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Vibration Spectra and Molecular Structures of *n*-Butyl Chloride and *n*-Butyl Bromide in Relation to Parallel (1 : 3) Interactions

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The vibration spectra of liquid *n*-butyl chloride and *n*-butyl bromide are observed in the region of 1500—100 cm^{-1}. From the analyses of spectra corresponding to the skeletal deformation vibrations, the molecular configurations are determined for both molecules. All the possible rotational isomers, the TT, GT, TG, GG, and GG′ forms, are observed for *n*-butyl chloride, while four isomers, the TT, GT, TG, and GG forms, are observed for *n*-butyl bromide. The results are compared with those of the electron-diffraction methods. It is shown that unfamiliar interactions must be considered for the parallel (1 : 3) interaction between methyl and chlorine substituents.

Ukaji and Bonham[1] studied the structures of *n*-butyl chloride by an electron-diffraction method and found that the concentration of the GG′ form is twenty-four percent in the gas phase at room temperature. This result is very important because the GG′ form is the most highly coiled among the five possible rotational isomers. Figure 1 shows the possible rotational isomers for $CH_3CH_2CH_2CH_2X$ type molecules. It can naturally be assumed from the figure that the GG′ form is the most unstable because of methyl/chlorine interactions.

The infrared spectra of this molecule have been studied by Snyder[2] for the crystalline state from the point of view of the molecular force field. Snyder concluded that the stable form in the crystalline state is the TT form.

The present work will be concerned with the confirmation of the electron-diffraction results through analyses of the vibration spectra of liquid *n*-butyl chloride and *n*-butyl bromide. The skeletal deformation vibrations will be discussed mainly, because they are characteristic in molecular geometry and are sensitive to any change in molecular configuration.[3]

Experimental

The samples used in the present work were commercial products. After fractional distillation, the purity was checked

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[1] T. Ukaji and R. A. Bonham, *J. Amer. Chem. Soc.*, **84**. 3627 (1962).

[2] R. G. Snyder and J. H. Sachtschneider, *J. Mol. Spectry.*, **30**, 290 (1969).

[3] T. Fujiyama, This Bulletin, **44**, 1194 (1971).

by gas chromatography.

The Raman spectra were recorded using a laser Raman spectrometer which was designed and constructed in our laboratory.[4] Figures 2 and 3 show the Raman spectra of *n*-butyl chloride and *n*-butyl bromide in the region of 100—1000 cm^{-1}. The Raman spectra of crystalline samples observed at the temperature of liquid nitrogen are illustrated in Figs. 4 and 5. The spectrometer was operated under a resolution of 5—10 cm^{-1}. The temperature dependence of the Raman spectra of *n*-butyl chloride was observed at low temperatures; the results are shown in Fig. 8. The temperature was observed by means of a thermocouple directly inserted in the sample.

The infrared spectra of liquid *n*-butyl chloride and *n*-butyl bromide in the region of 200—600 cm^{-1} are illustrated in Figs. 6 and 7. A Hitachi EPI-GII infrared spectrometer was used for the measurements. The observation of the infrared spectra at low temperatures reproduced the results of a previous author[2] quite well; therefore, those results are not illustrated here.

Normal Coordinate Treatment

In confirming the vibrational assignment, normal frequencies of *n*-butyl chloride and *n*-butyl bromide were calculated for all the possible rotational isomers by using the force constants obtained for a series of alkanohalides.[5] The method of calculation may be found described in the references.[6] In the present report, the results of the calculation will not be discussed in detail, but they are available upon request from the author.

Vibrations Spectra and Molecular Configuration

A molecule of the $CH_3CH_2CH_2CH_2X$ type can have the five rotational isomers of Fig. 1, because it has two axes of internal rotation. We define the two axes as:

$$CH_3CH_2\text{-(I)-}CH_2\text{(II)-}CH_2X$$

and call them the I axis and the II axis. In the case of *n*-butyl chloride or *n*-butyl bromide, configurations about the II axis can easily be determined by referring to the well known empirical rule of a stretching-vibration frequency of a carbon-halogen bond.[7] An empirical rule was previously proposed by the present author for the relationship between skeletal deformation vibrations and the molecular configurations of rotational isomers.[3] Based upon this rule, the molecular configuration will be discussed below.

