Tetrahedron Letters No.50, pp. 5225-5228, 1968. Pergamon Press. Printed in Great Britain.

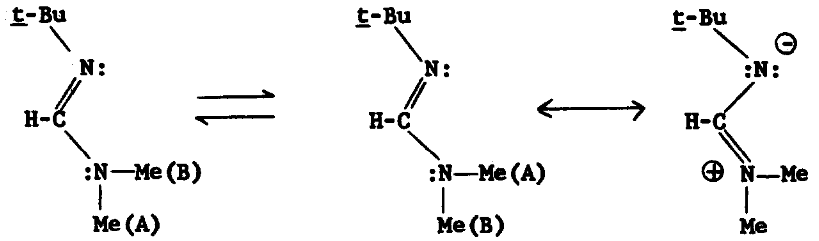
ACTIVATION PARAMETERS FOR HINDERED ROTATION IN N'-t-BUTYL-N,N-DIMETHYLFORMAMIDINE

David L. Harris and Keith M. Wellman(1)

Department of Chemistry, State University of New York at Buffalo
Buffalo, New York 14214

(Received in USA 22 July 1968; received in UK for publication 9 September 1968)

We wish to report the first successful measurement of the activation parameters for hindered rotation about the C-N bond in a trialkylated formamidine, namely, N'-t-butyl-N,N-dimethylformamidine (I).(2)



Ia Ib Ic

Recent attempts to detect slow rotation in trialkylamidines by magnetic resonance (nmr) methods have been unsuccessful.(3,4a) This lack of success may be a consequence of two phenomena: either the rotational barrier for a torsional process such as Ia $\rightleftarrows$ Ib is too rapid to be measured by the usual nmr techniques for exchange between two sites, or the magnetic non-equivalence requirement for the structurally different N-methyl groups may be unfavorable. In order to make a definitive study of I, we took advantage of the unusual solvent properties of pyridine-d_5 and toluene-d_8. By analogy with the use of benzene in other systems(4), it was anticipated that these solvents would provide a significant magnetic non-equivalence of the N-methyl groups while permitting nmr measurements at sufficiently low temperatures to analyze the process Ia $\rightleftarrows$ Ib.

The 60 MHz spectrum of the N-methyl region of I in pyridine-d_5, as a function of temperature, is shown in Figure 1. As can be seen in the Figure, the N-methyl signal broadens and separates into two peaks upon lowering the temperature. This observation can be reasonably attributed to a kinetically slow rate of rotation about the C-N bond of I on the nmr time scale.(5) A similar temperature dependence was observed with toluene-d_8 solvent.

Analysis of the temperature-dependent methyl signal was made using computer programs for total line-shape analysis as outlined recently by Gutowsky, et. al.(6) This method represents a distinct improvement in spectral analysis over earlier steady-state nmr approaches(7,8). In both solvents the chemical shift, Δ, between the two N-methyl signals in the absence of exchange was found to be temperature dependent. A plot of Δ vs. temperature was approximately linear, and extrapolation provided Δ values used in the fast exchange portions of the nmr analysis. The kinetic data are shown in Table I and the activation parameters computed by the usual method are given in Table II.

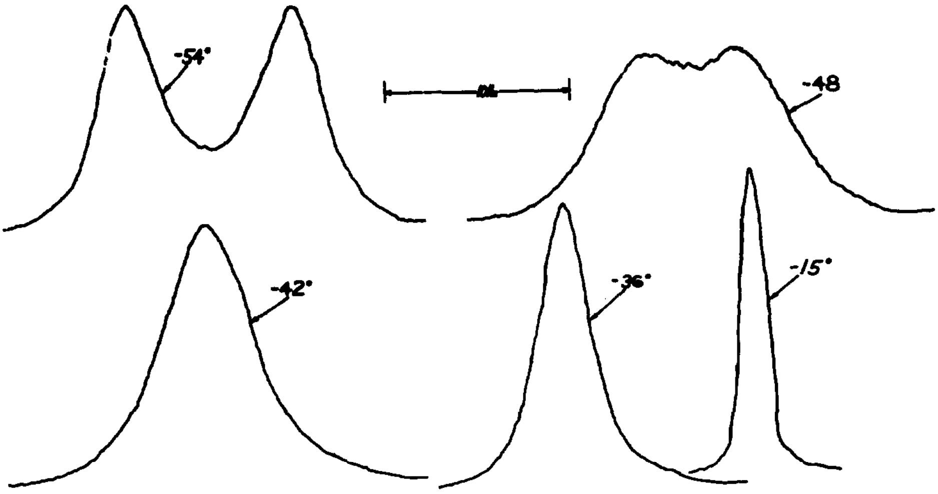


Figure 1. The experimentally observed N-CH_3 signals for 12% solution of N'-t-butyl-N,N-dimethylformamidine in pyridine-d_5.

