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CONFORMATIONAL ISOMERISM OF THE CH_2—CH_2 BOND IN POLYBUTADIENES

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Abstract—The energy difference ΔE between *gauche* and *trans* conformers, resulting from rotation about single bonds of the chain backbone in *trans*-1,4-polybutadiene, *cis*-1,4-polybutadiene and 1,5-hexadiene, was evaluated from i.r. measurements on the bands characteristic of bending vibration of CH_2 groups. Consideration of the experimental results, on the basis of the rotational isomeric state model, leads to the conclusion that a value of 0·1–0·2 kcal mole^{-1} is the best estimate of ΔE.

INTRODUCTION

THE PROBLEM of stability of *gauche* and *trans* conformers resulting from rotation about single bonds of the chain backbone in polydiolefins has been recently discussed.$^{(1-4)}$

In order to contribute to a better knowledge of this phenomenon, we subjected to i.r. examination two such polymers (*trans*-1,4- and *cis*-1,4-polybutadiene) and a low-mol. wt. model compound (1,5-hexadiene). Our experimental results, quoted in the work by Allegra$^{(4)}$ on the unperturbed dimensions of *cis*-1,4-polybutadiene, were treated on the basis of the relationship proposed by Mizushima$^{(5)}$ for the i.r. evaluation of the energy difference ΔE between *gauche* and *trans* rotational isomers of substituted ethanes:

$$\frac{A_g}{A_t} = \frac{\varkappa_g}{\varkappa_t} \cdot \frac{2f_g}{f_t} \exp\left(\frac{\Delta E}{RT}\right), \tag{1}$$

where A_g and A_t are the absorbances of the bands characteristic of the two conformers, $\varkappa_g$ and $\varkappa_t$ their absorptivities, and f_g and f_t their Boltzmann probabilities. According

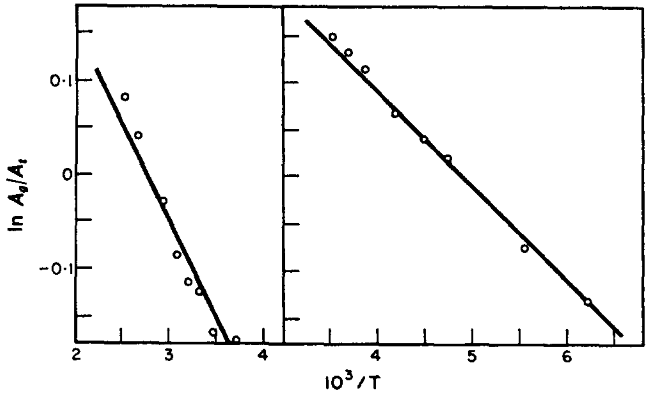

FIG. 1. Temperature variation of the absorbance ratio of the bands characteristic of *gauche* and *trans* conformers (left) in *trans*-1,4-polybutadiene, and (right) in 1,5-hexadiene.

to Eqn. (1), ln (A_g/A_t) is a linear function of $1/T$; from the slope of this straight-line one obtains ΔE. By applying this method (see Fig. 1), we found $\Delta E = +0 \cdot 2$, $+0 \cdot 4$ and $0 \cdot 0$ kcal mole^{-1} respectively, for 1,5-hexadiene, *trans*- and *cis*-1,4-polybutadiene, with an error of about $\pm$ 0·05 kcal mole^{-1}. By considering the essential similarity among the three molecules from the point of view of the investigated conformations and the possibility, neglected in our calculation, of solvent effects, an average value of $+0 \cdot 2$ kcal mole^{-1} was accepted for ΔE.

The representation of rotational isomerism given by Mizushima's model is over-simplified, in that it depicts conformers as arising from single rotations, whereas the successive rotational states along the chain are subjected to first-neighbour interactions so that the Boltzmann factors must be evaluated by taking into account the conformations of the whole chain.

On the basis of these considerations we have refined our procedure, by treating the problem in the light of the rotational isomeric state model, which accounts for the interdependence of bond rotational states. To this end, we followed a formalism like that employed by Mark,(2, 3) although somewhat simplified.

