Table VII. Data Obtained in Measurement of Dipole Moments

Compd	R_{20}	R_M	d^{25}	μ, D
IV	131.18 ± 1.53	28.80	1.043 ± 0.002	2.24 ± 0.02
trans-XII	223.25 ± 8.20	72.55	1.094 ± 0.010	2.71 ± 0.08
cis-XII	487.73 ± 4.68	73.69	1.0785 ± 0.005	4.50 ± 0.03

pounds VI–IX an Hp research chromatograph (Hewlett Packard) equipped with flame ionization was used.

Nmr Analysis. Nmr spectra of all compounds were recorded on a Varian Associates A-60A instrument. Samples were 20–25% in CCl_4, shifts are reported in hertz downfield from tetramethylsilane (TMS) at 60 MHz. (The instrument was acquired under NSF equipment Grant GP-6875.) Low- and high-temperature spectra were recorded in a commercially available variable-temperature probe. The temperature was measured by recording the chemical shift of methanol.

Dipole Moments. Measurements were effected in benzene at 25°. Three samples of different concentrations were used. Calculations were carried out as reported previously[2] (Table VII).

Acknowledgment. This work was supported under Grant AF-AFOSR-772 of the Air Force Office of Scientific Research and Grant GP-9379 of the National Science Foundation.

Conformational Analysis in Multisulfur Heterocycles. V. Activation Parameters for the Chair ⇄ Twist Equilibration in Duplodithioacetone by Direct Thermal Stereomutation and Total Nuclear Magnetic Resonance Line Shape Analysis

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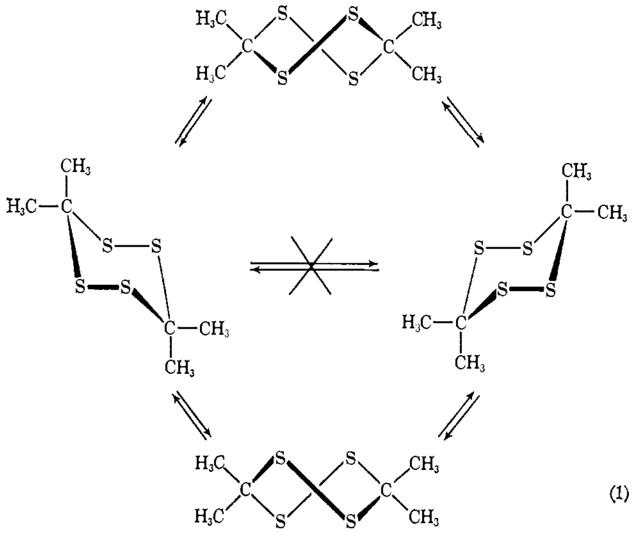
Contribution from the Department of Chemistry, Worcester Polytechnic Institute, Worcester, Massachusetts 01609. *Received November 29, 1969*

Abstract: Activation parameters for the chair-to-twist process (E_a = 16.5 ± 0.4 kcal/mole, $\Delta H^{\ddagger}$ = 15.9 ± 0.4 kcal/mole, $\Delta S^{\ddagger}$ = +1.2 ± 1.0 eu, $\Delta G^{\ddagger}$ = 15.6 ± 0.1 kcal/mole at 14°) and the twist-to-chair process (E_a = 17.4 ± 0.4 kcal/mole, $\Delta H^{\ddagger}$ = 16.5 ± 0.4 kcal/mole, $\Delta S^{\ddagger}$ = +2.8 ± 1.0 eu, $\Delta G^{\ddagger}$ = 16.0 ± 0.1 kcal/mole at 14°) in tetramethyl-*s*-tetrathiane (duplodithioacetone) have been determined by direct thermal equilibration of the pure twist conformer and by a total nmr line shape analysis at higher temperatures in carbon disulfide as solvent.

