

CHAPTER 6

CONFORMATIONAL ANALYSIS IN MODEL COMPOUNDS OF VINYL POLYMERS

The practical usefulness of the local interaction model in the NMR conformational analysis of chain molecules is demonstrated for 2,4-disubstituted pentanes, $\text{CH}_3\text{CHRCH}_2\text{CHRCH}_3$, which are model compounds of vinyl polymers. In the present treatment based on this model, the relative energies of all the possible conformers are expressed as sums of the five kinds of intramolecular interaction energy parameters, which are determined to reproduce the observed temperature dependence of the vicinal spin-spin coupling constants between the methine and methylene protons. The method was applied to the analyses of pentane-2,4-diol, 2,4-dichloropentane and 2,4-diphenylpentane on the basis of the NMR data in the literature. The energy parameters, the conformer energies, and the populations were determined. The observed solvent effect in pentane-2,4-diol can be interpreted directly as the variation in the intramolecular interaction energy between the two hydroxyl groups, -1.0 to 0.8 kcal mol⁻¹. In the analysis of this solvent effect, it is shown that the trans and gauche coupling constants, J_t and J_g , which are essential in NMR conformational analysis, can be obtained experimentally as $J_t = 11.5 \pm 1.0$ and $J_g = 2.1 \pm 1.0$ Hz. The energy parameters obtained in the present method may be used in calculations of the configurational statistics for polymer chains.

6.1 INTRODUCTION

It is well known that the conformational equilibria of molecules in solution can be effectively investigated by means of high-resolution nuclear magnetic resonance spectroscopy, especially by means of vicinal spin-spin coupling constants because of their sensitivity to dihedral angles.^{1,2} In practice, however, it has frequently seemed difficult to apply this method to chain molecules of n carbon-carbon skeletal bonds except for the

simplest ones with $n=1$, substituted ethanes,³ because, generally, 3^n possible conformers must be taken into account. In the simplest case, including 1,2-disubstituted propanes and 2,3-disubstituted butanes,⁴ the mole fractions of only three conformers, as unknown parameters, can be quantitatively determined, though it should always be necessary to estimate the *trans* and *gauche* coupling constants. The direct extension of such an orthodox treatment to longer chains which can take a number of conformers makes the analysis too complicated even for molecules with $n=2$ and prohibitive for those with larger n values.

Among compounds with $n=2$, 2,4-disubstituted pentanes, with *meso* and racemic isomers, have been extensively studied⁵⁻¹³ because they are model compounds of vinyl polymers. Figure 29 shows nine possible conformers, which can be reduced by symmetry to six distinguishable ones for each isomer. The designation of conformations, T , G , and \bar{G} (*trans*, *gauche*, and another *gauche*), is defined by the three Newman diagrams shown in Figure 30; T , G , and \bar{G} are characterized by the forms where CH_3 , R , and H , respectively, are located trans to CH . This designation is more convenient than that in the literature^{12,22} based on the direction of rotation, not only because of its simplicity, but more essentially because of the ease of its mathematical treatment¹⁴ based on the local interaction model.

Usually, most conformational studies⁵⁻¹¹ have focused on the preferred conformers, TG ($=GT$) for the *meso* and TT and GG for the racemic, which are regarded as the most stable forms from the viewpoint of steric hindrance. However, this simplification fails for some compounds, such as 2,4-dichloropentane and pentane-2,4-diol, where other conformers are detectable or are, especially in the latter compound, dominant. An infrared spectroscopic study of 2,4-dichloropentane by Schneider *et al*¹³ has disclosed the existence of less favored conformers. For pentane-2,4-diol, Fukuroi *et al*.¹² showed that TT for the *meso* and $T\bar{G}$ ($=\bar{G}T$) for the racemic are also preferred, presumably because of the stabilization by intramolecular hydrogen bonding. They successfully analyzed the solvent and temperature dependence of the coupling constants and chemical shifts, but it was necessary to assume *a priori* the order of stability of the conformers.

The main difficulty in analysis lies in the fact that there are too many possible conformers in chain molecules. This difficulty can be avoided by the use of an approximation, which might be called the local interaction model, in which the conformational energies of a chain molecule as a whole can be expressed as sums of the

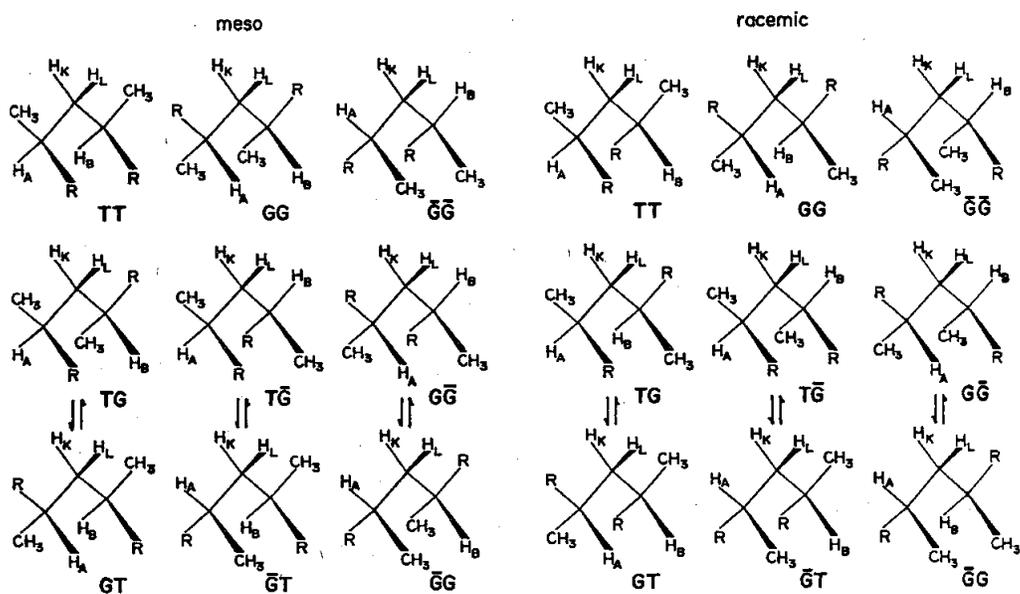


Figure 29 Staggered conformers in the *meso* and racemic isomers of 2,4-disubstituted pentanes. The pairs of conformers joined by arrows are forms equivalent to each other by symmetry.

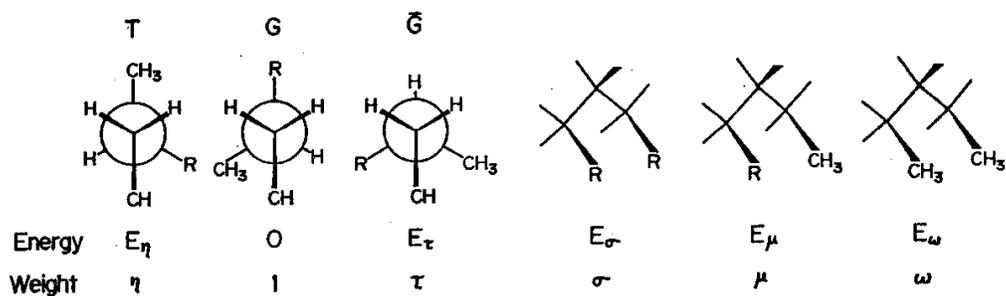


Figure 30 First-order and second-order intramolecular interactions considered to be present in 2,4-disubstituted pentane by a consideration of the local interaction model and the designations of their energies and statistical weights. The designations of the conformations, *T*, *G*, and \bar{G} , are defined by the three Newman diagrams.

local interaction energies contained in the conformers. Similar models have frequently been adopted since 1932¹⁴⁻²² in a number of theoretical investigations of the mean dimensions of polymer chains. The establishment of the mathematical treatment^{14,18-22} by means of matrix representation by Lifson,¹⁸ Nagai,¹⁹ Hoeve,²⁰ Flory^{14,21,22} and others has produced many kinds of statistical studies of polymers. However, the validity of the local interaction model has not been clearly demonstrated on an experimental molecular basis.

This paper will present a method for analyzing the temperature dependence of vicinal spin-spin coupling constants in 2,4-disubstituted pentanes by the use of the local interaction model; moreover, the NMR data for pentane-2,4-diol,¹² 2,4-dichloropentane¹³ and 2,4-diphenylpentane⁶ reported in the literature have been reanalyzed. In the present treatment, a small number of intramolecular interaction energies, usually five, are determined experimentally, instead of the energies of the conformers being determined directly. This procedure is significant in several ways and has the following characteristics:

- 1) The validity of the local interaction model is discussed on the basis of the experimental results.
- 2) A temperature-dependent phenomenon is analyzed on this model.
- 3) The mole fractions of all the possible conformers can be discussed and determined.
- 4) An experimental method for determining the energy parameters necessary for the statistical calculation of polymer chains is presented. As another method for the estimation of them, the theoretical calculation of interaction between non-bonded atom pairs has previously been recommended.²¹⁻²⁴ However, the experimental determination in the models corresponding to the respective polymers may be more straightforward. The theory of non-bonded interactions is still a very baffling problem.
- 5) Accordingly, the conformations of a polymer and its model compounds can be connected through the energy parameters as fundamental factors.
- 6) Intermolecular interactions, such as the solvent effect, can be interpreted quantitatively, as is shown for pentane-2,4-diol.
- 7) A side-group effect such as the internal rotation of the phenyl groups in 2,4-diphenylpentane can be treated semi-empirically.

It might be a significant result that the *trans* and *gauche* coupling constants, J_t and J_g , could be determined experimentally from the analysis of the solvent effect on the

temperature dependence of coupling constants in pentane-2,4-diol, because they play an important role in the conformational analysis, whereas they could not be determined experimentally in such chain molecules, so the corresponding values of ring compounds have until now been used.

6.2 THEORETICAL

6.2.1 Averaged Vicinal Coupling Constants

The vicinal spin-spin coupling constants between the methine and methylene protons are used as probes for this conformational analysis. They are averaged among the nine possible conformers in Figure 29 under the usual conditions of the rapid conformational motion.³

$$J_{obs} = \sum_i X_i J_i, \quad (1)$$

where X_i and J_i represent the mole fraction and the vicinal coupling constant of the conformer, i . The methine and methylene protons are labeled A and B, and K and L, respectively,²⁵ as is shown in Figure 29. That is,

1) For the *meso* isomer, K is syn to both A and B (anti to R), and L is anti to both A and B (syn to R).

2) For the racemic isomer, K is syn to A and anti to B, and L is anti to A and syn to B.

