# Vibration Spectra and Rotational Isomerism of Chain Molecules. II.[1) Butane, Pentane, Hexane, Pentane-$d_{12}$, and Hexane-$d_{14}$

Issei Harada, Hideo Takeuchi,* Masaaki Sakakibara, Hiroatsu Matsuura,
and Takehiko Shimanouchi
*Department of Chemistry, Faculty of Science, University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113*

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The Raman spectra of butane, pentane, hexane, pentane-$d_{12}$, and hexane-$d_{14}$ and infrared spectra of pentane-$d_{12}$ and hexane-$d_{14}$ were measured for the liquid and solid states. The rotational isomerism of normal paraffins was studied on the basis of the spectral observations and the normal coordinate calculations. The spectra of the deuterated compounds were useful in the confirmation of the less stable isomers and the establishment of the local symmetry force field of normal paraffins. The enthalpy differences among the rotational isomers were studied on pentane and hexane, which yielded some important data for the study of the conformations and properties of longer hydrocarbons.

The study of the vibrational spectra and rotational isomerism of normal paraffins was started by Mizushima and coworkers[2) and Sheppard and coworkers[3) about thirty years ago.

More recently, Snyder *et al.*[4) treated this problem by the use of the newly observed infrared data and normal coordinate analysis and obtained the refined valence force field that could correlate the calculated frequencies with the observed frequencies satisfactorily for various isomers of normal paraffins. As the result, it has become clear that some bands that had been used for the determination of the enthalpy differences are possibly assigned to more than one vibrations of one form or different forms. The enthalpy difference between the *trans-gauche* (TG) and the *trans-trans* (TT) forms and that between the *gauche-gauche* (GG) and the TG forms of pentane have been estimated to be 600±100 cal/mol and 670±100 cal/mol, respectively.[4c)

Verma *et al.*[5) studied the temperature dependence of the Raman spectra of gaseous butane, 2-methylbutane and 2,3-dimethylbutane. They could resolve the Raman bands which had been observed as single bands and obtained the enthalpy difference of 966±54 cal/mol between the G and T forms of butane.

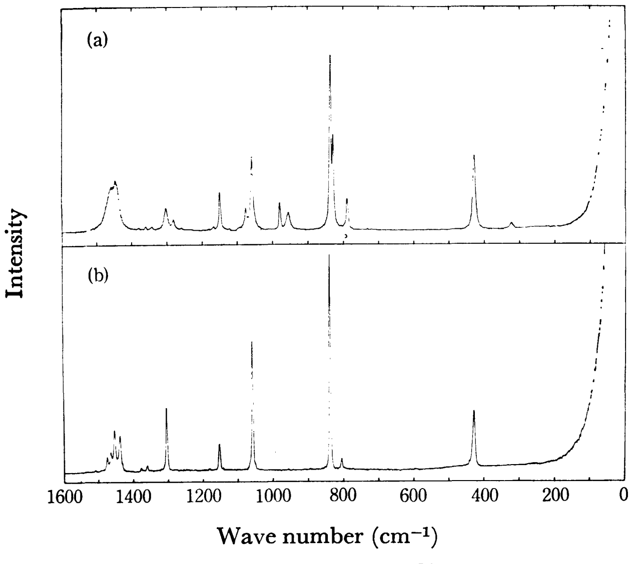

Fig. 1. Raman spectra of butane.
(a) Liquid (−70 °C), b) solid.

In pursuit of the studies on the vibration spectra and rotational isomerism of chain molecules,[1,6,7) we investigated the vibration spectra of normal paraffins and perdeuterated normal paraffins and obtained the refined local symmetry force field that explained the frequencies

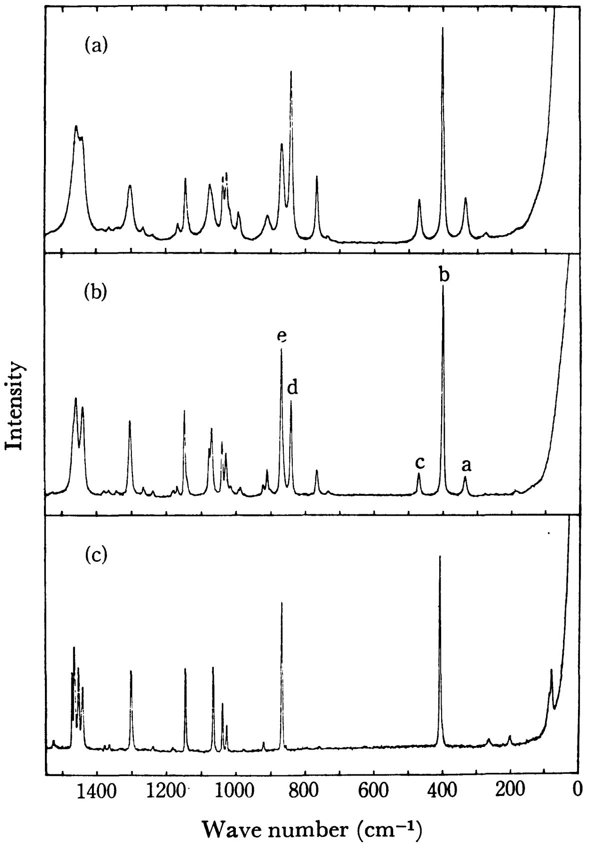

Fig. 2. Raman spectra of pentane.
(a) Liquid (25 °C), (b) liquid (−106 °C), (c) solid (−176 °C).
The temperature dependence of the intensities of the bands a through e was examined (see text and Tables 6 and 7).

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* Present address: Department of Chemical Engineering and Chemical Technology, Imperial College, London SW7 2BY, England.

