

## Conformational Isomerization in Hexahydro-1,3,5-trimethyl-s-triazine

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WE wish to report the thermodynamic activation parameters for the conformational isomerization of hexahydro-1,3,5-trimethyl-s-triazine (I). The analysis was carried out by observing the temperature dependency of the AB n.m.r. line pattern for the ring methylene protons over a range of 64° (229—293°K) using a Varian A-60 spectrometer. The experimental spectra were compared to computer-generated theoretical line shapes using a FORTRAN program written for the quantum-mechanical expression of the spectrum of two coupled nuclei undergoing intramolecular chemical exchange.<sup>1,2</sup> Temperature variation of the natural line-width was incorporated in the analysis of the Arrhenius energy of activation,  $E_a$ .<sup>3</sup>

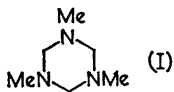


Table 1 lists the thermodynamic activation parameters for the chair-to-chair and chair-to-boat isomerizations.<sup>4</sup>

At 229°K the ring methylene protons gave an AB quartet with  $\delta\nu_{AB} = 52.8$  Hz and  $J = 10.2$  Hz

at a chemical shift of  $\tau = 6.8$  p.p.m. The methyl protons appeared as a sharp singlet at  $\tau = 7.7$  p.p.m. whose line-width did not change with temperature indicating rapid nitrogen inversion.

Of interest is the significance of the activation entropy. If symmetry variance in the ground and transition states is assumed to be the main contribution and that rotational and vibrational contributions may be neglected, then

$$\Delta S_{cb}^\ddagger = R \ln(\omega_2/\omega_1)/(\sigma_2/\sigma_1)$$

where  $\omega$  and  $\sigma$  are the statistical weight and symmetry number, respectively.<sup>5</sup> Using  $\omega_1 = 2$  and  $\sigma_1 = 3$  for a chair ground state and  $\omega_2 = 1$  and  $\sigma_2 = 6$  for a planar transition state, a value of  $\Delta S_{cb}^\ddagger = -2.8$  e.u. is obtained. If one assumes a "cyclohexene-like" transition state,  $\omega_2 = 6$  and  $\sigma_2 = 1$ , and  $\Delta S_{cb}^\ddagger$  is 4.4 e.u. The agreement of the latter  $\Delta S_{cb}^\ddagger$  value with the experimental value suggests that the barrier form possesses a "cyclohexene-like" conformation.<sup>6</sup> Methyl group steric interactions must be small as 1,3-interactions would lower the activation entropy. If the barrier form does resemble the preferred conformation for cyclohexene, it would be reasonable to assume that the reaction pathway for isomerization resembles

TABLE I.

*Activation parameters for conformational isomerization of (I)<sup>a</sup>*

$T_c(^{\circ}\text{K})$ .. .. .	$269.5 \pm 0.5$	$\Delta S_{cb}^{\ddagger}$ (e.u.)	$5.1 \pm 0.7$
$E_a$ (kcal./mole) .. .. .	$14.6 \pm 0.2^b$	$\Delta F_{ec}^{\ddagger}$ (kcal./mole)	$13.1 \pm 0.1$
$\nu_0$ (sec. <sup>-1</sup> ) .. .. .	$8.5 \pm 0.5 \times 10^{13}$	$\Delta F_{cb}^{\ddagger}$ (kcal./mole)	$12.8 \pm 0.1^c$
$\Delta S_{ec}^{\ddagger}$ (e.u.) .. .. .	$3.7 \pm 0.7$	$\Delta H^{\ddagger}$ (kcal./mole)	$14.1 \pm 0.2$

<sup>a</sup> 15% in CDCl<sub>3</sub> (w/v) in sealed tube under nitrogen.<sup>b</sup> Residuals represent statistical probable errors<sup>c</sup>  $12.6 \pm 0.2$ , F. G. Riddell and J. M. Lehn, *Chem. Comm.*, 1966, 376.

that proposed for cyclohexane.<sup>7,8</sup> The large  $\Delta F^{\ddagger}$  and  $\Delta H^{\ddagger}$  might be due to the valence angle strain within the ring and torsional strain introduced by

the rapidly exchanging lone pair-methyl group on nitrogen.

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