In previous reports,[2] we presented convincing evidence for a significantly lowered chair/twist energy difference in duplodithioacetone (tetramethyl-*s*-tetrathiane). Indeed, the twist is more stable than the chair. Although the twist form of cyclohexane is postulated as a discreet intermediate in the chair ⇆ chair equilibration,[3] the twist conformer of cyclohexane is too unstable to be detected by available spectroscopic techniques.

This report concerns the measurement of activation parameters for the chair ⇄ twist equilibration in duplodithioacetone (eq 1) using both the direct thermal stereomutation of the pure twist conformer[2b] at low temperatures and matching of experimental spectra to computer-generated theoretical spectra at higher temperatures. Strong evidence for the validity of total nmr line shape analysis for obtaining kinetic parameters by comparison with the direct equilibration technique is presented.



(1)

Results and Discussion

The previously reported temperature dependence of the nmr spectrum (60 MHz) of duplodithioacetone[2]

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[1] National Science Foundation Undergraduate Research Participant, Summer 1969.

[2] (a) C. H. Bushweller, *J. Am. Chem. Soc.*, **89**, 5978 (1967); (b) C. H. Bushweller, *ibid.*, **90**, 2450 (1968); (c) C. H. Bushweller, *ibid.*, **91**, 6019 (1969).

[3] F. A. L. Anet and A. J. R. Bourn, *ibid.*, **89**, 760 (1967); F. R. Jensen, D. S. Noyce, C. H. Sederholm, and A. J. Berlin, *ibid.*, **84**, 386 (1962). However, it should be noted that twist forms of *cis*-2,5-dialkyl-1,3-dithianes may be spectroscopically accessible, *e.g.*, see E. L. Eliel and R. O. Hutchins, *ibid.*, **91**, 2703 (1969). See also G. Binsch in "Topics in Stereochemistry," Vol. 3, N. L. Allinger and E. L. Eliel, Ed., Interscience Publishers, New York, N. Y., 1968.

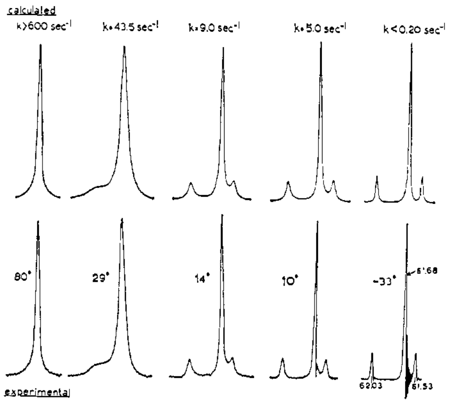

Figure 1. Calculated and experimental nmr spectra for duplodithioacetone at various rate constants and temperatures (k = rate constant for conversion of the chair to the twist).

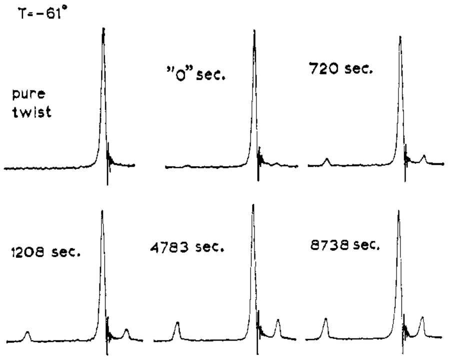

Figure 2. Nmr spectrum of duplodithioacetone at various times illustrating the direct thermal stereomutation of the twist at −61 °.

from approximately −20 to 80 ° illustrates behavior characteristic of intermediate exchange rates on the nmr time scale.[4] Since the nmr line shape for duplodithioacetone over this temperature range will be very much a function of the rate of chair ⇄ twist equilibration (eq 1), computer-calculated theoretical nmr spectra[5] have been generated and compared with the experimental spectra determined in carbon disulfide (Figure 1) in order to obtain a series of rate constants as a function of temperature (Table I). The rate constants shown in Figure 1 are for the chair-to-twist process.