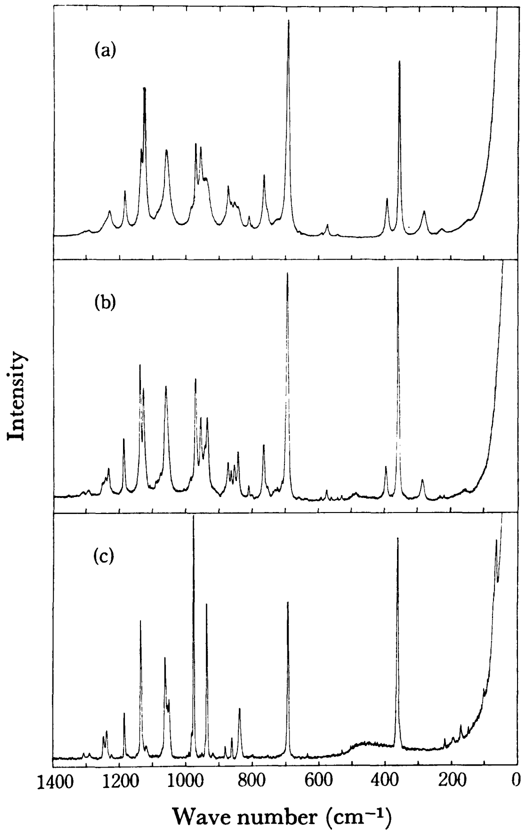

Fig. 3. Raman spectra of pentane-$d_{12}$.
(a) Liquid (23 °C), (b) liquid (−100 °C), (c) solid.

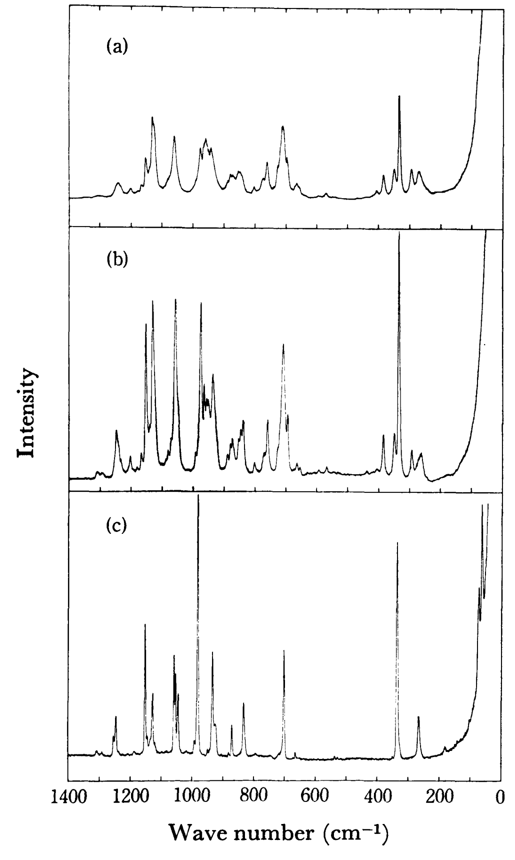

Fig. 5. Raman spectra of hexane-$d_{14}$.
(a) Liquid (23 °C), (b) liquid (−95 °C), (c) solid.

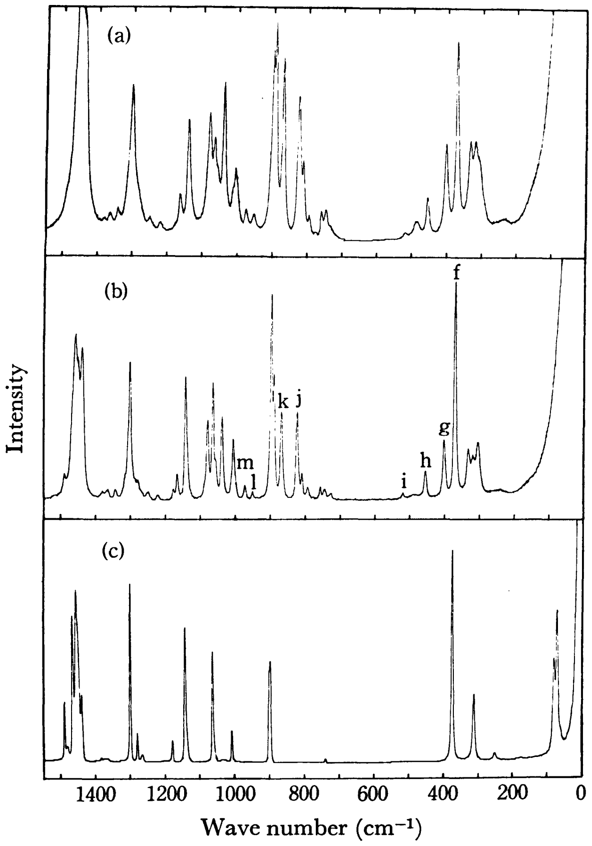

Fig. 4. Raman spectra of hexane.
(a) Liquid (23 °C), (b) liquid (−88 °C), (c) solid (−153 °C).
The temperature dependence of the intensities of the bands f through m was examined (see text and Tables 6 and 7).

of both species. In the course of the research, several new findings including the identification of the less stable rotational isomers and the determination of the enthalpy differences among the isomers of pentane and hexane in the liquid state have been obtained. The present paper describes the rotational isomerism and vibrational assignments of butane, pentane, hexane, pentane-$d_{12}$, and hexane-$d_{14}$.

