Tetrahedron Letters No.40, pp. 3459-3462, 1970. Pergamon Press. Printed in Great Britain.

ASYMMETRICAL NONBRIDGEHEAD NITROGEN. II[1]

INVESTIGATION OF INVERSION BY NMR SPECTRA OF THE N-ADJACENT METHYLENE PROTONS

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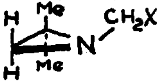
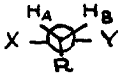
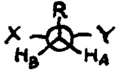
(Received in UK 17 February 1970; accepted for publication 29 July 1970)

Good agreement has been found between the nitrogen inversion parameters for both N-methylene diastereotopic[2] protons and ring substituents in the 

system (Fig.1), confirming that Roberts' method[3] is applicable and also satisfying van Gorkom and Hall's wish[4] to obtain some independent evidence for nitrogen inversion from the N-adjacent methylene protons. The theoretical concept of the latter authors seems erroneous since it does not take into account half rotamers with planar or pseudoplanar nitrogen in the rapid inversion nitrogen model. For example, for 

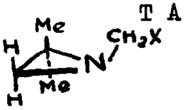
the possible one will be 

etc., whose existence results in averaging of the chemical enviroment of the *A* and *B* protons due to rapid rotation around the **N−C** bond (cf. ref.5).

Compound III (Table) was found to be the most convenient for an inversion study. The spectra of the methyl, methylene ring, and NCH_2N protons of III (50 molar %, toluene) were taken with a C-60-HL spectrometer using an internal lock system at 0.2 Hz/sec. scanning rate over a range of temperature from -30° to + 92°C (Fig.2). In each experiment the resolution was controlled by a standard signal and was not worse than 0.6 Hz. The temperature was determined by the peak separation in methanol (below + 20°C) and propyleneglycol (above + 20°C) in the standard Varian sealed ampoules. Temperature dependence of the static parameters in the AB spectra $\Delta\nu$ and T_2 was observed. The most rapid change of $\Delta\nu$ occurs between -25° and -12°C and corresponds to $\frac{1}{2\tau}$ change from 0.2 to 2 Hz. The minimal value of $\Delta\nu$ observed under conditions of slow exchange was taken for calculation. To take into account the change of T_2 at the intermediate rates of exchange, this parameter has been subjected to variation until the best fit of the theoretical and experimental spectra was obtained.

The computation, employing the usual Alexander formalism, was based on the SABEX program in the case of the N-CH_2 group and on the CLATUX[6] for the methylene and methyl ring protons. Both programs were translated from FORTRAN-IY into ALGOL-60 and some additions were introduced. The calculations were carried out on the "M-20" computer equipped with a plotter. Some of the theoretical and experimental NMR spectra are presented in Fig.2.

TABLE

PMR parameters of  under condition of very slow inversion

	δ p.p.m.	b)			Δν Hz			J^gem	
$X^{a)}$	Me	$CH_2^{c)}$	CH_2X	X	Me	CH_2	CH_2X	CH_2X Hz	Solvent
I Ph	1.05(d)	1.25(d)	3.42(s)	7.10(m)	2.5	62	-$^{d)}$	-	CCl_4
II HC≡C	1.13(d)	1.35(d)	3.10(m)$^{e)}$	2.23(t)	15.0	55	11.5	-16.2	CCl_4
III Me_2N	0.97(d)	1.13(d)	2.98(q)	2.21(s)	7.5	67	22.0	-10.6	$C_6H_5CH_3$

a) I and II were prepared by alkylation of 2,2-dimethylaziridine with benzyl and propargylchloride, respectively (I : b.p.54°/2 mm, n_D^{25} 1.5100; II : b.p.132°/4mm, n_D^{25} 1.4450). III has been described in ref.7.

b) The spectra were taken with a Varian HA-100 instrument with hexamethyldisiloxane as an internal standard, temperature -15°C.

c) J_{gem} of the ring protons in all these molecules appears to be almost zero and is unobservable in the spectra.

d) In CD_3COCD_3 $\Delta\nu_{CH_2X}$ 5.8 Hz and J_{gem} - 14.7 Hz. e) $J_{HC\equiv C-CH}$ 2.5 Hz.