As will be discussed later, we obtain a slightly lower value (0·1–0·2 kcal mole^{-1}) for ΔE, which however seems to confirm that the *trans* form is energetically favoured over the *gauche* form.

EXPERIMENTAL

The existence of *trans* and *gauche* rotational isomers in *trans*-1,4- and *cis*-1,4-polybutadiene in the amorphous state (molten polymer or solution) and in 1,5-hexadiene is revealed by a splitting into two components of the bending vibration of CH_2 groups near 1450 cm^{-1}. By comparison with the spectra of 1,2-disubstituted ethanes and of crystalline *trans*-1,4-polybutadiene (where the CH_2 groups lying between two double bonds are undoubtedly in the *trans* conformation, as proved by X-ray analysis,(6) and absorb at 1450 cm^{-1}), the higher frequency band (1450 cm^{-1}) was attributed to deformation of CH_2 groups in the *trans* form, and the lower frequency band (1435 cm^{-1}) to deformation of CH_2 groups in the *gauche* form.(7)

The spectra were recorded on a Perkin-Elmer (Mod. 125) spectrophotometer. The bands at 1450 and 1435 cm^{-1} largely overlap at all temperatures; the absorbance readings were made with reference to a common base line: a tentative graphical resolution of these bands gave the same results.

The examination of *trans*-1,4-polybutadiene was carried out on the benzene extract of a sample, prepared as described by Natta *et al.*,(6) dissolved in tetrachloroethylene, over the temperature range −8° to +120°; lower temperatures could not be used because of the lack of solubility of the sample.

1,5-hexadiene was examined as such between −120° and +20°.

Cis-1,4-polybutadiene, prepared according to Natta *et al.*,(8) was examined both in C_2Cl_4 solution and in the amorphous phase, over the range 0° to +120°.

TRANS-1,4-POLYBUTADIENE

Trans-1,4-polybutadiene may be described by assigning to each skeletal bond a certain number of rotational states corresponding to minima in the bond torsional potentials (Table 1).

All rotational states are characterized by statistical weights, the values of which depend on those of the immediately adjacent skeletal bonds. In the case of interdependent rotational states, the conformational partition function for a chain may be obtained by means of matrices whose elements are the statistical weights relevant to the various conformations assumed by rotations about adjacent bond pairs: rows of these matrices are associated with rotational states of a given bond, and columns with states of the next bond.

TABLE 1. LOCATIONS OF ROTATIONAL STATES OF *trans*-1,4-POLYBUTADIENE CHAIN, MEASURED FROM A *cis* STATE OF 0°*

Bonds	Rotational states and angles
$=\mathrm{CH} \ominus \mathrm{CH_2}-$	*cis* (0°), *skew* (± 120°)
$-\mathrm{CH_2} \ominus \mathrm{CH_2}-$	*trans* (180°), *gauche* (± 60°)
$-\mathrm{CH_2} \ominus \mathrm{CH}=$	*cis* (0°), *skew* (± 120°)
$-\mathrm{CH}=\mathrm{CH}-$	*trans* (180°)

* Here and in the following discussion, we adopt the nomenclature of the Italian school (0° = *cis* conformation), which is different from that of Mark who uses 0° = *trans* conformation.

The values assigned by Mark to the various states(3) are listed in Table 2, in which all statistical weights are expressed relative to unity for the conformation (*skew*, *trans*, *skew*, *trans*) of the repeat units -[-CH_2—CH=CH—CH_2-]-.

TABLE 2. STATISTICAL WEIGHTS OF ROTATIONAL STATES IN *trans*-1,4-POLYBUTADIENE

From \ To	*trans*	*skew*	*gauche*	*cis*
*trans**		1		α
skew	1		σ	
gauche		1		$\beta\alpha$
cis	1		$\beta\sigma$	

* This state is characteristic both of double bonds (where it represents the only possibility) and of CH_2—CH_2 bonds (where also *gauche* states are possible).

