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THE ACTIVATION ENTHALPY AND ENTROPY FOR THE INVERSION–ROTATION PROCESS IN DIBENZYLMETHYLAMINE

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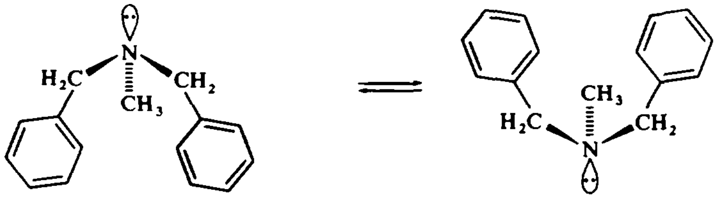
Abstract The temperature dependence of the PMR spectrum of the diastereotopic benzyl protons of dibenzylmethylamine has provided the activation parameters for nitrogen inversion. A method is described to account for the substantial variation in T_2 of the benzyl protons resonances as a function of temperature in the intermediate exchange region.

RECENTLY there has been considerable interest in the direct observation of rotation[1] or inversion[2] processes in acyclic amines using DNMR spectroscopy.[3,4] An important compound in the investigation of rate processes in acyclic trialkylamines has been dibenzylmethylamine (I). In the event of slow nitrogen inversion (eq. 1) on the NMR time scale, the diastereotopic benzyl protons of a given benzyl group of I are nonequivalent giving rise to an AB spectrum.[2] Fast nitrogen inversion with concomitant rotation about the benzyl carbon–nitrogen bond will render the two diastereotopic benzyl protons equivalent.[5]



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In all previous reports concerning the measurement of the rate of nitrogen inversion in I using the DNMR method, the rate was determined at only one temperature enabling the calculation of just the free energy of activation ($\Delta G^{\ddagger}$).[2] However, for the purpose of comparing the DNMR data to the enthalpy of activation ($\Delta H^{\ddagger}$) for other amines obtained from microwave or vibrational spectroscopy or theoretical calculations,[4] it is important to extract $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ (entropy of activation) from the variable temperature NMR spectra.

This report concerns the measurement of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for nitrogen inversion in I (eq. 1) using the DNMR technique and employing an empirical method to account for a significant temperature dependence of T_2 for the benzyl proton resonances at very low temperatures.

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RESULTS AND DISCUSSION

Examination of the ^1H NMR spectrum (60 MHz) of I (0·08 M in CH_2CHCl) at about −100° reveals two sharp singlet resonances for the NCH_3 (δ 2·08) and NCH_2 (δ 3·42) groups consistent with rapid nitrogen inversion on the NMR time scale. Upon lowering the temperature, the NCH_3 resonance broadens substantially but remains Lorentzian indicating a decreasing T_2 at lower temperatures (increasing viscosity). The temperature dependence of the width-at-half-height ($W_{\frac{1}{2}}$) of the NCH_3 peak is illustrated in Fig 1. The NCH_2 peak also broadens substantially at lower temperatures separating clearly into an AB spectrum ($\Delta\nu_{AB}$ = 17 Hz; J_{AB} = 13 Hz) at *ca.* −152° (Fig 2) consistent with slow nitrogen inversion on the NMR time scale.[2] Each component of the AB spectrum at −155° has a substantially greater $W_{\frac{1}{2}}$ than that observed at higher temperatures and it is evident that in the intermediate exchange region both the nitrogen inversion rate process and a decreasing T_2 at lower temperatures will contribute to the benzyl protons line shape. Neglect of the variation in T_2 with temperature will introduce serious errors into the activation parameters derived from the total NMR line shape analysis.[3]

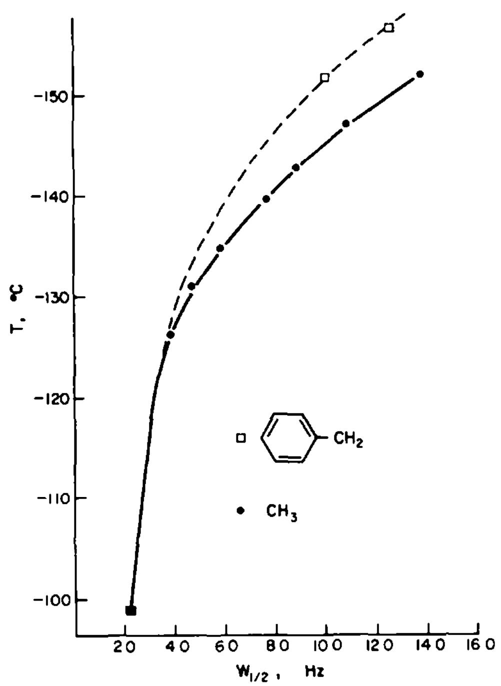

FIG 1. Temperature dependence of the width-at-half-height ($W_{\frac{1}{2}}$) of the N—CH_3 resonance and interpolated behavior for NCH_2 peaks in I (0·08 M in CH_2CHCl). The $W_{\frac{1}{2}}(NCH_2)$ at low temperatures (slow exchange) was obtained from a total line shape analysis.

