Conformational Enthalpy Difference of *n*-Alkanes

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ABSTRACT: Pentane-3,3-d_2, pentane-3-*d*, hexane-3-*d*, heptane-3-*d* and nonane-4-*d* were synthesized. Normal coordinate calculations of these molecules were carried out to show that the frequencies of the CDH rocking vibration are in the region $700\,\mathrm{cm}^{-1}$–$650\,\mathrm{cm}^{-1}$ where protonated homologues are transparent. The frequencies were classified into three groups according to the conformation of the two bonds connected directly with the carbon atom in the CDH group. The enthalpy differences between the TG and TT types of the molecules were obtained from the temperature dependence of infrared spectra and found to be $580 \pm 20\,\mathrm{cal\,mol}^{-1}$.

KEY WORDS Rotational Isomer / *n*-Alkane / Deuterium Labelling / Enthalpy Difference / Infrared Spectra /

The enthalpy difference between the *gauche* (G) and *trans* (T) forms, $\Delta H_{\text{G-T}}$, of long *n*-alkanes, has a great importance in the study of short range interactions in polymer chains. The temperature dependence of vibrational spectra has been studied to determine the value of $\Delta H_{\text{G-T}}$. Verma *et al.*[1] obtained $966\,\mathrm{cal\,mol}^{-1}$ for the $\Delta H_{\text{G-T}}$ of gaseous butane from Raman spectra. Snyder[2] obtained $600\,\mathrm{cal\,mol}^{-1}$ for the enthalpy difference between the TG and TT forms, $\Delta H_{\text{TG-TT}}$, for liquid pentane using infrared spectra. He also obtained $1270\,\mathrm{cal\,mol}^{-1}$ for the $\Delta H_{\text{GG-TT}}$ of pentane. Shimanouchi and his co-workers[3] obtained $581\,\mathrm{cal\,mol}^{-1}$ for the $\Delta H_{\text{TG-TT}}$ of liquid pentane using Raman spectra. They also measured Raman spectra of hexane and hexane-d_{12}, to estimate the $\Delta H_{\text{TTG-TTT}}$ of these molecules and found the values to be in the range from 400 to $600\,\mathrm{cal\,mol}^{-1}$, but could not determine the precise value of $\Delta H_{\text{TTG-TTT}}$ because of the uncertainty in the relative contributions of other isomers. They suggest that the value of $\Delta H_{\text{TTG-TTT}}$ is on the side of $400\,\mathrm{cal\,mol}^{-1}$.

For higher homologues, the number of rotational isomers increases greatly with an increase in the number of carbon atoms in the chain. Since differences in vibrational frequencies of these isomers are too small to be resolved in the spectra and to be assigned definitely to the isomers, no reliable value

of $\Delta H_{\text{G-T}}$ for higher *n*-alkanes has as yet been reported. If the value of $\Delta H_{\text{G-T}}$ is $400\,\mathrm{cal\,mol}^{-1}$ for hexane, the value of $\Delta H_{\text{G-T}}$ for polymethylene must be smaller than $500\,\mathrm{cal\,mol}^{-1}$, which has been inferred from the value of $\Delta H_{\text{G-T}}$ of pentane without experimental evidence.[4]

In the study of local polymer conformations using model compounds, it is not necessary to know the total conformation of the model compounds, but just the local conformation at the assigned position of a model compound. In this report, an attempt has been made to elucidate the $\Delta H_{\text{G-T}}$ of higher *n*-alkanes in the liquid state from the analysis of local conformations in which deuterium is used as the label for infrared spectra.

EXPERIMENTAL

Deuterated samples were prepared at our laboratory. Pentane-3-*d*, hexane-3-*d*, and heptane-3-*d* were synthesized from the corresponding ketones *via* Grignard reagents as follows.

$$\begin{array}{l} C_2H_5\underset{\underset{O}{\|}}{C}C_nH_{2n+1} \xrightarrow[\quad]{} C_2H_5CHBrC_nH_{2n+1} \\ \qquad\qquad 1)\ LiAlH_4 \\ \qquad\qquad 2)\ HBr \\ \qquad\qquad \xrightarrow[\quad]{} C_2H_5CHDC_nH_{2n+1} \\ \qquad\qquad 1)\ Mg \\ \qquad\qquad 2)\ D_2O \end{array}$$