The parameters α, β and σ are defined as $\alpha = \exp(-E_\alpha/RT)$, $\beta = \exp(-E_\beta/RT)$ and $\sigma = \exp(-E_\sigma/RT)$, the E's being the energies of the conformation associated with each statistical weight. The partition function Q for a chain containing N monomeric units may then be written:

$$Q = \left\{ \overline{\underline{\alpha\ 2}} \begin{bmatrix} 1 & 2\beta\sigma \\ 1 & 2\sigma \end{bmatrix} \begin{bmatrix} \alpha & 2 \\ \beta\alpha & 2 \end{bmatrix} \begin{bmatrix} 1 \\ 1 \end{bmatrix} \right\}^N = \{(2+\alpha)^2 + 2\sigma(2+\beta\alpha)^2\}^N$$

where the matrix $\overline{\underline{\alpha\ 2}}$ (= U_c with the Mark notation) is associated with transitions from rotational states of CH = CH bonds to those of CH—CH_2 bonds; the matrix $\begin{bmatrix} 1 & 2\beta\sigma \\ 1 & 2\sigma \end{bmatrix}$ (= U_d) with transitions from CH—CH_2 to CH_2—CH_2 bonds; the matrix $\begin{bmatrix} \alpha & 2 \\ \beta\alpha & 2 \end{bmatrix}$ (= U_a) with transitions from CH_2—CH_2 to CH_2—CH bonds; and the matrix $\begin{bmatrix} 1 \\ 1 \end{bmatrix}$ (= U_b) with transitions from CH_2—CH to CH=CH bonds. Factor 2 in the three former matrices accounts for the two possibilities of *skew* and *gauche* rotations. The ratio between the concentrations of *gauche* and *trans* bonds is thus given by

$$\frac{C_g}{C_t} = \frac{2\sigma(2+\beta\alpha)^2}{(2+\alpha)^2}. \tag{2}$$

According to Mark, $E_\alpha = 0{\cdot}03$ kcal mole^{-1}, $E_\sigma \sim 0$ and $E_\beta = 1{\cdot}1$ kcal mole^{-1}. With these values, when temperature is changed from 100° to 0°, C_g/C_t decreases from 1·135 to 1·04, i.e. by 8·4 per cent. The values of E_α, E_σ and E_β were deduced by Mark from the values of $\mathrm{d}\ln \langle r^2\rangle_0/\mathrm{d}T$ obtained from stress–temperature measurements; in several cases, the values of this derivative obtained by viscosity measurements in Θ solvents are drastically different.(9)

Hence it is not too surprising that the temperature variation of C_g/C_t, derived from our i.r. measurements, does not agree with the above result: in fact A_g/A_t amounts to 1·03 at 100° and to 0·84 at 0°; although this ratio cannot be transformed into the concentration ratio C_g/C_t (the absorptivities of the two bands being not known), the quantity $R = 1{\cdot}03/0{\cdot}84$ indicates that C_g/C_t decreases by 18·5 per cent between 100° and 0°.

Since Eqn. (2) contains three empirical parameters, our experimental result cannot be obviously reproduced by a unique set of values of α, β and σ; however, the direction in which these quantities should be varied may be found by trial, in order to improve the agreement. For this purpose, we will leave $E_\alpha = 0$ unaltered throughout the calculations* and change E_β from 0·5 to 1·5 kcal mole^{-1} and E_σ from 0 to 0·5 kcal

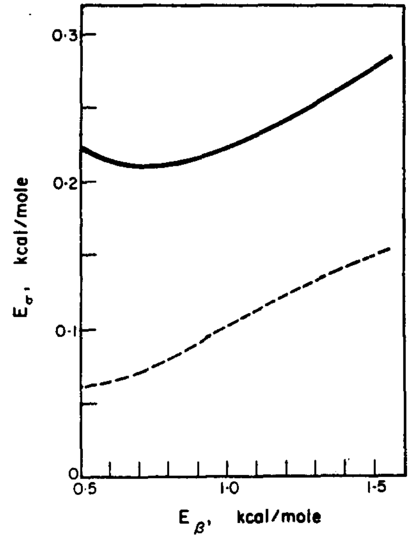

FIG. 2. Curves for which values of R, deduced from i.r. measurements, agree with values calculated by means of Eqn. (2). Solid curve refers to *trans*-1,4-polybutadiene, and dashed curve to 1,5-hexadiene.