Unfortunately, in the case of I, the variations in T_2 for the NCH_3 and NCH_2 resonances are different at very low temperatures. The behavior of the NCH_3 resonance is illustrated in Fig 1. Although the $W_{1/2}$ of the NCH_3 and NCH_2 resonances are essentially identical at −100°, the $W_{1/2}$ of each NCH_2 peak (13·0 Hz obtained from a total line shape analysis) at −155° is significantly different from the $W_{1/2}$ of NCH_3 (19·3 Hz) a phenomenon observed by other workers.[2d] Thus, in order to obtain the effective T_2 (or $W_{1/2}$) of the NCH_2 resonances in the region of partial peak collapse, the temperature dependence of $W_{1/2}$ of NCH_2 was estimated by assuming the same general but attenuated temperature dependence of $W_{1/2}$ (NCH_2) as observed for $W_{1/2}$ (NCH_3).

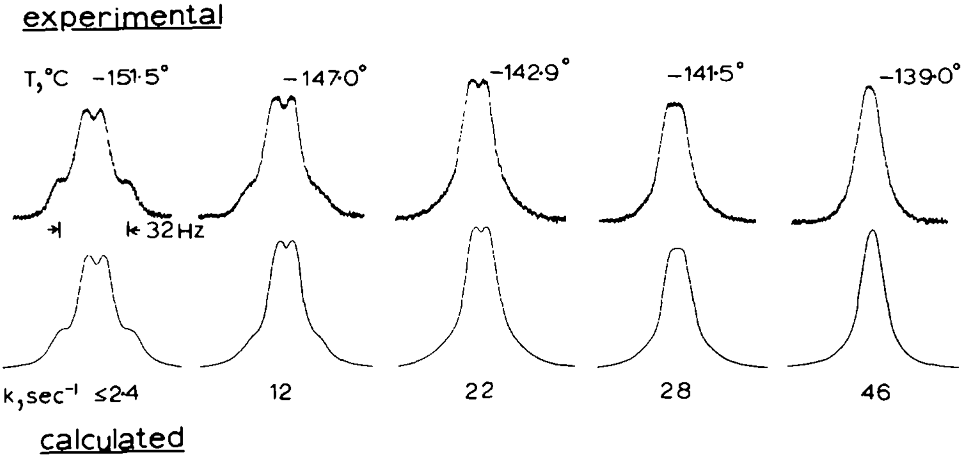

FIG 2. Temperature dependence of the ^1H NMR spectrum (60 MHz) of the NCH_2 protons of I (0·08 M in CH_2CHCl) and theoretical spectra as a function of the rate of nitrogen inversion.

Thus, the temperature dependence of $W_{1/2}$ (NCH_2) in the region of peak collapse was approximated by interpolation between a fast exchange $W_{1/2}$ (NCH_2) and two values obtained from total line shape analysis under slow exchange conditions (See dotted line in Fig 1). Accounting for the variation in T_2 in this manner, a series of normalized theoretical DNMR spectra[6] were calculated and fit by superposition to the experimental spectra (Fig 2) at various temperatures. A least squares fit of an Arrhenius plot gave $E_a = 7{\cdot}5 \pm 0{\cdot}4$ kcal/mole, $\Delta H^{\ddagger} = 7{\cdot}2 \pm 0{\cdot}4$ kcal/mole, $\Delta S^{\ddagger} = 4 \pm 3$ eu, and $\Delta G^{\ddagger}_{-141^\circ} = 6{\cdot}6 \pm 0{\cdot}1$ kcal/mol for the nitrogen inversion process. The error limits reported above are maximum errors obtained from an alternate straight line drawn through the Arrhenius plot which gave a reasonable though poorer fit than the line used. We prefer to report the error limits in this way because there still may be undetermined systematic errors in our analysis,[3] e.g., systematic errors resulting from our treatment of T_2 of the NCH_2 peaks (Fig 1). Although there is apparently no variation in the AB chemical shift as a function of temperature from −152° to −160° (slow exchange conditions), a small variation could easily be obscured by the very broad lines observed at these low temperatures.

