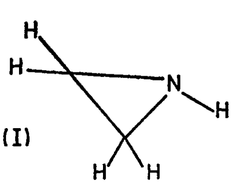
Observation of Temperature-dependent ^{1}H Nuclear Magnetic Resonance Spectra for Aziridine and [*N*-^{2}H]Aziridine in the Gas Phase

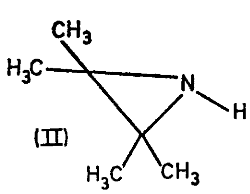
By Robert E. Carter* and Torbjörn Drakenberg

(*Organic and Physical Chemistry* 2, *Chemical Center, Box* 740, S-220 07 *Lund* 7, *Sweden*)

Summary The n.m.r. spectra of the methylene protons in aziridine and [*N*-^{2}H]aziridine have been obtained in the gas phase at 35 °C by means of Fourier transform spectroscopy at 100 MHz, and it is found that as the temperature is raised, a 'coalescence point' is observed at 68 °C, corresponding to a free energy of activation ($\Delta G_c^\ddagger$) of 17·3 kcal/mol (72·4 kJ/mol); the coalescence temperature in the case of [*N*-^{2}H]aziridine is 79 °C, corresponding to a $\Delta G_c^\ddagger$ value of 17·9 kcal/mol (74·9 kJ/mol).

The ^{1}H n.m.r. spectrum of the methylene protons of aziridine (I) in condensed phases is invariably reported as a singlet, although Mortimer[1] estimated all the proton–proton couplings in the $CH_2{\cdot}CH_2$ part of the molecule by an analysis of the ^{13}C-satellite pattern. The singlet nature of the main n.m.r. peak may be due to accidental shift equivalence of the aziridine ring protons, fast nitrogen inversion, or rapid intermolecular N–H proton exchange. We considered the latter alternative most likely to be correct in view of the work of Saitô *et al.*,[2] who demonstrated the presence of intermolecular hydrogen bonds (NH···N) in aziridine by dilution studies, and a kinetic study[3] on nitrogen inversion in a 'carefully dehydrated' sample of 2,2,3,3-tetramethylaziridine (II), originally reported[4] to exhibit a single, sharp n.m.r. peak for all 12 methyl protons.


(I)


(II)

In order to minimize intermolecular interactions, and thereby study the 'free' aziridine molecule, we have obtained† the n.m.r. spectrum of the methylene protons of aziridine in the gas phase [see Figure (a)] (probe temperature 35 °C). Since spinning of the n.m.r. tube gave interfering sidebands, the spectra were recorded on a non-spinning sample, which may have led to some inhomogeneity broadening of the lines. The possibility of line-broadening due to ^{14}N-quadrupole coupling was briefly examined by means of ^{14}N-decoupling at 7·2 MHz, but very little effect on the line shape could be observed. Line-broadening can also occur owing to decreased longitudinal relaxation times in the gas phase compared to those in the liquid state.[5,6] Finally, the aziridine methylene resonances at probe temperature are most certainly also broadened by some exchange process(es).

The broad (*ca.* 40 Hz), slightly unsymmetrical band due to the aziridine methylene protons is centred at δ 1·43 p.p.m. [see Figure (a)].‡ The splitting in the downfield half is *ca.* 9 Hz, while that in the upfield half is *ca.* 6 Hz. We ascribe the difference in splitting to stereospecific long-range H–N–C–H coupling. By analogy with the results of Saitô *et al.*,[2] we tentatively assign the low-field resonance to the *anti*-CH_2 protons.

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† Varian XL-100-15 spectrometer equipped with VFT-XL Fourier transform spectroscopy equipment. The sample was a mixture of aziridine and Me_4Si at the bottom of a 12 mm n.m.r. tube, sealed at *ca.* 10^{-3} mmHg.

‡ Under the conditions of our experiment, the N–H proton signal—probably quite near the Me_4Si lock signal[2]—could neither be observed nor irradiated.

