Tetrahedron Letters No. 12, pp 1079 - 1080, 1977. Pergamon Press. Printed in Great Britain.

# CONFORMATIONAL STUDIES BY DYNAMIC NMR. IX[1] ACTIVATION PARAMETERS FOR THE BARRIER TO C-N ROTATION IN N,N-DIMETHYLBENZAMIDINE : A CORRECTION

Lodovico Lunazzi
Istituto di Chimica Organica, Università, Bologna, Italy

Alessandro Dondoni
Istituto Chimico, Università, Ferrara, Italy

Gaetano Barbaro and Dante Macciantelli
Laboratorio C.N.R., Ozzano Emilia, Italy

(Received in UK 4 February 1977; accepted for publication 14 February 1977)

The entropies of activation obtained from the complete line shape analysis (CLSA) of NMR spectra of thermally induced rotational processes are usually negligible[1-4] and in the few cases in which large positive or negative values have been reported it is likely that experimental errors are involved.[4-6]

Owing to our interest in the rotational barriers around the C-N bond,[7] there came to our attention a study[8] on N,N-dimethylbenzamidine, $C_6H_5C(=NH)-NMe_2$, in $CDCl_3$ as a solvent, where apparently there is a large $\Delta S^{\neq}$ value. This becomes evident when the reported[8] $E_a$ value (18.2 kcal $mol^{-1}$) is compared with $\Delta G^{\neq}$ (11.3 kcal $mol^{-1}$)[9] obtained by approximate equations.[10] This energy barrier $E_a$ has been accepted and even quoted as $\Delta G^{\neq}$ elsewhere.[11]

We have repeated the rate-temperature study on the title compound[12] in the same solvent ($CDCl_3$) and the spectra were analysed by CLSA.[13] The $E_a$ value (14.3±.3 kcal $mol^{-1}$) calculated therefrom, although smaller than reported,[8] still shows a considerable difference from $\Delta G^{\neq}$ (11.4±.1 kcal $mol^{-1}$) owing to a substantial positive $\Delta S^{\neq}$ value (11.0±1 cal $mol^{-1}$ $deg^{-1}$). The identical values of $\Delta G^{\neq}$ obtained from CLSA and the Gutowsky-Holm equation[10] prove that the approximation of measuring $\Delta G^{\neq}$ at the coalescence temperature is correct in this case. Since temperature measurements have been made with a good degree of accuracy,[14] the most likely source of error for the 'anomalous' $\Delta S^{\neq}$ is the determination of the linewidth (and consequently of $T_2$) in the absence of exchange. This occurs expecially when measurements are made over a range of temperature close to the freezing point of the solvent[5] where the linewidth is strongly viscosity dependent, thus preventing its use as a measure of $T_2$ at higher temperatures.

In order to show that this fact is responsible for the high $E_a$ value reported in ref. 8, which we attributed to an incorrect determination of $\Delta S^{\neq}$, we have repeated the rate-temperature study in $CHF_2Cl$ since this solvent has a lower freezing point (-150°C) than $CDCl_3$. In this case the linewidth is not appreciably affected by changes of viscosity of the solvent in the range of temperature over which the rotational process has been observed (-48°– -67°C). As expected, $\Delta S^{\neq}$ was found to be negligible and $E_a$ almost identical with $\Delta G^{\neq}$ (Table). The slight decrease of $\Delta G^{\neq}$ in $CHF_2Cl$, which becomes more significant in $(CD_3)_2CO$, with respect to $CDCl_3$, indicates the existence of a solvent effect on the rotational process.

TABLE : Methyl Chemical Shift Differences (at 60 MHz), Coalescence Temperatures, and Activation Parameters for the C-N Rotation in $C_6H_5C(=NH)-NMe_2$.

| Solvent | $\Delta\nu$ (in Hz) | $T_c$ (°C) | $\Delta G^{\neq a}$ | $\Delta H^{\neq a}$ | $\Delta S^{\neq b}$ | $E_a{}^{a}$ | log A |
|---|---|---|---|---|---|---|---|
| $CHF_2Cl$ | 14.8(-88°C) | -59 | 11.0±.05 | 11.4±.4 | 2.1±1 | 11.9±.4 | 13.6±.4 |
| $CDCl_3{}^{c}$ | 17.8(-71°C) | -49 | 11.4 | | | | |
| $(CD_3)_2CO$ | 15.0(-93°C) | -78 | 9.9 | | | | |

[a] kcal $mol^{-1}$; [b] cal $mol^{-1}$ $deg^{-1}$; [c] plus 10% *n*-pentane to decrease the freezing point.

The present work underlines the importance of a proper choice of the solvent and of CLSA for a correct determination of $E_a$ and $\Delta S^{\neq}$ from DNMR studies and emphasizes that $\Delta G^{\neq}$ is a more reliable parameter than $E_a$ or $\Delta H^{\neq}$ since its evaluation is not affected by experimental errors due to some physical properties of the solvent.

## REFERENCES AND NOTES

[1] Part VIII, L. Lunazzi, G. Placucci, and G. Cerioni, J.C.S. Perkin II, in press.

[2] I.O. Sutherland in 'Annual Reports on NMR Spectroscopy', Vol. 4, E.F. Mooney Ed., Academic Press, New York, 1971, p. 71.

[3] F.A.L. Anet and Ragini Anet in 'Determination of Organic Structures by Physical Methods', Vol. 3, F.C. Nachod and J.J. Zuckerman Ed., Academic Press, New York, 1971, p. 344.

[4] 'Dynamic NMR Spectroscopy', L. Jackman and F.A. Cotton Ed., Academic Press, New York, 1975.

[5] R.E. Carter, T. Drakenberg, and C. Russel, J.C.S. Perkin II, 1690 (1975).

[6] C. Piccinni-Leopardi, O. Fabre, and J. Reisse, Org. Mag. Resonance, **8**, 233 (1976).

[7] A. Dondoni, L. Lunazzi, P. Giorgianni, and D. Macciantelli, J. Org. Chem., **40**, 2979 (1975).

[8] G. Schwenker and H. Rosswag, Tetrahedron Lett., 2691 (1968).

[9] Due to the lack of data in ref. 8, we have determined the methyl signal splitting and the coalescence temperature (see Table) from which $\Delta G^{\neq}$ was calculated applying the Gutowsky-Holm approximation.[10]

[10] H.S. Gutowsky and C.H. Holm, J. Chem. Phys., **25**, 1228 (1956).

[11] G. Fodor and B.A. Phillips in 'The Chemistry of Amidines and Imidates', S. Patai Ed., Interscience, London, 1975, ch. 2, p. 109.

[12] A. Dondoni and G. Barbaro, J.C.S. Chem. Commun., 761 (1975).

[13] G. Binsch and D.A. Kleier, Program 140, Q.C.P.E., Indiana Univ., Bloomington.

[14] Spectra were recorded on a JEOL 60 MHz instrument. Errors on temperature readings (thermocouple, before and after each spectral determination) were ±0.5°C.