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ACTIVATION PARAMETERS FOR TERT-BUTYL ROTATION IN TERT-BUTYLDIMETHYLAMINE

TOTAL NMR LINE SHAPE ANALYSIS

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Abstract—Unequivocal evidence for tert-butyl rotation in tert-butyldimethylamine (I) has been obtained using dynamic NMR spectroscopy. A total NMR line shape analysis which accounts for a significant variation in T_2 with temperature for the tert-butyl resonance gives $E_a = 6{\cdot}4 \pm 0{\cdot}3$ kcal/mole. $\Delta H^{\ddagger} = 6{\cdot}2 \pm 0{\cdot}3$ kcal/mole. $\Delta G^{\ddagger} = 6{\cdot}0 \pm 0{\cdot}1$ kcal/mole at $-153°$. and $\Delta S^{\ddagger} = 1{\cdot}3 \pm 2{\cdot}0$ eu for tert-butyl rotation.

THE AVAILABILITY of potential barriers to fundamental nondestructive rate processes, i.e. rotation and inversion. in simple acyclic compounds is important for the understanding of conformational dynamics in larger cyclic systems. The few published studies of the barrier to rotation about carbon–nitrogen single bonds have employed principally the methods of microwave spectroscopy,[1] e.g. $MeNH_2$ ($\Delta H^{\ddagger} = 2{\cdot}0$ kcal/mole),[2] $(Me)_3N$ ($\Delta H^{\ddagger} = 4{\cdot}4$ kcal/mole),[3] $MeNO_2$ ($\Delta H^{\ddagger} = 0{\cdot}006$ kcal/mole).[4] However, much information concerning C—N bond rotation in amides and related compounds is available due to varying degrees of π-bonding across the carbonyl C—N bond raising the rotational barrier into a range accessible to study by dynamic NMR (DNMR) spectroscopy.[5] Until recently, there had been few reports using DNMR to measure the rate of rotation about a C—N single bond.[6]

Although there may be some ambiguity regarding the nature of the pathway for conformational isomerism. i.e. pure rotation or rotation–inversion,[7] this report concerns the observation of slow *net* rotation of tert-butyl in tert-butyldimethylamine (I) using the DNMR method.[6]

Examination of the PMR spectrum (60 MHz) of I (15% v/v in CH_2CHCl) at $-50°$ revealed two sharp singlet resonances due to the tert-butyl (δ 1·00) and $N(Me)_2$ (δ 2·14) groups (Fig. 1). Upon lowering the temperature, the tert-butyl resonance broadens and separates into two broad overlapping peaks at δ 0·84 and δ 1·08 with a respective area ratio of 1:2 (Fig. 1). The shape of the $N(Me)_2$ resonance remains Lorentzian over the temperature range of interest, although significant broadening occurs at very low temperatures (Fig. 1). The variation of the width-at-half-height ($W_{\frac{1}{2}}$) of the $N(Me)_2$ resonance with temperature is summarized in Table 1. The source of the peak broadening exclusive of exchange processes, i.e. a shortened T_2, observed for both the $N(Me)_2$ and tert-butyl resonances at low temperatures is most likely due to spin–spin relaxation mechanisms dependent on viscosity and excluding ^{14}N quadrupolar relaxation.[8] The observation of a sharp singlet at room temperature for the $N(Me)_2$ resonance of I revealing the absence of any ^{14}N–Me spin–spin coupling ($J_{N,H} \sim 0{\cdot}6$ Hz)[8f] indicates that the ^{14}N quadrupolar relaxation time (T_q)[8g] is short enough even at room temperature to cause rapid ^{14}N spin state interconversion and decoupling of ^{14}N from the Me

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[*] Alfred P. Sloan Research Fellow. 1971–73.

