Vibration Spectra and Rotational Isomerism of Chain Molecules. VIII.[1) 1-Chloro-, 1-Bromo-, and 1-Iodopentanes, and 1,4-Dichloro- and 1,4-Dibromobutanes

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The Raman and infrared spectra of 1-chloro-, 1-bromo-, and 1-iodopentanes $CH_3(CH_2)_4X$ (X=Cl, Br, and I), and 1,4-dichloro- and 1,4-dibromobutanes $X(CH_2)_4X$ (X=Cl and Br) were measured for the gaseous, liquid, glassy, and crystalline states. The normal coordinates were calculated for these molecules by the use of a consistent set of force constants. The rotational isomerism was studied by analyzing the spectra with reference to the results of the calculation. The study clarified the isomers present not only in the crystalline state but also in other states of aggregation. In the crystal, 1-chloro-, 1-bromo-, and 1-iodopentanes take the *trans-trans-trans* form and 1,4-dichloro- and 1,4-dibromobutanes take the *gauche-trans-gauche′* form.

Many studies have been made of the rotational isomerism of 1-halogenopentanes[2—7) and 1,4-dihalogenobutanes[8—11) by means of Raman, infrared, and NMR measurements. As a result, the conformer in the crystalline state has been made clear for each of these molecules. However, the rotational isomers existing in other states such as liquid and glass have not yet been fully explored.

In the preceding paper of this series,[1) we reported the vibration spectra and the rotational isomerism of 1-halogenopropanes and 1-halogenobutanes, and obtained information on the conformational stabilities of these molecules. In the present work, we extended our studies to longer halogenoalkanes: 1-halogenopentanes $CH_3(CH_2)_4X$ (X=Cl, Br, and I) and 1,4-dihalogenobutanes $X(CH_2)_4X$ (X=Cl and Br). The rotational isomerism was studied by analyzing the Raman and infrared spectra with reference to the results of the normal coordinate calculation.

Experimental

All the samples used in this study were purchased from Tokyo Kasei Kogyo Co., Ltd. and were distilled prior to the spectroscopic measurements. The Raman and infrared spectra were measured for the gaseous (only for 1-chloropentane), liquid, glassy, and crystalline states by the method reported previously.[12,13) The glassy state for Raman measurements was obtained by immersing the liquid sample enclosed in an ampoule in liquid nitrogen for rapid cooling, and the glassy state for infrared measurements by depositing the gaseous sample onto a cooled plate of KBr or KRS-5. The glassy state of 1,4-dichloro- and 1,4-dibromobutanes for Raman measurements and that of 1,4-dibromobutane for infrared measurements could not be obtained because of rapid crystallization.

Normal Coordinate Treatment

The normal coordinate calculations were carried out with a computer program NCTB2[14) and a HITAC 8800/8700 computer system at the Computer Center of the University of Tokyo. The detailed procedure of the calculations on unbranched halogenoalkanes has been described in the previous paper.[1) The observed frequencies for the molecules treated in this study together with those of the shorter molecules (1-halogenopropanes, 1-halogenobutanes, and 1,3-dihalogenopropanes) were used in the refinement of the force constants.

In the analyses of the observed spectra, the calculation of the normal coordinates plays an important role, since the assignments of the bands to individual conformers rely largely on the calculated frequency values. Therefore, the accuracy of the calculated frequencies has to be high enough to allow the spectral analyses. The high accuracy is particularly required for large molecules, such as those studied in this work, which give many bands in the spectra.

The force constants used in this study have been obtained by the least-squares procedure from about 340 observed frequencies for chloroalkanes, 400 for bromoalkanes, and 400 for iodoalkanes,[15) with root-mean-square deviations of 5.6, 6.1, and 6.5 cm^{-1}, respectively, between the observed and calculated frequencies. These accuracies of the calculations, we believe, are high enough to analyze the spectra of 1-halogenopentanes and 1,4-dihalogenobutanes in this study.

Results

Figures 1—10 show the observed spectra of the 1-halogenopentane and 1,4-dihalogenobutane molecules in various states of aggregation in comparison with the calculated frequencies.[17)

1-Halogenopentane molecules have, as given in Table 1 of Part I of this series,[12) fourteen possible rotational isomers, TTT, TTG, TGT, GTT, TGG, GTG, GGT, TGG′, GTG′, GG′T, GGG, GGG′, GG′G, and GG′G′, where the first conformation symbol in each isomer designation is that for the CH_3CH_2–CH_2CH_2 axis and the last for the CH_2CH_2–CH_2X axis. Of these, the isomers with a sequence of the GG′ conformation, *i.e.* TGG′, GG′T, GGG′, GG′G, and GG′G′ are unlikely to exist because of the strong

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Table 1. ROTATIONAL ISOMERS OF 1-HALOGENOPENTANES AND 1,4-DIHALOGENOBUTANES

Molecule	Gas	Liquid	Glass	Crystal
$CH_3(CH_2)_4F$[a]	—[b]	TTG TTT TGT GTT	—[b]	TTG
$CH_3(CH_2)_4Cl$	TTT TTG TGT TGG GTG GTG′	TTT TTG TGT TGG GTG GTG′	TTT TTG TGT TGG GTG GTG′	TTT
$CH_3(CH_2)_4Br$	—[b]	TTT TTG TGT GTT TGG GTG GTG′ GGG	TTT TTG TGT TGG GTG GTG′	TTT TTG[c]
$CH_3(CH_2)_4I$	—[b]	TTT TTG TGT GTT TGG GTG GTG′ GGG	TTT TTG TGT GTT TGG GTG GTG′	TTT
$Cl(CH_2)_4Cl$	—[b]	GTG′ TTT TTG TGG GTG GGG	GTG′ TTT TTG GTG GGG	GTG′
$Br(CH_2)_4Br$	—[b]	GTG′ TTT TTG TGT TGG GTG GGG	—[b]	GTG′

a) Ref. 6. b) Spectral measurements were not made. c) Two crystal modifications have been obtained. For the TTG form, see Ref. 20.

steric hindrance. In fact, existence of the GG′ form of pentane[18] or of 1-halogenobutanes[1] has not been identified in any state of aggregation. 1,4-Dihalogenobutane molecules have ten possible rotational isomers, TTT, TTG, TGT, TGG, GTG, TGG′, GTG′, GGG, GGG′, and GG′G. Of these, the TGG′, GGG′, and GG′G forms are again unlikely to exist.