## Experimental

Butane (stated purity of 98%) was supplied by Tokyo Kasei Kogyo Co., Ltd. and was used without further purification. Highly pure samples (stated purity of 99.9%) of pentane and hexane were purchased from Tokyo Kagaku Seiki Co., Ltd. and were distilled prior to the measurements. Pentane-$d_{12}$ and hexane-$d_{14}$ (stated purity of 98%) were obtained from Merck, Sharp, and Dohme of Canada and were transferred to ampoule Raman cells by the use of a vacuum system. The spectrometers used are the same as those in the previous study.[1]

The Raman spectra were recorded in the region below 1600 cm$^{-1}$. The measurements of the spectra at low temperatures were performed in the same way as that in a previous study.[8] Liquid nitrogen and liquid-nitrogen cooled ethanol were used as the cooling agent. For the determination of the enthalpy difference, the Raman spectra were recorded twice

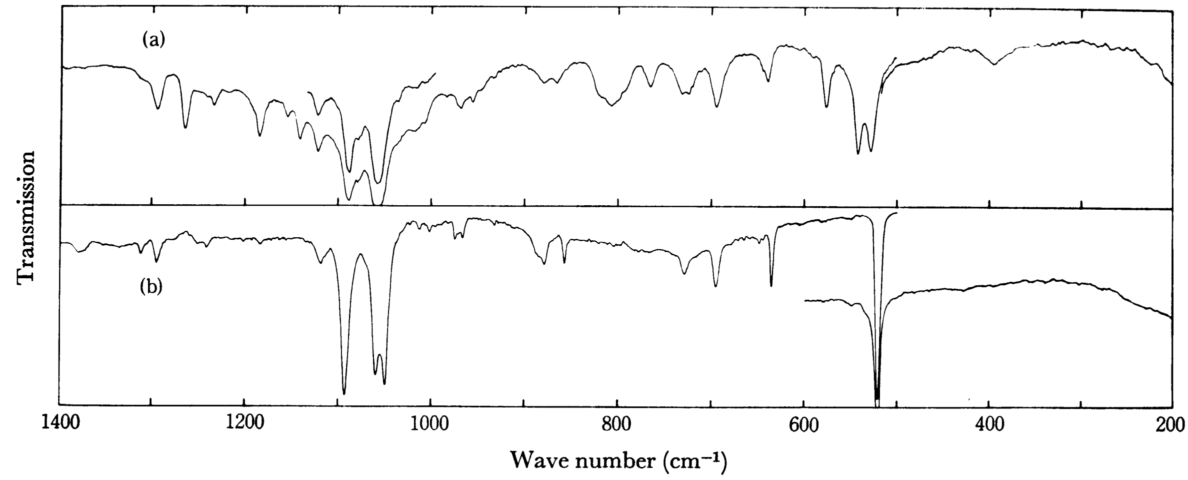

Fig. 6. Infrared spectra of pentane-$d_{12}$.
(a) Liquid, (b) solid.

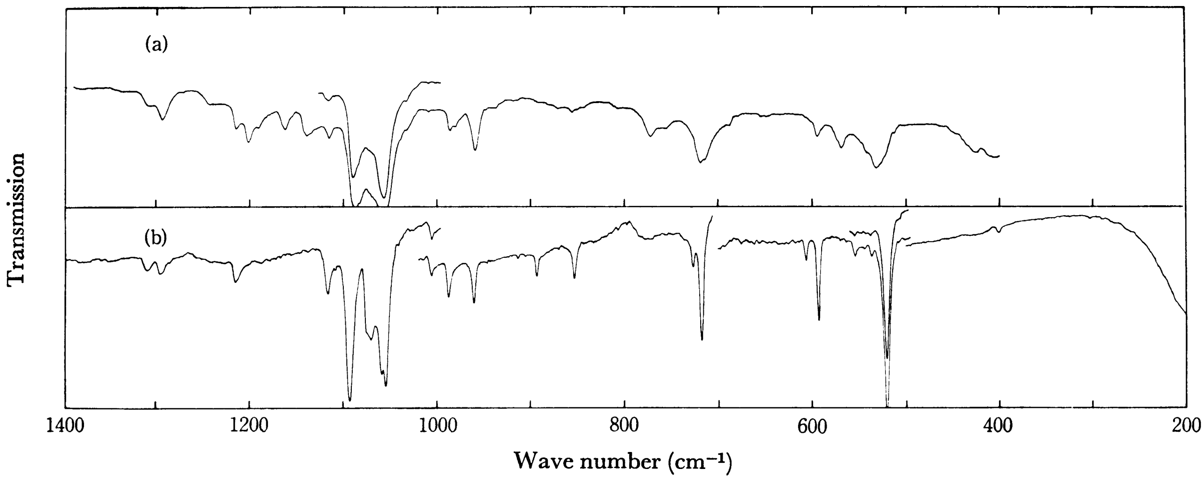

Fig. 7. Infrared spectra of hexane-$d_{14}$.
(a) Liquid, (b) solid.

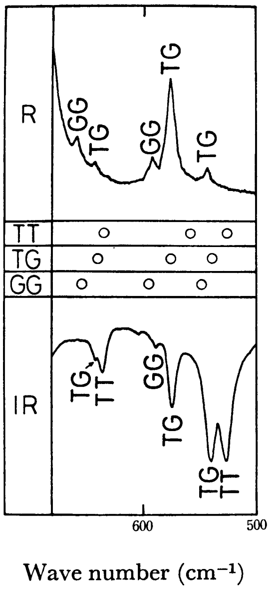

Fig. 8. Comparison of the observed spectra and calculated frequencies of pentane-$d_{12}$.

at each of ten different temperatures between −111 and 23 °C for pentane and at each of eight different temperatures between −89 and 23 °C for hexane.

Infrared spectra of pentane-$d_{12}$ and hexane-$d_{14}$ in the solid and liquid states were measured in the region 1600—400 cm$^{-1}$.

## Normal Coordinate Treatment

The normal coordinate treatment of normal paraffin molecules was carried out in a way similar to the case of the ethers.[1] The molecules treated are: butane, pentane, hexane, pentane-$d_{12}$, hexane-$d_{14}$, poly(ethylene), and poly(ethylene-$d_4$). Detailed results including structural parameters, symmetry coordinates, and force constants are reported in a separate paper.[9]

A total of 45 force constants of normal paraffins were determined from 254 Raman and infrared frequencies of 14 forms of the seven molecular species.**

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** Some of the observed frequencies were assigned to more than one vibrations of the same isomer or different isomers. However each of these frequencies was counted as one.