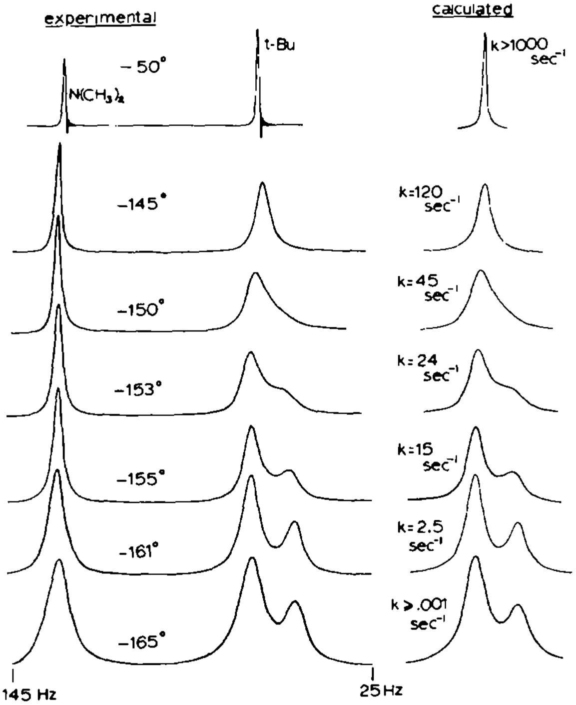


FIG 1. The experimental PMR spectra (60 MHz) of tert-butyldimethylamine (I) as a function of temperature and calculated spectra for the tert-butyl resonances as a function of the rate of tert-butyl rotation (k = rate constant for disappearance of any Me from any one of the three sites on tert-butyl).

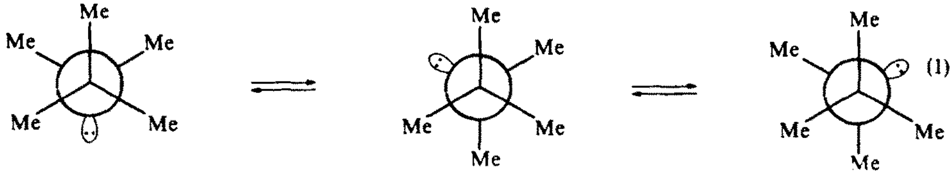
protons. If T_q is of the order of the Larmor period for the Me protons. Kintzinger and Lehn[8g] have suggested that ^{14}N quadrupolar relaxation can act as an additional mechanism for proton spin–spin relaxation via the ^{14}N—^{1}H scalar spin–spin coupling. Approximating the shape of I as a sphere[8g] with a radius of approximately 5 Å and

TABLE 1. THE WIDTH-AT HALF-HEIGHT ($W_{\frac{1}{2}}$) OF THE $N(Me)_2$ RESONANCE IN TERT-BUTYLDIMETHYLAMINE AS A FUNCTION OF TEMPERATURE

Temperature	$W_{\frac{1}{2}}$, Hz
− 45·0°	1·0
−127·3°	1·6
−137·0°	1·7
−140·0°	1·8
−145·0°	2·1
−149·6°	2·8
−155·3°	3·7
−158·0°	4·6
−161·3°	6·2
−164·5°	8·3
−165·0°	8·7

assuming a 100-fold change in viscosity in going from room temperature to -170°. our calculated T_q at -170° ($\sim 1 \times 10^{-6}$ sec) is still significantly greater than the proton Larmor period ($1{\cdot}2 \times 10^{-8}$ sec). Although T_q will certainly shorten at lower temperatures with increasing viscosity, we feel that it does not get short enough to contribute significantly to T_2. The most reasonable source of the significant peak broadening observed for I at low temperatures is a shortening of the proton relaxation time due to other relaxation mechanisms related to viscosity.[9]