In the following subsections, the rotational isomerism of the individual molecules is described. For the spectral analyses, the bands due to the skeletal deformation, skeletal stretching, and CH_2 rocking vibrations were primarily used to identify the existing rotational isomers.

1-Chloropentane (See Figs. 1 and 2). The crystalline-state spectra are explained by the existence of the TTT form, since the Raman bands at 263, 347, 448, 714, 737, 759, 835, 892, (and 900), and 955 cm^{-1} are all assigned consistently to this form. The calculated frequencies are 256, 354, 462, 727, 729, 754, 833, 901, and 956 cm^{-1}, respectively.

In the liquid and glassy states, the spectra exhibit many bands to be assigned to various rotational isomers. It is evidently shown that the TTT and TTG forms exist in these states. The relative intensities of the Raman bands at 400, 455, 653, 788, 838, 908, and 923 cm^{-1}, together with those of the bands which have been assigned to the TTT form, increase in going from the liquid state at room temperature to the glassy state at liquid nitrogen temperature. All of these bands correspond to the calculated frequencies for the TTG form: 401, 456, 656, 791, 838, 916, and 929 cm^{-1}.

The liquid- and glassy-state spectra have further additional bands. Spectral observations indicate that these bands lose their intensities largely, when temperature is lowered, as compared with the bands which have been assigned to the TTT and TTG forms. According to the results of the normal coordinate treatment, the bands at 375 and 822 cm^{-1} are assigned to the GTG form (the calculated frequencies: 369 and 823 cm^{-1}), those at 387 and 878 cm^{-1} to the TGG form (384 and 886 cm^{-1}), those at 712, 764, and 855 cm^{-1} to the TGT form (714, 761, and 856 cm^{-1}), and that at 933 cm^{-1} to the GTG′ form (938 cm^{-1}).

Existence of the GTT form is uncertain, since all of the calculated frequencies of this form are almost coincident with those of the other forms mentioned above. For the GGG and GGT forms, no positive evidence of their existence was obtained. According to the calculation, the former form is expected to exhibit bands around 325 and 410 cm^{-1} and the latter at 475 cm^{-1}, but no recognizable bands are actually observed in these frequency regions. Therefore, the GGG and GGT forms do not seem to exist in the liquid or glassy state.

The gaseous-state Raman spectrum is essentially the same as the liquid-state Raman spectrum but relative intensities of several bands are different between them. This suggests that the gaseous and liquid molecules have the same kinds of rotational isomers with different distributions.

The temperature dependence of the liquid-state Raman spectra shows that the TTT and TTG forms have much higher stabilities than the other forms in this state. These two forms are also dominant conformers in the glassy state at liquid nitrogen temperature. These observations are consistent with the result obtained for 1-chlorobutane that the TT and TG forms are more stable than the other forms.[1]

1-Bromopentane (See Figs. 3 and 4). The spectra of the crystalline state is explained by the existence of the TTT form, since the Raman bands at 216, 334, 433, 638 (and 644), 731, 753, 828, 894 (and 899), and 944 cm^{-1} are assigned consistently only to this form. The calculated frequencies are 215, 341, 446, 642, 729, 751, 825, 899, and 943 cm^{-1}, respectively.

In the liquid and glassy states, the existence of the TTT and TTG forms is clear, similarly to the case of 1-chloropentane. In going from the liquid state to

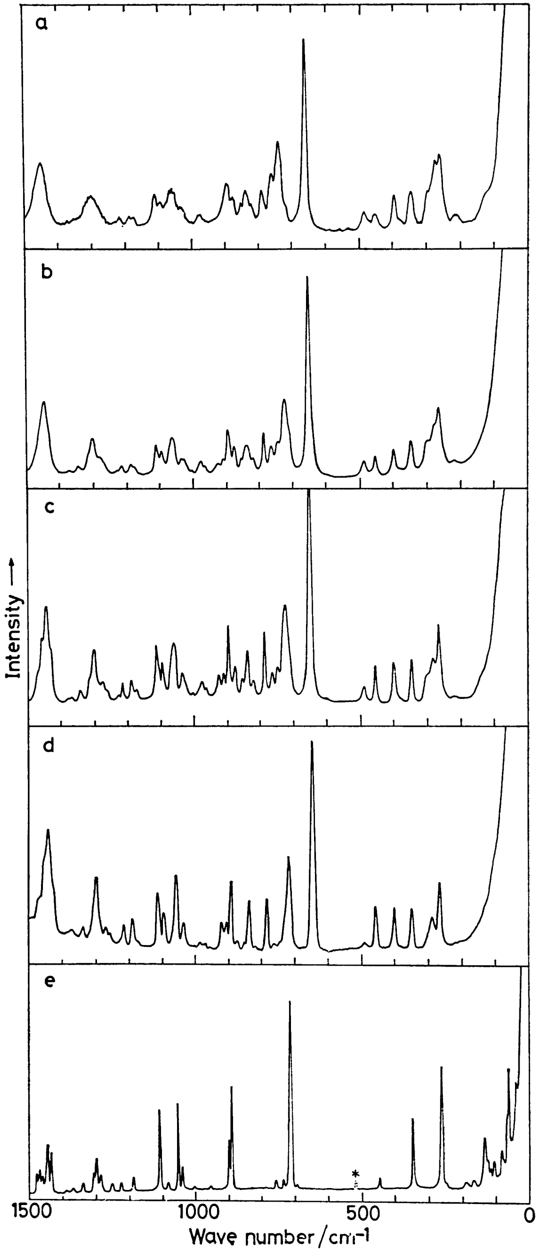

Fig. 1. Raman spectra of 1-chloropentane. a: Gas (23 °C), b: liquid (23 °C), c: liquid (−90 °C), d: glass (liquid nitrogen temperature), e: crystal (liquid nitrogen temperature). The following symbols are used in Figs. 1—10. *: Emission line of Ar$^+$ laser, △: origin unknown.

