

CONFORMATIONAL ISOMERIZATION IN 1,3,3-TRIMETHYL-4,5-DIOXACYCLOHEXENE

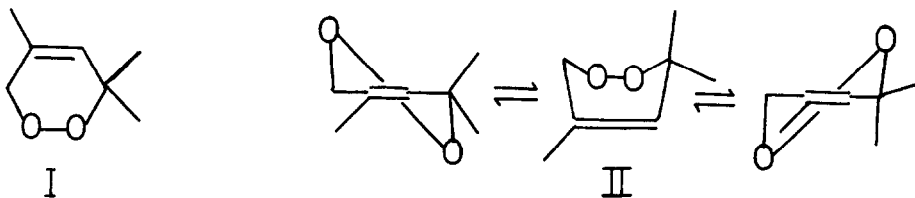
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The study of rate processes in flexible ring systems has been facilitated by the use of nuclear magnetic resonance spectroscopy.¹⁻³ More work has appeared concerning the conformational isomerization of cyclohexene and its derivatives than of rings of other sizes⁴ due probably to the accessibility of the appropriate temperature ranges with NMR instruments and the relative simplicity of the spectra obtained. Once unsaturation is introduced into the six-membered ring distinct changes in conformational mobilities result. Four atoms now lie in a plane such that a half-chair or a boat are possible. Calculations have shown the half-chair of cyclohexene to be more stable by 2.7 kcal/mole⁵ and in fact X-ray^{6,7} and infrared and raman studies^{8,9} of derivatives have confirmed its existence.

The half-chair conformers of cyclohexene may interconvert. This ring inversion process has been observed in the variable temperature NMR spectra of cyclohexene-cis-3,3,4,5,6,6-d₆,¹⁰ cyclohexene-2,3,3,4,5,5,6,6-d₈ and derivatives,^{11,12} substituted tetrahydropyridazines,¹³ and polyfluorinated cyclohexenes.¹⁴ The barriers in the deuterated cyclohexenes are quite low (ΔF^* 5.3 kcal/mole)^{10,11} placing their determination by NMR at the limits of the technique. The kinetic parameters for the conformational changes occurring in 1,3,3-trimethyl-4,5-dioxacyclohexene (I), a representative of a little known class of compounds, is the



subject of this report. Preparation of I was achieved by treatment of 2,4-dimethyl-1,3-pentadiene with singlet oxygen.¹⁵ The NMR spectra of an 8% solution of I in CS₂

were recorded on a JEOL C60-HL spectrometer in the temperature range +25° to -100°C. Because of the absence of proton couplings the resonance lines of the gem-dimethyl groups are of particular interest. At room temperature they appear as a single sharp line at 8.80 τ which broadens as the temperature is lowered until -58.5°C when the coalescence temperature is reached. By -64°C the two lines which have appeared reach their maximum separation of 11.8 Hz (Figure 1). The line broadening observed at temperatures above coalescence was used to calculate the rate constant for the

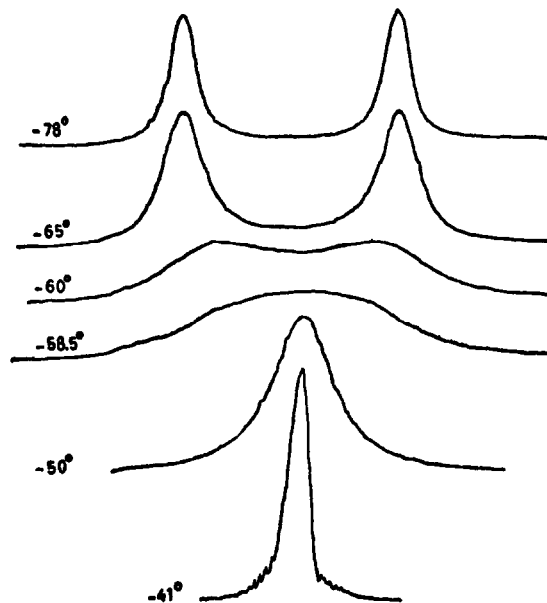


Figure 1 - NMR Spectra of the Geminal Methyl Resonances of I at Various Temperatures