Since slowing of the nitrogen *inversion* process does not generate a dissymmetric center in I as it does in an amine such as dibenzylmethylamine.[8e, 10] slow nitrogen inversion alone cannot account for the spectral transitions for tert-butyl in Fig. 1. The most plausible rationalization is a slowing of *net tert-butyl rotation*. Perusal of Fig. 1 indicates that in any of the three equivalent rotamers (Newman projection looking down the central tert-butyl C—N bond). the N-Me groups always experience equivalent environments and should display an NMR spectrum independent of any rate process except Me—N rotation. However. for the tert-butyl group in any rotamer (Eq. 1). there are two equivalent Me's bisected by the nitrogen lone pair and one other different Me which bisects the $N(Me)_2$ group. In the event of slow rotation of tert-butyl (Eq. 1). the tert-butyl resonance should consist of two singlets of relative intensity 1:2 as observed (Fig. 1). It is also clear from Eq. 1 that the three Me's of the tert-butyl group do indeed exchange environments *via* net rotation and that rapid net tert-butyl rotation on the NMR time scale will result in a singlet resonance.



(1)

Total line shape analyses for the tert-butyl resonance in the region of peak collapse should give the activation parameters for tert-butyl rotation. As mentioned above. there is a significant variation in the $W_{\frac{1}{2}}$ (or T_2) of the peaks in the NMR spectrum of I (Fig. 1). Neglect of these variations in T_2 in computing theoretical spectra will introduce serious error into the derived activation parameters. However. examination of the NMR spectrum of I at -165° (Fig. 1) under slow exchange conditions reveals equal intensities for the $N(Me)_2$ peak and the larger of the two tert-butyl resonances. Since these peaks should have an area ratio of 1:1. the data strongly imply equal widths-at-half-height. Indeed. the best "fit" of theoretical* to experimental spectra for the tert-butyl resonances at -165° was obtained using $W_{\frac{1}{2}}$ for both tert-butyl resonances equal to that of the $N(Me)_2$ peak. Also. the $W_{\frac{1}{2}}$ of $N(Me)_2$ and tert-butyl resonances at -80° (fast exchancge conditions) are equal. In all subsequent theoretical tert-butyl line shape calculations under conditions of intermediate rates of tert-butyl rotation (Fig. 1), it was assumed that the $W_{\frac{1}{2}}$ of the $N(Me)_2$ peak accurately

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* The computer program used to generate the theoretical spectra was written by Professor M. Saunders (Yale U.) For a description of the program. see M. Saunders in *Magnetic Resonance in Biological Systems*. A. Ehrenberg. Ed.. Pergamon Press. New York. (1967). For other examples of papers concerned with the selection of an effective T_2. see: K.-I. Dahlquist. and S. Forsen. *J. Magnetic Resonance* **2**. 61 (1970); T. Drakenberg. K.-I. Dahlquist. and S. Forsen. *Acta Chem. Scand.* **24**. 694 (1970)

reflects the $W_{\frac{1}{2}}$ (or T_2) of the two tert-butyl resonances at the various temperatures. In addition, the chemical shift of the tert-butyl resonance under conditions of fast exchange (e.g. δ1·00 at −50°) is predicted accurately using the properly weighted chemical shifts of the two tert-butyl peaks at −165° (δ 1·08; δ 0·84), i.e. the chemical shifts of the two tert-butyl resonances are essentially independent of temperature. The chemical shift difference between the two tert-butyl peaks, i.e. 0·24 ppm, under slow exchange conditions (−165°) was obtained from a total line shape analysis which takes into account overlap due to the large widths-at-half-height. Of course, the *apparent* chemical shift difference is smaller than 0·24 ppm due to the overlap phenomenon. Thus, a series of first order rate constants (k) for the disappearance of any Me of the tert-butyl group from any one of the three sites (Eq. 1) as a function of temperature was obtained by matching calculated to experimental NMR spectra (Fig. 1). A least squares treatment of ln k *vs.* $1/T$ (Fig. 2; correlation coefficient = 0·998) gave