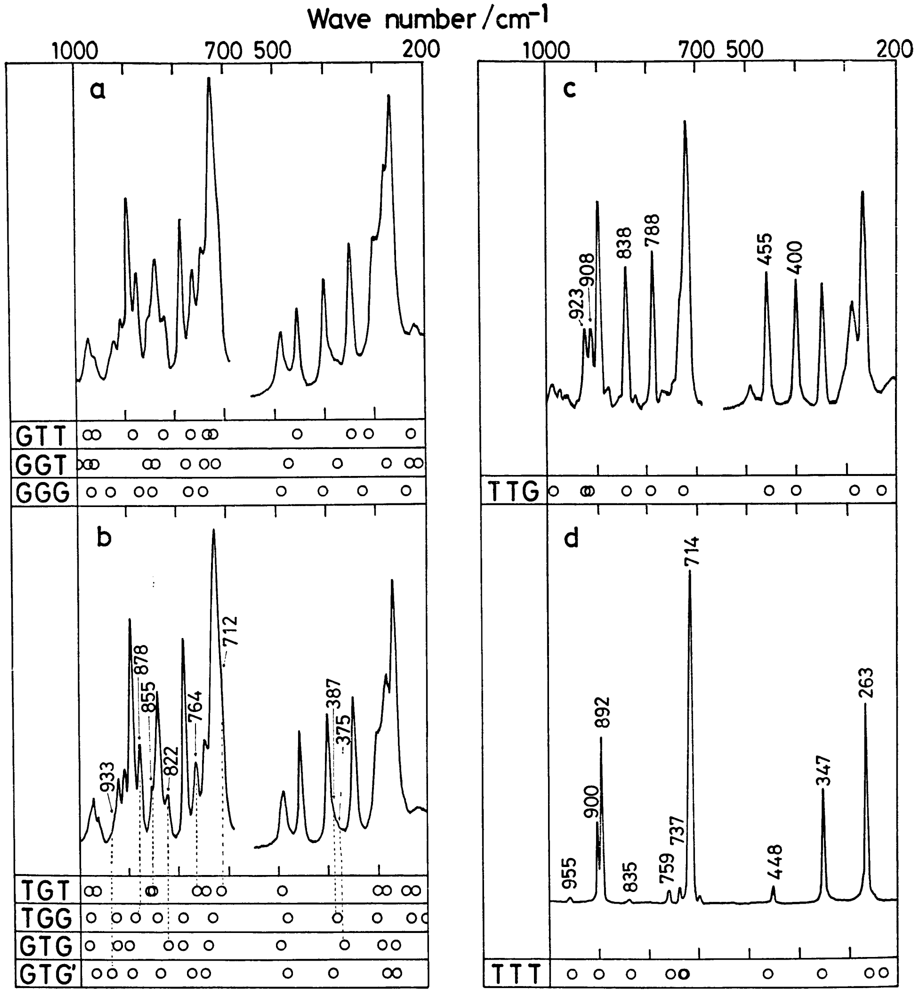

Fig. 2. Comparison between the Raman spectra and the calculated freqencies of 1-chloropentane. a: Liquid (23 °C), b: liquid (−90 °C), c: glass (liquid nitrogen temperature), d: crystal (liquid nitrogen temperature).

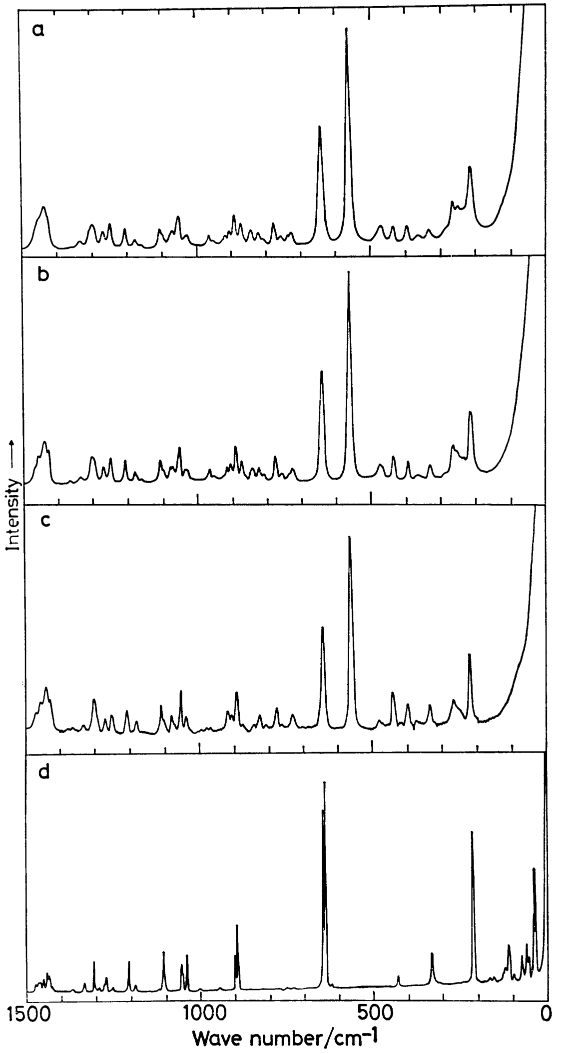

Fig. 3. Raman spectra of 1-bromopentane. a: Liquid (23 °C), b: liquid (−85 °C), c: glass (liquid nitrogen temperature), d: crystal (liquid nitrogen temperature).