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* It may be easily seen that, of the three quantities contained in Eqn. (2), the smallest effect is exerted by α, whose value is certainly not very different from unity.(3) On the other hand, the calculations required in the case of three variable parameters are very complex. Therefore our assumption $E_\alpha = 0$ ($\alpha = 1$) is justified from both theoretical and practical points of view.

mole^{-1}, determining the pairs (E_σ, E_β) for which $R_{\text{calc}} = R_{\text{exp}}$. As can be seen from Fig. 2, Eqn. (2) is more sensitive to variations of E_σ than of E_β, and the agreement with our data can be obtained only by assigning to E_σ a positive non negligible value, of at least 0·2 kcal mole^{-1}.

This result implies that the intrinsic internal energy associated with a *gauche* state of a —CH_2—CH_2 bond is higher than that associated with a *trans* state.

1,5-HEXADIENE

As far as the investigated conformations are concerned, 1,5-hexadiene is quite similar to *trans*-1,4-polybutadiene; hence consideration of its rotational states leads again to Eqn. (2). Such a result may be obtained either by the procedure followed for *trans*-1,4-polybutadiene, or by a procedure, described below, which does not resort to matrix techniques. The 1,5-hexadiene chain is schematically represented in Fig. 3.

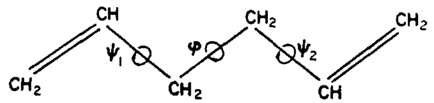

FIG. 3. Representation of the chain of 1,5-hexadiene with the angles of rotation about single bonds.

The splitting of the bending vibration of CH_2 groups observed in the i.r. spectrum arises from the possibility for the rotation angle φ about the CH_2—CH_2 bond to be in the *trans* or in the *gauche* form.*

According to the various conformations assumed by the CH—CH_2 and CH_2—CH bonds, conformers characterized by the statistical weights reported in Table 3 are obtained.

TABLE 3. STATISTICAL WEIGHTS FOR THE VARIOUS CONFORMERS IN 1,5-HEXADIENE

ψ_1	ψ_2	Multiplicity	w	
			$\varphi = \pm$ *gauche*	$\varphi =$ *trans*
± *skew*	± *skew*	4	$\sigma \cdot 1$	$1 \cdot 1$
cis	± *skew*	2	$\alpha \cdot \beta\sigma$	$\alpha \cdot 1$
± *skew*	*cis*	2	$\sigma \cdot \beta\alpha$	$\alpha \cdot 1$
cis	*cis*	1	$\alpha \cdot \beta\sigma \cdot \beta\alpha$	$\alpha \cdot \alpha$

The concentration ratio of *gauche* and *trans* bonds is given by the ratio of the sums of the terms of the two last columns of Table 3, each taken with its multiplicity:

$$\frac{C_g}{C_t} = \frac{2\sigma(4 + 4\alpha\beta + \alpha^2\beta^2)}{4 + 4\alpha + \alpha^2} = \frac{2\sigma(2 + \beta\alpha)^2}{(2 + \alpha)^2}.$$

It would be then expected that the temperature variation of C_g/C_t is equal to that found for *trans*-1,4-polybutadiene. Our i.r. measurements give a lower result:

$$R' = \frac{(C_g/C_t)_{0^\circ\text{C}}}{(C_g/C_t)_{-100^\circ\text{C}}} = \frac{1 \cdot 13}{0 \cdot 92} = 1 \cdot 23.$$

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* The *gauche* form may be realized in two ways.

Also in this case, application of Eqn. (2) with the numerical values of Mark gives a too low value, viz. $R' = 1{\cdot}04/0{\cdot}97 = 1{\cdot}07$. The determination of the pairs (E_σ, E_β) such that $R'_{\mathrm{calc}} = R'_{\mathrm{exp}}$ leads to values of E_σ smaller than those found for *trans*-1,4-polybutadiene (Fig. 2).

