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HINDERED ROTATION IN DEUTERATED *p*-NITROSODIMETHYLANILINE

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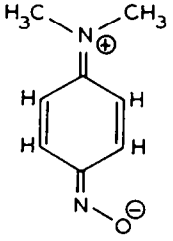
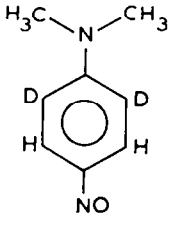
Abstract—An NMR study at $-60°$ to $+100°$ of selectively deuterated *p*-nitrosodimethylaniline leads to values of $\Delta H^{\ddagger} = 14{\cdot}9 \pm 0{\cdot}1$ kcal mol^{-1} and $\Delta S^{\ddagger} = 4{\cdot}8 \pm 0{\cdot}4$ cal mol^{-1} deg^{-1} for the rotational barrier round the C—NO bond.

IN A recent publication[1] Brand *et al.* reported on hindered rotation in *p*-nitrosodimethylaniline by studying NMR spectra at various temperatures. From the variation of an A_2X_2 pattern of the aromatic protons at room temperature to an ABKX pattern at $-60°$, they found a strong hindrance in the rotation of the NO group round the C—N bond. The barrier is due to the contribution of the mesomeric structure I. Despite the rather complex spin patterns, Brand *et al.* were able to calculate the energy and entropy of activation.

As part of a programme on hindered rotations we prepared *p*-nitrosodimethylaniline, selectively deuterated at the *ortho*-positions (II) in order to simplify the spin patterns.



I



II

RESULTS AND DISCUSSION

The spectra of the normal and of the deuterated compound at temperatures between $-60°$ and $+40°$ are given in Figs. 1 and 2.

A theoretical treatment of the influence of time-dependent processes on the shape of the absorption bands is given by several authors (cf. Ref. 7). The rate constant can be evaluated directly from the spectra by relating them to easily measurable components of the line shape function. We used two independent methods to obtain the rate constants:

(1) *Method of Woodbrey and Rogers*[2]

This method consists of the recording of the resonances due to the aromatic protons in *meta*-positions at temperatures *below* the coalescence temperature and

[1] D. D. McNicol, R. Wallace and J. C. D. Brand, *Trans. Faraday Soc.* **61**, 1 (1965).
[2] J. C. Woodbrey, Diss. Michigan State University 1960. *Diss. Abstr.* **22**, 4202 (1962).

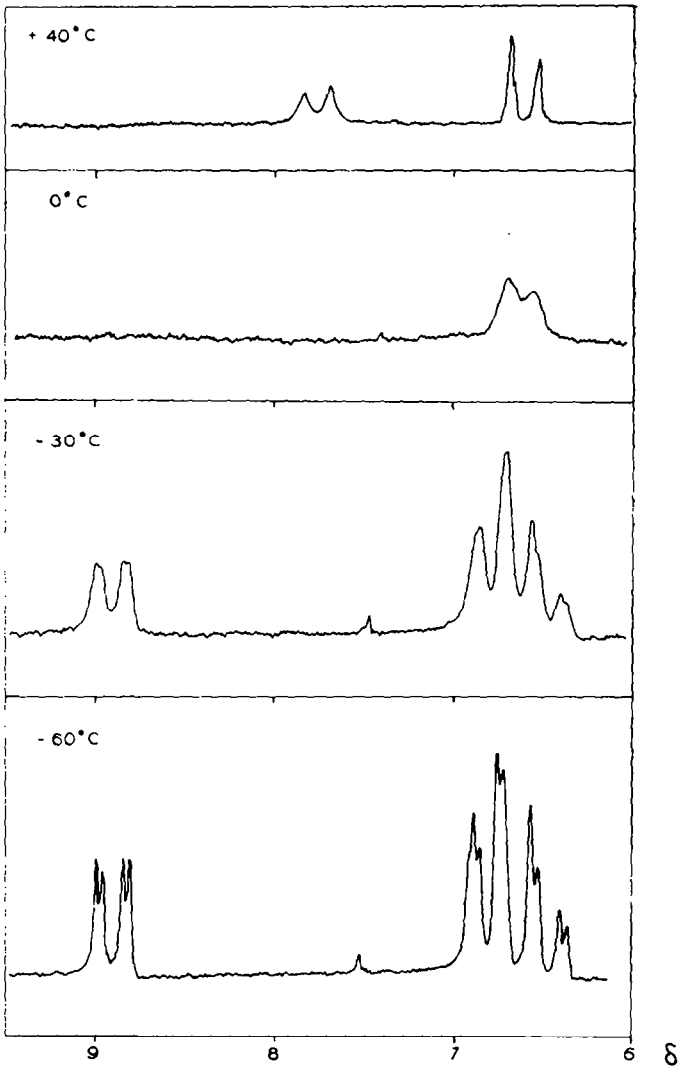


FIG. 1

measuring

$$r \equiv \frac{I_{max}}{I_{min}}$$

(for definitions of I_{max} and I_{min} see Fig. 3). The rate constant k is given by the formula:

$$k = \frac{\pi}{\pm\sqrt{2}} [r \pm (r^2 - r)^{1/2}]^{-1/2} \cdot \delta\nu$$

in which $\delta\nu$ is the difference in chemical shift when no rotation is observed.† With $k = (RT/Nh) \times e^{-\Delta G^*/RT}$ values for ΔH^* and ΔS^* can be determined. Results are given in Table 1.