TABLE 1. OBSERVED RAMAN FREQUENCIES OF BUTANE IN $cm^{-1}$ AND ASSIGNMENTSa)

| Liquid (−70 °C) | Solid | Assignment |
|---|---|---|
| 1474 VW, sh$^{b),c)}$ | 1475 VW$^{b)}$ | $CH_3$ ip-d-deform (**T**) |
| 1463 VW, sh$^{b),c)}$ | 1464 VW$^{b)}$ | |
| 1455 W | 1454 VW | $CH_3$ op-d-deform (**T**, G) |
| 1441 W | 1438 VW | $CH_2$ scis (**T**),<br>$CH_3$ ip-d-deform (G) |
| | 1377 VW | $CH_3$ s-deform (**T**) |
| 1360 VW | 1360 VW | $CH_2$ wag (**T**) |
| 1343 VW | | $CH_2$ wag (**G**) |
| 1303 VW | 1304 W | $CH_2$ twist (**T**) |
| 1281 VW | | $CH_2$ twist (**G**) |
| 1181 VW | 1182 W | $CH_2$ rock (**T**) |
| 1168 VW | | $CH_2$ rock (**G**) |
| 1150 W | 1153 VW | $CH_3$ ip-rock (**T**) |
| 1076 VW | | CC stretch (**G**) |
| 1058 M | 1059 S | CC stretch (**T**) |
| 979 VW | | $CH_3$ ip-rock (**G**) |
| 956 VW | | CC stretch (**G**) |
| 837 VS | 838 VS | CC stretch (**T**) |
| 829 M | | CC stretch (**G**) |
| | 805 VW | $CH_3$ op-rock (**T**) |
| 789 VW | | $CH_3$ op-rock (**G**) |
| 430 M | 428 W | CCC deform (**T**) |
| 323 VW | | CCC deform (**G**) |

a) There is a possibility that the bands observed only in the solid state are components of crystal field splittings. For the notation and definition of the local symmetry coordinates, see Ref. 10. VS: very strong, S: strong, M: medium, W: weak, VW: very weak, sh: shoulder. b) The two Raman bands are due to the Fermi resonance between the $CH_3$ ip-d-deform vibration ($a_g$) and the overtone of the $CH_2$ rocking vibration ($a_u$). c) Observed at −140 °C.

TABLE 2. OBSERVED RAMAN FREQUENCIES OF PENTANE IN $cm^{-1}$ AND ASSIGNMENTSa)

| Liquid (−106 °C) | Solid (−176 °C) | Assignment |
|---|---|---|
| 1526 VW | 1527 VW | 2 × $CH_2$ rock ($a_2$) (**TT**) |
| | 1473 M | $CH_2$ scis (**TT**) |
| 1465 W, sh | 1467 M | $CH_3$ op-d-deform (**TT**) |
| 1458 M | 1454 M | $CH_3$ ip-d-deform (**TT**) |
| 1450 W, sh$^{b)}$ | | $CH_3$ ip-d-deform (**TG**) |
| 1438 M | 1442 W | $CH_2$ scis (**TT**) |
| 1379 VW | 1378 VW | $CH_3$ s-deform (**TT**, TG) |
| 1365 VW | 1365 VW | $CH_2$ wag (**TT**, TG) |
| 1343 VW | | $CH_2$ wag (**TG**) |
| 1303 W | 1303 M | $CH_2$ twist (**TT**),<br>$CH_2$ wag (TG) |
| 1265 VW | | $CH_2$ twist (**TG**) |
| 1238 VW | 1239 VW | $CH_2$ twist (**TT**, TG) |
| 1179 VW | 1182 VW | $CH_2$ rock (**TT**) |
| 1167 VW | | $CH_2$ rock (**TG**) |
| 1146 M | 1146 M | $CH_3$ ip-rock (**TT**) |
| 1140 VW, sh | | $CH_3$ ip-rock (**TG**) |
| 1075 W | | CC stretch (**TG**) |
| 1068 W | 1066 M | CC stretch (**TT**) |
| 1038 W | 1039 W | CC stretch (**TT**) |
| 1027 W | 1027 VW | CC stretch (**TT**, TG) |
| 1015 VW | | $CH_3$ op-rock (**TG**) |
| 992 VW | | CC stretch (**TG**) |
| 986 VW | 982 VW | $CH_3$ op-rock (**TT**) |
| 920 VW | 921 VW | CC stretch (**TT**) |
| 909 VW | | $CH_3$ ip-rock (**TG**) |
| 900 VW | | $CH_3$ ip-rock (**GG**) |
| 868 S | 870 S | $CH_3$ ip-rock (**TT**),<br>$CH_3$ op-rock (TG) |
| | 857 VW | $CH_3$ op-rock (**TT**) |
| 841 M | | CC stretch (**TG**) |
| 766 W | 760 VW | $CH_2$ rock (**TT**, TG) |
| 733 VW | | $CH_2$ rock (**TG**) |
| 471 W | | CCC deform (**TG**) |
| 403 VS | 409 VS | CCC deform (**TT**) |
| 337 W | | CCC deform (**TG**) |
| 276 VW$^{b)}$ | | CCC deform (**TG**) |
| | 265 VW | CCC deform, torsions |
| 190 VW | 203 VW | |
| | 86 VW, sh | Lattice vibrations |
| | 80 W | |

a) The observed bands are assigned to the individual vibrations of the TT and TG forms. The vibration of the GG form is identified in the table when the band is assigned only to this form. There is a possibility that the bands observed only in the solid state are components of crystal field splittings. For the notation and definition of the local symmetry coordinates, see Ref. 10. VS: very strong, S: strong, M: medium, W: weak, VW: very weak, sh: shoulder. b) Observed at room temperature.

## Results and Discussion

Figures 1—7 show the Raman and infrared spectra in the liquid and solid states of the molecules. In Figs. 2 and 4, the comparatively isolated bands for which the dependence of the relative intensities on temperature has been examined are identified by letters a through e for pentane and f through m for hexane. The observed frequencies and the assignments based on the calculated potential-energy distributions are listed in Tables 1—5. In the column of assignment in each table, the conformation symbol given by boldface indicates that the corresponding frequency is definitely assigned to the rotational isomer based solely on the experimental result or almost definitely assigned based on the combined results of the experiments and normal vibration calculations. The apparent enthalpy differences calculated by assuming that the intensity of each of the bands is due to one rotational isomer are tabulated in Table 6 and possible assignments of the bands a through m are listed in Table 7. Part of the observed spectra and calculated frequencies of pentane-$d_{12}$ are compared in Fig. 8.