CIS-1,4-POLYBUTADIENE

The conformational analysis of the molecule of *cis*-1,4-polybutadiene can be made with reference to a simplified geometrical model$^{(2)}$ in which the two simple bonds adjacent to the double bond are extended so as to replace the three coplanar bonds by two effective (virtual) bonds (Fig. 4).

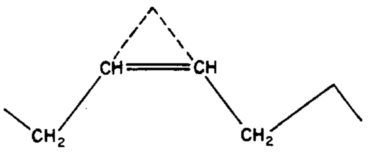

FIG. 4. Simplified representation of the *cis*-1,4-polybutadiene chain.

The statistical weight matrices are:

$$\begin{bmatrix} 1 & 2 \\ 1 & 2 \end{bmatrix} \quad (= U_a, \text{ with the Mark notation})$$

for transition from rotational states of bond CH_2—CH_2 to rotational states of bond CH_2—CH (the first CH_2 group belongs to the preceding molecule);

$$\begin{bmatrix} 0 & 2 \\ 1 & 2\gamma \end{bmatrix} \quad (= U_b) \text{ from bond } CH_2{-}CH \text{ to bond } CH{-}CH_2;$$

$$\begin{bmatrix} 1 & 2\sigma \\ 1 & 2\sigma \end{bmatrix} \quad (= U_c) \text{ from bond } CH{-}CH_2 \text{ to bond } CH_2{-}CH_2$$

(the last CH_2 group belongs to the subsequent molecule).

Here $\gamma = \exp(-E_\gamma/RT)$ is the statistical weight assigned to rotational pairs (+ *skew*, + *skew*) and (+ *skew*, − *skew*) about the two single bonds adjacent to the same double bond, relative to a statistical weight of unity for the pair (*trans*, + *skew*) and (+ *skew*, *trans*), and $\sigma = \exp(-E_\sigma/RT)$ is the statistical weight (relative to unity for *trans*) corresponding to + *gauche* states, irrespective of the rotational state of the preceding bond.

The conformational partition function for *cis*-1,4 polybutadiene can be then written*

$$Q = \mathrm{Spur}\left\{\begin{bmatrix} 1 & 2 \\ 1 & 2 \end{bmatrix} \begin{bmatrix} 0 & 2 \\ 1 & 2\gamma \end{bmatrix} \begin{bmatrix} 1 & 2\sigma \\ 1 & 2\sigma \end{bmatrix}\right\}^N =$$

$$= \mathrm{Spur}\begin{bmatrix} 2 + 4\gamma & 4\sigma + 8\sigma\gamma \\ 2 + 4\gamma & 4\sigma + 8\sigma\gamma \end{bmatrix}^N .$$

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* The different formalism employed for the evaluation of Q in *trans*-1,4- and *cis*-1,4-polybutadiene is due to the fact that a correlation exists in the latter case between single bonds separated by a double bond, whereas such a correlation does not exist in the former case.

For N large, indicated by λ the largest eigen value of the matrix, we have

$$Q = \lambda^N = (2 + 4\gamma + 4\sigma + 8\sigma\gamma)^N.$$

Hence the concentration ratio of the *gauche* and *trans* conformers is

$$\frac{C_g}{C_t} = \frac{4\sigma + 8\sigma\gamma}{2 + 4\gamma} = 2\sigma.$$

The analysis of our experimental data shows that the points on the plot (ln A_g/A_t, $1/T$) are more scattered than in the cases of *trans*-1,4-polybutadiene and of 1,5-hexadiene, and the variations of A_g/A_t over the whole temperature range are only slightly greater than the uncertainties at a given temperature. We might conclude that no significant difference exists between the energies of *gauche* and *trans* conformers; however, the dependence of A_g/A_t upon T, if any, is opposite to that found by Mark:⁽²⁾ a least-square calculation of the relationship between ln A_g/A_t and $1/T$ (assumed to be linear) gives $\Delta E \sim 0{\cdot}05$ kcal mole^{-1}, but the correlation coefficient, which indicates the goodness of fit, is low and the existence of such a linear relationship is rather doubtful.

