# Activation Parameters for Chair–Twist Equilibration in 3,3,6,6-Tetramethyl-1,2,4,5-tetrathian by Direct Thermal Stereomutation and Total Nuclear Magnetic Resonance Line-shape Analysis

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*Summary* Activation parameters ($E_a$, $\Delta G^‡$, $\Delta H^‡$, $\Delta S^‡$) for the chair–twist process in 3,3,6,6-tetramethyl-1,2,4,5-tetrathian have been obtained from the direct equilibration of the pure twist conformer and from matching experimental n.m.r. spectra with theoretical spectra over an appropriate temperature range.

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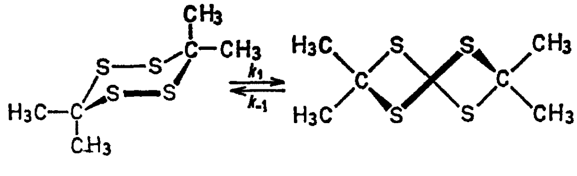
IN previous reports,[1] we presented evidence for a significantly lowered chair–twist energy difference in 3,3,6,6-tetramethyl-1,2,4,5-tetrathian (I) (tetramethyl-*s*-tetrathian): the twist-form is more stable than the chair-form.



(1)

We report the activation parameters for the chair/twist equilibration in (I) (Equation 1) using both a total n.m.r. line-shape analysis and direct thermal stereomutation of the pure twist-conformer.[1]

A matching of computer-generated theoretical n.m.r. spectra and experimentally determined n.m.r. spectra (60 MHz) at various temperatures[1] gave a series of rate constants for conversion of the chair-form to the twist-form ($k_1$, Equation 1) and the twist to the chair ($k_{-1}$, Equation 1).

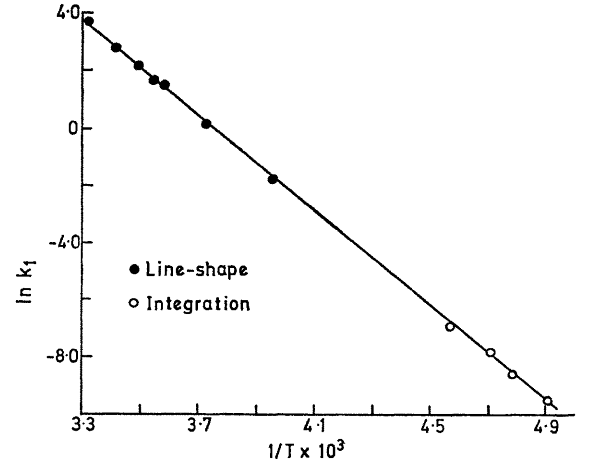


FIGURE. *Arrhenius plot for the chair-to-twist process in* (I).

Another series of rate constants was obtained by isolation of the conformationally pure twist form[1] at lower temperatures and direct measurement of the rate of equilibration to the chair by n.m.r. peak-area integrations as a function of time. The solvent used in both cases was carbon disulphide.

*Activation parameters for chair-twist equilibration in* (I)

| | Chair-to-twist | Twist-to-chair |
|---|---|---|
| $E_a$(kcal/mole) .. .. | 16·5 ± 0·4 | 17·4 ± 0·4 |
| $\Delta H^\ddagger$ (kcal./mole) .. .. | 15·9 ± 0·4 | 16·5 ± 0·4 |
| $\Delta G^\ddagger_{14^\circ}$ (kcal./mole) .. | 15·6 ± 0·1 | 16·0 ± 0·1 |
| $\Delta S^\ddagger$ (eu) .. .. .. | 1·2 ± 1·0 | 2·8 ± 1·0 |

An Arrhenius plot for the chair to twist process in (I) (Figure) illustrates good agreement between the rate constants obtained from the two different techniques and supplies further evidence for the validity of total n.m.r. line-shape analysis for obtaining kinetic parameters.[2]

The entropies of activation (Table) for both processes in (I) are small and positive consistent with data available for cyclohexane ($\Delta S^\ddagger$ for chair-to-boat +2·8 eu)[3] and bromocyclohexane ($\Delta S^\ddagger$ for axial isomer-to-boat +3·6 eu)[4] but at variance with data for 3,3,6,6-tetramethyl-1,2,4,5-tetroxan ($\Delta S^\ddagger$ for chair-to-chair −12·1 eu),[5] 3,3,6,6-tetramethyl-1,2-dioxan ($\Delta S^\ddagger$ for chair-to-chair +14·4 eu),[6] and another report on (I) ($\Delta S^\ddagger$ for twist-to-chair 21 ± 7 eu).[7]

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