† The broadening due to the coupling J_{AX} (2·5 c/s) has been neglected because $\delta\nu_{AX} \gg J_{AX}$.

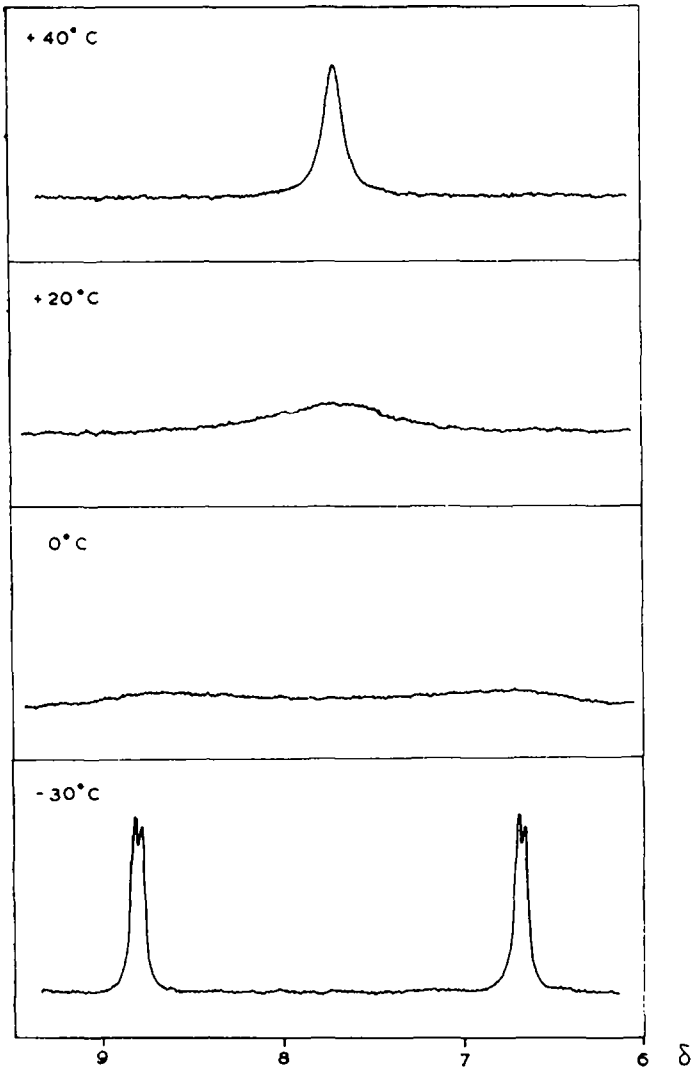


FIG. 2

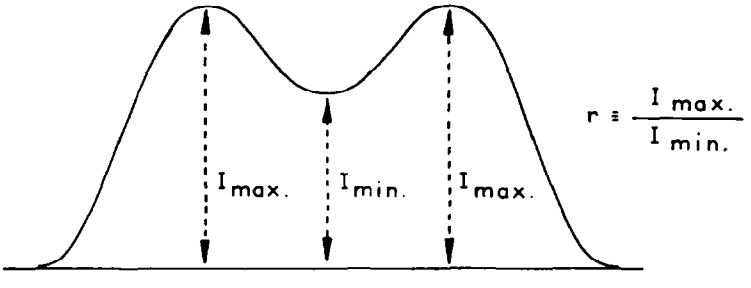


FIG. 3

TABLE 1

T_{abs}	266·9	268·2	270·3	272·1	274·2	276·8
r	8·54	5·54	4·31	2·84	1·94	1·31
log k	1·85	1·95	2·01	2·11	2·20	2·31

$\delta\nu = 129$ c/s
$\Delta H^* = 14{\cdot}6 \pm 1{\cdot}0$ kcal mol^{-1}
$\Delta S^* = 1{\cdot}1 \pm 3{\cdot}6$ cal deg^{-1} mol^{-1}

(2) *Method of Alexander*[3]