*Butane (See Fig. 1 and Table 1).* Verma *et al.*5) studied the Raman spectra of this molecule in the gaseous and solid states for the purpose of determining the enthalpy difference between the rotational isomers, but reported only the spectra in the regions 900—750 $cm^{-1}$ and 450—300 $cm^{-1}$. Figure 1 and Table 1 give the Raman frequency data below 1600 $cm^{-1}$ obtained in the present measurements and the assignments. The band at 421 cm$^{-1}$ observed and assigned to the G form by Verma *et al.*[5] is missing in the spectrum in the liquid state at −70 °C. By comparison of the relative intensities of the band and other *gauche* bands, this band is assigned to a hot band or combination band of the T form. The two bands at 842 and 833 cm$^{-1}$ observed in the gaseous state[5] are also resolved at 837 and 829 cm$^{-1}$ in the liquid state at −70 °C. The bands at 1475 and 1464 cm$^{-1}$ observed in the solid state may be due to the Fermi resonance between the $CH_3$ ip-d-deformation vibration ($a_g$) and the overtone of the $CH_2$ rocking vibration ($a_u$).

*Pentane and Pentane-*$d_{12}$ *(See Figs. 2, 3, 6 and 8, and Tables 2 and 3).* The possible conformations are TT, TG, GG, and GG′, of which GG′ may be the least stable because of the steric hindrance. The spectra in the solid state are consistent with the calculated frequencies for the TT form. The spectra in the liquid state are mostly explained by the coexistence of the TT and TG forms. The intensities of the bands at 659 and 592 cm$^{-1}$ of pentane-$d_{12}$ observed at room temperature decrease significantly on cooling compared with those of the TG

Table 3. Observed frequencies of pentane-$d_{12}$ in cm$^{-1}$ and assignments[a]

| Liquid | | Solid | | Assignment |
|---|---|---|---|---|
| Raman (−100 °C) | Infrared | Raman | Infrared | |
| 1307 VW[b] | 1310 VW, sh[b] | 1307 VW[b] | 1312 VW[b] | |
| 1292 VW[b] | 1294 VW[b] | 1290 VW[b] | 1295 VW[b] | |
| 1247 VW, sh[b] | 1254 W[b] | 1247 VW[b] | 1252 VW[b] | |
| 1238 VW | | 1238 VW | 1242 VW | CC stretch (**TT**) |
| 1230 VW | 1233 VW | | | CC stretch (**TG**) |
| 1184 W | 1185 W | 1184 VW | 1184 VW | CC stretch (**TT**, TG) |
| | 1156 VW | | | CC stretch (**GG**) |
| 1142 VW, sh | 1143 VW | | | CC stretch (**TG**) |
| 1135 M | | 1135 M | | CC stretch (**TT**) |
| 1125 M | 1124 W | | | $CD_2$ scis (**TG**) |
| | | 1119 VW | 1119 VW | $CD_2$ scis (**TT**) |
| 1088 VW, sh | 1090 VS | | 1092 VS | $CD_2$ scis (**TT**) |
| 1074 VW, sh | 1079 VW, sh | | | $CD_2$ scis (**TG**) |
| 1057 M | 1057 VS | 1062 M | 1059 VS | $CD_3$ s-deform (**TT**, TG) |
| | | 1055 W, sh | | $CD_3$ s-deform (**TT**) |
| | | 1050 W | 1049 VS | $CD_3$ d-deform (**TT**) |
| | 1036 VW, sh | | | $CD_2$ wag (**TG**) |
| | 1020 VW[b] | | | |
| | 1008 VW, sh | | 1013 VW | $CD_2$ wag (**TT**) |
| | | | 1002 VW[b] | |
| 984 VW, sh | | 982 VW, sh | | $CD_2$ rock (**TT**, TG) |
| 968 M | 970 VW | 976 VS | 975 VW | $CD_2$ scis (**TT**), $CD_3$ op-rock (**TT**, TG) |
| | | | 967 VW | $CD_2$ twist (**TT**) |
| 953 M | 957 VW | | | $CD_2$ twist (**TG**) |
| 942 VW, sh | | | | $CD_2$ scis (**TG**) |
| 934 W | | 937 VS | | $CD_2$ twist (**TT**, TG) |
| | | | 896 VW, sh[b] | |
| | 881 VW | 882 VW | 879 VW | CC stretch (**TT**) |
| 873 VW | 867 VW | | | CC stretch (**TG**) |
| 863 VW | | 862 VW | 857 VW | $CD_2$ wag (**TT**) |
| 853 VW | | | | $CD_2$ wag (**TG**) |
| 842 W | | 838 W | | $CD_2$ wag (**TT**) |
| | 820 VW, sh[b] | | | |
| 810 VW[b] | 808 W, b[b] | | | |
| 802 VW | 794 VW, sh | | | $CD_2$ twist (**GG**) |
| 764 W | 767 VW | | | $CD_2$ wag (**TG**) |
| 753 VW, sh | | | | $CD_2$ twist (**TG**) |
| 730 VW | 732 VW | | 728 VW | $CD_3$ ip-rock (**TT**) |
| 723 VW | 726 VW | | | $CD_3$ ip-rock (**TG**) |
| 629 VS | 695 W | 693 S | 695 VW | $CD_3$ ip-rock (**TT**, TG) |
| 659 VW, sh | | | | $CD_2$ rock (**GG**) |
| 641 VW | 643 VW, sh | | | $CD_3$ op-rock (**TG**) |
| | 638 VW | 635 VW | 635 W | $CD_3$ op-rock (**TT**) |
| 592 VW | 589 VW | | | $CD_3$ op-rock (**GG**) |

