

## Retarded Rate of Inversion in Aziridines

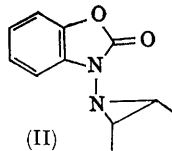
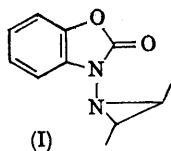
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EARLY work by Bottini and Roberts using n.m.r. demonstrated that the normal inversion rate of trialkyl-substituted nitrogen is considerably retarded in the case of aziridines.<sup>1</sup> The effect of various *N*-substituents upon the rate of inversion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

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<sup>4</sup> and 7-chloro-7-aza-bicyclo[4,1,0]heptane.<sup>5</sup> 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  $> 180^\circ$ .<sup>6</sup>

This Communication deals with the recently reported<sup>7</sup> 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  $\delta$  (CCl<sub>4</sub>)‡ 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 ( $\Delta\nu$ ) has the value of 62 c./sec. in CCl<sub>4</sub> (48 c./sec. in CDCl<sub>3</sub>) 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.



For the isochronous<sup>8</sup> aziridine ring protons in (II) a complex signal is observed from  $\delta$  (CCl<sub>4</sub>) 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  $160^\circ$ ,

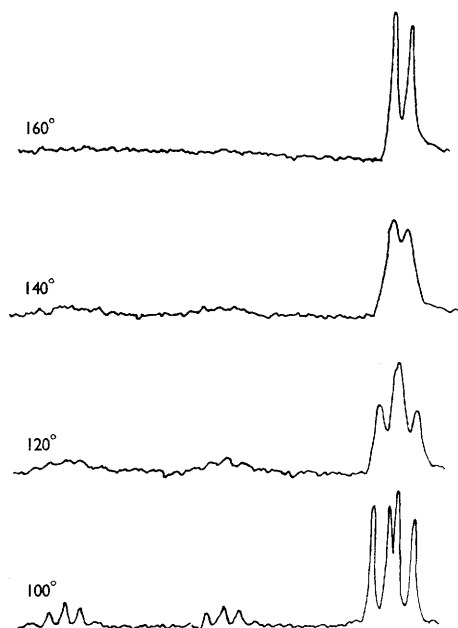


FIGURE. Effect of increasing temperature upon the n.m.r. spectrum of (I) in dichlorobenzene obtained by using a Varian A60. (Aromatic signals omitted.)

vanishing nature of the two signals at  $\delta$  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.<sup>9</sup>

No change was observed in the n.m.r. spectrum of (II) up to  $180^\circ$  where the large free energy disparity between the two invertomers involved leads to no manifestation of  $T_c$  as in (I).<sup>8</sup>

This present case should be compared both with

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‡ In p.p.m. from Me<sub>4</sub>Si 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 ( $\delta$ , 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,<sup>10</sup> and with various *N*-substituted phosphorus aziridines,<sup>11</sup> where rapid inversion was reported even at  $-100^{\circ}$  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.

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<sup>1</sup> A. T. Bottini and J. D. Roberts, *J. Amer. Chem. Soc.*, 1956, **78**, 5126.

<sup>2</sup> F. A. L. Anet and J. M. Osyany, *J. Amer. Chem. Soc.*, 1967, **89**, 352; F. A. L. Anet, R. D. Trepka, and D. J. Cram, *J. Amer. Chem. Soc.*, 1967, **89**, 357; A. L. Logothetis, *J. Org. Chem.*, 1964, **29**, 3049.

<sup>3</sup> S. J. Brois, *J. Amer. Chem. Soc.*, 1967, **89**, 4242.

<sup>4</sup> S. J. Brois, *J. Amer. Chem. Soc.*, 1968, **90**, 508.

<sup>5</sup> D. Felix and A. Eschenmoser, *Angew. Chem.*, 1968, **79**, 197.

<sup>6</sup> J. M. Lehn and J. Wagner, *Chem. Comm.*, 1968, 148—see also references to examples of hindered inversion in azetidines, diazetidinones and oxazetidines.

<sup>7</sup> R. S. Atkinson and C. W. Rees, *Chem. Comm.*, 1967, 1230.

<sup>8</sup> Y. Shvo, E. C. Taylor, K. Mislow, and M. Raban, *J. Amer. Chem. Soc.*, 1967, **89**, 4910.

<sup>9</sup> For analogous examples in the annulenes see F. Sondheimer *et al.* in "Aromaticity" Special Publ. no. 21, The Chemical Society, London.

<sup>10</sup> A. Mannschreck, R. Radeglia, E. Gründemann, and R. Ohme, *Chem. Ber.*, 1967, **100**, 1778. Slow inversion is also observed in the related oxaziridines, W. D. Emmons, *J. Amer. Chem. Soc.*, 1957, **79**, 5739.

<sup>11</sup> V. F. Bystrov, R. G. Kostyanovskii, O. A. Panshin, A. U. Stepanyants, and O. A. Iuzhakova, *Optics and Spectroscopy*, 1965, **19**, 122.