Table I. Rate Constants from the Total Nmr Line Shape Analysis at Various Temperatures

Temp, °K	k_1,[a] sec^{-1}	k_{-1},[b] sec^{-1}
302.0	43.5	22.5
293.8	16.0	8.2
286.9	9.0	4.4
282.8	5.0	2.3
279.0	4.5	2.2
252.4	0.20	0.08

[a] k_1 = rate constant for conversion of the chair to the twist. [b] k_{-1} = rate constant for the conversion of the twist to the chair.

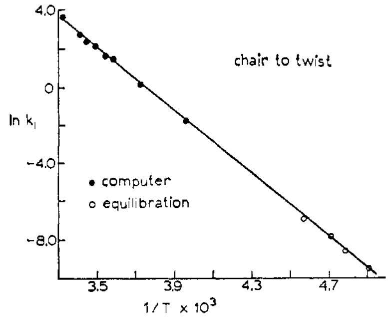

Figure 3. Arrhenius plot for the chair to twist process in duplodithioacetone (E_a = 16.5 ± 0.4 kcal/mole, $\Delta H^{\ddagger}$ = 15.9 ± 0.4 kcal/mole, $\Delta G^{\ddagger}_{287°\mathrm{K}}$ = 15.6 ± 0.1 kcal/mole, $\Delta S^{\ddagger}$ = +1.2 ± 1.0 eu).

The theoretical spectra were matched to the experimental spectra by a comparison of peak widths at various fractions of the peak height, by a comparison of peak-to-valley ratios in appropriate spectra, and by superposition of normalized theoretical spectra on experimental spectra. The relative populations of the chair and twist conformers at temperatures where broadening of the nmr spectrum is substantial were obtained by extrapolation of the chair:twist ratio as a function of temperature from −50 to −10°. The model used for calculation of the theoretical nmr spectra is essentially that illustrated in eq 1, *i.e.*, equilibration of two equivalent chairs with two equivalent twists with *no direct chair ⇄ chair interconversion.* In the computer program used, one may introduce transition probabilities from one resonance line to another, *i.e.*, from one conformer to another. The best "fit" was obtained assuming the transition probability for a direct chair to chair process to be zero or very small. Thus, it would seem that the model used (eq 1) is valid and data presented below from a direct equilibration technique are consistent with that model.

Another series of rate constants was obtained by isolation of the conformationally pure twist form in carbon disulfide by a previously described technique[2] at lower temperatures and measurement of the rate of chair ⇄ twist equilibration by nmr peak area measurements as a function of time. A run performed at −61° is illustrated in Figure 2. The kinetic treatment of such an equilibration is summarized in eq 2–6[6]

$$\text{chair} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \text{twist} \tag{2}$$

$$\frac{-\mathrm{d}[\text{twist}]}{\mathrm{d}t} = k_{-1}[\text{twist}] - k_1[\text{chair}] \tag{3}$$

If only the twist is present at the beginning

$$[\text{twist}]_0 - [\text{twist}] = [\text{chair}] \tag{4}$$

$$\frac{-\mathrm{d}[\text{twist}]}{\mathrm{d}t} = (k_1 + k_{-1})[\text{twist}] - k_1[\text{twist}]_0 \tag{5}$$

Integration and introduction of the equilibrium concentration of the twist ([twist]$_e$) gives

$$\ln\frac{[\text{twist}]_0 - [\text{twist}]_e}{[\text{twist}] - [\text{twist}]_e} = (k_1 + k_{-1})t \tag{6}$$

It is apparent from eq 6 that equilibration of the twist is

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[4] J. W. Emsley, J. Feeney, and L. H. Sutcliffe, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, New York, N. Y., 1965, pp 481–588.

[5] The computer program used in this study was written by Professor Martin Saunders (Yale University). For a detailed description and background of the program, see M. Saunders in "Magnetic Resonance in Biological Systems," A. Ehrenberg, Ed., Pergamon Press, New York, N. Y., 1967, and C. S. Johnson, Jr., in "Advances in Magnetic Resonance," Vol. I, Academic Press, New York, N. Y., 1965.