The observed activation parameters for the process Ia$\rightleftharpoons$Ib merit some discussion. Both calculated free energies of activation are less than that for any other accurately determined barriers in molecules of the type RC(=X)-NMe_2 including amides,(3,7-9) thioamides(3,10) and N-aryl-N,N-dimethylformamidines.(4) This observation implies that the double bond character in the C-N bond arising from electron delocalization (see contributing structure Ic) is relatively less than in the other systems. The small entropies of activation compare favorably with the values of -1.6 eu for a similar process in N,N-dimethylcarbamoyl chloride;(10) they do not indicate any unusual solvent-solute interaction complex as suggested previously(4) for a different

Table I. Kinetic Data for the Exchange Process, Ia$\rightleftharpoons$Ib

Toluene-d_8		Pyridine-d_5	
T°K	k	T°K	k
248.7	125.	247.5	111.
241.5	78.9	244.0	64.6
238.5	42.8	241.5	52.7
233.0	23.4	236.0	44.9
227.5	13.9	235.5	31.2
225.5	7.3	233.0	37.5
220.7	5.2	230.5	15.9
		229.5	15.5
		225.0	9.0
		223.5	7.2
		221.0	6.4
		216.0	3.7
		212.0	2.4

Table II. Activation Parameters for Hindered Rotation in N'-t-Butyl-N,N-dimethylformamidine

Solvent	E_a kcal/mole	$\Delta G^{\ddagger}$ kcal/mole	$\Delta H^{\ddagger}$ kcal/mole	$\Delta S^{\ddagger}$ eu
Toluene-d_8	13.0 ± 0.7	11.9 ± 0.6	12.4 ± 0.7	1.6 ± 2.8
Pyridine-d_5	11.4 ± 0.7	12.4 ± 0.8	10.8 ± 0.7	-5.4 ± 2.7

benzene-amidine system. Finally, the frequency factors (log A = 12.5 in pyridine-d_5 and 13.6 in toluene-d_8) are in excellent agreement with other accurately determined values(7,8,10) and serve to justify confidence in the present results.

Acknowledgement: We wish to thank Professor J. Jonas for kindly furnishing a CURVE 4 FORTRAN program. Partial support for this work was provided by the Petroleum Research Fund, administered by the American Chemical Society. We also wish to thank the Computer Center of the State University of New York at Buffalo for donation of computer time.

References:

1. Address inquiries to this author at Department of Chemistry, University of Miami, Coral Gables, Florida 33124

2. N'-t-butyl-N,N-dimethylformamidine (I) was synthesized in low yield by refluxing equi-molar amounts of t-butylamine, triethyl orthoformate, and dimethylamine hydrochloride in ethanol for three days followed by neutralization of the hydrochloride salts and fractional distillation. The nmr of I in $CDCl_3$ at 25° exhibited singlets at 8.84τ (*t*-butyl) 7.21τ (N,N-dimethyl) and 2.71τ (CH) with intensities 9.2 : 5.9 : 0.8, respectively. The C,H analysis was satisfactory.

3. R.C. Neuman, Jr., and L.B. Young, *J. Phys. Chem.*, 2770 (1965).

4. (a) J.P. Marsh, Jr., and L. Goodman, *Tetrahedron Letters*, *No. 8*, 683(1967); (b) D.J. Bertelli and J.T. Gerig, *ibid.*, *No. 26*, 2481 (1967).

5. An alternate explanation, suggested by a referee, that the kinetic process could be due to inversion of the imino nitrogen lone pair is not plausible, since the low temperature methyl signals are of equal area and require that the *cis* and *trans* isomers be present in equal amounts--a most unlikely expectation on steric grounds. Nmr studies on the formamidinium ion of I support this steric preference of the *t*-butyl group.

6. J. Jonas, A. Allerhand, and H.S. Gutowsky, *J. Chem. Phys.*, **42**, 3396,(1965).

7. H.S. Gutowsky, J. Jonas, and T.H. Siddall, III, *J. Am. Chem. Soc.*, **89**, 4300 (1967).

8. R.C. Neuman, Jr., D.N. Roark, and V. Jonas, *ibid.*, 3412.

9. J.C. Woodbrey and M.T. Rogers, *J. Am. Chem. Soc.*, **84**, 13 (1962).

10. R.C. Neuman, Jr., and V. Jonas, *ibid.*, **90**, 1970 (1968).