Slight asymmetry in the spectra of the methyl and methylene ring protons may arise from a preferential broadening of the trans-groups due to incomplete quadrupolar relaxation of the ^{14}N-C-H and ^{14}N-C-C-H couplings.[8]

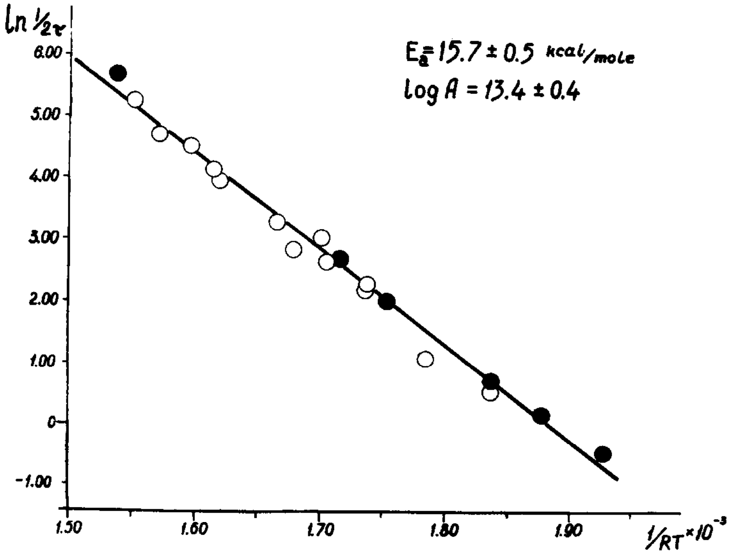


FIG.1

Arrhenius plot for inversion of III in toluene.

○ - determined from the signals of the $N-CH_2-N$ protons.

● - determined from the signals of the methyl and methylene ring protons.

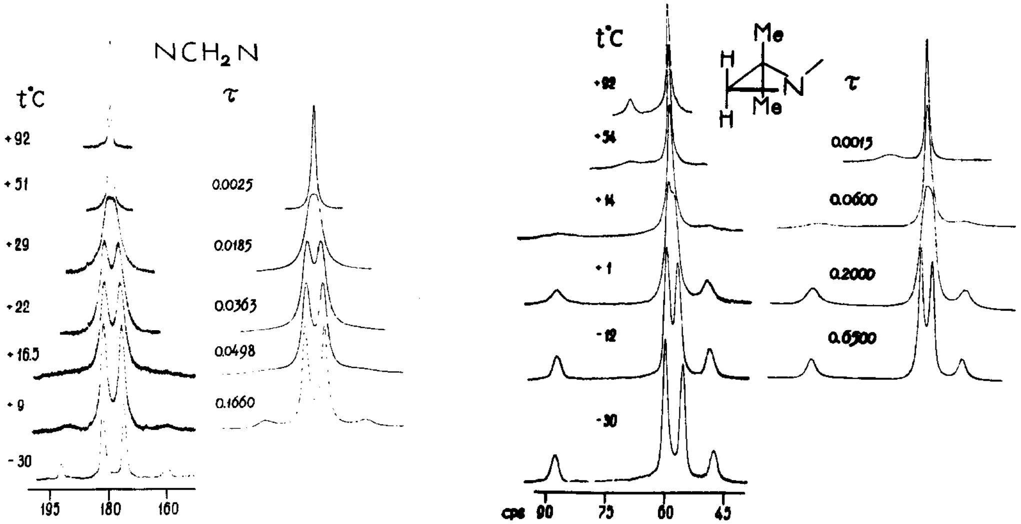


FIG.2. Experimental (60 MHz) and computed spectra of III at various inversion rates ($\Delta\nu_{NCH_2N}$ 11.5 Hz, J^{gem} -10.6 Hz; $\Delta\nu$ Me 2.9 Hz; $\Delta\nu\, CH_2$ 38.9 Hz; T_2 varied from 0.15 to 0.5 sec/rad)

Thus, different T_{2A} and T_{2B} values were taken for calculating the theoretical plots.

The inversion rates were determined by the complete line-shape method. In each case τ was adjusted until the theoretical spectra were superimposable on the observed ones. The possibility of observing the inversion in III by means of the three nonidentical AB systems having different $\Delta\nu$'s (Fig.2) enabled us to determine the τ magnitudes with an equal reliability over a rather wide temperature range. There was a sufficient number of experimental points to make use of the complete least squares technique[9] for the calculation of E_a and log A (Fig.1) and their r.m.s. errors.

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AKNOWLEDGEMENTS

The authors are grateful to Professor J.D.Roberts for the courteous gift of the SABEX algorithm. We would also like to thank Dr. A.J.Boulton, G.E. Hall and J. Feeney for valuable advice and helpful discussion.