines was not possible owing to prior decomposition upon heating but for *N*-chloro-2,2-dimethylaziridine T_c was believed to be $> 180°$.[6]

This Communication deals with the recently reported[7] benzoxazolinone-substituted aziridines (I) and (II) where nitrogen is the hetero-atom bound to the aziridine ring nitrogen and in which there is a larger inversion barrier than in the alkylaziridines. The n.m.r. spectrum of (I) includes two quintets (two overlapping quartets) with *J* 5·6 c./sec. centred at δ (CCl_4)[‡] 2·25 and 3·31 corresponding to aziridine ring protons *trans* and *cis* to the benzoxazolinone substituent respectively; the methyl signals are doublets at 1·28 and 1·37 (*J* 5·6 c./sec.). The difference in chemical shift between protons *cis* and *trans* to the benzoxazolinone substituent (Δν) has the value of 62 c./sec. in CCl_4 (48 c./sec. in $CDCl_3$) at 60 Mc./sec. This abnormally large value is attributed to additional deshielding effects of aromatic ring and carbonyl group in the benzoxazolinone substituent upon the *cis* aziridine ring protons.



(I)



(II)

For the isochronous[8] aziridine ring protons in (II) a complex signal is observed from δ (CCl_4) 2·76—3·02; the methyl signals coincide as a doublet at 1·37 (*J* 5·0 c./sec.).

The reversible change in the n.m.r. spectrum upon heating a solution of (I) in dichlorobenzene is shown in the Figure. With increasing temperature, the gradually broadening and, by 160°, vanishing nature[§] of the two signals at δ 2·25 and 3·31 is characteristic of the resonance signals from protons moving at an increasing rate between positions of widely separated chemical shift.[9]

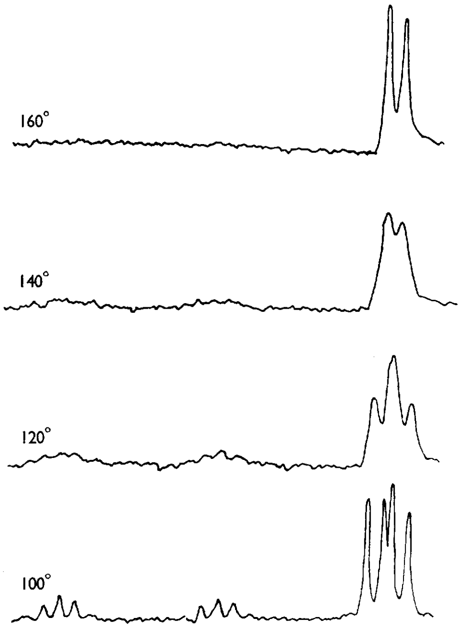


FIGURE. *Effect of increasing temperature upon the n.m.r. spectrum of* (I) *in dichlorobenzene obtained by using a Varian* A60. (*Aromatic signals omitted.*)

No change was observed in the n.m.r. spectrum of (II) up to 180° where the large free energy disparity between the two invertomers involved leads to no manifestation of T_c as in (I).[8]

This present case should be compared both with

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[‡] In p.p.m. from Me_4Si as internal standard. Spectra run at 100 Mc./sec.

[§] At even higher temperatures, the signal from the aziridine ring protons in (I) would be expected to reappear as a quartet at the mean position (δ, 2·78) but this was not experimentally feasible.

that of the diaziridines, where both adjacent nitrogens are within a three-membered ring and in which slow inversion of nitrogen has been demonstrated,[10] and with various *N*-substituted phosphorus aziridines,[11] where rapid inversion was reported even at −100° but in which a low operating frequency (20·5 Mc./sec.) would mask a probably low value for $\Delta\nu$.

I thank Professor C. W. Rees for helpful discussions.

(*Received, April 8th*, 1968; *Com.* 432.)

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