[6] A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," 2nd ed, John Wiley & Sons, Inc., New York, N. Y., 1965, p 186.

a first-order process and one needs to know only the *relative concentration* of the twist as a function of time. These data can be taken directly from the nmr spectrum (Figure 2). A series of rate constants obtained using this technique is compiled in Table II.

Table II. Rate Constants from Direct Thermal Stereomutation of the Pure Twist Conformer

Temp, °K	k_1,^{a} sec^{-1}	k_{-1},^{b} sec^{-1}
218.2	9.3×10^{-4}	1.9×10^{-4}
212.4	4.3×10^{-4}	0.88×10^{-4}
209.0	1.9×10^{-4}	0.34×10^{-4}
204.2	0.79×10^{-4}	0.12×10^{-4}

^{a} k_1 = rate constant for conversion of chair to twist. ^{b} k_{-1} = rate for conversion of twist to chair.

Arrhenius plots for both the chair-to-twist process (Figure 3) and the twist-to-chair process gave the activation parameters listed in Table III. The reported activation parameters (Table III) were derived from a *combination* of the nmr line shape analysis and the direct equilibration data. Perusal of Figure 3 illustrates good agreement between the slopes of the lines defined by the computer-derived rate constants and the equilibration-derived rate constants. Such data give us confidence in the derived activation parameters (Table III) and provide additional convincing evidence for the validity of total nmr line shape analysis for obtaining kinetic parameters. Mannschreck and coworkers[7a] have reported a similar study involving various substituted N,N-dialkylbenzamides. Although their data provide evidence for the validity of the total nmr line shape technique, the equilibration experiments and the line shape analysis were performed on *different* compounds.

Table III. Activation Parameters for the Chair ⇄ Twist Equilibration in Duplodithioacetone^a

Process	E_a, kcal/mole	$\Delta H^{\ddagger}$, kcal/mole	$\Delta G^{\ddagger}$,^{b} kcal/mole	$\Delta S^{\ddagger}$, eu
Chair to twist	16.5 ± 0.4	15.9 ± 0.4	15.6 ± 0.1	$+1.2 \pm 1.0$
Twist to chair	17.4 ± 0.4	16.5 ± 0.4	16.0 ± 0.1	$+2.8 \pm 1.0$

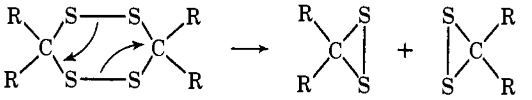
^{a} The reported errors are maximum errors obtained by drawing alternative lines through the Arrhenius plot (Figure 3) while still giving a reasonable though poorer fit than the line used. The principal sources of error lie in the value of the rate constant (±5%) and the temperature measurement (±0.1°). ^{b} At 14° using the Eyring equation and assuming a transmission coefficient = 1.

The availability of activation parameters (Table III) for chair ⇄ twist interconversion in duplodithioacetone provides the opportunity to predict the half-life of either conformer at various temperatures. The half-lives of the twist conformer at various temperatures are compiled in Table IV. At −100°, it is clear that the twist and chair forms are in fact two *separate compounds* and might no longer be considered *conformers*.

Table IV. The Half-Life of the Twist Form of Duplodithioacetone at Various Temperatures