Pentane-3.3-d_2 was obtained from 3-pentanone *via* tosylhydrazone using the following reaction.

$$C_2H_5\underset{\underset{O}{\|}}{C}C_2H_5 \xrightarrow{\quad NH_2NHT_s \quad} C_2H_5\underset{\underset{NNHT_s}{\|}}{C}C_2H_5$$

$$\xrightarrow[\substack{1)\ LiAlD_4 \\ 2)\ D_2O}]{\quad\quad} C_2H_5CD_2C_2H_5$$
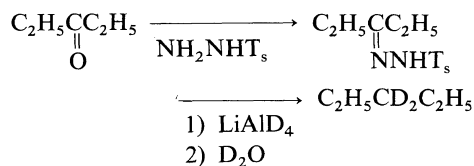
Nonane-4-*d* was obtained from 4-nonanone *via* tosylhydrazone with LiAlH$_4$ and D$_2$O.

These samples were purified with silver nitrate on an alumina column chromatograph to remove the main byproducts, alkenes, and were them carefully distilled. All samples showed single peaks on *glpc*. The deuterium content measured by a mass spectrometer was at least 95%.

Infrared spectra of these samples in the liquid state were recorded by an IR-G Infrared Spectrophotometer (Japan Spectroscopy Co.). For determination of the enthalpy difference, infrared spectra were recorded at several temperatures with a home-made KBr window cell which controlled temperature within $\pm 0.5°$C. Spectra were converted to optical densities and their overlapping bands were resolved by assuming a symmetrical shape for the TT and GG bands. The band intensities were measured by a graphical method.

Normal coordinate treatment of deuterated *n*-alkanes was carried out by the method of Wilson's GF matrix. Force constants of the local symmetry force field used were taken from the work of Shimanouchi *et al.*[5,6] Numerical computation was made on an M-200 at the Computer Center, Kyushu University, using the programs developed by the authors.

RESULTS AND DISCUSSION

Pentane-3,3-d_2

For pentane-3,3-d_2, the possible conformations are the TT, TG and GG forms, GG′ form being excluded owing to its steric hindrance. The spectrum of liquid pentane-3,3-d_2 in the 800 cm^{-1}–600 cm^{-1} region at room temperature is shown in Figure 1. There are three bands in the 680 cm^{-1}–600 cm^{-1} region and two bands in the 800 cm^{-1}–730 cm^{-1} region. These bands were analyzed on the basis of calculated potential energy distributions. The results are as follows. The frequencies due to the CD$_2$ rocking vibration lie between 680 cm^{-1}
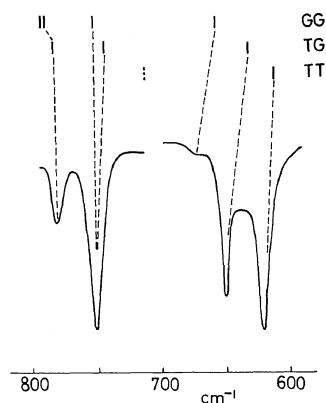
Figure 1. Infrared spectra of pentane-3,3-d_2. Vertical bars indicate the calculated wavenumbers for the rotational isomers.

and 600 cm^{-1}. The band at 621 cm^{-1} is assigned to the TT form. (The calculated value is 613 cm^{-1} and hereafter, calculated values are shown in parentheses.) The bands at 650 cm^{-1} is assigned to the TG form (633 cm^{-1}). The very weak shoulder at 670 cm^{-1} is assigned to the GG form (659cm^{-1}). The bands in the range between 800 cm^{-1} and 730 cm^{-1} are assigned to the CH$_2$ rocking vibrations. For the TT form, the a_2 species of CH$_2$ rocking mode of vibration (713 cm^{-1}) is infrared inactive due to molecular symmetry. The bands at 781 cm^{-1} and 752 cm^{-1} are overlapping bands of the TG form (785 cm^{-1} and 745 cm^{-1}) and GG form (792 cm^{-1} and 754 cm^{-1}), respectively. The agreement between the observed and calculated values is very satisfactory.