(The syn and anti relations are defined as those between the two vicinal protons on the same side and on the opposite side, respectively of the backbone plane when the chain takes the planar zigzag conformation, *TT* in this case. These terms should be conceptually distinguished from the terms, *trans* and *gauche*, which are available for the temporal relations between the two vicinal protons among the various conformations.)

According to the above designations, the following relations between average J_{AK} , J_{AL} , J_{BK} and J_{BL} values should be present by symmetry:

$$meso: \quad J_{AK} = J_{BK} (J_{syn}), \quad J_{AL} = J_{BL} (J_{anti}), \quad (2)$$

$$racemic \quad J_{AK} = J_{BL} (J_{syn}), \quad J_{AL} = J_{BK} (J_{anti}). \quad (3)$$

Therefore, two different coupling constants, denoting “syn” coupling and “anti” coupling, can be expected not only in the *meso* isomer, but also in the racemic isomer; in the latter case, the K and L protons are symmetrically equivalent but are magnetically nonequivalent.² The two averaged coupling constants, J_{syn} and J_{anti} , for the two isomers can be expressed by the same formula as follows:

$$J_{\text{syn}} = X_{TT}J_g + X_{TG+GT}(J_g + J_t)/2 + X_{T\bar{G}+\bar{G}T}J_g \\ + X_{GG}J_t + X_{G\bar{G}+\bar{G}G}(J_g + J_t)/2 + X_{\bar{G}\bar{G}}J_g, \quad (4)$$

$$J_{\text{anti}} = X_{TT}J_t + X_{TG+GT}(J_g + J_t)/2 + X_{T\bar{G}+\bar{G}T}(J_g \\ + J_t)/2 + X_{GG}J_g + X_{G\bar{G}+\bar{G}G}J_g + X_{\bar{G}\bar{G}}J_g, \quad (5)$$

where X_{TT} , for example, is the mole fraction of the *TT* conformer, and where J_t and J_g represent the *trans* and *gauche* coupling constants. All the values of J_t and J_g are assumed to be common among all the conformers. By denoting the difference and the sum of J_{anti} and J_{syn} by ΔJ and ΣJ , respectively, we obtain

Table 10 The energies, weights, and mole fractions of the conformers in the *meso* and racemic isomers of 2,4-disubstituted pentane, expressed in terms of the interaction energy factors and weight factors. Z_m and Z_r denote the conformational partition functions, which are given by *Equations* (10) and (11) in the text

Conformer	Energy		Weight		Conformer	Mole fraction	
	<i>Meso</i>	Racemic	<i>Meso</i>	Racemic		<i>Meso</i>	Racemic
<i>TT</i>	$2E_\eta + E_\sigma$	$2E_\eta$	$\eta^2\sigma$	η^2	<i>TT</i>	$\eta^2\sigma/Z_m$	η^2/Z_r
<i>TG(=GT)</i>	E_η	$E_\eta + E_\mu$	η	$\eta\mu$	<i>TG+GT</i>	$2\eta/Z_m$	$2\eta\mu/Z_r$
<i>T\bar{G}(=\bar{G}T)</i>	$E_\eta + E_\tau + E_\mu$	$E_\eta + E_\tau + E_\sigma$	$\eta\tau\mu$	$\eta\tau\sigma$	<i>T\bar{G}+\bar{G}T</i>	$2\eta\tau\mu/Z_m$	$2\eta\tau\sigma/Z_r$
<i>GG</i>	E_ω	0	ω	1	<i>GG</i>	ω/Z_m	$1/Z_r$
<i>G\bar{G}(=\bar{G}G)</i>	$E_\tau + E_\mu$	$E_\tau + E_\omega$	$\tau\mu$	$\tau\omega$	<i>G\bar{G}+\bar{G}G</i>	$2\tau\mu/Z_m$	$2\tau\omega/Z_r$
<i>\bar{G}\bar{G}</i>	$2E_\tau + E_\sigma + E_\omega$	$2E_\tau + 2E_\mu$	$\tau^2\sigma\omega$	$\tau^2\mu^2$	<i>\bar{G}\bar{G}</i>	$\tau^2\sigma\omega/Z_m$	$\tau^2\mu^2/Z_r$

$$\Delta J = J_{\text{amti}} - J_{\text{syn}} = \delta J (X_{TT} + X_{T\bar{G}+\bar{G}T} / 2 - X_{GG} - X_{G\bar{G}+\bar{G}G} / 2), \quad (6)$$

where $\delta J = J_t - J_g$, and

$$\begin{aligned} \sum J = J_{\text{amti}} + J_{\text{syn}} &= (J_t + J_g)(X_{TT} + X_{TG+GT} + X_{GG}) \\ &+ (J_t + 3J_g)(X_{T\bar{G}+\bar{G}T} + X_{G\bar{G}+\bar{G}G}) / 2 + 2X_{\bar{G}\bar{G}}J_g \end{aligned} \quad (7)$$

for either isomer.

The mole fraction, X_i , is related to the energy of each isomer and can be calculated from the Boltzmann statistics:

$$X_i = f_i \exp(-E_i / RT) / \sum_i f_i \exp(-E_i / RT), \quad (8)$$

where E_i is the conformational energy and where f_i is the partition function including the contributions from the vibration, the rotation, the internal rotation other than that about skeletal bonds, and the intermolecular interactions. In many cases, f_i can be set equal among all the conformers to a good approximation and may be eliminated from *Equation* (8). The case where f_i plays an influential role will be discussed later. The relative energies E_i 's, and the *trans* and *gauche* coupling constants, J_t and J_g , can be determined, in principle, from the analysis of the temperature dependence of the coupling constants on the assumption that E_i 's, J_t and J_g as parameters are independent of the temperature. Such a treatment was performed by Fukuroi *et al.*¹² in the conformational analysis of pentane-2,4-diol by means of its ΔJ . As has been mentioned in Sec. 6.1, however, the direct fitting of *Equation* (6) to the observed data presents some difficulties because *Equation* (6) does not contain all the possible X_i 's and because the estimation of E_i is difficult. The following improvement will make the analysis easier and more practical.

6.2.2 Interaction Energies and Statistical Weights

The following assumption is introduced in the present treatment (local interaction model).

Assumption: The energy of each conformer can be expressed as a sum of the energies of the first-order (i.e., three bond) and second-order (i.e., four bond) intramolecular interactions contained in each. The intramolecular interactions to be taken into consideration in the molecules in question are shown in Figure 30. The statistical weight factors, α , corresponding to the respective interaction energies, E_a 's,

are defined as ²²

$$\alpha = \exp(-E_\alpha/RT). \quad (9)$$

The weight factors, η , unity, and τ , are assigned to the first-order interactions in the T , G , and \overline{G} conformations, respectively. These interactions involve pairs of groups (CH_3 , CH , or R) separated by three bonds. The T conformation contains CH_3 *trans* and R *gauche* with respect to CH . The G conformation, which is adopted as an energy reference, contains CH_3 *gauche* and R *trans* to CH . In another conformation, \overline{G} , both CH_3 and R are *gauche* with respect to CH . The designation of the conformations by T , G , and \overline{G} is convenient for the present purpose because they are directly related to the first-order interactions;¹⁴ the situation is complicated by definitions based on the direction of rotation.²² The value of η may be less than unity (consequently, $E_\eta \begin{smallmatrix} > \\ < \end{smallmatrix} 0$) according to the substituent, R . In general, $\tau < 1$ ($E_\tau > 0$) can be expected.

The σ , μ , and ω factors characterize the second-order, interactions, which depend upon rotation about two neighboring skeletal bonds and which refer to the interactions between the groups separated by four bonds. They are assigned to the $\cdot\text{R}\cdots\text{R}$, $\cdot\text{R}\cdots\text{CH}_3$ and $\cdot\text{CH}_3\cdots\text{CH}_3$ interactions, respectively. The weights for the $\cdot\text{CH}_3\cdots\text{H}$ and $\cdot\text{R}\cdots\text{H}$ interactions are taken as unity.

According to the local interaction model, the conformational energy and the statistical weight of each conformer can be easily deduced by the summation of the included interaction energy factors and by the multiplication of the related weight factors, with reference to Figure 29. For example, the energy and the weight of the TT form of the *meso* isomer are $2E_\eta + E_\sigma$ and $\eta^2\sigma$, respectively, because the T conformation occurs twice and there is an $\cdot\text{R}\cdots\text{R}$ interaction. All the energies and the weights of conformers can be expressed in the same manner; they are listed in Table 10. The conformational partition function, which is the sum of the weights of all the possible conformers, is then given for the *meso* (Z_m) and the racemic (Z_r) isomers by

$$Z_m = \eta^2\sigma + 2(\eta + \eta\tau\mu + \tau\mu) + \omega + \tau^2\sigma\omega, \quad (10)$$

$$Z_r = \eta^2 + 2(\eta\mu + \eta\tau\sigma + \tau\omega) + 1 + \tau^2\mu^2. \quad (11)$$

The mole fractions of conformers, X_i 's in *Equations* (6) and (7) are equal to the respective weights divided by the above partition function. *Equations* (6) and (7) can,

then, be represented by

$$\Delta J_m = \delta J(\eta^2 \sigma + \eta \tau \mu - \omega - \tau \mu) / Z_m, \quad (12)$$

$$\Delta J_r = \delta J(\eta^2 + \eta \tau \sigma - 1 - \tau \omega) / Z_r, \quad (13)$$

$$\Sigma J_m = [(J_g + J_t)(\eta^2 \sigma + 2\eta + \omega) + (3J_g + J_t)(\eta \tau \mu + \tau \mu) + 2J_g \tau^2 \sigma \omega] / Z_m, \quad (14)$$

$$\Sigma J_r = [(J_g + J_t)(\eta^2 + 2\eta \mu + 1) + (3J_g + J_t)(\eta \tau \sigma + \tau \omega) + 2J_g \tau^2 \mu^2] / Z_r. \quad (15)$$