Temp, °C	25	−10	−70	−100
Half-life	0.034 sec	1.5 sec	6.1 hr	1 yr

Three mechanisms seem possible for the chair ⇄ twist interconversion in duplodithioacetone: (1) a concerted electronic redistribution leading to fragmentation (eq 7); (2) a radical dissociation leading to thiyl radicals (eq 8); (3) a nondissociative process involving bond rotation and angle distortion *via* transition states such as I, II, and III. If the concerted fragmentation mechanism were important, heating a mixture of two *s*-tetrathianes might be expected to give some crossover products. However, heating equimolar amounts of duplodithioacetone and 3,3:6,6-bis(tetramethylene)-*s*-tetrathiane at 70° for 24 hr in tetrachloroethylene gave no exchange and no evidence of decomposition (eq 9) which speaks against the fragmentation process. The presence of thiyl radicals appears very unlikely in light of the sharp nmr lines observed at high and low temperatures as well as the substantial S–S bond dissociation energy (63 kcal/mole).[8] The most likely mechanism for chair ⇄ twist equilibration is *via* transition states such as I, II, or III. Available data for hydrogen disulfide indicate a high potential barrier (~6 kcal/mole) for the *cis* configuration (hydrogens eclipsed).[9] Thus the most probable transition state for chair ⇄ twist interconversion in duplodithioacetone would be that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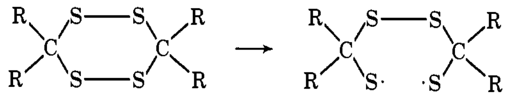
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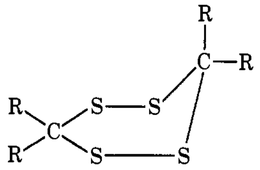
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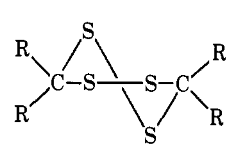
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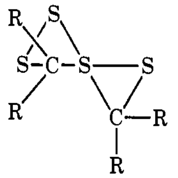
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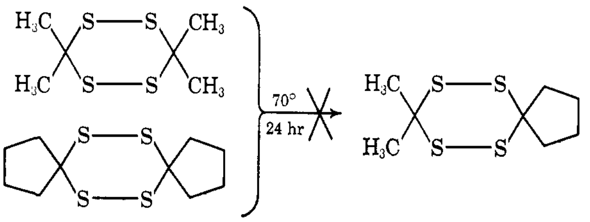

(9)

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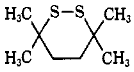
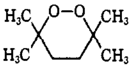
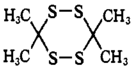
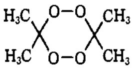
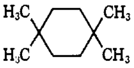
(7) (a) A. Mannschreck, A. Mattheus, and G. Rissman, *J. Mol. Spectrosc.*, **23**, 15 (1967). See also (b) H. S. Gutowsky, J. Jonas, and T. H. Siddall, III, *J. Am. Chem. Soc.*, **89**, 4300 (1967); (c) F. A. L. Anet and A. J. R. Bourn, *ibid.*, **89**, 760 (1967).

(8) C. C. Price and S. Oae, "Sulfur Bonding," The Ronald Press Co., New York, N. Y., 1962.

(9) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960.

Table V. Activation Parameters for Ring Inversion in Tetramethyl 6-Rings

Compound	$\Delta H^{\ddagger}$, kcal/mole	$\Delta S^{\ddagger}$, eu	$\Delta G^{\ddagger}$, kcal/mole
	15.6[a,e]	6.7	13.8 (−2°)
	17.9[a,e]	14.4	14.6 (12°)
	15.9[b,f]	1.2	15.6 (14°)
	11.7[c,g]	−10.7	15.0 (30°)
			11.6 (−53°)[d,e]

[a] F. Claeson, F. Androes, and M. Calvin, *J. Am. Chem. Soc.*, **83**, 4357 (1961). [b] This work. [c] R. W. Murray, P. R. Story, and M. L. Kaplan, *ibid.*, **88**, 526 (1966). [d] H. Friebolin, W. Faisst, and H. F. Schmid, *Tetrahedron Letters*, 1317 (1966). [e] For the chair-to-chair process. [f] For the chair-to-twist process. [g] For the chair to assumed boat process.

which avoids the *cis* configuration for the C–S–S–C moiety (*e.g.*, II), *i.e.*, that which avoids maximized vicinal lone pair–lone pair repulsions across the S–S bond. Such interactions would seem to be better minimized in I or III than in II and we favor the semiplanar transition state (I). If it is reasonable to assume that the entropy of activation may be estimated from $\Delta S^{\ddagger} = R \ln(n)$ in which n = number of reaction pathways,[7c] $\Delta S^{\ddagger} = R \ln 2 = +1.4$ eu is in qualitative agreement with the entropy of activation for the chair-to-twist process (+1.2 eu) in duplodithioacetone. The twist-to-chair process is apparently more complicated.