Pentane-3-d

The possible conformations of pentane-3-*d* are the TT, TG$_+$, TG$_-$, and GG forms. The spectrum of liquid pentane-3-*d* in the 800 cm^{-1}–600 cm^{-1} region at room temperature is shown in Figure 2. There are three bands in the 710 cm^{-1}–640 cm^{-1} region and at least four bands in the 800 cm^{-1}–720 cm^{-1} region. Assignment of these bands based on calculated potential energy distributions was made as follows. The bands in the 710 cm^{-1}–640 cm^{-1} region are assigned mainly to the CDH rocking vibration. The band at 660 cm^{-1} is assigned to the TT form (651 cm^{-1}). The band at 682 cm^{-1} is assigned to the overlapping band of the TG$_+$ (664 cm^{-1}) and TG$_-$ form (668 cm^{-1}). The very weak
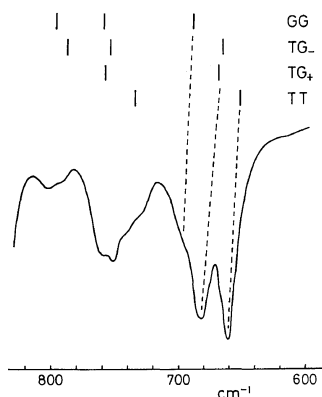
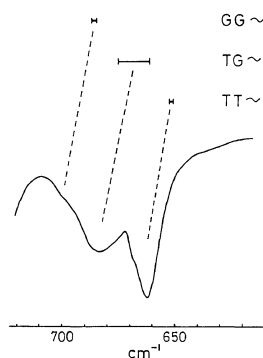Figure 2. Infrared spectra of pentane-3-*d*. Vertical bars indicate the calculated wavenumbers for the rotational isomers.

Figure 3. Infrared spectra of hexane-3-*d*. Horizontal bars indicate the range of calculated wavenumbers for the rotational isomers.

shoulder at 690 cm^{-1} is assigned to the GG form (688 cm^{-1}). The frequencies of the CH$_2$ rocking vibrations are in the 800 cm^{-1}–720 cm^{-1} range. The resolution of these complicated bands is so difficult that no assignment could be made for these bands.

Hexane-3-d

The spectrum of liquid hexane-3-*d* in the region 700 cm^{-1}–600 cm^{-1} at room temperature is shown in Figure 3. Three bands are seen at 662 cm^{-1}, 686 cm^{-1}, and 697 cm^{-1}. The number of possible conformations of hexane-3-*d* is 17, except the GG$'$ form. The calculated frequencies in the range 700 cm^{-1}–600 cm^{-1} are listed in Table I. These frequencies can be assigned to the CDH and the CH$_2$ rocking vibrations on the basis of calculated potential energy distributions. The calculated frequencies are classified into three groups. The frequencies around at 650 cm^{-1} are due to the TTT, TTG$_+$, and TTG$_-$ forms. The frequencies in the 670 cm^{-1}–660 cm^{-1} range are assigned to the TG$_+$X and the TG$_-$X forms, where X is either T, G$_+$, or G$_-$. The G$_+$G$_+$X and G$_-$G$_-$X forms have their frequencies in the 680 cm^{-1} region. It can be seen clearly that the frequencies of the CDH rocking vibrations mainly depend on the conformations of the two bonds connected directly to the carbon atom in the CDH group, and is less influenced by the conformations of the bonds not directly connected to the carbon atom in the CDH group. From this consideration, the bands in the 700 cm^{-1}–650 cm^{-1} region can be assigned as follows. The band at 662

Table I. The calculated frequencies of the CDH rocking vibration of the rotational isomers of hexane 3-*d*

Rotational isomer	Wavenumber cm^{-1}
TTT	653
TTG$_+$	652
TTG$_-$	650
TG$_+$T	668
TG$_-$T	662
G$_+$TT	666
G$_-$TT	672
TG$_+$G$_+$	667
TG$_-$G$_-$	662
G$_+$TG$_+$	667
G$_+$TG$_-$	664
G$_-$TG$_+$	673
G$_-$TG$_-$	667
G$_+$G$_+$T	686
G$_-$G$_-$T	687
G$_+$G$_+$G$_+$	687
G$_-$G$_-$G$_-$	686