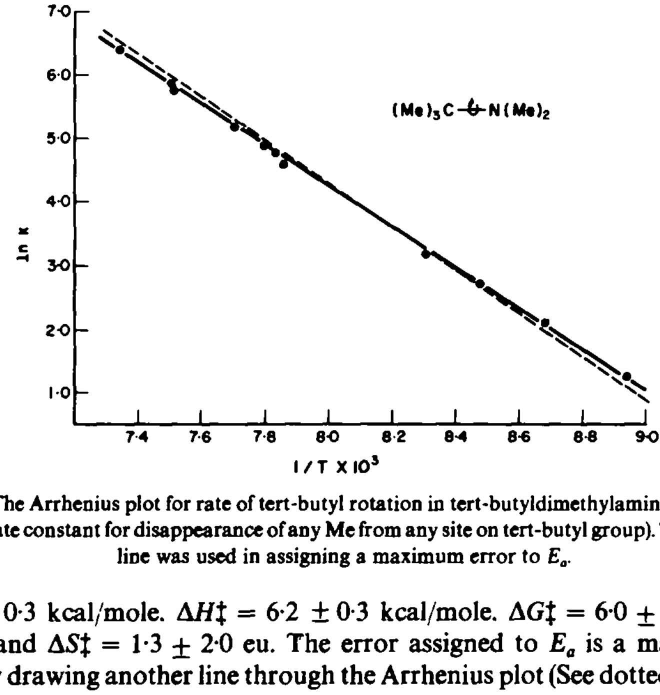
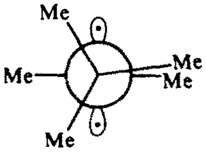


Fig 2. The Arrhenius plot for rate of tert-butyl rotation in tert-butyldimethylamine (k = first order rate constant for disappearance of any Me from any site on tert-butyl group). The dotted line was used in assigning a maximum error to E_a.

$E_a = 6{\cdot}4 \pm 0{\cdot}3$ kcal/mole, $\Delta H\ddagger = 6{\cdot}2 \pm 0{\cdot}3$ kcal/mole, $\Delta G\ddagger = 6{\cdot}0 \pm 0{\cdot}1$ kcal/mole at −153°, and $\Delta S\ddagger = 1{\cdot}3 \pm 2{\cdot}0$ eu. The error assigned to E_a is a maximum error obtained by drawing another line through the Arrhenius plot (See dotted line in Fig. 2) which gave a reasonable though worse fit than the line used. We prefer to report our error limit in this way because a good straight line may be obtained for the Arrhenius plot in spite of undetermined systematic errors. Assignment of an error limit based on a least squares treatment may be too optimistic. In addition, a plot of ln (k/T) versus ($1/T$) using the Eyring treatment[11] gave $\Delta H\ddagger = 6{\cdot}1$ kcal/mole and $\Delta S\ddagger = 0{\cdot}8$ eu in excellent agreement with the values derived from the Arrhenius treatment.

The potential barrier to rotation about the central tert-butyl C—N single bond in I ($\Delta H\ddagger = 6{\cdot}2$ kcal/mole) is higher than the comparable barriers in $MeNH_2$ ($\Delta H\ddagger = 2{\cdot}0$ kcal/mole)[2] or $(Me)_3N$ ($\Delta H\ddagger = 4{\cdot}4$ kcal/mole)[3] and significantly higher than the six-fold barrier in $MeNO_2$ ($\Delta H\ddagger = 0{\cdot}006$ kcal/mole).[4] This attests to increased non-bonded repulsions in the transition state for tert-butyl rotation in I as compared to the other compounds. However, the nature of the transition state for tert-butyl rotation is somewhat in doubt. The observation that the barriers to tert-butyl rotation and nitrogen inversion in tert-butylbenzylmethylamine are essentially identical ($\Delta G\ddagger = 6{\cdot}2$ kcal/mole at $-138°$)[12] suggests a common transition state for rotation and inversion in hindered trialkylamines. By analogy with the similar tert-butylbenzylmethylamine,[12] the most likely transition state for tert-butyl rotation in I involves sp^2 hybridized nitrogen and one Me–Me eclipsing interaction (II) obviously not analogous to the rotational process in ethane for which no rehybridization of carbon occurs in the transition state. Although the energy associated with rehybridization of nitrogen contributes to the total energy of II, the nonbonded repulsions in II are analogous to those for a low barrier six-fold rotational process. Using this model, the barrier to the *separate* tert-butyl rotation process in I is *lower* than that for rotation involving no rehybridization of nitrogen and two methyl–methyl eclipsings.[12]