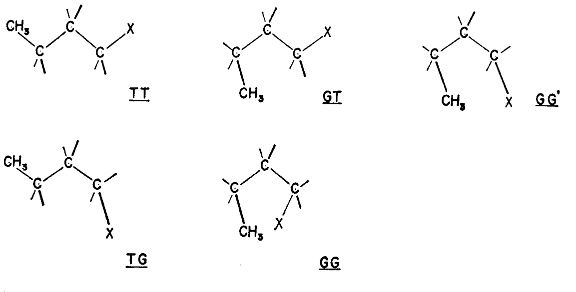

Fig. 1. Possible rotational isomers for the $CH_3CH_3CH_2CH_2X$ type molecules.

n-*Butyl Chloride*. Among the three skeletal deformation vibrations of *n*-butyl chloride, the so-called A type vibration is expected to occur in the region of about 350—500 cm^{-1} in this frequency order:[3]

$$\nu(GG') > \nu(GG) > \nu(TG) > \nu(GT) > \nu(TT),$$

where ν(TG) refers to, for example, a frequency of the A type vibration corresponding to a rotational isomer whose configurations is *trans* and *gauche* about the I axis and the II axis respectively.

In Figs. 2 and 5, we can see five Raman lines, at 529, 476, 465, 438, and 382 cm^{-1}, and seven infrared counterparts, namely, the 525, 472, 456, 435, 399, 388, and 375 cm^{-1} bands. The Raman shift at 382 cm^{-1} can be explained as an unresolved band which corresponds to the infrared bands at 399, 388, and 375 cm^{-1}. The observed bands may be assigned to molecular configurations of *n*-butyl chloride if the location of the TT form band is determined, because it occurs at the lowest frequency of all the five bands.

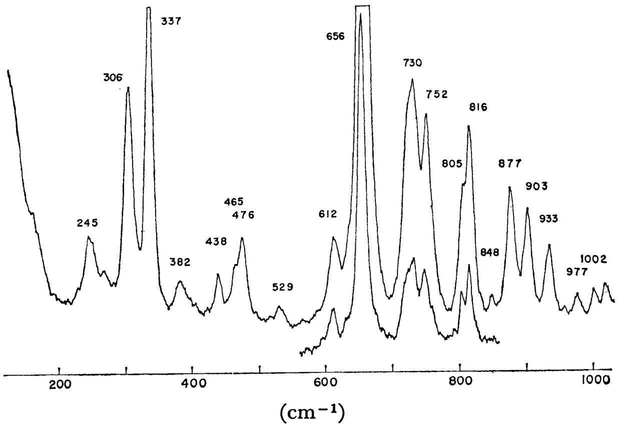

Fig. 2. Raman spectra of liquid *n*-butyl chloride at 25°C.

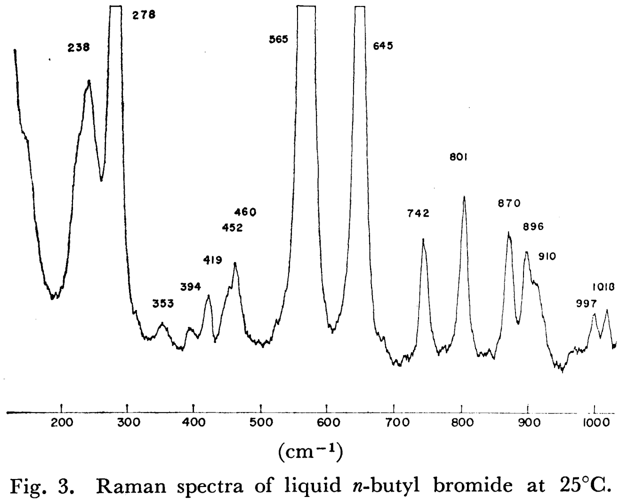

Fig. 3. Raman spectra of liquid *n*-butyl bromide at 25°C.

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[4] T. Fujiyama and M. Tasumi, *Bunko Kenkyu*, **20**, 28 (1971).

[5] M. Tasumi and T. Shimanouchi, *Polymer J.*, **2**, 66 (1971).

[6] T. Shimanouchi, *J. Chem. Phys.*, **17**, 245, 734, 848 (1949).

[7] S. Mizushima, T. Shimanouchi, K. Nakamura, M. Hayashi, and T. Tsuchiya, *ibid.*, **26**, 970 (1957).

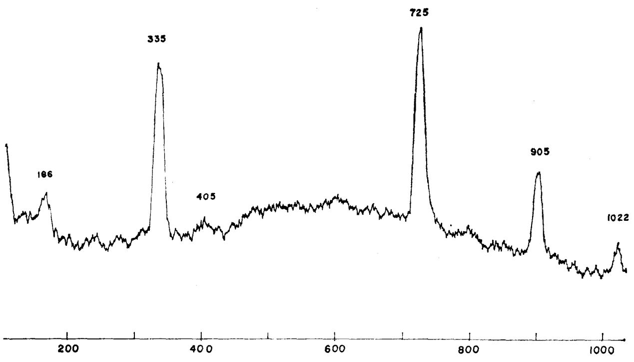

Fig. 4. Raman spectra of crystalline *n*-butyl chloride at −160°C.