We have observed the temperature dependence of the lineshape as far as the 'coalescence point' (68 °C). Estimation of the free energy of activation at the coalescence temperature ($\Delta G^{\ddagger}_{c}$), using the approximate equation (1)

$$\Delta G^{\ddagger}_{c} = RT_{c} \ln [(kT_{c}\sqrt{2})/(h\pi\Delta\nu)] \qquad (1)$$

with $\Delta\nu = 25$ Hz (see below), provides 17·3 kcal/mol (72·4 kJ/mol), which should primarily reflect the nitrogen inversion barrier. Any residual proton exchange would increase the observed inversion rate, but the 'true' rate cannot be larger than the observed value.§

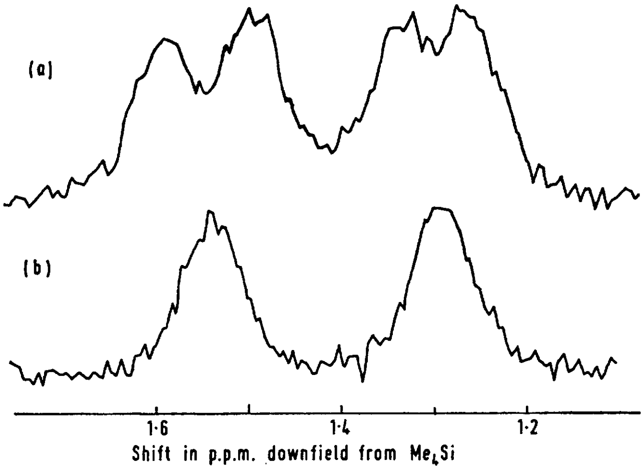

FIGURE. *100 MHz gas phase Fourier transform n.m.r. spectra of methylene protons in* (a) *aziridine and* (b) [N-^{2}H]*aziridine at* 35 °C.

The spectrum of [*N*-^{2}H]aziridine consists of two equally broad lines separated by 25 Hz [see Figure (b)]. The coalescence temperature for these two lines was 79 °C, corresponding to $\Delta G^{\ddagger}_{c}$ 17·9 kcal/mol (74·9 kJ/mol). The absolute error in the $\Delta G^{\ddagger}_{c}$ values could at worst be as much as ±0·5 kcal/mol, since temperatures were measured by the replacement technique, using a copper–constantan thermocouple in an empty, non-spinning 12 mm n.m.r. tube. However, the *relative* error is not more than ±0·2 kcal/mol, since the two measurements were made in exactly the same way. The isotope effect on the inversion barrier will be given detailed consideration in the full paper.

At least in the case of [*N*-^{2}H]aziridine, the entire sample was in the gas phase over the temperature range of our measurements, and thus the density of the sample was constant. In the case of aziridine itself, a small residual amount of liquefied sample was at the bottom of the n.m.r. tube, but we observed no significant shifts between the spectra of the two samples [*cf.* Figure (a) and (b)]. It is of interest that Raynes, Buckingham, and Bernstein[7] studied the pressure dependence of the chemical shifts of HCl, H_2S, CH_4, and C_2H_6, and found small shift changes (*ca.* −0·1 to −0·4 Hz/atm) over a pressure range of 0—55 atm. for HCl and CH_4, 0—20 atm. for H_2S, and 0—30 atm. for ethane. For aziridine (b.p. 56 °C), the change in pressure over the entire temperature range of our experiment can hardly be more than 1—2 atm.

Recent theoretical work on the nitrogen inversion barrier in aziridine has provided values ranging from 13·8[8] to 34[9] kcal/mol. *Ab initio* calculations by Lehn *et al.*[10] and by Clark[11] give barriers of 18·3 and 15·5 kcal/mol, respectively. The only previously available experimental values for the inversion barrier[12] have been two microwave 'lower-limit' estimations[13,14] of 12 and 11·6 kcal/mol. A comparison between theory and experiment must await the results of detailed complete lineshape analyses now in progress in our laboratories, in order to establish a value for the entropy of activation. It should be possible to differentiate between inversion and hydrogen exchange processes by observing the N–H proton signal.‡ The only available data on entropies of activation for the nitrogen inversion process in aziridines[12] almost invariably refer to condensed phases, and vary from large negative values [*e.g.* −14 e.u. estimated from the data of Bardos *et al.*[3] for (II)] to very large positive values (*e.g.* +14 to +38 e.u. for 1,2,2-trimethylaziridine in various solvents.[15]

Recent work[16] on 1,2,2-trimethylaziridine in both the gas and condensed phases provides a value of 2·3 ± 3 e.u. for $\Delta S^{\ddagger}$ in $Me_8Si_4O_4$ solution from a complete lineshape analysis. The $\Delta G^{\ddagger}_{c}$ value in the gas phase is only 0·4 kcal/mol lower than that in $Me_8Si_4O_4$.

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§ *Cf.* discussion in ref. 3. The $\Delta G^{\ddagger}_{c}$ value for (II) calculated from the data of these authors is 17·0 kcal/mol.

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