cm^{-1} is due to an overlapping of the bands of the TTX type rotational isomers. The broad band at 686 cm^{-1} is due to overlapping of the bands of the TGX (and GTX) type rotational isomers. The weak shoulder at 697 cm^{-1} is due to overlapping of the bands of the GGX type rotational isomers. It is evident that the GGX type rotational isomers exist in the liquid state at room temperature.
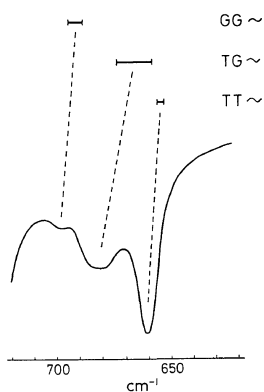
Figure 4. Infrared spectra of heptane-3-d. Horizontal bars indicate the range of calculated wavenumbers for the rotational isomers.
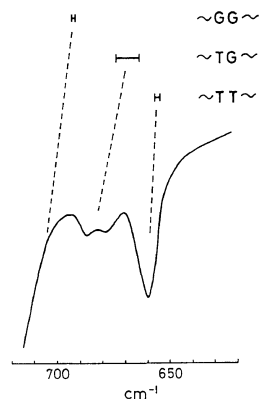

Figure 5. Infrared spectra of nonane-4-d. Horizontal bars indicate the range of calculated wavenumbers for the rotational isomers.

Heptane-3-d

The spectrum of liquid heptane-3-d in the 700 cm^{-1}–650 cm^{-1} region at room temperature is shown in Figure 4 in which three bands can be seen. For heptane-3-d, the number of possible conformations is 41. It is impossible to resolve and assign the observed bands to respective rotational isomers. Normal vibrational calculations of several rotational isomers of heptane-3-d showed that the frequencies of the CDH rocking vibration are in the 700 cm^{-1}–650 cm^{-1} region and can be classified into three groups as in the case of hexane-3-d. The calculated frequencies of the TTXY type rotational isomers are about 650 cm^{-1}. For the TGXY type rotational isomers, the calculated frequencies lie between 680 cm^{-1} and 660 cm^{-1}. For the GGXY type rotational isomers, the calculated values are approximately 690 cm^{-1}. (The symbols X and Y indicate T, G$_+$, or G$_-$, respectively.) The observed bands are assignable as follows. The band at 661 cm^{-1} is assigned to the TT type rotational isomers. The broad band at 682 cm^{-1} is assigned to the TG type rotational isomers. The weak shoulder at 698 cm^{-1} is assigned to the GG type rotational isomers. The shoulder at 698 cm^{-1} is the first reported evidence for the existence of the GG type rotational isomers in an *n*-alkane longer than hexane.

Nonane-4-d

The spectrum of liquid nonane-4-d at room temperature in the 700 cm^{-1}–600 cm^{-1} region is shown in Figure 5. A very strong tail of the 720

cm^{-1} band for the CH$_2$ rocking vibtation makes it difficult to analyzed the region between 700 cm^{-1} and 670 cm^{-1}. Two bands are observed in this region. Normal coordinate calculations also showed that the frequencies due to the CDH rocking vibrations were sensitive to the conformation of the two bonds connected directly to the carbon atom in the CDH group, but were insensitive to the conformation of other bonds, as in the cases of hexane-3-d and heptane-3-d. The band at 661 cm^{-1} may certainly be assigned to the TT type rotational isomers. The very broad double peak band at 680 cm^{-1} may be assigned to the TG type rotational isomers. The reason for the double peak is not clear at present, but it is evident that the peak at 690 cm^{-1} can not be assigned to the GG type rotational isomers because these two peaks have similar intensities and a similar temperature dependence. Clarification of these peaks will require further study.

Enthalpy Difference

In Figure 6, an example of band resolution is shown (hexane-3-d at 282.8 K). When the band shapes were symmetrical, the resolved area for the TT band could be determined certainly. The uncertainty of the GG band area had little influence on the TG band area since the GG area is about one-fifth of the TG band area. For determination of the enthalpy differences, the logarithm of the ratio between the band intensities of the TT type and of the TG type were plotted against the reciprocal of
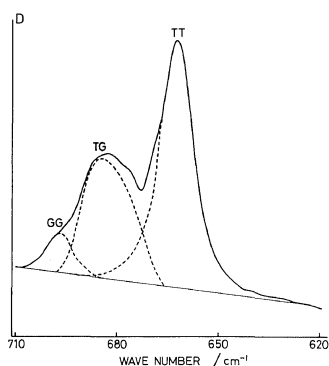
Figure 6. An example of band resolution. The sample is hexane-3-*d* at 282.8 K.
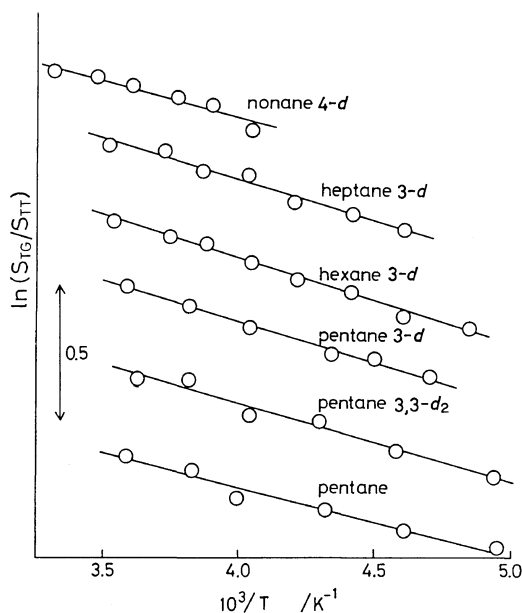