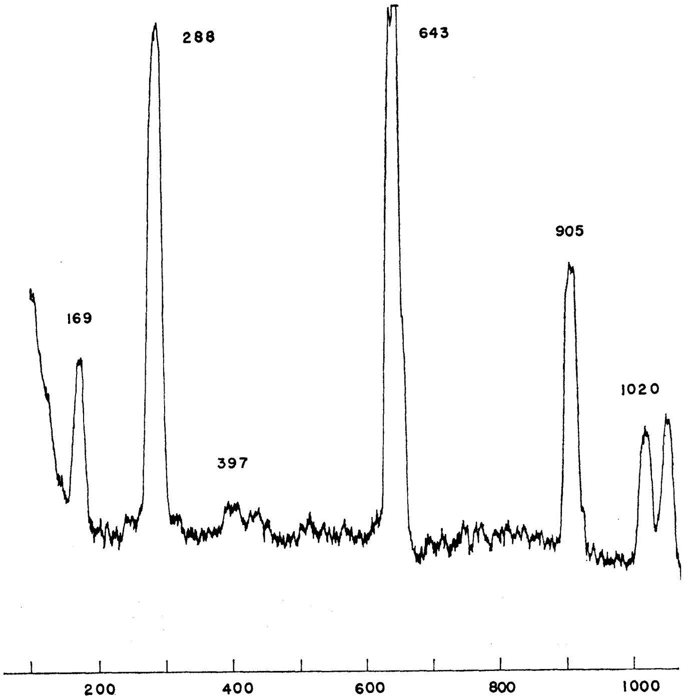

Fig. 5. Raman spectra of crystalline *n*-butyl bromide at −162°C.

Snyder[2)] reports a band at 411 cm^{-1} observed in the infrared spectra of crystalline *n*-butyl chloride. The band corresponds clearly to the Raman line at 405 cm^{-1} of Fig. 6. The results of the normal coordinate treatment of Snyder and of the present work show that the Raman shifts at 405, 355, and 166 cm^{-1} of Fig. 6 can be definitely assigned to the skeletal deformation vibrations of the TT form in the crystalline state.

A little observation of Figs. 2 and 6 leads to the conclusion that the remaining four bands can be assigned to the remaining four rotational isomers. The band at 405 cm^{-1} of Fig. 6 is assumed to be buried in the wing part of the Raman shift at 382 cm^{-1} of Fig. 2. By referring to the frequency order of the empirical rule, the four bands at 438, 465, 476, and 529 cm^{-1} of Fig. 2 can be assigned to the GT, TG, GG, and GG′ forms respectively.

n-*Butyl Bromide*. The vibration spectra of *n*-butyl bromide may be analyzed in a manner similar to that used for *n*-butyl chloride. The frequencies of the A type skeletal deformation vibrations of this molecule can be expected to be slightly lower than those of *n*-butyl chloride. In Figs. 3 and 7, we see four Raman lines, at 460, 452, 419, and 394 cm^{-1}, and four infrared counterparts, at 460, 448, 417, and 394 cm^{-1}.

The Raman lines at 169, 288, and 397 cm^{-1} of Fig. 5 can be expected to correspond to the three skeletal deformation vibrations of the TT form from analogy with the results obtained for *n*-butyl chloride. Actually, the normal frequencies of these vibrations are calculated to be 155, 267, and 381 cm^{-1}. Thus, *n*-butyl bromide takes the TT form in the crystalline state and the band at 394 cm^{-1} of Fig. 5 can definitely be assigned to the A type skeletal deformation vibration of the TT form. The remaining three bands, at 460, 452, and 419 cm^{-1}, can reasonably be assigned to the GG, TG, and GT forms of *n*-butyl bromide respectively. The close similarity of the spectral patterns observed for *n*-butyl chloride and *n*-butyl bromide in the region of 350—500 cm^{-1} probably support the validity of the above-described assignments (see Figs. 2 and 3).

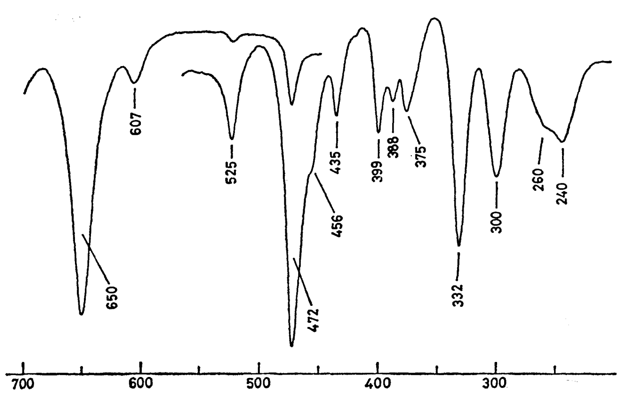

Fig. 6. Infrared spectra of liquid *n*-butyl chloride at 25°C.