$$(\pi\delta\nu\tau)^{-1} = [(\delta\nu/W^*)^2 - (W^*/\delta\nu)^2 + 2]^{1/2} \quad (1)$$

isomerization ($1/2\tau$) from Equation 1.¹⁶ In this equation $\delta\nu$ is the maximum peak separation while W^* is the full line-width at half-maximum intensity. At temperatures below the coalescence point the experimentally observed peak separation $\delta\nu_e$ was used¹⁷

$$1/2\tau = (\pi\sqrt{2})(\delta\nu^2 - \delta\nu_e^2)^{1/2}$$

An Arrhenius plot of the rate constants obtained permitted the determination of E_a , and the Eyring formulation was used to calculate the thermodynamic parameters for the

transition state. The results are presented in Table 1. These data point to a similar process for inversion of I as that postulated in cyclohexene-cis-3,3,4,5,6,6-d₆¹⁰ wherein a boat structure is an intermediate in the half-chair inversion (II). In contrast, it should be mentioned that the boat form of cyclohexene has been interpreted by others^{11,14} to be a true transition state.

	Coalescence Temperature °C	E _a kcal/mole	kcal/mole		eu	Ref.
			ΔF^*_{cc}	ΔH^*_{cc}	ΔS^*_{cc}	
Cyclohexene-cis-3,3,4,5,6,6-d ₆	-164°		5.3	5.3	0 ^a	10
Cyclohexene-2,3,3,4,5,5,6,6-d ₈	-166°		5.37	5.5	1.4 ^a	11
I	- 58.5°	13.0±1.8	11.0	12.6±1.8	+7.4 ^b	this work

^a theory; ^b experiment-Measured entropy values have large inherent errors and perhaps all that should be said is that ΔS^* may be small and positive.

Table 1 - Transition State Parameters for Half-Chair Inversion of Deuterated Cyclohexenes and I

Significant increases in barriers to 6-membered ring inversions have been noted previously in saturated systems when peroxidic oxygens are present.^{18,19} It seems reasonable that the interconversion of chair forms of I is also slowed by a combination of factors including lone pair interactions, bond angle strain, and Van der Waals forces. Two possible potential energy surfaces for the conformational inversion are visualized. One is that suggested for cyclohexene¹⁰ having an intermediate boat form (B) and two higher energy half-boat (HB) transition states (Figure 2b) which, due to the asymmetry of I, must have different energies. However, models indicate that the boat conformation of I may be the highest energy form due to its very unfavorable 1,4-Van der Waals repulsion, O-O torsional interactions and electrostatic effects. If these interactions are greater than the bond angle deformation effects of the half-boat form, the potential energy surface is simplified to that of a single maximum (Figure 2a).¹⁸ No matter which of these surfaces is more accurately descriptive, it is apparent as in the cyclohexene case that a completely planar intermediate or transition state is extremely unfavorable because of large torsional interactions, acute bond angle distortions and electrostatic effects.

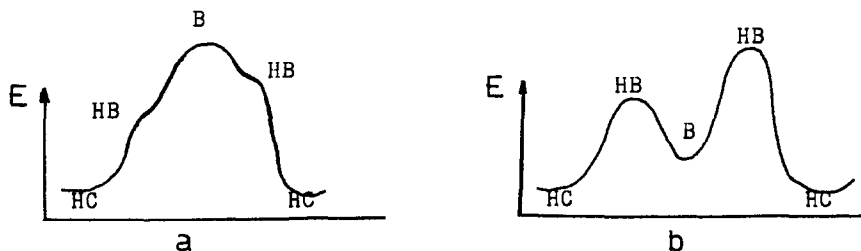


Figure 2 - Diagrammatic Representation of Possible Reaction Pathways in the Half-Chair Inversion of I

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