Table 3. (Continued)

| Liquid | | Solid | | Assignment |
|---|---|---|---|---|
| Raman (−100 °C) | Infrared | Raman | Infrared | |
| 575 VW | 576 VW | | | $CD_2$ rock (**TG**) |
| | | | 550 VW | $CD_2$ rock (**TT**) |
| 542 VW | 542 M | | | $CD_2$ rock (**TG**) |
| 530 VW | 528 M | 529 VW | 522 VS | $CD_2$ rock (**TT**) |
| 397 VW | | | | CCC deform (**TG**) |
| 358 VS | | 362 VS | | CCC deform (**TT**) |
| 287 VW | | | | CCC deform (**TG**) |
| 233 VW | | | | CCC deform (**TG**) |
| | | 195 VW | | CCC deform, torsions |
| | | 172 VW | | |
| 157 VW | | | | |
| | | 69 W | | Lattice vibration |

a) The observed bands are assigned to the individual vibrations of the TT and TG forms. The vibration of the GG form is identified in the table when the band is assigned only to this form. There is a possibility that the bands observed only in the solid state are components of crystal field splittings. For the notation and definition of the local symmetry coordinates, see Ref. 10. VS: very strong, S: strong, M: medium, W: weak, VW: very weak, sh: shoulder, b: broad. b) Assigned to the partially deuterated compounds or origin unknown.

TABLE 4. OBSERVED RAMAN FREQUENCIES OF HEXANE IN $cm^{-1}$ AND ASSIGNMENTS[a)]

| Liquid (−88 °C) | Solid (−153 °C) | Assignment |
|---|---|---|
| 1489 VW | 1489 W | $CH_2$ scis (**TTT**, TTG, TGT) |
| | 1480 VW | 2 × $CH_2$ rock ($b_g$) (**TTT**) |
| | 1466 S | $CH_3$ op-d-deform (**TTT**) |
| 1457 S | 1456 S | $CH_3$ ip-d-deform (**TTT**, TTG),<br>$CH_2$ scis (TGT) |
| 1450 VW, sh | 1450 VW, sh | 2 × $CH_2$ rock ($a_u$) (**TTT**) |
| 1438 S | 1440 W | $CH_2$ scis (**TTT**, TTG),<br>$CH_3$ ip-d-deform (TGT) |
| 1380 VW | 1383 VW | $CH_3$ s-deform (**TTT**, TTG, TGT) |
| 1365 VW | 1370 VW | $CH_2$ wag (**TTT**, TTG, TGT) |
| 1343 VW | | $CH_2$ wag (**TTG**) |
| 1315 VW, sh | | $CH_2$ wag (GTG) |
| 1302 S | 1301 VS | $CH_2$ twist (**TTT**, TTG),<br>$CH_2$ wag (**TTT**, TGT) |
| 1280 VW | 1280 VW | $CH_2$ twist (**TTT**, TTG) |
| | 1265 VW[b)] | |
| 1250 VW | | $CH_2$ wag (**TTG**) |
| 1222 VW | | $CH_3$ op-rock (TTG, TGT) |
| 1178 VW | 1179 VW | $CH_2$ rock (**TTT**) |
| 1167 VW | | $CH_2$ rock (TTG, TGT) |
| 1143 M | 1143 S | $CH_3$ ip-rock (**TTT**),<br>CC stretch (TGT) |
| 1080 W | | CC stretch (TTG, TGT) |
| 1065 M | 1064 M | CC stretch (**TTT**) |
| 1057 VW, sh | | CC stretch (**TTG**) |
| 1039 W | | CC stretch (TTG),<br>$CH_3$ ip-rock (TGT) |
| 1007 W | 1008 W | CC stretch (**TTT**, TGT),<br>$CH_2$ twist (TTG) |
| 975 VW | | CC stretch (**TTG**) |
| 952 VW | | CC stretch (GTG, GTG′) |
| | 900 VW, sh | $CH_3$ ip-rock (**TTT**) |
| 899 VS | 898 M | $CH_3$ op-rock (**TTT**, TTG, TGT) |
| 891 M | | $CH_3$ ip-rock (**TTG**) |
| 870 M | | CC stretch (**TTG**) |
| 824 M | | CC stretch (**TGT**) |
| 811 VW | | $CH_2$ rock (**TGT**) |
| 794 VW | | $CH_2$ rock (**TTG**) |
| 758 VW | | $CH_2$ rock (**TTG**) |
| 746 VW | | $CH_2$ rock (**TGT**) |
| | 739 VW | $CH_2$ rock (**TTT**) |
| 727 VW | | $CH_2$ rock (TTG, TGT) |
| 520 VW | | CCC deform (**TGT**) |
| 488 VW, b | | CCC deform (TGG, GTG) |
| 456 VW | | CCC deform (**TTG**) |
| 402 W | | CCC deform (**TTG**) |
| 372 VS | 376 VS | CCC deform (**TTT**) |
| 332 W | | CCC deform (**TGT**) |
| 320 VW | | CCC deform (**TTG**) |
| 305 VW | 313 W | CCC deform (**TTT**) |
| 240 VW, b | 251 VW | Torsions |
| | 175 VW, b | |
| | 81 M | Out-of-plane rotatory lattice vibration[c)] |
| | 72 S | In-plane rotatory lattice vibration[c)] |

a) The observed bands are assigned to the individual vibrations of the TTT, TTG, and TGT forms. The vibrations of the TGG, GTG, and GTG′ forms are identified in the table when the bands are assigned to these forms but not to the TTT, TTG, or TGT form. The crystal structure of hexane is P1 ($C_i^1$), $Z = 1$ [N. Norman and H. Mathisen, *Acta Chem. Scand.*, **15**, 1755 (1961)]. Accordingly, no crystal field splitting is expected in the spectrum of the solid state. For the notation and definition of the local symmetry coordinates, see Ref. 10. VS: very strong, S: strong, M: medium, W: weak, VW: very weak, sh: shoulder, b: broad. b) Origin unknown. c) H. Takeuchi, T. Shimanouchi, M. Tasumi, G. Vergoten, and G. Fleury, *Chem. Phys. Lett.*, **28**, 449 (1974).