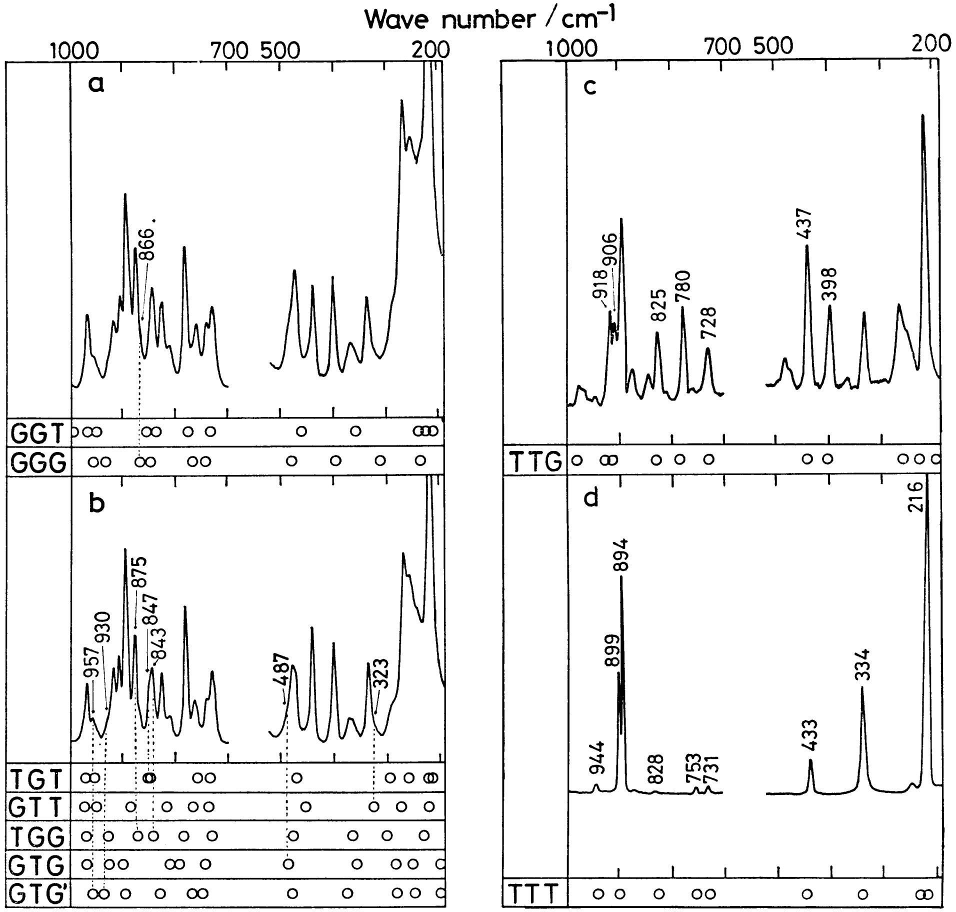

Fig. 4. Comparison between the Raman spectra and the calculated frequencies of 1-bromopentane. a: Liquid (23 °C), b: liquid (−85 °C), c: glass (liquid nitrogen temperature), d: crystal (liquid nitrogen temperature).

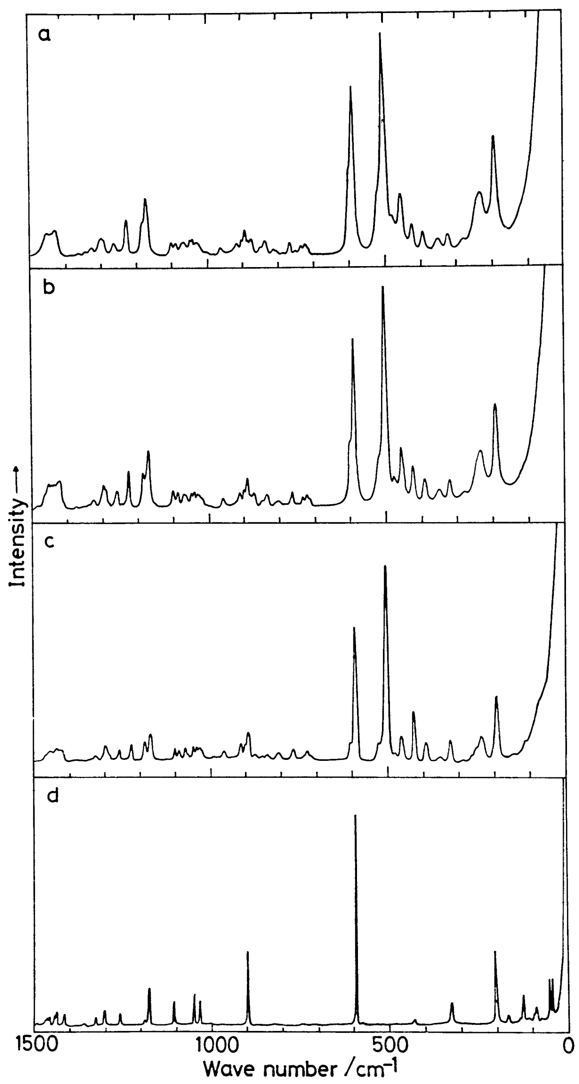

Fig. 5. Raman spectra of 1-iodopentane. a: Liquid (23 °C), b: liquid (−80 °C), c: glass (liquid nitrogen temperature), d: crystal (liquid nitrogen temperature).