The subscripts, m and r , refer to *meso* and *racemic*. *Equations* (12) - (15) can be expressed in the exponential form, including E_α and the temperature, by the substitution of *Equation* (9). This procedure results in the same formulation by the direct expression of the E_i 's in *Equation* (8) in terms of sums of the energies in Table 10 according to the assumption stated at the beginning of this subsection. Then, one obtains

$$\Delta J_m = \delta J \{ \exp(-2E_\eta / RT) + \exp[-(E_\eta + E_\tau + E_\sigma) / RT] - \exp(-E_\omega / RT) - \exp[-(E_\tau + E_\mu) / RT] \} / Z_m, \quad (16)$$

$$\Delta J_r = \delta J \{ \exp(-2E_\eta / RT) + \exp[-(E_\eta + E_\tau + E_\sigma) / RT] - 1 - \exp[-(E_\tau + E_\omega) / RT] \} / Z_r, \quad (17)$$

$$\begin{aligned} \Sigma J_m = & ((J_g + J_t) \{ \exp[-(2E_\eta + E_\sigma) / RT] + 2\exp[-E_\eta / RT] + \exp(-E_\omega / RT) \} \\ & + (3J_g + J_t) \{ \exp[-(2E_\eta + E_\tau + E_\sigma) / RT] + \exp[-(E_\tau + E_\mu) / RT] \} + 2J_g \exp[-(2E_\tau + E_\sigma + E_\omega) / RT]) / Z_m, \end{aligned} \quad (18)$$

$$\begin{aligned} \Sigma J_r = & ((J_g + J_t) \{ \exp[-(2E_\eta / RT) + 2\exp[-(E_\eta + E_\mu) / RT] + 1 \} + (3J_g + J_t) \{ \exp[-E_\eta + E_\tau + E_\sigma] / RT \\ & + \exp[-(E_\tau + E_\omega) / RT] \} + 2J_g \exp[-(2E_\tau + E_\mu) / RT]) / Z_r, \end{aligned} \quad (19)$$

where

$$\begin{aligned} Z_m = & \exp[-(2E_\eta + E_\sigma) / RT] + 2\exp[-(E_\eta / RT) + \exp[-(2E_\eta + E_\tau + E_\mu) / RT]] \\ & + \exp[-(E_\tau + E_\mu) / RT] + \exp(-E_\omega / RT) + \exp[-(2E_\tau + E_\sigma + E_\omega) / RT], \end{aligned} \quad (20)$$

$$\begin{aligned} Z_r = & \exp(-2E_\eta / RT) + 2 \{ \exp[-(E_\eta + E_\mu) / RT] + \exp[-(E_\eta + E_\tau + E_\sigma) / RT] \} \\ & + \exp[-(E_\tau + E_\omega) / RT] + 1 + \exp[-2(E_\tau + E_\mu) / RT]. \end{aligned} \quad (21)$$

These equations indicate explicitly how ΔJ and ΣJ depend upon the temperature, including five intramolecular interaction energies, E_η , E_τ , E_σ , E_μ , and E_ω , as unknown parameters. These five E_α 's are the parameters to be determined, instead of the energies of the conformers in themselves, by an examination of the temperature dependence of ΔJ

and ΣJ . The E_α 's as well as the J_g and J_t values are assumed to be independent of temperature.

6.2.3 Numerical Calculations of ΔJ and ΣJ

The theoretical temperature dependence of ΔJ and ΣJ was calculated by the use of *Equations* (16)-(21) for various values of five parameters, E_η , E_τ , E_σ , E_μ , and E_ω , in order to investigate their effects. Typical examples are shown in Figure 31, where ΔJ_m , ΔJ_r , ΣJ_m , and ΣJ_r as functions of $1/T$ are depicted by a number of curves corresponding to the respective variations in the value of one of the parameters, E_η , E_τ , E_σ , E_μ , and E_ω with the values of -0.42, 0.4, 0.4, 0.9, and 2.0 kcal mol⁻¹, respectively. This is an optimum set for pentane-2,4-diol, as will be discussed in the Sec. 6.3. The $J_t = 11.5$ and $J_g = 2.1$ Hz values were used; their determination is also described there.

An inspection of Figure 31 shows that the temperature dependence of ΔJ and ΣJ is affected mainly by E_η and E_σ , slightly by E_μ , and little by E_τ and E_ω . From its definition, E_η is expected to be sensitive to the size of the substituent; therefore, the results for compounds with different substituents will mainly show changes in E_η . On the other hand, E_σ is related to the interaction between substituents. The solvent effects are reflected in the changes in E_σ for molecules with the substituents which interact appreciably with solvents, pentane-2,4-diol, for example. This will be discussed in a later section on experimental results.

It is worth noticing that all the curves cross at a particular point in the figure of the E_σ dependence of the $\Delta J_r \cdot 1/T$ relations [Figure 31 (h)]. This crossing occurs independently of the other parameter values so long as ΔJ is positive, and the ΔJ_r value at this point should be equal to $\delta J/2$, that is, $(J_t - J_g)/2$. This fact can be verified as follows.

Let ΔJ_r be equal to $\delta J/2$ in *Equation* (13), i.e.,

$$1/2 = (\eta^2 + \eta\tau\sigma - 1 - \tau\omega) / [\eta^2 + 2(\eta + \eta\tau\sigma + \tau\omega) + 1 + \tau^2\mu^2]. \quad (22)$$

Then, one obtains

$$\eta^2 - 3 - 3\tau\omega - 2\eta\mu - \tau^2\mu^2 = 0, \quad (23)$$

where the term including σ has vanished. The substitution of *Equation* (9) yields

$$\exp(-2E_\eta/RT) - 3 \cdot 3 \exp[-(E_\tau + E_\eta)/RT] - 2 \exp[-(E_\eta + E_\mu)/RT] - \exp[-2(E_\tau + E_\mu)/RT] = 0. \quad (24)$$

Let the T which satisfies *Equation* (24) be T^0 ; then, the $\Delta J_r \cdot 1/T$ curves necessarily pass through a point $(1/T^0, \delta J/2)$ irrespective of E_σ , because *Equation* (24) does not contain E_σ .

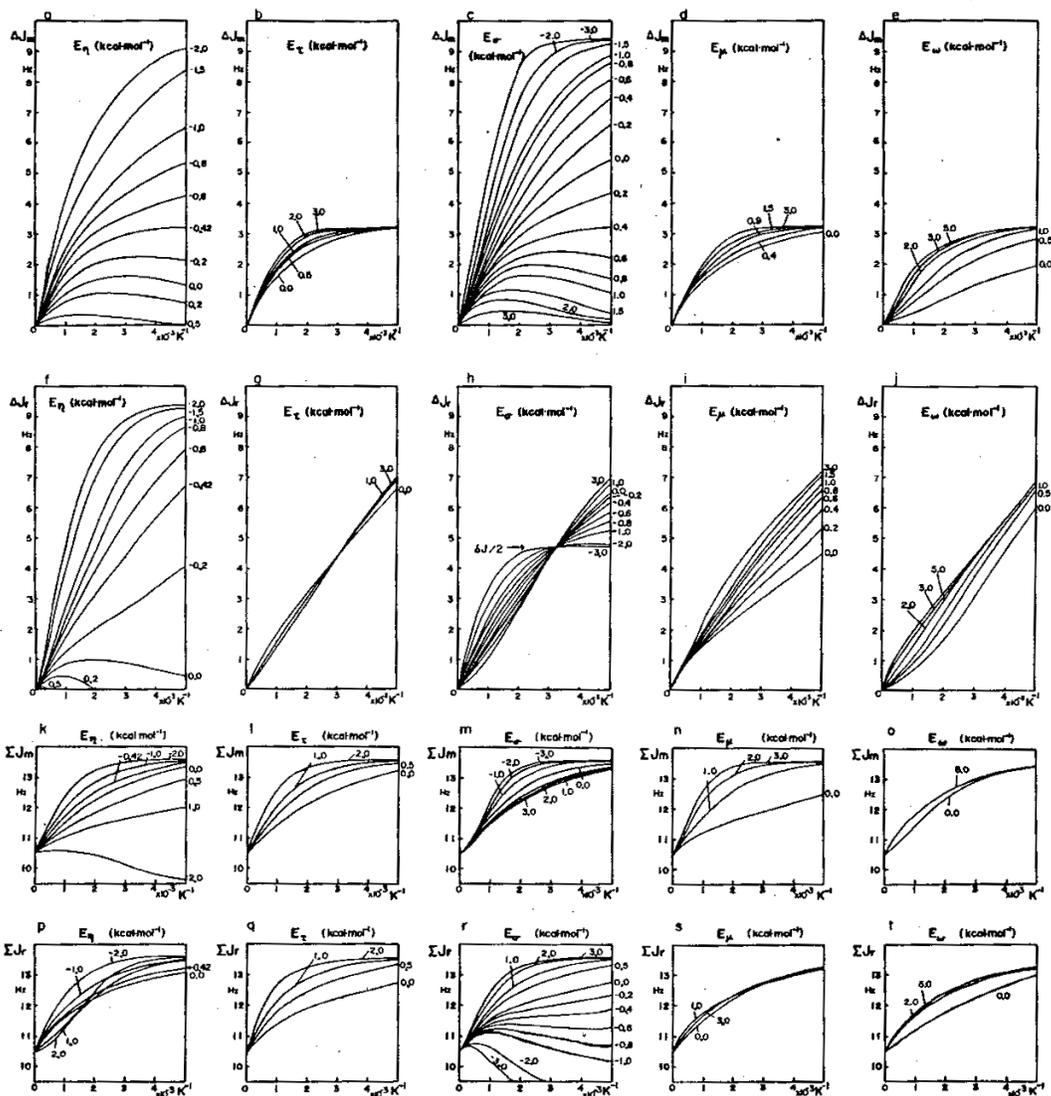


Figure 31 Calculated temperature dependence of ΔJ_m , ΔJ_r , ΣJ_m , and ΣJ_r for the various values of five energy parameters, E_n , E_v , E_o , E_μ , and E_w . The abscissa indicates the reverse of the temperature. A number of curves correspond to the respective variations in the values of one of the parameters, E_n , E_v , E_o , E_μ , and E_w with the values of -0.42, 0.4, 0.9, and 2.0 kcal mol⁻¹, respectively.

6.2.4 The Case where $E_\sigma = E_\mu = E_\omega$ is Assumed

Frequently the three second-order interactions are assumed to be equal^{14,21,22} when the substituent can be taken as effectively commensurate in size with the methyl group. Thus, when $\sigma = \mu = \omega$, that is, when $E_\sigma = E_\mu = E_\omega$, the theoretical temperature dependence of ΔJ and ΣJ is shown in Figure 32 for several values of E_η . The other parameters are fixed at $E_r = 0.4$ and $E_\sigma = E_\mu = E_\omega = 2.0$ kcal mol⁻¹. It is found that the effects of the temperature and E_η are small for ΔJ_m but large for ΔJ_r . This feature can be attributed to the dominant role of the "preferred conformations." That is to say, only the $TG(=GT)$ conformer is favored in the *meso* isomer, while in the racemic isomer the relative populations of the two possible preferred conformers, TT and GG , can be affected by the temperature are by E_η .