II

This report is one of a number of observations of nonequivalence in tert-butyl.[13]

We are continuing this research especially with respect to the effect of the size of alkyl groups on the rotation-inversion barrier.

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 audio-modulation technique using a Hewlett-Packard 651A 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 $\pm 0{\cdot}3°$ 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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REFERENCES

[1] E. B. Wilson, Jr., *Advan. Chem. Phys.* **2**, 367 (1959); D. J. Millen, *Progress in Stereochemistry* **3**, 138 (1962)
[2] T. Nishikawa, T. Itoh and K. Shimoda, *J. Chem. Phys.* **23**, 1735 (1955)
[3] D. R. Lide, Jr., and D. E. Mann, *Ibid.* **28**, 572 (1958)
[4] E. Tannenbaum, R. J. Myers and W. D. Gwinn, *Ibid.* **25**, 42 (1956)
[5] W. E. Stewart and T. H. Siddall, III, *Chem. Revs.* **70**, 517 (1970)
[6] C. H. Bushweller, J. W. O'Neil and H. S. Bilofsky, *J. Am. Chem. Soc.* **92**, 6349 (1970); H. Kessler, *Angew. Chem. Internat. Edit.* **9**, 219 (1970)

[7] A. Rauk, L. C. Allen and K. Mislow, *Ibid.* **9**, 400 (1970)

[8] [a] J. A. Pople. *Molecular Physics* **1**. 168 (1958); [b] E. L. Meutterties and W. D. Phillips. *J. Am. Chem. Soc.* **81**. 1084 (1959);
[c] J. D. Roberts. *Ibid.* **78**. 4495 (1956);
[d] H. Beall. C. H. Bushweller. W. J. Dewkett and M. Grace. *Ibid.* **92**. 3484 (1970);
[e] M. J. S. Dewar and W. B. Jennings. *Tetrahedron Letters*. 339 (1970);
[f] D. W. Larsen. *J. Phys. Chem.* **75**. 505 (1971);
[g] J. P. Kintzinger and J. M. Lehn. *Mol. Phys.* **14**. 133 (1968)

[9] J. W. Emsley. J. Feeney and L. H. Sutcliffe. *High Resolution Nuclear Magnetic Resonance Spectroscopy*. Vol. 1-2. Pergamon Press. New York. (1965)

[10] C. H. Bushweller and J. W. O'Neil. *J. Am. Chem. Soc.* **92**. 2159 (1970); M. Saunders and F. Yamada. *Ibid.* **85**. 1882 (1963); W. R. Morgan and D. E. Leyden. *Ibid.* **92**. 4527 (1970); S. Brownstein. E. C. Horswill and K. U. Ingold. *Ibid.* **92**. 7217 (1970)

[11] G. Binsch. *Top. Stereochem.* **3**. 97 (1968)

[12] C. H. Bushweller. J. W. O'Neil. and H. S. Bilofsky. *J. Am. Chem. Soc.* **93**. 542 (1971)

[13] C. H. Bushweller. H. Beall. W. J. Dewkett. and J. W. O'Neil. *Tetrahedron Letters* 4955 (1970); W. E. Heyd and C. A. Cupas. *J. Am. Chem. Soc.* **91**. 1559 (1969); H. Kessler. *Angew. Chem. Internat. Edit.* **9**. 219 (1970)