CONCLUSIONS

The results of the i.r. examination of conformational isomers of *trans*- and *cis*-1,4-polybutadiene and of 1,5-hexadiene should be critically discussed before drawing conclusions that may either support or contradict the results obtained by other techniques. The main problem concerns their reliability. Except for *cis*-1,4-polybutadiene, accidental errors are rather low, so that application of error theory leads to confidence limits for E_σ within $\pm\, 0{\cdot}05$ kcal mole^{-1}, both in *trans*-1,4-polybutadiene and in 1,5-hexadiene.

However, we did not take into account possible solvent effects; it is perhaps reasonable to believe that they are mainly responsible for the actual differences among the figures obtained by us. As a consequence, the results found by means of i.r. spectroscopy may be more safely utilized for the evaluation of an average value of E_σ than for the comparison of the values relevant to the three substances examined.

As pointed out in the previous sections, our experimental results may be reproduced by an infinite set of values of the energies associated with the various concentrations; a reasonable choice would be:

for *trans*-1,4-polybutadiene	$E_\sigma = 0{\cdot}2 \div 0{\cdot}3$ kcal mole^{-1} $E_\beta = 0{\cdot}5 \div 1{\cdot}5$ kcal mole^{-1} $(E_\alpha = 0)$
for *cis*-1,4-polybutadiene	$E_\sigma = 0 \div 0{\cdot}05$ kcal mole^{-1}
for 1,5-hexadiene	$E_\sigma = 0{\cdot}05 \div 0{\cdot}15$ kcal mole^{-1} $E_\beta = 0{\cdot}5 \div 1{\cdot}5$ kcal mole^{-1} $(E_\alpha = 0)$.

By averaging the above figures, the best estimate for E_σ may be taken as $0{\cdot}1 \div 0{\cdot}2$ kcale mole^{-1}.

As far as allowed by the limitations of the experimental method outlined above, such a result supports the assumption made by Allegra(1) that the energy E_σ is positive in *cis*-1,4-polybutadiene, even if his value is probably exceedingly high.

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Résumé—A partir de mesures sur les bandes caractéristiques en i.r. de la vibration de flexion des groupements CH_2, on a évalué la différence d'énergie ΔE entre les conformations *gauche* et *trans* provenant d'une rotation autour de simples liaisons dans les squelettes du trans-polybutadiène-1,4, du *cis*-polybutadiène 1,4 et de l'hexadiène-1,5. L'interprétation des résultats expérimentaux à l'aide du modèle de l'état isomérique rotationnel conduit à prendre 0,1–0,2 kcal mole^{-1} comme valeur la plus probable de ΔE.

Sommario—Mediante misure all'i.r. sulle bande caratteristiche della vibrazione di bending del gruppo CH_2 si è valutata la differenza di energia ΔE fra i conformeri *gauche* e *trans* originati dalla rotazione intorno ai legami semplici della catena nel polibutadiene-1,4 *trans*, nel polibutadiene-1,4 *cis* e nell' esadiene-1,5. La considerazione dei risultati sperimentali in base al modello dello stato isomerico rotazionale porta alla conclusione che un valore medio di 0,1–0,2 kcal per mole può essere assunto come la migliore stima di ΔE.

Zusammenfassung—Die Energiediffer nz ΔE zwischen *gauche* und *trans* Konformationen, die in trans-1,4-Polybutadien, *cis*-1,4-Polybutadien und 1,5-Hexadien bei Rotation um Einfachbindungen der Hauptkette entstehen wurde durch Infrarotmessungen der für die Deformations-Schwingungen der CH_2-Gruppen charakteristischen Banden bestimmt. Eine Betrachtung der experimentellen Ergebnisse unter Zugrundelegung des Modells des Rotations-isomeren Zustandes führt zu dem Schluß, daß ein Wert von 0,1–0,2 kcal. Mol^{-1} die beste Abschätzung für ΔE darstellt.