

## Ring Inversion in Cyclohexane and Piperazine Derivatives

By R. J. ABRAHAM and D. B. MACDONALD

(*The Robert Robinson Laboratories, The University of Liverpool*)

DESPITE many investigations,<sup>1-5</sup> the values of the entropy and energy of activation for the ring inversion process of cyclohexanes are still in dispute (*cf.* Table). In order to resolve this problem we have studied the temperature-dependence of the methyl proton resonance spectra of 1,1,4,4-tetramethoxycyclohexane (I) and *NNN*<sup>1</sup>*N*<sup>1</sup>-tetramethylpiperazinium dichloride (II). In these systems we have the simplest possible n.m.r. system, of two lines collapsing to one when the temperature is raised, in which there is no spin-spin coupling and there are equal populations and lifetimes of the exchanging species. If we also assume that the transverse relaxation times of the hydrogen nuclei are very long, then the complex line-shape function<sup>6</sup> simplifies to give explicit equations for the rate constant.

The n.m.r. spectrum of (I) in *ca.* 20% w/v

solution in toluene was recorded at temperatures in the range -30 to -90° c and that of (II) in *ca.* 10% w/v solution in liquid sulphur dioxide at temperatures in the range +20 to -60°c. The values of the first-order rate constants at a series of temperatures for the two compounds were obtained from the equations.

The values of *k* derived from the equations are the rate constants for the chair-to-chair equilibrium. Arrhenius plots of log *k* against 1/*T* for both compounds gave good straight lines from which by a least-mean-squares treatment, the thermodynamic parameters given in the Table were deduced. The errors shown are the values for 90% confidence limits.

The values obtained for the entropy of activation are of particular interest because of the widely different values found for cyclohexane itself

(cf. Table). The calculated value of +4.9 e.u. for  $\Delta S^\ddagger$ , assuming an unsymmetrical barrier<sup>2</sup> form, does not appear to be correct.

It is now well accepted<sup>7</sup> that the transition state for the chair-to-boat interconversion is the

same, and will be less (more negative) by *ca.* 2 e.u. than for cyclohexane itself.

Despite the considerable experimental error in the determination of  $\Delta S^\ddagger$ , our results support those obtained by spin-echo measurements which yield

TABLE

Compound	Reference	$\Delta F_{cb}^\ddagger$	$\Delta H^\ddagger$	$\Delta S_{cb}^\ddagger$
(I)		$10.5 \pm 0.4^*$	$8.6 \pm 1.2$	$-9.5 \pm 6^*$
(II)		$12.9 \pm 0.3^\ddagger$	$9.3 \pm 1.2$	$-13.5 \pm 5.6^\ddagger$
Cyclohexane	5	10.3	$9.1 \pm 0.5$	$-5.8 \pm 2.4$
[ <sup>2</sup> H <sub>11</sub> ]Cyclohexane	4	10.3	$10.9 \pm 0.6$	$2.9 \pm 2.3$
"	3	10.2	$10.5 \pm 0.5$	$1.4 \pm 1.0$
"	5	10.3	$9.1 \pm 0.1$	$-5.8 \pm 0.4$
1,1-Difluorocyclohexane (in CFCl <sub>3</sub> )	8	9.5	9.64	-3.6
Perfluorocyclohexane	9	10.5	$7.5 \pm 0.3$	-8.8
"	10	10.8	$9.9 \pm 0.2$	-3.0

\* at 200°K

† at 273°K

"cyclohexene-like" half-chair form with four planar carbon atoms. This has  $C_2$  symmetry and hence a symmetry number of 2 (not 1 as previously reported<sup>2</sup>), and therefore  $\Delta S^\ddagger$  equals  $R \ln 6$ , *i.e.*, +3.6 e.u.

For a 1,1,4,4-substituted cyclohexane with  $C_{2h}$  symmetry and symmetry number 2,  $\Delta S^\ddagger$  equals +1.4 e.u. The calculation predicts that the entropies for the two compounds studied here will be the

negative values of  $\Delta S^\ddagger$ . It is difficult to see why the values of  $\Delta S^\ddagger$  obtained by steady-state methods are so widely and consistently different. It may be that the nuclear Overhauser effect caused by the deuterium decoupling in [<sup>2</sup>H<sub>11</sub>]cyclohexane affects the proton relaxation time so much that the results obtained are seriously in error.

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