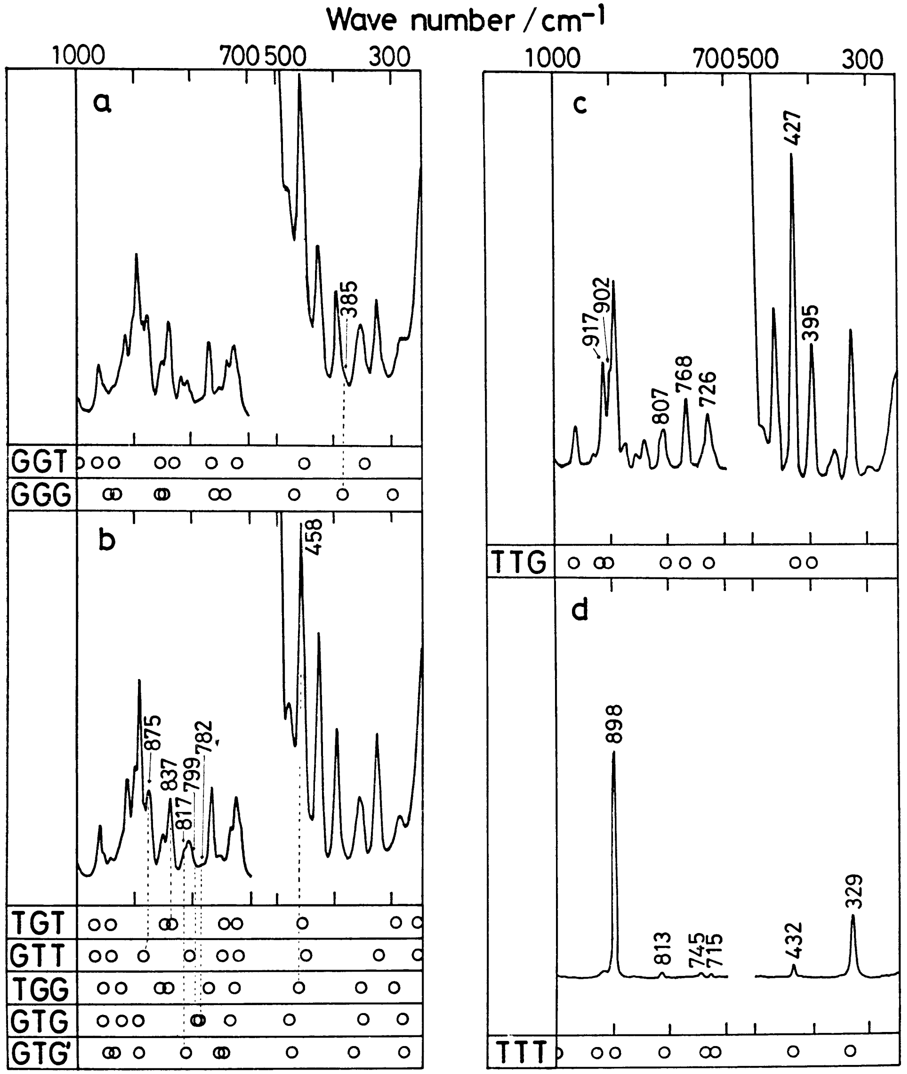

Fig. 6. Comparison between the Raman spectra and the calculated frequencies of 1-iodopentane. a: Liquid (23 °C), b: liquid (−80 °C), c: glass (liquid nitrogen temperature), d: crystal (liquid nitrogen temperature).

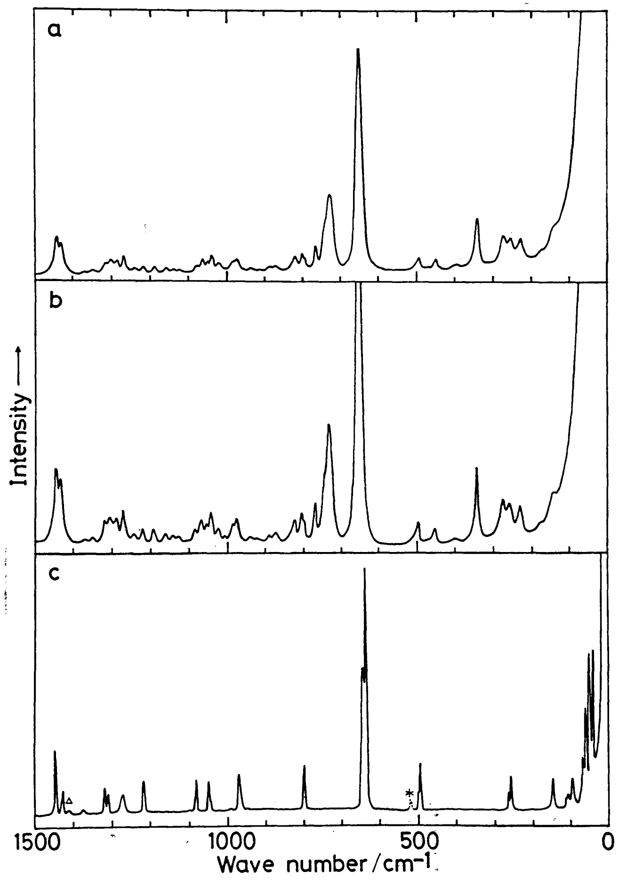

Fig. 7. Raman spectra of 1,4-dichlorobutane. a: Liquid (23 °C), b: liquid (−35 °C), c: crystal (liquid nitrogen temperature).