Only the preferred conformers are permitted in the approximation that $\sigma = \mu = \omega = 0$, i.e., $E_\sigma, E_\mu, E_\omega \rightarrow \infty$. In the case, *Equations* (10)-(15) become

$$Z_m = 2\eta \quad \text{and} \quad Z_r = \eta^2 + 1 \quad (25)$$

$$\Delta J_m = 0 \quad \text{and} \quad \Sigma J_m = J_t + J_g \quad (26)$$

$$\Delta J_r = \delta J(\eta^2 - 1)/(\eta^2 + 1) \quad \text{and} \quad \Sigma J_r = J_t + J_g \quad (27)$$

From *Equation* (27), we obtain

$$\eta^2 = (\delta J + \Delta J_r)/(\delta J - \Delta J_r). \quad (28)$$

The mole fractions of TT and GG in the racemic isomer are given by

$$P_{TT} = \eta^2 / (\eta^2 + 1) \quad \text{and} \quad P_{GG} = 1 / (\eta^2 + 1) \quad (29)$$

from Table 10. The substitution of *Equation* (28) yields

$$P_{TT} = (\delta J + \Delta J_r)/(2\delta J) \quad \text{and} \quad P_{GG} = (\delta J - \Delta J_r)/(2\delta J). \quad (30)$$

The last well-known equations have been used in most conformational analyses.⁵⁻¹¹ Similarly, only the $TG(=GT)$ conformer is permitted in the *meso* isomer, and $\Delta J_m = 0$ at any temperature.

6.2.5 The Sign of ΔJ

Care must be taken in the determination of the relative magnitudes of the syn and anti vicinal couplings, that is, the sign of ΔJ , because only its absolute value can be

deduced experimentally by spin analysis. As is shown in Figure 32, the sign of ΔJ is dependent mainly upon that of E_η in the usual case where all the second-order interaction energies are higher. In practice, the sign is closely related to the relative stability of the two preferred conformers in the racemic isomer, TT and GG , because Equation (29) implies that if $\eta > 1$, and if, accordingly, $E_\eta < 0$ and $\Delta J_r > 0$, the TT conformer should predominate over GG and vice versa. For the definite determination, it will be necessary to have other experimental information; the solvent effect is found to be a determinant for pentane-2,4-diol and the temperature dependence of the chemical shift in the methine protons may be used for 2,4-dichloropentane and 2,4-diphenylpentane.

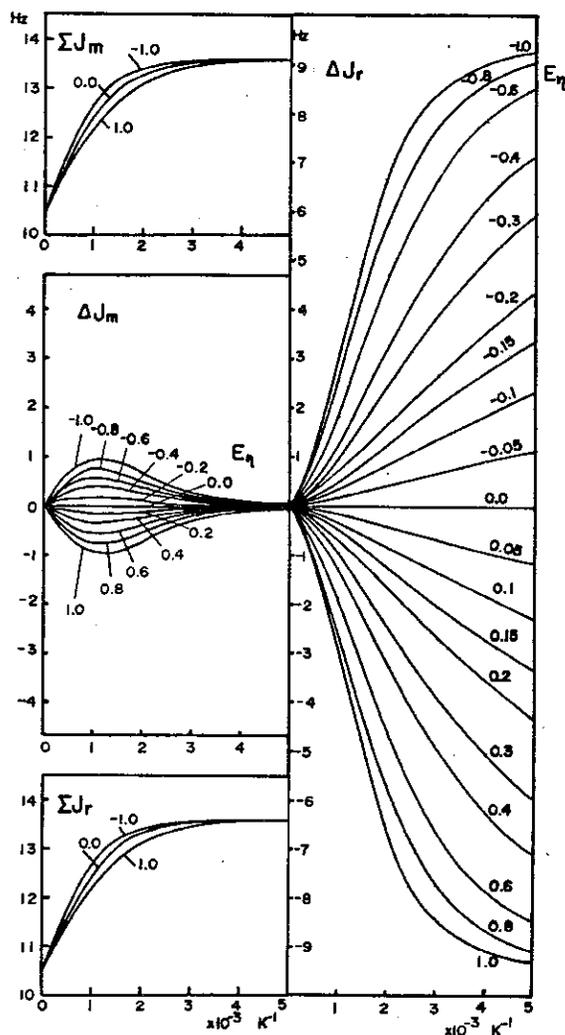


Figure 32 Calculated temperature dependence of ΔJ_m , ΔJ_r , ΣJ_m , and ΣJ_r for the various values of E_η . The other parameters are taken as $E_r = 0.4$ and $E_\sigma = E_\mu = E_\omega = 2.0 \text{ kcal mol}^{-1}$.

6.2.6 Pre-exponential Factor

In the preceding calculations, the partition function f_i and Equation (8), which includes the degree of freedom of motions other than the internal rotation about skeletal bonds, was set equal among all the conformers in Equation (8). This seems to be a good approximation for the molecules with small substituents, as will be shown later for pentane-2,4-diol and 2,4-dichloropentane. However, the above treatment fails in the analysis of the temperature dependence of ΔJ_r for 2,4-diphenylpentane. This is probably a result of the neglect of f_i , which must have a great effect on the molecules with larger substituents such as the phenyl group.

The vibrational and rotational partition functions are calculated as

$$f_i^{\text{vib}} = \prod_j \{ \exp(-hv_j / 2kT) [1 - \exp(-hv_j / kT)]^{-1} \},$$

$$f_i^{\text{rot}} = K(I_A I_B I_C)^{1/2},$$

where ν_j is the normal frequency, where I_A , I_B , and I_C are the moments of inertia, and where K represents a constant independent of the conformers. The estimates of f_i^{rot} 's for the *TT* and *GG* forms in the racemic isomer of 2,4-diphenylpentane revealed a difference of about 10% between them but this is not sufficient to interpret the experimental results. The evaluation of f_i^{vib} is difficult because the normal frequencies for each isomer are unknown. The difference, however, must be negligibly small as far as small vibrations are concerned.

On the other hand, the internal rotation of substituents must play an important role, especially in the case of the molecules with bulky and stiff substituents, such as phenyl group. The potential function of such an internal rotation, however, is so complicated that its theoretical partition function can not be calculated. Instead of the *a priori* calculation, the f_i term can be treated semi-empirically, as will be shown below.

Consider now the case where σ , μ , and ω are negligibly small; then the mole fractions of *TT* and *GG* for the racemic isomer can be determined by a parameter, η , from Equation (29). If the corresponding interaction energy, E_η , is formally defined by Equation (9), then E_η may depend upon the temperature, because the more rapid rotation at higher temperatures may result in a considerable interference between R and CH groups, whereupon E_η should increase. Let the variation of E_η with the temperature be expressed as

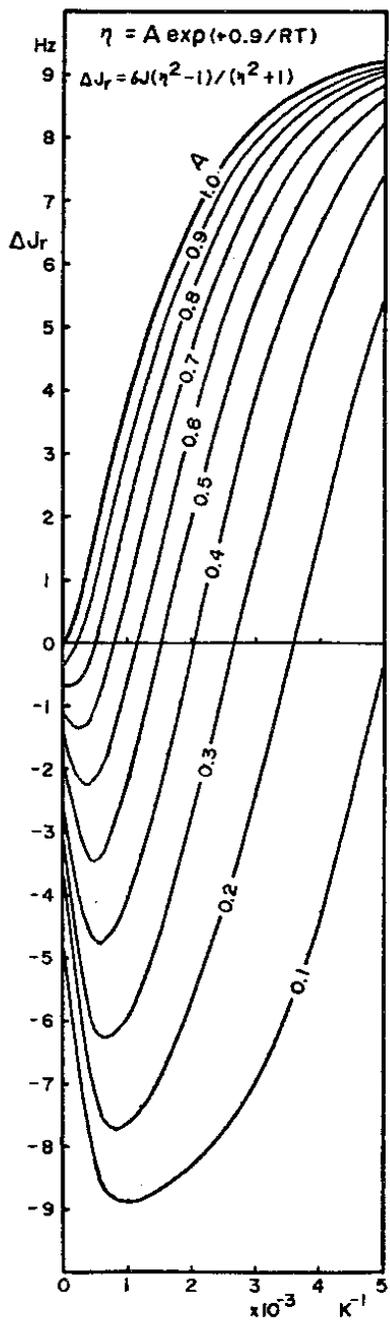


Figure 33 Calculated temperature dependence of ΔJ_r for the various values of A , the pre-exponential factor in η . The other parameters are taken as $E_r = 0.4 \text{ kcal mol}^{-1}$ and $\sigma = \mu = \omega = 0$.

$$E_{\eta} = E_{\eta}^0 - ST \quad (31)$$

where E_{η}^0 is the E_{η} value at absolute zero and where S is a coefficient parameter with the dimension of entropy. The substitution of this equation into Equation (9) yields

$$\eta = \exp(-E_{\eta}/RT) = \exp[-(E_{\eta}^0 + ST)/RT] = A \exp[-(E_{\eta}^0/RT) \quad (32)$$

where

$$A = \exp(S/R). \quad (33)$$

In the present problem, $S \leq 0$; therefore, $0 < A \leq 1$ can be expected, because E_{η} should increase with an increase in the temperature. In other words, the G conformation is favored by entropy because a considerable interference with the internal rotation may be expected in T , whereas the substituent rotates more freely in G .

The influence of the above pre-exponential factor, A , upon ΔJ_r was calculated; it is shown in Figure 33 on the assumption that A is independent of the temperature. This figure also shows that the ΔJ_r value for a small values of A decrease more sharply with an increase in the temperature than that for the large value of A .

6.3 APPLICATION TO PENTANE-2,4-DIOL

6.3.1 Solvent Effect

The temperature dependence of the spin-spin coupling constant between the methine and methylene protons and their solvent effect were investigated by Fukuroi *et al.*¹² The examples of spectra are shown in Figure 34. The spectrum shape for methylene proton in *meso* isomer shows remarkable solvent effects due to the changes of conformation and chemical shifts. The values of vicinal coupling constants have been obtained from the analyses of the spectra. The results are plotted in Figure 35 in terms of ΔJ and ΣJ as functions of $1/T$. The solvent effect is most striking in ΔJ_m and ΔJ_r . The former curves are clearly affected by solvents in absolute value as well as in slope; some decrease with the temperature, while others increase. On the other hand, the latter curves concentrate on a small region, and they are affected by the solvent only in slope; they all decrease with an increase at the temperature. The slopes of the curves are greater for ΔJ_m than for ΔJ_r in methylene chloride, chloroform, and carbon

tetrachloride solutions, while this tendency is reversed in pyridine, dimethyl sulfoxide, and deuterium oxide solutions.

The features observed above correspond well with the theoretical curves in Figures 31(c) and 31(h), that is, the curves for the E_σ dependence of ΔJ_m and ΔJ_r , respectively. This correspondence is reasonable, because E_σ is defined as an interaction energy between substituents. The intramolecular hydrogen-bond formation between hydroxyl groups results in a decrease in E_σ . Solvation depresses this effect because *intermolecular* hydrogen bonding may become dominant instead. Theoretical curves corresponding to various E_σ 's are also shown in Figure 35. E_σ is smaller in methylene chloride, chloroform and carbon tetrachloride, which are considered to have weaker solvating abilities, while E_σ is larger in deuterium oxide and dimethyl sulfoxide with stronger solvating abilities. This tendency is clearly shown in the results for ΔJ_m , where E_σ is found to vary between -1.0 to $+0.8$ kcal mol⁻¹, depending upon the solvent.