The presence of adjacent atoms possessing lone pairs of electrons leads to substantial enhancements in the barriers to ring inversion in a number of tetramethyl six-membered heterocycles as compared to the cyclohexane analog. The data are summarized in Table V. Although differing force constants for bond angle deformation in the transition state must account for some of the barrier increase, lone pair–lone pair repulsions cannot be ruled out as a significant contributor.[9]

A recent paper reported activation parameters for the twist-to-chair process in duplodithioacetone ($\Delta H^{\ddagger} = 22.2 \pm 2$ kcal/mole, $\Delta S^{\ddagger} = 21.0 \pm 7$ eu, $\Delta G^{\ddagger} = 16.1 \pm 0.2$ at 20°)[10] at significant variance with the values reported here. However, the kinetic parameters were obtained *only* by the line shape method and no comparison to equilibration data was performed.[11]

Experimental Section

The nmr spectra were recorded on a Varian HR-60A spectrometer equipped with a custom-built variable-temperature probe.

Temperature was measured using a calibrated copper-constantan thermocouple placed about 1 in. below the sample. Temperature readings were taken simultaneously with the recording of the spectrum and are accurate to ±0.1° at the sample.

Computer calculations were performed on an RCA Spectra 70-46 computer.

Acknowledgment. We are grateful to Professor M. Saunders for supplying the computer programs used and for invaluable advice and assistance. We thank the Worcester Area College Computation Center for many hours of donated computer time as well as Research Corporation and the National Science Foundation (COSIP Grant) for financial support.

[10] B. Magnusson, B. Rodman, and S. Rodmar, *Arkiv Kemi*, **31** (7), 65 (1969).

[11] In a personal communication, Professor Magnusson indicated that temperature stability was not of a high order in his equipment providing a source for the discrepancy in $\Delta S^{\ddagger}$.

Conformational Analysis of Tricarbonyl(diene)iron Compounds

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Contribution from the Department of Chemistry, University of Massachusetts, Amherst, Massachusetts 01002. *Received October 6, 1969*

Abstract: Tricarbonyl(diene)iron complexes bearing terminal 1-hydroxyethyl groups have been prepared by sodium borohydride reduction of complexed dienones and direct complexation of dienols. Conformational analysis allows firm predictions of preferred conformations which have been used as a basis for assigning *R,R* and *S,S* relative stereochemistry to compounds **1** and **11** and *R,S* and *S,R* relative stereochemistry to **2** and **12**. Compounds **1** and **11** in which the hydroxy group prefers to be *exo* to iron are designated *ψ-exo* and **2** and **12** in which hydroxy is *endo* with respect to iron are designated as *ψ-endo* compounds. Uncomplexed dienones exist as mixtures of *s-cis* and *s-trans* enones; however the complexed dienones appear to prefer the *s-cis* conformation of the enone unit. Reduction of complexed dienones with sodium borohydride is highly stereospecific, producing 95% or more of the *ψ-endo* diastereomer in agreement with the transition state model developed by Karabatsos.

Tricarbonyl(diene)iron compounds which contain one additional asymmetric carbon exist as two diastereomeric forms, *e.g.*, **1** and **2**, owing to the asymmetry of the complexed diene moiety.[2] Diastereomeric tricarbonyl(*trans,trans*-3,5-heptadien-2-ol)iron complexes **1** and **2** have been prepared in pure

[1] (a) Texaco Research Fellow 1965–1966; (b) Alfred P. Sloan Foundation Fellow 1969–1971.

[2] Compound **1** is a mixture of *R,R*, and *S,S* enantiomers and **2** a mixture of *R,S*, and *S,R* enantiomers. For the purpose of assigning configuration, each carbon of the diene is considered to be bonded to iron.[3]

[3] J. E. Mahler and R. Pettit, *J. Am. Chem. Soc.*, **85**, 3955 (1963).