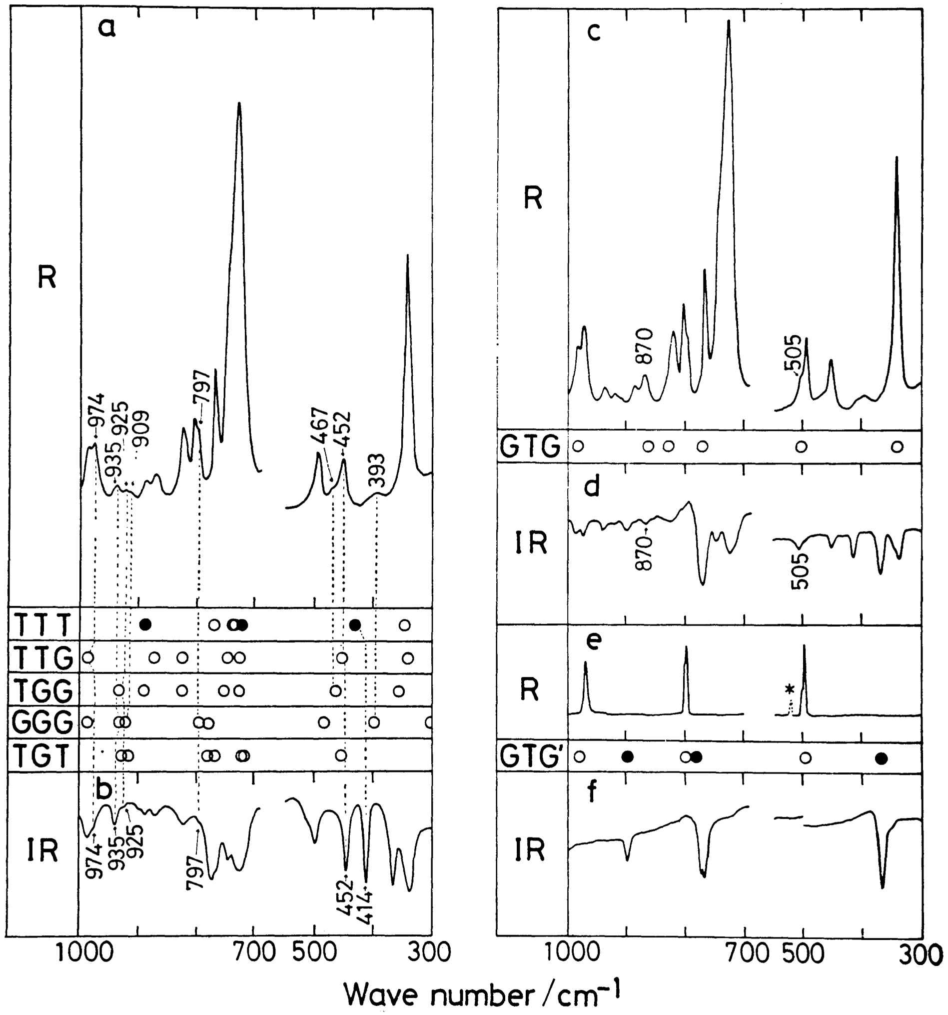

Fig. 8. Comparison between the observed spectra and the calculated frequqncies of 1,4-dichlorobutane. a: Liquid (Raman, 23 °C), b: liquid (infrared, room temperature), c: liquid (Raman, −35 °C), d: glass (infrared), e: crystal (Raman, liquid nitrogen temperature), f: crystal (infrared). For the TTT and GTG′ forms, the open and filled circles indicate Raman- and infrared-active vibrations, respectively.

the glassy state, the relative intensities of the Raman bands at 398, 437, 562, 728, 780, 825, 906, and 918 cm^{-1} of the TTG form increase together with those of the TTT form. The calculated frequencies of the TTG form are 400, 438, 563, 731, 784, 827, 912, and 926 cm^{-1}, respectively.

In addition to the Raman bands of the TTT and TTG forms, the liquid- and glassy-state spectra exhibit many other bands. On the basis of the results of the normal coordinate treatment, the band at 323 cm^{-1} is assigned to the GTT form (the calculated frequency: 326 cm^{-1}), that at 487 cm^{-1} to the GTG form (485 cm^{-1}), those at 843 and 875 cm^{-1} to the TGG form (844 and 874 cm^{-1}), that at 847 cm^{-1} to the TGT form (847 and 850 cm^{-1}), and those at 930 and 957 cm^{-1} to the GTG′ form (936 and 955 cm^{-1}). It is likely that the GGG form is also present in the liquid state, since a very weak Raman band is observed as a shoulder at 866 cm^{-1}, which corresponds to the calculated frequency 867 cm^{-1} of this form.

Existence of the GGT form in the liquid and glassy states is uncertain, as all of the calculated frequencies of this form are almost coincident with those of the other forms mentioned above. Also, the GTT and GGG forms are not confirmed to exist in the glassy state, because their characteristic bands are too weak to identify them in this state.

The TTT and TTG forms are far more stable than the other forms in the liquid state as shown from the temperature dependence of the Raman intensities, and are also predominating isomers in the glassy state. These findings are similar to those for 1-chloropentane.

1-Iodopentane (See Figs. 5 and 6). The molecule takes the TTT form in the crystalline state, since the observed Raman bands at 205, 329, 432, 593, 715, 745, 813, and 898 cm^{-1} are assigned consistently to this form which gives calculated frequencies 191, 331, 438, 590, 721, 736, 811, and 898 cm^{-1}.

The existence of the TTT and TTG forms in the liquid and glassy states is clearly shown from the spectral observation that the bands whose intensities increase at lower temperature are assigned to these forms. The Raman bands of the TTG form are those at 395, 427, 506, 726, 768, 807, 902, and 917 cm^{-1} which are compared with the calculated frequencies 399, 426, 506, 731, 769, 808, 908, and 922 cm^{-1}, respectively.

In addition to the TTT and TTG forms, the existence of other forms in the liquid and glassy states is confirmed by the spectral observations incorporated with the normal coordinate treatment. Of the Raman bands which have not been assigned to the TTT or TTG form, the bands at 458 and 525 cm^{-1} are interpreted to be due to the TGG form (the calculated frequencies: 463 and 516 cm^{-1}), those at 602 and 837 cm^{-1} to the TGT form (598 and 837 cm^{-1}), those at 782 and 799 cm^{-1} to the GTG form (784 and 791 cm^{-1}), that at 817 cm^{-1} to the GTG′ form (814 cm^{-1}), and that at 875 cm^{-1} to the GTT form (883 cm^{-1}).

It is likely that the GGG form exists in the liquid state, since a very weak Raman band is observed at 385 cm^{-1} at room temperature, which is in agreement with the calculated frequency 387 cm^{-1} of this form. However, in the glassy-state spectrum, this band is too weak to confirm existence of this form. Therefore, it is not certain whether the GGG form is present in this state. Existence of the GGT form in the liquid and glassy states is also uncertain, since all of the calculated frequencies are almost coincident with those of the other forms.