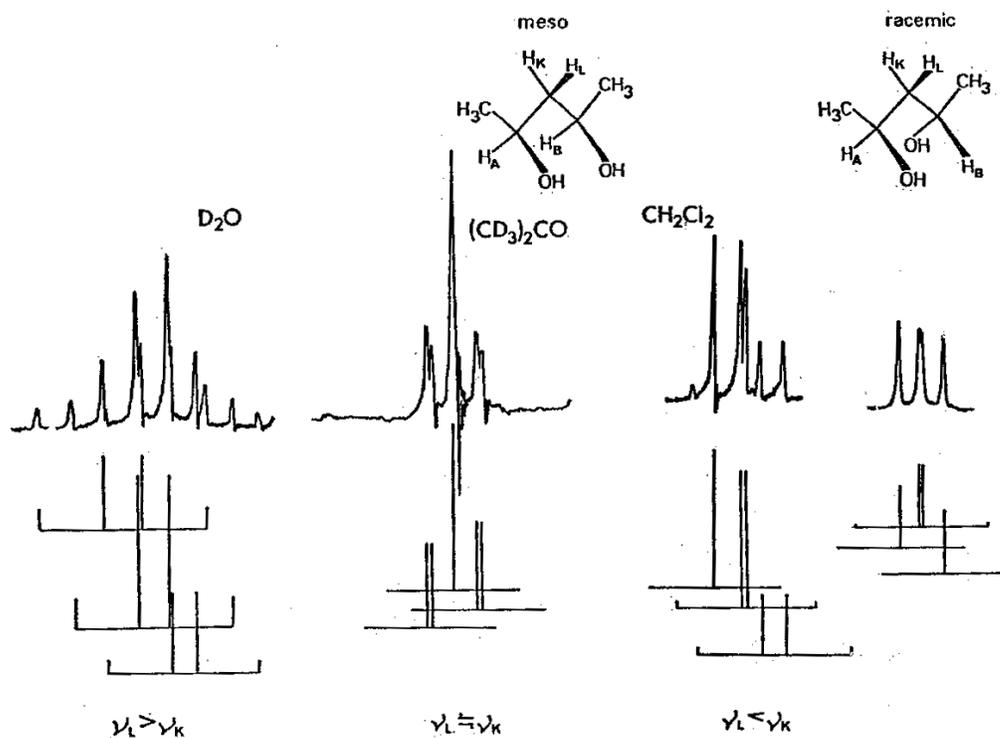


Figure 34 ¹H NMR spectra of pentane-2,4-diol.

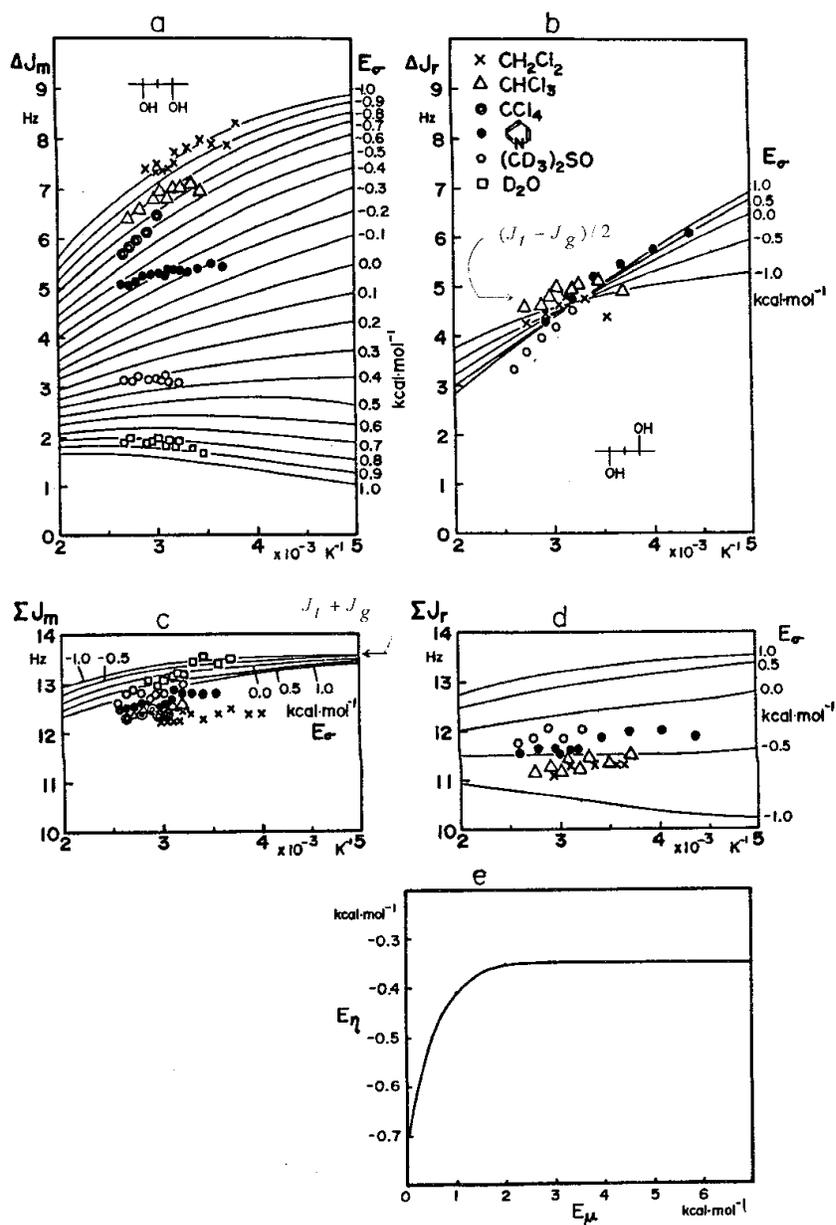


Figure 35 (a) - (d) Experimental and theoretical temperature dependence of ΔJ_m , ΔJ_r , ΣJ_m , and ΣJ_r in pentane-2,4-diol. The data observed by Fukuroi et al.¹² in the various solvents are plotted. The solid line indicate the curves calculated for the various values of E_σ with other parameter values, with $E_\eta = -0.42$, $E_\tau = 0.4$, $E_\mu = 0.9$, and $E_\omega = 2.0$ kcal mol⁻¹. (e) The relation between E_η and E_μ , which reproduces the experimental value on the abscissa for the crossing point of the curves in (b).

Table 11 The conformational energies in kcal mol⁻¹ (a) and the mole fractions of conformers at 25°C (b) for the meso and racemic isomers of pentane-2,4-diol in the various solvents. The energy parameters and weight factors determined are also listed

Solvent	E σ	Meso						Racemic					
		TT	TG(=GT)	TG(=GT)	GG	GG(=GG)	GG	TT	TG(=GT)	TG(=GT)	GG	GG(=GG)	GG
CH ₂ Cl ₂	-1.0	-1.8 ₄	-0.42	0.8 ₈	2.0	1.3	1.8	-0.8 ₄	0.4 ₈	-1.0 ₂	0	2.4	2.6
CHCl ₃	-0.75	-1.5 ₉				2.1				-0.7 ₇			
CCl ₄	-0.6	-1.4 ₄				2.2				-0.6 ₂			
Pyridine	-0.3	-1.1 ₄				2.5				-0.3 ₂			
(CD ₃) ₂ SO	0.3	-0.5 ₄				3.1				0.2 ₈			
D ₂ O	0.8	-0.0 ₄				3.6				0.7 ₈			

Solvent	σ	Meso (%)						Racemic (%)					
		TT	TG+GT	TG+GT	GG	GG+GG	GG	TT	TG+GT	TG+GT	GG	GG+GG	GG
CH ₂ Cl ₂	4.87	79.8	16.8	2.2	0.0 ₃	1.1	0.0 ₅	23	5.9	63.7	6.3	0.1	0.0 ₅
CHCl ₃	3.28	72.7	22.8	2.9	0.0 ₅	1.5	0.0 ₄	30	7.5	54.1	8.0	0.1	0.0 ₇
CCl ₄	2.59	67.7	26.9	3.4	0.0 ₅	1.8	0.0 ₄	34	8.4	48.2	9.0	0.1	0.0 ₈
Pyridine	1.61	56.6	36.2	4.6	0.0 ₈	2.4	0.0 ₃	41	10.3	36.6	11.0	0.2	0.1
(CD ₃) ₂ SO	0.62	33.6	55.5	7.1	0.1	3.6	0.0 ₂	53	13.3	18.3	14.2	0.2	0.1
D ₂ O	0.28	18.6	68.0	8.7	0.2	4.5	0.0 ₁	59	14.8	9.2	15.8	0.3	0.1

E_η	E_τ	E_μ	E_ω	η	τ	μ	ω
-0.42	0.4	0.9	2.0	1.94	0.5	0.24	0.04

In spite of such a satisfactory correspondence between theory and experiment in ΔJ , the situation in ΣJ is not so good. This is probably because systematic errors in the treatment of the spin-spin coupling constants effectively cancel each other out in their difference, but are revealed in their sum.

6.3.2 The Determination of J_t and J_g

The $\Delta J_r - 1/T$ curves with various E_o values have a crossing point located at $\delta J/2$, as has been stated previously. Therefore, δJ can be determined experimentally from the solvent effect in racemic pentane-2,4-diol. The experimental crossing point is located at about 4.7 Hz in Figure 32. Then, $\delta J = J_t - J_g = 9.4$ Hz. The uncertainty of this value is estimated to be about ± 0.5 Hz. On the other hand, the asymptotic value of ΣJ_m in Figure 31(m) at a lower temperature is $J_t + J_g$. The observed value in the case of the deuterium oxide solvent is about 13.6 Hz. Thus, $J_t = 11.5$ and $J_g = 2.1$ Hz are obtained; they may be regarded as reasonable values. The errors inherent in $J_t + J_g$, J_t and J_g thus obtained must be about ± 1.0 Hz larger than that of δJ , judging from the unsatisfactory correspondence between theory and experiment.

6.3.3 The Determination of Energy Parameters

The five interaction energy parameters, E_η , E_τ , E_o , E_μ , and E_ω , were determined to reproduce the observed temperature dependence of ΔJ_m , ΔJ_r , ΣJ_m , and ΣJ_r by an investigation of the theoretical curves in Figure 31 as well as by a consideration of their physical meanings.