TABLE 5. OBSERVED FREQUENCIES OF HEXANE-$d_{14}$ IN $cm^{-1}$ AND ASSIGNMENTS[a]

| Liquid | | Solid | | Assignment |
|---|---|---|---|---|
| Raman (−95 °C) | Infrared | Raman | Infrared | |
| 1309 VW[b] | 1306 VW[b] | 1307 VW[b] | 1309 VW[b] | |
| 1293 VW[b] | 1293 W[b] | 1290 VW[b] | 1294 VW[b] | |
| | | 1252 VW[b] | | |
| 1246 W | | 1245 VW | | CC stretch (**TTT**) |
| 1241 VW | 1242 VW | | | CC stretch (**TTG**) |
| 1232 VW | | | | CC stretch (**TGT**) |
| | 1214 W | | 1214 VW | CC stretch (**TTT**, TGT) |
| 1201 VW | 1201 M | | | CC stretch (**TTG**) |
| | 1190 W[b] | 1186 VW[b] | | |
| 1179 VW | | | | CC stretch (TGG, GTG, GTG′) |
| 1166 VW | 1162 W | | | CC stretch (**TTG**) |
| 1152 S | | 1151 M | | CC stretch (**TTT**), $CD_2$ scis (TGT) |
| | | 1144 VW[b] | | |
| 1138 VW | 1139 W | | | $CD_2$ scis (**TTG**) |
| | | 1135 VW, sh[b] | | |
| 1130 S | | 1127 W | | $CD_2$ scis (**TTT**, TGT), CC stretch (TTG, TGT) |
| | | 1118 VW, sh[b] | | |
| | 1115 W | | 1115 W | CC stretch (**TTT**) |
| | 1090 VS | | 1092 VS | $CD_2$ scis (**TTT**) |
| 1080 VW | | | | $CD_2$ scis (TTG, TGT) |
| 1070 VW[b] | 1070 W, sh[b] | | 1070 S[b] | |
| 1057 S | 1057 VS | 1058 M | 1059 VS | $CD_2$ scis (**TTT**, TTG, TGT), $CD_3$ s-deform (**TTT**, TTG, TGT) |
| | | | 1054 VS | $CD_3$ d-deform (**TTT**) |
| | | 1053 W | | $CD_3$ s-deform (**TTT**) |
| | | 1045 W | | $CD_3$ d-deform (**TTT**) |
| | 1042 VW | | | $CD_3$ d-deform (**TTG**, TGT) |
| | | 1017 VW[b] | | |
| | 1004 VW[b] | | 1005 VW[b] | |
| 991 VW | | 992 VW | | $CD_2$ rock (**TTT**) |
| | 987 W | | 988 W | $CD_2$ wag (**TTT**), $CD_2$ rock (TTG) |
| | 981 W | | 980 VW, sh | $CD_2$ rock (**TTT**, TGT) |
| 975 S | | 982 VS | | $CD_2$ scis (**TTT**), $CD_2$ twist (**TTT**), $CD_2$ rock (TTG, TGT) |
| 964 M | | | | $CD_2$ twist (TTG, TGT) |
| | | | 960 W | $CD_2$ twist (**TTT**) |
| 957 M | 959 M | | | $CD_2$ twist (**TGT**) |
| 951 M | | | | $CD_2$ twist (TTG, TGT), $CD_2$ scis (TTG) |
| 936 M | 933 VW | 935 M | | $CD_2$ twist (**TTT**, TTG, TGT) |
| | | 925 VW[b] | | |
| 889 VW | 892 VW | | 893 VW | $CD_2$ wag (**TTT**), CC stretch (TGT) |
| | | 881 VW[b] | | |
| 880 VW | | | | CC stretch (**TTG**) |
| 873 VW | 872 VW | 871 VW | | CC stretch (**TTT**), $CD_2$ wag (TTG) |
| 854 VW | 856 VW | | 853 W | $CD_2$ wag (**TTT**, TGT) |
| 846 W | | | | $CD_2$ wag (**TGT**) |
| 839 W | | 833 W | | $CD_2$ wag (**TTT**, TTG) |
| 803 VW[b] | | | | |
| | | 795 VW[b] | | |
| 771 VW | 773 W | | | $CD_2$ wag (**TGT**) |
| 760 W | 760 W | | | $CD_2$ wag (**TTG**) |
| | 752 VW, sh | | | $CD_2$ twist (TTG, TGT) |
| 727 VW, sh | | | | $CD_2$ wag (**GTG′**) |
| | | | 726 W | $CD_2$ twist (**TTT**) |
| | 719 M | | 717 S | $CD_3$ ip-rock (**TTT**, TTG) |
| 709 S | | 704 M | | $CD_3$ ip-rock (**TTT**, TTG, TGT) |
| 695 W | | | | $CD_3$ ip-rock (**TGT**) |

Table 5. (Continued)

| Liguid | | Solid | | Assignment |
|---|---|---|---|---|
| Raman (−95 °C) | Infrared | Raman | Infrared | |
| 665 VW | | 666 VW | | CD$_3$ op-rock (**TTT**, TTG) |
| 655 VW | | | | CD$_3$ op-rock (**TGT**) |
| 638 VW | | | | CD$_3$ op-rock (**TGT**) |
| | | | 605 VW[b)] | |
| 594 VW | 595 W | | 592 M | CD$_3$ op-rock (**TTT**, **TTG**) |
| 570 VW | 569 M | | | CD$_2$ rock (**TTG**) |
| | | | 553 VW[b)] | |
| | 540 W, sh | | | CD$_2$ rock (**TGT**) |
| | | 538 VW | | CD$_2$ rock (**TTT**) |
| | | | 536 VW[b)] | |
| | 532 S | | | CD$_2$ rock (**TTG**) |
| | 524 S | | 520 VS | CD$_2$ rock (**TTT**) |
| 438 VW | | | | CCC deform (**TGT**) |
| | 425 W | | | CCC deform (**TGG**) |
| 408 VW | 405 W | | 401 VW | CCC deform (**TTT**, GTG, GTG′) |
| 385 VW | | | | CCC deform (**TTG**) |
| 350 VW | | | | CCC deform (**TTG**) |
| 335 VS | | 338 VS | | CCC deform (**TTT**) |
| 294 VW | | | | CCC deform (**TGT**) |
| 270 VW, sh | | | | CCC deform (**TTG**) |
| 263 VW | | 266 VW | | CCC deform (**TTT**) |
| 179 VW, b | | 176 VW | | Torsion |
| | | 73 W | | Out-of-plane rotatory lattice vibration[c)] |
| | | 63 M | | In-plane rotatory lattice vibration[c)] |