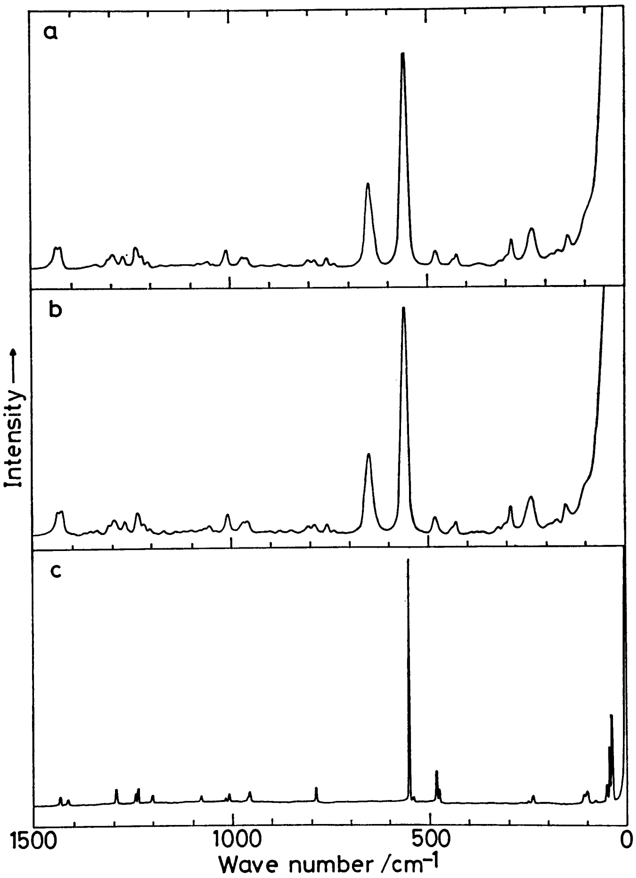

Fig. 9. Raman spectra of 1,4-dibromobutane. a: Liquid (23 °C), b: liquid (−20 °C), c: crystal (liquid nitrogen temperature).

The glassy-state spectra and the temperature dependence of the liquid-state spectra show that the conformational stabilities of the TTT and TTG forms are higher than those of the other forms.

The spectra of the liquid and glassy states exhibit in the C–I stretching region four Raman bands at 506, 525, 592, and 602 cm^{-1} and the corresponding infrared bands at 506, 522, 593, and 603 cm^{-1}. According to the normal coordinate calculation, the TTG, GTG, and GTG′ forms (having the *trans-gauche* conformation about the CC–C–CI axes) give the C–I stretching frequencies of about 505 cm^{-1}, the TGG and GGG forms (having the *gauche-gauche* conformation) about 515 cm^{-1}, the TTT and GTT forms (having the *trans-trans* conformation) about 590 cm^{-1}, and the TGT and GGT forms (having the *gauche-trans* conformation) about 600 cm^{-1}. The observed bands are reasonably assigned to these four groups of conformers. This spectral observation indicates that the C–I stretching frequency can be used to examine the conformation not only about the CC–CI axis but also about the adjacent CC–CCI axis.

1,4-Dichlorobutane (See Figs. 7 and 8). In the crystalline state, the Raman and infrared spectra are quite different from each other and the mutual exclusion in the Raman and infrared activities is clearly observed. Of the two conformers TTT and GTG′ having a center of symmetry, the observed C–Cl stretching frequencies of about 640 cm^{-1} are consistent only with the latter form. The observed frequencies of other bands are also explained by this form. Thus, the molecule in the crystal is found to take the centrosymmetrical GTG′ form.

The observed spectra in the liquid state are explained by the coexistence of the GTG′, TTT, TTG, GTG, GGG, and TGG forms. The bands which are characteristic of the individual conformers are: 175, 452, and 974 cm^{-1} of the TTG form (the calculated frequencies: 181, 456, and 988 cm^{-1}); 230 (Raman) and 414 cm^{-1} (infrared) of the TTT form (213 and 428 cm^{-1}); 393, 797, 909, and 935 cm^{-1} of the GGG form (400, 798, 923, and 933 cm^{-1}); 467 and 925 cm^{-1} of the TGG form (465 and 932 cm^{-1}); and 505 and 870 cm^{-1} of the GTG form (504 and 864 cm^{-1}). In the glassy-state infrared spectrum, most of the liquid-state bands persist but the bands assignable to the TGG form are not observed definitely. Accordingly, the conformers mentioned above for the liquid state but the TGG form are confirmed to be present in the glassy state as well. Existence of the TGT form is not certain in the liquid and glassy states, since all of their frequencies are almost coincident with those of the other forms.

The spectral change with temperature variation in the liquid state shows that the Raman bands at 494, 505, 803, 870, and 974 cm^{-1} are enhanced at lower temperature. This indicates that the GTG′ and GTG forms, to which these bands are assigned, are more stable than the other forms coexisting in the liquid state.

1,4-Dibromobutane (See Figs. 9 and 10). In the crystalline state, the Raman and infrared spectra show the mutual exclusion activities, similarly to the case of 1,4-dichlorobutane. The observed frequencies and the Raman and infrared activities of the individual vibrations agree with those for the GTG′ form, indicating the existence of this form in the crystalline state.

Analyses of the liquid-state Raman and infrared spectra show that all of the seven possible conformers, GTG′, TTT, TTG, GTG, GGG, TGG, and TGT, are present in this state. The following bands give evidences for the existence of these conformers: 148 (Raman), 325 (Raman), 354 (infrared), and 743 cm^{-1} (infrared) of the TTT form (the calculated frequencies: 142, 331, 366, and 735 cm^{-1}); 190, 368, 474, and 787 cm^{-1} of the GGG form (200, 371, 464, and 787 cm^{-1}); 303, 484, and 817 cm^{-1} of the GTG form (305, 481, and 819 cm^{-1}); 318, 443, and 873 cm^{-1} of the TGG form (321, 435, and 878 cm^{-1}); 387 cm^{-1} of the TGT form (399 cm^{-1}); and 428 and 289 cm^{-1} of the TTG form (432 and 289 cm^{-1}).

In the liquid-state Raman spectra, the intensities of the bands at 481, 787, and 959 cm^{-1} are enhanced at lower temperature as compared with those of other bands. The GTG′ form, giving these bands, is thus found to have higher stability than others in the liquid state.

Rotational Isomerism in Comparison with Previous Results. In Table 1, the rotational isomerism of the five molecules studied in this work is summarized. The result of 1-fluoropentane $CH_3(CH_2)_4F$ is also included in this table.