E_ω , which is the interaction energy between methyl groups, is estimated to be about 2.0 kcal mol⁻¹ from the values reported in the literature.²² The error in E_ω has little effect on the spin-spin coupling constants and mole fractions of the conformers. E_τ , which also has little effect, is estimated to be 0.4 kcal mol⁻¹. The location of the crossing point on the abscissa in Figure 31 (h) is probably determined mainly by E_η and E_μ . The observed value is 3.2×10^{-3} K⁻¹. The relation between E_η and E_μ , which is consistent with these experimental results, is indicated in Figure 35(e). The range of E_η is probably restricted to $-0.7 < E_\eta \leq -0.35$, because E_μ can be expected to be positive. The best values of E_η and E_μ to reproduce the experimental data are determined to be -0.42 and 0.9 kcal mol⁻¹, respectively. Another parameter, E_o , which depends upon the solvents, can be determined from Figure 35(a). The values thus obtained are listed in Table 11.

6.3.4 The Determination of the Energies and Mole Fractions of Conformers

The energies of all the conformers can readily be given as the respective sums of the determined energy parameters by reference to Table 10. The results are listed in Table 11(a). The energies of the conformers including the σ interaction are necessarily dependent upon the solvents. Similarly, the mole fractions of conformers at 25°C are calculated from Table 10 by the use of the weight factors, η , τ , σ , μ , and ω , computed from Equation (9) at 25°C. They are indicated in Table 11.

As is shown in Table 11(b), pentane-2,4-diol can take various kinds of conformers and their populations vary considerably with the solvents. These conclusions were drawn out by Fukuroi *et al.*¹² They also showed that TT for the *meso* and $T\bar{G}$ ($=\bar{G}T$) for the racemic isomers predominate in methylene chloride presumably due to the stabilization by the intramolecular hydrogen bonding in such a solvent with weaker solvating ability. This interpretation is also supported by the present work, but more directly and quantitatively; the solvent effect can be explained as a change in the interaction energy, E_{σ} .

The mole fractions are indicated in Table 11(b) for the racemic isomer in carbon tetrachloride and deuterium oxide in spite of the lack of experimental data on them. They were calculated from the data of the *meso* isomer, because it is characteristic of this analysis to treat both stereochemical isomers at the same time.

As discussed in Chapter 3, the NMR spectra of the hydroxyl protons have been investigated in poly(vinyl alcohol) and its model compounds including pentane-2,4-diol, where the triad tacticity has been accurately determined and where a systematic variation in coupling constants $J(\text{HCOH})$ with the configurational structures has been observed.^{26,27} The change in $J(\text{HCOH})$ can be explained in terms of the conformations both of the hydroxyl group and of the chain skeleton, as shown in Appendix 2.

6.4 APPLICATION TO 2,4-DICHLOROPENTANE AND 2,4-DIPHENYLPENTANE

The temperature dependence of the coupling constants for 2,4-dichloropentane and 2,4-diphenylpentane can be analyzed in a similar manner. The NMR data reported by

Schneider *et al.*¹³ and by Bovey *et al.*⁶ were used. The ΔJ , but not the ΣJ , was investigated by the present method, because the former is more sensitive to the conformation than is the latter, as is shown by pentane-2,4-diol. The δJ values for both the compounds are assumed to be equal to that of pentane-2,4-diol, 9.4 Hz, a value experimentally determined in Sec. 6.3.

6.4.1 2,4-Dichloropentane

Figure 36 shows the reported values of ΔJ_m and ΔJ_r observed in neat 2,4-dichloropentane and the best-fitting theoretical curves. The parameter values thus determined and the conformer population are listed in Table 12. According to these results, the small infrared absorption bands observed by Schneider *et al.*¹³ can probably be assigned to the TT or $T\bar{G}$ ($=\bar{G}T$) conformer for the *meso* isomer, and to the $TG(=GT)$ conformer for the racemic isomer. More detailed data in various solvents will make possible a precise investigation of the conformational equilibrium of this compound.

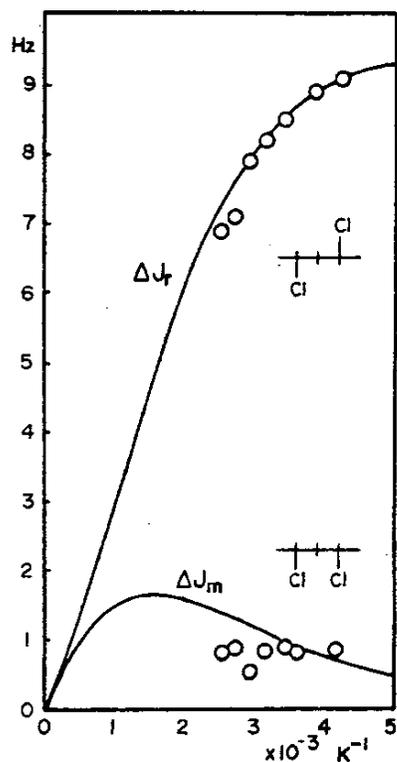


Figure 36 Experimental and theoretical temperature dependence of ΔJ_m and ΔJ_r in 2,4-dichloropentane. The plotted data are those reported by Schneider *et al.*¹³ The solid curves indicate the best-fitting ones calculated for $E_\eta = -1.0$, $E_\tau = 0.4$, $E_\sigma = 1.9$, $E_\mu = 1.5$, and $E_\omega = 2.0$ kcal mol⁻¹.

Table 12 The mole fractions of conformers of the *meso* and racemic isomers of 2,4-dichloropentane at 25°C. The energy parameters (kcal mol⁻¹) and weight factors determined are also listed

(%)	<i>TT</i>	<i>TG+GT</i>	$\overline{T\overline{G}}+\overline{G}T$	<i>GG</i>	$\overline{G\overline{G}}+\overline{G}G$	$\overline{G}\overline{G}$			
<i>Meso</i>	10	85	4	0.1	0.9	0			
Racemic	92	3	1	4	0	0			
E_η	E_τ	E_σ	E_μ	E_ω	η	τ	σ	μ	ω
-1.0	0.4	1.9	1.5	2.0	4.9	0.5	0.05	0.09	0.04

6.4.2 2,4-Diphenylpentane

In Figure 37(a) are plotted the reported values of ΔJ for racemic 2,4-diphenylpentane in three solvents. Such small solvent effects are observed that the data for the three solvents may be treated together. At any temperature, $\Delta J = 0$ is observed for the *meso* isomer. It is noticed that ΔJ_r decreases much more rapidly with an increase in the temperature than in the preceding cases. This feature cannot be interpreted in the same manner as before. As was stated in the theoretical section, the internal rotation of the phenyl groups is expected to play an important role and to make E_η depend upon the temperature. By the substitution of the experimental ΔJ_r value into *Equation* (13) or *Equation* (28) for an approximate calculation, η and E_η can be obtained. The E_η 's thus derived are plotted in Figure 37(b) as functions of the temperature. They have an apparently linear relation to the temperature; therefore, the coefficient, S, in *Equation* (31) may be regarded as a constant with the

value of $-1.7 \text{ cal mol}^{-1}\text{deg}^{-1}$ in the observed temperature region. Extrapolating to absolute zero degree, $E_\eta^0 = -0.9 \text{ kcal mol}^{-1}$ was obtained. It follows that

$$E_\eta = -0.9 + 1.7 \times 10^{-3}T. \quad (34)$$

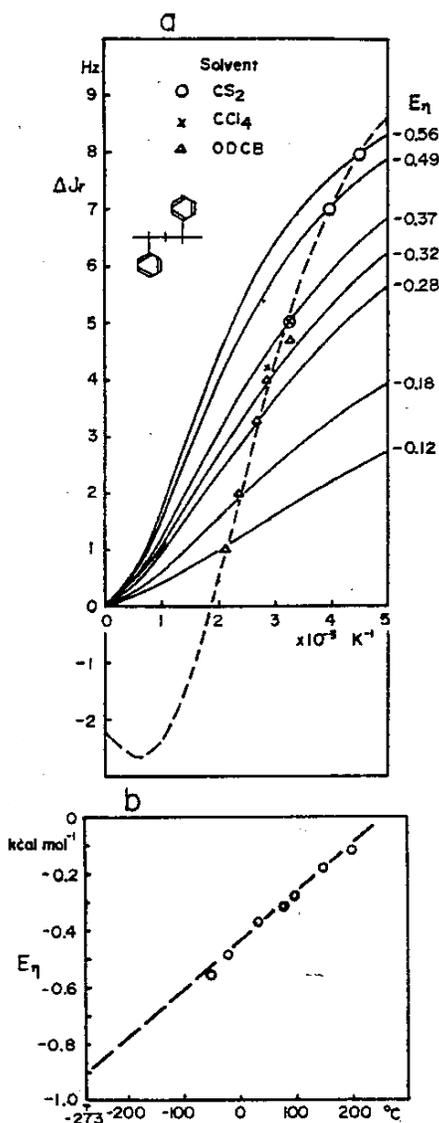


Figure 37 (a) The experimental and theoretical temperature dependence of ΔJ_r in 2,4-diphenylpentane. The plotted data are those reported by Bovey et al.⁶ The dashed curve indicates the best-fitting ones calculated for $\eta = 0.43 \exp(0.9/RT)$, $E_r = 0.4$, and $E_\sigma = E_\mu = E_\omega = 2.0$ kcal mol $^{-1}$, while the solid curves indicate those calculated for the various values of E_η in $\eta = \exp(-E_\eta/RT)$ without the pre-exponential factor. (b) The E_η 's obtained experimentally as a function of the temperature. See text.

Therefore η can be written in a form including a pre-exponential factor, such as

$$\eta = 0.43 \exp(0.9/RT). \quad (35)$$

The η value expressed by Equation (35), with $E_r = 0.4$ and $E_\sigma = E_\mu = E_\omega = 2.0$ kcal mol $^{-1}$, gives the calculated dependence of ΔJ_r shown by the dashed curve in Figure 37(a). The experimental results can be satisfactorily interpreted by a constant pre-exponential

factor. The solid curves represent the relations between ΔJ_r and $1/T$, assuming that E_η is independent of the temperature. Similar arguments were put forth by Bovey *et al.*⁶ and Williams and Flory,²⁸ but in the present treatment the temperature dependence of ΔJ_r is explicitly investigated. Conformer populations at various temperatures are listed in Table 13.