Figure 7. The plot of $\ln(S_{TG}/S_{TT})$ *vs.* $1/T$ for pentane and deuterated *n*-alkanes, where $S_{i,j}$ is the optical density (area) of the i, j rotational isomer.

temperature in Figure 7. The enthalpy difference of protonated pentane was determined using the bands in the 930 cm^{-1}–890 cm^{-1} region according to Snyder.[2] These bands were assigned to the CH$_3$ rocking vibration. The resolution of bands assigned to the CH$_2$ rocking vibration at about 720 cm^{-1} were very difficult. The obtained values of the $\Delta H_{TG\text{-}TT}$ were 492($\pm$37) cal mol^{-1}, 561($\pm$55) cal mol^{-1}, and 598($\pm$23) cal mol^{-1}, for pentane, pentane-3,3-*d*$_2$ and pentane-3-*d*, respectively. (The

value in parentheses is the standard deviation.) These values are in good agreement with each other and reported values by Snyder, 600 cal mol^{-1},[2] and by Shimanouchi *et al.*, 581 cal mol^{-1}.[3] The obtained values of the $\Delta H_{TG\text{-}TT}$ of hexane-3-*d*, heptane-3-*d*, and nonane-4-*d* were 619($\pm$21) cal mol^{-1}, 596($\pm$52) cal mol^{-1}, and 525($\pm$70) cal mol^{-1}, respectively. These values are in very good agreement with each other and the values of pentanes. This indicates that $\Delta H_{TG\text{-}TT}$ becomes constant, 580($\pm$20) cal mol^{-1}, for *n*-alkanes longer than butane. This value also may be correct for the value of the $\Delta H_{TG\text{-}TT}$ of polymethylene. The enthalpy difference $\Delta H_{GG\text{-}TT}$, could not be determined in this study, since the intensities of the bands related to the GG type of rotational isomers were very weak. According to Snyder,[2] about twice the value of $\Delta H_{TG\text{-}TT}$ was obtained for the $\Delta H_{GG\text{-}TT}$ of pentane. However, a more detailed analysis of the value of $\Delta H_{GG\text{-}TT}$ is necessary for higher *n*-alkanes.

CONCLUSION

n-Alkanes labelled by deuterium at assigned positions (pentane-3,3-*d*$_2$ pentane-3-*d*, hexane-3-*d*, heptane-3-*d*, and nonane-4-*d*) were synthesized. The temperature dependence of infrared spectra was measured. Normal coordinate calculations of these molecules were carried out for all rotational isomers of pentanes and hexane-3-*d*, and several rotational isomers of other molecules. These measurements and calculations showed that the frequencies of the CDH rocking vibrations are in the region of 700 cm^{-1}–650 cm^{-1}, where protonated homologues are transparent, and that the frequencies are classified into three regions, according to the conformation of the two bonds connected directly with the carbon atom in the CDH group. This means that the deuterium labelling is a powerful tool for studying local polymer conformations. The values of the enthalpy difference between the TG and TT forms for the above compounds were the same being, 580 ± 20 cal mol^{-1}. From this result, it follows that the value of $\Delta H_{TG\text{-}TT}$ for polymethylene is substantially equal to that for *n*-alkanes longer than butane.

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6. One of the referees kindly checked the frequencies of these molecules using a MVIB program. He indicated that the frequencies by MVIB are slightly higher (5—20 cm^{-1}) than ours and agree better with the observed values. The authors gratefully acknowledge this comment.