This method deals with the exchange narrowing of the absorption band at temperatures *above* the coalescence temperature. The height (A) of the absorption band at a certain temperature relative to the height (A_0) at "infinite" temperature is related to the mean lifetime τ† by the equation:

$$\frac{A}{A_0} = 1 - \frac{2T_2\delta\nu^2\tau + (T_2^2\delta\nu^4 + \delta\nu^2)\tau^2}{4 + 4\left(\frac{1}{T_2} + T_2\delta\nu^2\right)\tau + \left\{\left(\frac{1}{T_2} + T_2\delta\nu^2\right)^2 + J_{AX}{}^2\right\}\tau^2}$$

with $T_2\delta\nu^2 \gg 1$ and $T_2{}^2\delta\nu^4 \gg J_{AX}{}^2$, we get

$$k = \frac{1}{2\tau} = \frac{T_2\delta\nu^2}{4\left(\frac{A_0}{A} - 1\right)}$$

Results obtained by this method are given in Table 2.

TABLE 2

T_{abs}	290·0	293·7	299·8	303·0	306·6
A/A_0	0·0429	0·0579	0·0935	0·1202	0·163
T_{abs}	312·2	319·5	323·2	327·7	331·6
A/A_0	0·226	0·352	0·403	0·492	0·572

$\delta\nu = 129$ c/s
$T_2 = 2$ sec‡
From these data we calculate: $\Delta H^* = 14{\cdot}9 \pm 0{\cdot}1$ kcal mol^{-1}
$\Delta S^* = 4{\cdot}8 \pm 0{\cdot}4$ cal mol^{-1} deg^{-1}.

The value of $\Delta H^* = 14{\cdot}9 \pm 0{\cdot}1$ kcal mol^{-1} obtained by method 2 is in excellent agreement with $\Delta H^* = 14{\cdot}6 \pm 1{\cdot}0$ kcal mol^{-1} obtained by method 1. The difference between our value and the one reported by Brand *et al.*[1] ($11{\cdot}2 \pm 1{\cdot}1$ kcal mol^{-1}), might be due to the fact that we used a different solvent, i.e. deuterated chloroform instead of acetone.

† $\tau \equiv \tau_A\tau_B/(\tau_A + \tau_B)$ in which τ_A and τ_B are the lifetimes in positions A and B respectively. With $\tau_A = \tau_B = 1/k$ we get $k = 1/2\tau$.

‡ T_2, the experimental transversal relaxation time, was determined by the method of Tiers.[5] The error in k is mainly determined by the error in T_2. Since T_2 does not vary much over a limited temperature range, the influence on the error in ΔH^* is small.

[3] S. Alexander, *J. Chem. Phys.*, **37**, 967 (1962).
[4] A. I. Vogel, *Practical Organic Chemistry* 3rd ed., p. 573. Longmans Green, London (1956).
[5] G. V. D. Tiers, *J. Phys. Chem.* **65**, 1916 (1961).

Further experiments are necessary to establish whether there is a significant correlation between rotational barriers and the nature of the solvent.

EXPERIMENTAL

2,4,6-*Trideutero*-N,N-*dimethylaminobenzene*. Dimethylaniline (5 g) was dissolved in 10 ml D_2O, acidified with 1 ml 40% DCl in D_2O. The solution was heated at 100° in a sealed ampoule for 24 hr. The dimethylaniline was recovered and the process repeated. After three successive treatments the dimethylaniline was found to be selectively deuterated at the *ortho*- and *para*-positions for 99% (analysis by NMR).

2,6-*Dideutero*-4-*nitroso*-N,N-*dimethylaminobenzene*. 2,4,6-Trideutero-N,N-dimethylaniline was converted into the *para*-nitroso compound by nitrosation with nitrous acid.[4] The product was purified by column chromatography over "Woelm" basic alumina with $CHCl_3$ as an eluent. The deuterium content at the *ortho*-positions was 96% (by NMR analysis).

NMR spectra. The NMR spectra were obtained with a Varian A-60 spectrometer equipped with a Varian V 6440 variable temperature accessory. Temperatures are accurate within 0·1° by direct measurement in the spinning sample tube with a copper–constantane thermocouple immediately before and after scanning a spectrum. Concentrations were 15% (by weight) in $CDCl_3$. Absorption peak heights, as used in method 2, were measured relative to $CHCl_3$ as an internal standard. Above a certain temperature, the relative height of the absorption peak is no longer dependent upon the temperature. This height was taken as "A_0". T_2 was measured from the wiggle decay of the signal of TMS.[5] The spectrometer was calibrated following the method of Jungnickel.[6]

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[6] J. L. Jungnickel, *Anal. Chem.* **35**, 1985 (1963).
[7] J. A. Pople, W. G. Schneider and H. J. Bernstein, *High Resolution Nuclear Magnetic Resonance* p. 222. McGraw-Hill, New York (1959).