Table 13 The mole fractions of conformers of the meso and racemic isomers of 2,4-diphenylpentane at various temperatures. The energy parameters and the weight factors at 25°C are also listed

Temp		Meso (%)							Racemic (%)					
(°C)	E_η	η	TT	$TG+GT$	$\overline{TG}+\overline{GT}$	GG	$\overline{GG}+\overline{GG}$	\overline{GG}	TT	$TG+GT$	$\overline{TG}+\overline{GT}$	GG	$\overline{GG}+\overline{GG}$	\overline{GG}
-50	-0.52	3.53	0.2	99.7	0.04	0.01	0.01	0.00	91.2	0.06	0.02	8.7	0.00	0.00
0	-0.44	2.24	0.4	99.2	0.2	0.08	0.08	0.00	82.9	0.3	0.1	16.6	0.06	0.00
25	-0.39	1.94	0.6	98.8	0.3	0.2	0.2	0.00	78.3	0.5	0.3	20.8	0.1	0.00
100	-0.28	1.44	1.2	96.5	1.0	0.6	0.7	0.00	65.1	1.6	0.9	31.8	0.6	0.00
200	-0.12	1.11	2.1	91.5	2.5	1.7	2.2	0.02	50.4	3.7	2.4	41.1	2.2	0.02
		E_τ	E_σ	E_μ	E_ω	η	τ	σ	μ	ω				
		0.4	2.0	2.0	2.0	1.94	0.5	0.04	0.04	0.04				

6.4.3 The Signs of ΔJ_r and E_η

In the above discussion, it was assumed, without proof, that E_η is negative and accordingly, that the TT conformer predominates over the GG conformer in the racemic isomer, and also that ΔJ is positive. These assumptions were adopted by Bovey *et al.*⁶ in their analysis of 2,4-diphenylpentane. Strictly speaking, however, it is necessary to prove these points by experimental facts. The following data suggest that $E_\eta < 0$ for both 2,4-dichloropentane and 2,4-diphenylpentane.

Figure 38 shows the temperature dependence of the chemical shifts of the methine protons in both compounds. This is a graphical illustration of the reported values in the literature.^{6,13} Apparently, temperature affects the chemical shift of the two compounds to the opposite direction. If the polar effect²⁹ due to C-Cl bonds and the magnetic anisotropy effect³⁰ due to phenyl groups play predominant roles in the chemical shift of the methine protons in 2,4-dichloropentane and 2,4-diphenylpentane, respectively the

predominance of the *TT* form is supported by the above shift data, because the former effect is expected to make methine protons shift downfield, while the latter shift upfield in the *TT* form, where the methine proton is located near the substituent; the decrease in *TT* with an increase in the temperature must reduce such effects.

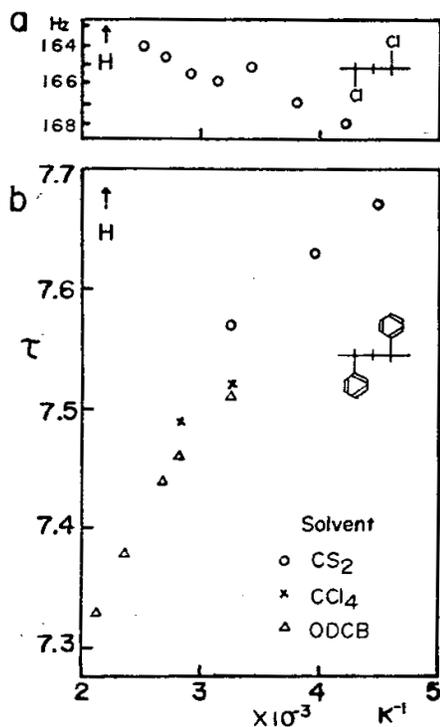


Figure 38 Experimental temperature dependence of the chemical shifts of the methine protons in 2,4-dichloropentane (a) and 2,4-diphenylpentane (b), which were observed by Schneider *et al.*¹³ and by Bovey *et al.*⁶ respectively.

6.5 DISCUSSION

6.5.1 *Trans and Gauche Coupling Constants*

It is one of the most significant conclusions in this paper that the difference between *trans* and *gauche* coupling constants, $\delta J = J_t - J_g$, can be determined experimentally from the solvent effect in the temperature dependence of ΔJ_r of pentane-2,4-diol. Although this quantity plays an important role in conformational analysis using NMR coupling data, a direct means for its determination in chain molecules has not yet been

found. A similar treatment may permit the determination of δJ for other compounds, if an appropriate solvent effect is found in them as is observed in pentane-2,4-diol.

6.5.2 *Approximations*

The main assumptions of the present treatment are as follows:

- (I) Rotational isomeric state approximation.^{22,23}
- (II) Common J_t and J_g values among all the conformers.
- (III) Neglect of the effects of the temperature and the solvent upon J_t and J_g .
- (IV) Local interaction model approximation.
- (V) Neglect of the temperature dependence of the interaction energy parameters.

The assumption (IV) is characteristic of the present analysis. Though it seems to be quite a bold assumption, it holds to a good approximation, because the solvent effect upon the temperature dependence of ΔJ in the *meso* and racemic pentane-2,4-diols can be well explained in terms of the intramolecular interaction energy parameters based on this model. The merits of adopting this assumption are as follows:

- (1) It makes it practical to analyze the conformational equilibrium of chain molecules, because usually only five parameters are necessary.
- (2) The interaction energy between non-bonded groups as a parameter is a straightforward concept and gives useful results in the interpretation of solvent effects.
- (3) The stereochemical isomers can be treated simultaneously by the use of the common parameters. Either isomer can be analyzed complementarily and the reliability of the parameter values thus determined must be increased. In the previous analysis of *meso* pentane-2,4-diol in a dimethyl sulfoxide solution by Fukuroi *et al.*,¹² two possible sets of values were reported; one of them can be eliminated by the use of the present method.
- (4) Similarly, this model makes it possible to treat and interpret the conformations of homologous molecules of different chain lengths in terms of a unified theory.

The assumption (V) is discussed in the theoretical section; it requires care in its application, as has been explained in detail for 2,4-diphenylpentane.

6.5.3 *Application to Homologous Polymer Chains*

The statistical weight factors defined in this article constitute a concept essentially identical to those introduced by Nagai,¹⁹ Flory^{14,21,22} and others in their statistical

calculation of polymer chains. For details of the theory and a number of applications, their articles^{14,22,31} should be referred to. The statistical weight matrices for a vinyl polymer chain corresponding to their formulation¹⁴ may be expressed by the present system of designation as

$$U' = \begin{matrix} & T & G & \bar{G} \\ \begin{matrix} T \\ G \\ \bar{G} \end{matrix} & \begin{pmatrix} h & 1 & t \\ h & w & t \\ h & 1 & tw \end{pmatrix} \end{matrix}, \quad (36)$$

$$U_m'' = \begin{pmatrix} \eta\sigma & 1 & \tau\mu \\ \eta & \omega & \tau\mu \\ \eta\mu & \mu & \tau\sigma\omega \end{pmatrix}, \quad (37)$$

$$U_r'' = \begin{pmatrix} \eta & \mu & \tau\sigma \\ \eta\mu & 1 & \tau\omega \\ \eta\sigma & \omega & \tau\mu^2 \end{pmatrix}, \quad (38)$$

The configurational partition function of the vinyl polymer chain as a whole can be obtained by the multiplication of the above matrices in the serial order dictated by the structure of the chain^{14,21,22}

$$Z = (1 \ 0 \ 0) \prod_{i=1}^{n-1} (U' U_i'') \begin{pmatrix} 1 \\ 1 \\ 1 \end{pmatrix}. \quad (39)$$

In spite of the elementary importance of the statistical weight parameters in such a calculation of polymer chains in solution, no satisfactory method of evaluating them has yet been presented. They have been estimated from the spectroscopic or diffraction data on the small molecules in the gas phase or from theoretical calculations of the interactions between non-bonded atoms.^{22,23} The present NMR method of analyzing the model compounds in the solvent in question must provide more reliable values for them for use in calculations for homologous polymer chains.

APPENDIX 1 Conformation of PVAL

The conformation of PVAL in water has been obtained from the combination of the experimental data on pentane-2,4-diol and the theoretical calculation based on multiplication of matrices. Calculation has been made for PVAL chains of 50 monomer units with stereoregularity. The results are shown in Figure 39, where dyad conformations are shown for the eight monomer units in chain end. The effects of chain end are observed only for the second units. Thus the present investigation offers a consistent method treating conformation for polymer and its model compounds.

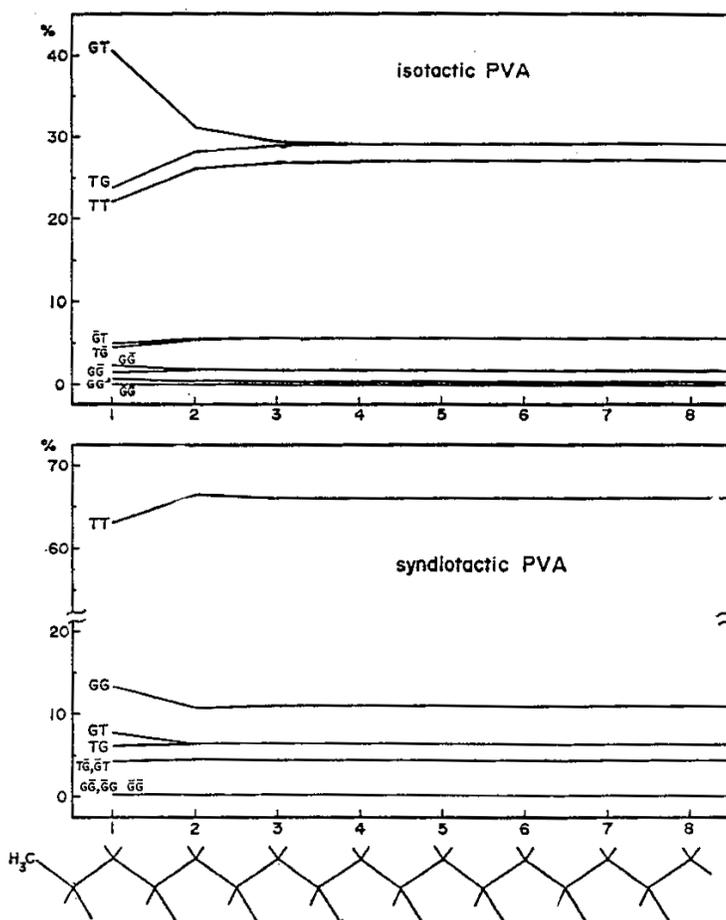


Figure 39 Conformation of PVAL in water. Theoretical calculation based on multiplication of matrices and the experimental data on pentane-2,4-diol. Calculation has been made for PVAL chains of 50 monomer units with stereoregularity.