With regard to the line broadening, we have also observed that at relatively high amine concentrations (>0·2 M), the AB pattern becomes less well resolved, *i.e.*, greater $W_{\frac{1}{2}}$, consistent with a smaller T_2 due to increased viscosity at higher amine concentrations. The source of the peak broadening exclusive of exchange processes observed for both the NCH_3 and NCH_2 resonances at very low temperatures is most likely due to the usual spin–spin relaxation mechanisms dependent on viscosity and *not* to ^{14}N quadrupolar relaxation.[2d, 7] The observation of sharp singlets at −100° for the NCH_3 and NCH_2 resonances in I revealing the absence of any $^{14}N—^1H$ spin–spin coupling ($J_{N,H} = 0·6$ Hz)[7c] indicates that the ^{14}N quadrupolar relaxation time (T_q)[7d] is short enough at −100° to cause rapid ^{14}N spin state interconversion and decoupling of ^{14}N from ^1H. Indeed, as the temperature is lowered and the viscosity increases, T_q should decrease and more effectively wash out the $^{14}N—^1H$ coupling rendering the lines *more sharp*.

It is apparent from the activation parameters determined for I that the major contribution to $\Delta G^\ddagger$ is $\Delta H^\ddagger$ and that $\Delta S^\ddagger$ is relatively small. Such an observation is consistent with a simple rate process such as nitrogen inversion.[3, 4] The positive $\Delta S^\ddagger$ is also consistent with a transition state involving planar nitrogen (i.e., expanded CNC bond angles as compared to the pyramidal ground state) and a greater degree of rotational freedom as compared to the ground state. In order to render the diastereotopic NCH_2 protons isochronous on the NMR time scale, it is also necessary to have rotation about the $N—CH_2$ bond. Thus, the activation parameters reported here may also include a torsional contribution due to $CH_2—N$ rotation.

The $\Delta H^\ddagger$ for the inversion-rotation process in I ($\Delta H^\ddagger = 7·2 \pm 0·4$ kcal/mole) is comparable to that for $(CH_3)_3N$ obtained from application of the valency force model to vibrational spectroscopic data ($\Delta H^\ddagger = 7·5$ kcal/mole)[8] or from MINDO SCF-MO calculations ($\Delta H^\ddagger = 6·5$ kcal/mole).[9]

The barrier to nitrogen inversion in I ($\Delta H^\ddagger = 7·2$ kcal/mole) is also significantly greater than the rotational barrier in trimethylamine ($\Delta H^\ddagger = 4·4$ kcal/mole)[10] and consistent with our recently criticized statement[2c] that the $\Delta H^\ddagger$ for the process being observed in I is significantly different from the rotational $\Delta H^\ddagger$ in trimethylamine. That criticism[2c] was included in a paper reporting negative entropies of activation as large as −36 eu for rate processes in a series of neopentyl amines. The slowed rate process observed in the neopentyl amines was assigned to C—N bond rotation,[2c] although nitrogen inversion cannot unequivocally be ruled out. The very large negative $\Delta S^\ddagger$ obtained for certain neopentyl amines[2c] is not consistent with an inversion process. Also, it does not seem reasonable that the assigned rotation process would have such a large negative $\Delta S^\ddagger$. Usually, large positive or negative entropies of activation for simple conformational equilibrations obtained using the DNMR method result from systematic errors in the line shape analysis or inaccurate temperature measurement.[3]

EXPERIMENTAL

The NMR spectra were obtained using a Varian HR-60A spectrometer equipped with a custom-built variable temperature probe. Spectral calibrations were performed by the audiomodulation technique using a Hewlett-Packard 641A audio oscillator and 5221B electronic counter.

Temperature measurement was performed using a calibrated copper-constantan thermocouple permanently in place in the probe and is done simultaneously with the recording of the spectrum. Temperature measurement is accurate to ±0·3° at the sample.

Matching of theoretical to experimental spectra was performed by superposition of normalized theoretical spectra on the experimental spectra. In all cases, the fit was essentially perfect and a calculated spectrum involving a 5% deviation in the chosen rate constant gave an obviously poor fit for all rate constants used in the Arrhenius plot. Thus we assign a maximum error of ± 5% to each rate constant.

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