Many studies have been made of the rotational isomerism of 1-halogenopentanes[2–7] and 1,4-dihalogenobutanes.[8–11] Brown and Sheppard[2,9] studied the infrared spectra of many halogenoalkane molecules in the liquid and crystalline states. They concluded that the crystalline-state isomer of 1-bromopentane has a planar conformation of the carbon and bromine atoms. For 1,4-dichloro- and 1,4-dibromobutanes, they showed that these molecules take in the crystalline state the GTG′ conformation with a center of symmetry.

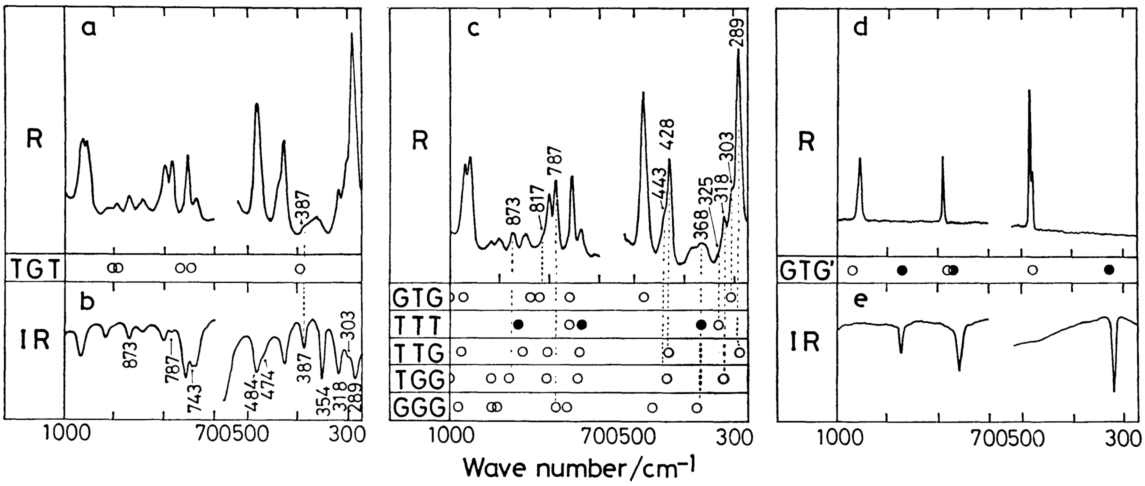

Fig. 10. Comparison between the observed spectra and the calculated frequencies of 1,4-dibromobutane. a: Liquid (Raman, 23 °C), b: liquid (infrared, room temperature), c: liquid (Raman, −20 °C), d: crystal (Raman, liquid nitrogen temperature), e: crystal (infrared). For the TTT and GTG′ forms, the open and filled circles indicate Raman- and infrared-active vibrations, respectively.

Snyder and Schachtschneider[5] measured the infrared spectra of $CH_3(CH_2)_nCl$ (n=1—5) in the crystalline and glassy states. For 1-chloropentane, they concluded on the basis of the normal coordinate analysis that the spectrum of the former state could be explained by the existence of the TTT form and that of the latter state by the coexistence of the TTT and TTG forms.

Crowder and coworkers, on the other hand, interpreted the infrared spectra of 1-iodopentane[7] and 1-fluoropentane[6] in the liquid, glassy, and crystalline states, taking account of only two among various isomers, the TTT and TTG forms. Their observed data for 1-fluoropentane were analyzed in the light of our normal coordinate calculation,[1,14] and it is now shown that the TGT and GTT forms, in addition to the TTT and TTG forms they mentioned, are confirmed to exist in the liquid state. Crowder and Ali[11] also measured the spectra of 1,4-diiodobutane.

The present results of the rotational isomerism in the crystalline state agree with the previous results mentioned above. This study further clarified the rotational isomers present in the liquid and glassy states as well on the basis of the careful spectral observations and the systematic normal coordinate calculation.

Discussion

In our previous study,[1] it was demonstrated that the skeletal deformation vibrations were important for studying the rotational isomerism of halogenoalkanes. In the present study on the longer molecules, the bands in the skeletal deformation region were efficiently used in analyzing the spectra and identifying the rotational isomers present in various states of aggregation. The bands due to the skeletal stretching and the CH_2 rocking vibrations were also found to be useful for studying the rotational isomers.

From the results in this and previous[1] studies on $CH_3(CH_2)_nX$ (n=2—4; X=Cl, Br, and I) and $X(CH_2)_4X$ (X=Cl and Br), it has become clear that the *gauche* conformation about the CC–CX axis is more stable than or as stable as the *trans* conformation in the liquid state. However, in the crystalline state, the accessible conformation about this axis is likely to depend on the subtle balance between the intramolecular forces favoring the *gauche* conformation rather than the *trans* and the intermolecular forces favoring the *trans* conformation. For $X(CH_2)_3X$ (X=Cl, Br, and I)[9,19] and $X(CH_2)_4X$ (X=Cl and Br), the non-planar GG and GTG′ forms exist in the crystalline state. On the other hand, for $CH_3(CH_2)_nX$ (n=2—4; X=Cl, Br, and I), the all-*trans* form exists in the crystalline state. A crystal consisting of the TTG form of $CH_3(CH_2)_4Br$ has also been obtained.[20] It is thus probable that the balance of the intra- and intermolecular forces mentioned above is responsible, at least in part, for the thermodynamic properties of these molecular crystals.

Through this series of studies on the vibration spectra and the rotational isomerism of chain molecules, a reliable and consistent set of force constants has been obtained, which has been satisfactorily utilized for predicting vibrational frequencies of various molecules. The present method of analyzing the spectra in conjunction with the use of the refined force field encourages us to make further studies on the rotational isomerism of large molecules.

The present series of studies has also provided us with various important information for making more advanced investigations in the field of structural chemistry. The conformational polymorphism of halogenoalkane molecules[20] has been in fact investigated in close relation to our fundamental studies in this series.

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