a) The observed bands are assigned to the individual vibrations of the TTT, TTG, and TGT forms. The vibrations of the TGG, GTG, and GTG′ forms are identified in the table when the bands are assigned to these forms but not to the TTT, TTG, or TGT form. The crystal structure of hexane is P1 ($C_i^1$), $Z=1$ [N. Norman and H. Mathisen, *Acta Chem. Scand.*, **15**, 1755 (1961)]. Accordingly, no crystal field splitting is expected in the spectra of the solid state. For the notation and definition of the local symmetry coordinates, see Ref. 10. VS: very strong, S: strong, M: medium, W: weak, VW: very weak, sh: shoulder, b: broad. b) Assigned to the partially deuterated compounds or origin unknown. c) H. Takeuchi, T. Shimanouchi, M. Tasumi, G. Vergoten, and G. Fleury, *Chem. Phys. Lett.*, **28**, 449 (1974).

Table 6. APPARENT ENTHALPY DIFFERENCES IN cal/mol

| Molecule | Band pair | | $\Delta H_{x-y}$[a)] |
|---|---|---|---|
| | x | y | |
| Pentane | b | a | 581(28) |
| | b | c | 574(31) |
| | a | c | 17(34) |
| | e | d | 619(20) |
| Hexane | f | g | 600(11) |
| | f | h | 370(50) |
| | h | i | 3(56) |
| | j | k | 52(18) |
| | m | l | 661(51) |

a) $\Delta H_{x-y}=H_x—H_y$. The value in parentheses is the standard deviation.

Table 7. POSSIBLE ASSIGNMENTS OF THE BANDS USED IN THE CALCULATION OF ENTHALPY DIFFERENCES

| Molecule | Raman band | Frequency (cm$^{-1}$) | Possible assignments |
|---|---|---|---|
| Pentane | a | 337 | TG |
| | b | 403 | TT, GG |
| | c | 471 | TG, GG |
| | d | 841 | TG, GG |
| | e | 868 | TT, TG, GG |
| Hexane | f | 372 | TTT, GTG[a)] |
| | g | 402 | TTG, TGG[a)] |
| | h | 456 | TTG |
| | i | 520 | TGT |
| | j | 824 | TGT, TGG |
| | k | 870 | TTG, GTG, GTG′ |
| | l | 952 | GTG, GTG′ |
| | m | 975 | TTG, TGG |

a) The value of the enthalpy difference between the TTT and TTG forms depends on the relative amounts of the contributions from these forms to the intensities of the bands f and g (see text).

bands. These bands are explained only by the calculated frequencies of the GG form. Hence, it is certain that the GG form exists at room temperature to some extent.

*Hexane and Hexane-*d$_{14}$ *(See Figs. 4, 5, and 7 and Tables 4 and 5).* The spectra in the solid state are explained by the calculated frequencies for the TTT form. Among the liquid-state bands that are due to forms other than the TTT form, the bands at 456 and 520 cm$^{-1}$ of hexane and the bands at 350 and 294 cm$^{-1}$ of hexane-$d_{14}$ are assigned only to the TTG and TGT forms, respectively. The temperature dependence of the intensity of the Raman band at 952 cm$^{-1}$ of hexane is much more significant than those of the above bands. Since this frequency matches the calculated frequencies for the GTG and GTG′ forms, the existence of one or both of these forms is evident.

*Enthalpy Differences (See Figs. 2 and 4 and Tables 6 and 7).* *Pentane*: As the intensity of the band b in the solid state is very strong, the contribution, if any, from the vibration of the GG form to this band in the liquid state may be small. Hence, the apparent enthalpy difference obtained for the band pair of b and a, 581 cal/mol, may be a good approximate value of the enthalpy difference between the TG and TT forms.

*Hexane*: It is evident from the value of $\Delta H_{\text{i-h}}$ that the TGT form is as stable as the TTG form. The great difference between the values of $\Delta H_{\text{g-f}}$ and $\Delta H_{\text{h-f}}$ indicates the fair amount of the contribution from the TGG form to the band g. From these values, it is apparent that the enthalpy difference between the TTG and TTT forms lies in the range between 400 and 600 cal/mol. However, since the relative amount of the contribution from the GTG form to the band f is considered to be far less than that from the TGG form to the band g, it may be safely concluded that the enthalpy difference between the TTG and TTT forms is on the side of 400 cal/mol. Moreover, by assuming that the TGG, GTG, and GTG′ forms are approximately of the same stability, it may be concluded from the value of $\Delta H_{\text{l-m}}$ that the GTG form is less stable than the TTG form by 650 cal/mol.

In conclusion, the present study shows that the TGT form is as stable as the TTG form in the liquid state of hexane and that $\Delta H_{\text{TTG-TTT}}$ (400 cal/mol) of hexane is less than $\Delta H_{\text{TG-TT}}$ (600 cal/mol) of pentane. These results add to the data for the understanding of the stable structure and properties of longer hydrocarbon molecules. It is to be noted that these enthalpy-difference values are appreciably smaller than $\Delta H_{\text{G-T}}$ (966 cal/mol) reported for gaseous butane.[5]

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