APPENDIX 2 *Spin-spin splitting in ^1H NMR of hydroxyl proton*

As reported in Chapter 3, the ^1H NMR of hydroxyl proton for PVAL and its model compounds has shown a systematic change of spin-spin splitting. This can be explained by conformation of chain skeleton and of hydroxyl group as shown in Figure 40. $J(\text{H-C-O-H})$ increases in the order of mm, me, mr, re, rr according to the nomenclature considering ends of models shown in Figure 41. The conformers which make it possible to form hydrogen bonding between neighboring hydroxyl groups are TT for *meso* and $T\bar{G}$ or $\bar{G}T$ for racemic dyads. In these conformers, the probability weight where a hydroxyl group makes hydrogen bonding is assumed to γ . From the experimental data on pentane-2,4-diol in this work, γ has been determined as 8. Calculation has been done for 81 conformers of heptane-2,4,6-triol and $J(\text{H-C-O-H})$ has been obtained. The results are shown in Figure 41. $J(\text{H-C-O-H})$ is expressed as a function of the weight factor σ . Considering $\sigma=0.62$ determined from the experiment before, the observed systematic change can be explained.

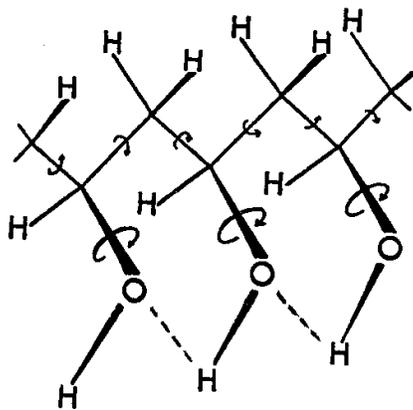


Figure 40 Conformation of chain skeleton and hydroxyl group.

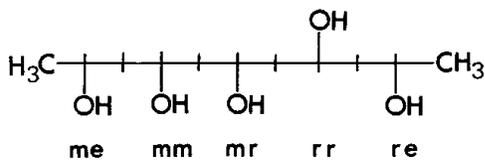
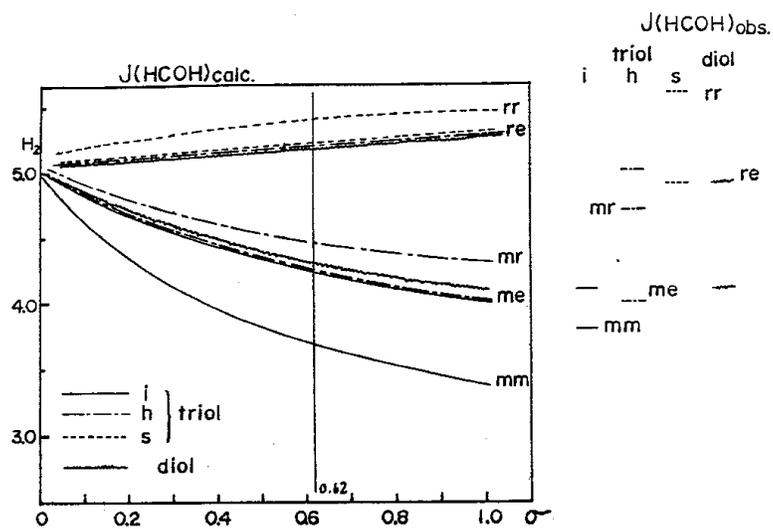


Figure 41 Theoretical calculation and observed values for $J(\text{H-C-O-H})$ for heptane-2,4,6-triol (triol) and pentane-2,4-diol (diol).

APPENDIX 3 *Trans and Gauche Coupling Constants, J_t and J_g*

Although the *trans* and *gauche* coupling constants, J_t and J_g , are basically important constants in NMR conformational analysis, not so many studied have been reported for determining them before and after this work. The values in the literature are listed below. They were determined using cyclic compounds.^{32,33,36} In chain molecules, J_t and J_g were usually estimated or determined through the analysis of conformer populations.^{5,6,37,38} In this work, J_t and J_g have been determined independently from the data on temperature dependence and solvent effects for coupling constants.

Table *Trans and gauche coupling constants, J_t and J_g reported in the literature*

Author	Molecule	J_t and J_g (Hz)
Karplus ¹	(Theoretical)	$J_t=11.9$
Gutowsky and Juan ³²	2,2-Metacyclophane	$J_t= 12.3, J_g= 3.2$
McMahon and Tincher ⁵	2,4-Disubstituted pentanes	$J_t \cdot J_g= 10 \pm 1.5$
Yoshino, Kikuchi and Komiyama ³³	Trimethyl <i>cis</i> -hydrotrimesate	$J_t= 12, J_g= 3$
Bovey, Hood III, Anderson and Snyder ^{6,34}	2,4-Diphenyl pentane	$J_t + J_g= 14.8 \pm 0.2$
Moritani and Fujiwara³⁵ (This work)	Pentane-2,4-diol	$J_t= 11.5 \pm 1.0, J_g= 2.1 \pm 1.0$
Matsuzaki and Ito ³⁶	Dioxane	$J_t= 9.7, J_g= 2.7$
Viti, Indovina, Podo, Radics, and Nemethy ³⁷	1,2-Dimethoxyetane	$J_t= 11.91, J_g= 5.76, J'_g= 2.36$
Tasaki and Abe ³⁸	1,2-Dimethoxyetane	$J_t= 11.4, J_g= 2.3$

REFERENCES

- 1 Karplus, M., *J. Chem. Phys.*, 1959, **30**, 11.
- 2 Emsley, J. W., Feeney, J. and Sutcliffe, L. H., *High Resolution Nuclear Magnetic Resonance Spectroscopy*, Pergamon, Vol. 1, New York, 1965.
- 3 Gutowsky, H. S., Belford, G. G. and McMahon, P. E., *J. Chem. Phys.*, 1962, **36**, 3353.
- 4 Bothner-By, A. A. and Naar-Colin, C., *J. Am. Chem. Soc.*, 1962, **84**, 743.
- 5 McMahon, P. E. and Tincher, W. C., *J. Mol. Spectrosc.*, 1965, **15**, 180.
- 6 Bovey, F. A., Hood III, F. P., Anderson, E. W. and Snyder, L. C., *J. Chem. Phys.*, 1965, **42**, 3900.
- 7 Abe, Y., Tasumi, S., Shimanouchi, T., Satoh, S. and Chujo, R., *J. Polym. Sci. Part A-1*, 1966, **4**, 1413.
- 8 Murano, M. and Yamadera, R., *J. Polym. Sci. Part A-1*, 1967, **5**, 1855.
- 9 Doskocilova, D., Sykora, S., Pivcova, H., Obereigner, B. and Lim, D., *J. Polym. Sci. Part C*, 1968, **23**, 365.
- 10 Murano, M. and Harwood, H. J., *Macromolecules* 1970, **3**, 605.
- 11 Matsuzaki, K., Sakota, K. and Okada, M., *J. Polym. Sci. Part A-2*, 1969, **7**, 1444.
- 12 Fukuroi, T., Fujiwara, Y., Fujiwara, S. and Fujii, K., *Anal. Chem.*, 1968, **40**, 879.
- 13 Schneider, B., Stokr, J., Doskocilova, D., Sykora, S., Jakes, J. and Kolinsky, M., *J. Polym. Sci. Part C*, 1969, **22**, 1073.
- 14 Flory, P. J. and Fujiwara, Y., *Macromolecules*, 1969, **2**, 315.
- 15 Eyring, H., *Phys. Rev.*, 1932, **39**, 746.
- 16 Kuhn, H., *J. Chem. Phys.*, 1947, **15**, 843.
- 17 Volkenshtein, M. V. and Ptitsyn, O. B., *Dokl. Akad. Nauk SSSR*, 1951, **78**, 657; *Zh. Fiz. Khim.*, 1952, **26**, 1061.
- 18 Lifson, S., *J. Chem. Phys.*, 1958, **29**, 80.
- 19 Nagai, K., *J. Chem. Phys.*, 1959, **31**, 1169.
- 20 Hoeve, C. A. J., *J. Chem. Phys.*, 1960, **32**, 888.
- 21 Abe, A., Jernigan, R. L. and Flory, P. J., *J. Am. Chem. Soc.*, 1966, **88**, 631.
- 22 Flory, P. J., *Statistical Mechanics of Chain Molecules*, Interscience, New York, 1969.
- 23 Birshstein, T. M. and Ptitsyn, O. B., *Conformations of Macromolecules* (translated

from the 1964 Russian edition, edited by Timasheff, S. N. and Timasheff, M. J.) Interscience, New York, 1966.

- 24 McCullough, R. L. and McMahon, P. E., *Trans. Faraday Soc.*, 1964, **60**, 2089; McMahon, P. E., *Trans. Faraday Soc.*, 1965, **61**, 197.
- 25 Fujiwara, Y. and Fujiwara, S., *Bull. Chem. Soc. Jap.*, 1964, **37**, 1005; Fujiwara, Y., Fujiwara, S. and Fujii, K., *J. Polym. Sci. Part A-1*, 1966, **4**, 257.
- 26 DeMember, J. R., Haas, H. C. and MacDonald, R. L., *J. Polym. Sci. Part B*, 1972, **10**, 385.
- 27 Chapter 3 in this thesis; Moritani, T., Kuruma, I., Shibatani, K. and Fujiwara, Y., *Macromolecules*, 1972, **5**, 577.
- 28 Williams, A. D. and Flory, P. J., *J. Am. Chem. Soc.*, 1969, **91**, 3111.
- 29 Buckingham, A. D., *Can. J. Chem.*, 1960, **38**, 300.
- 30 Johnson, C. E. and Bovey, F. A., *J. Chem. Phys.*, 1958, **29**, 1012.
- 31 Flory, P. J. and Fujiwara, Y., *Macromolecules*, 1969, **2**, 327; Fujiwara, Y. and Flory, P. J., *Macromolecules*, 1970, **3**, 43; *Macromolecules*, 1970, **3**, 280; *Macromolecules*, 1970, **3**, 288.
- 32 Gutowsky, H.S. and Juan, C., *J. Chem. Phys.*, 1962, **37**, 120.
- 33 Yoshino, T., Kikuchi, Y. and Komiyama, J., *J. Phys. Chem.*, 1966, **70**, 1059.
- 34 Bovey, F. A., *High Resolution NMR of Macromolecules*, Academic Press, Inc., London, 1972.
- 35 This thesis; Moritani, T. and Fujiwara, Y., *J. Chem. Phys.*, 1973, **59**, 1175.
- 36 Matsuzaki, K. and Ito, H., *J. Polym. Sci., Polym. Phys. Ed.*, 1974, **12**, 2507.
- 37 Viti, V., Indovina, P.L., Podo, F., Radics, L. and Nemethy, G., *Mol. Phys.*, 1974, **27**, 541.
- 38 Tasaki, K. and Abe, A., *Polym. J.*, 1985, **17**, 641.