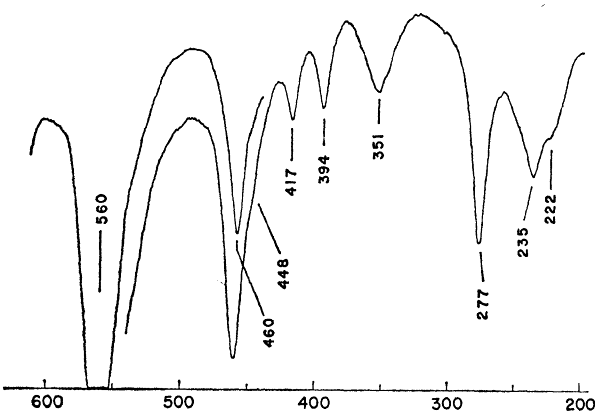

Fig. 7. Infrared spectra of liquid *n*-butyl bromide at 25°C.

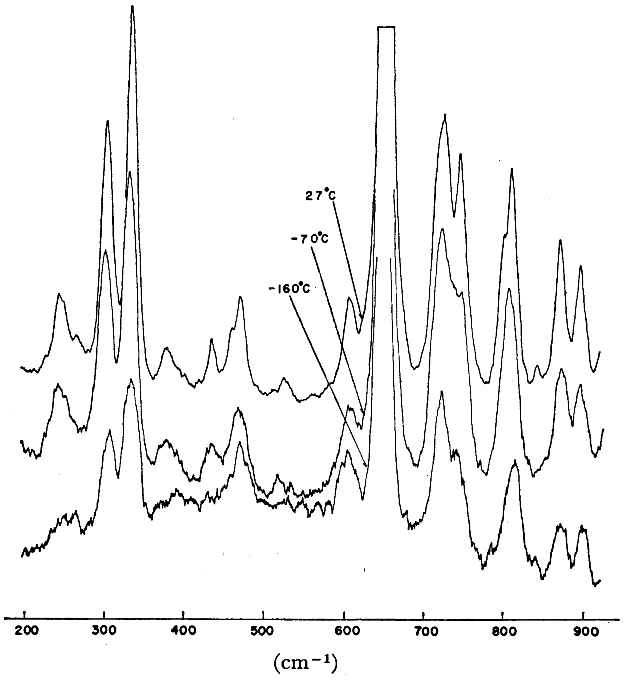

Fig. 8. Raman spectra of liquid *n*-butyl chloride at low temperature.

Table 1. Isomer percentages for the $CH_3CH_2CH_2CH_2X$ type molecules (After Bonham *et al.* (1, 9, 10))

Isomer	Concentration (per cent)		
	n-Pentane	*n*-Butyl chloride	*n*-Butyl bromide
TT	43	11	36
GT	25	11	24
TG	25	37	24
GG	7	17	16
GG′	—	24	—

Discussion

The GG′ Form and the Parallel (1 : 3) Interaction. It may be concluded from the spectral analyses that the numbers of rotational isomers observed in the vibration spectra of liquid *n*-butyl chloride and *n*-butyl bromide are five and four respectively. Only the TT form remains in the crystalline state of both molecules. The most remarkable finding is the existence of the GG′ form of *n*-butyl chloride in the liquid state. In the GG′ form, strong methyl/chlorine interactions are assumed to occur, because substituents on the carbon atoms, 1 and 3, give rise to parallel C–Cl and $C–CH_3$ bonds on the same side of the carbon skeleton. Actually, it has been widely agreed to reject the possibility of the existence of molecular configurations in which parallel (1 : 3) interactions are involved. We call those interaction by the term "parallel (1 : 3) interactions" following the suggestion of Sheppard.[8]

Table 1 shows the isomer percentage of the $CH_3CH_2CH_2CH_2X$-type molecules ($X–CH_3$, Cl, and Br) observed by the gas electron diffraction methods.[1,9,10] It may be seen from the table that these good agreement between the electron diffraction data and the present results in the senses that the GG′ form of *n*-butyl chloride is present in a considerable concentration and that the GG′ form of *n*-butyl bromide is not present in a readily measurable concentration. The qualitative agreement between the two sets of experimental results, namely, for the gas and liquid phases, is naturally accepted because the change in a dipole moment due to the change in molecular configuration is very small for the $CH_3CH_2CH_2CH_2X$ type molecules; therefore, the relative stabilities of the rotational isomers change little on passing from the vapour to the liquid phase. This only emphasizes that parallel (1 : 3) interactions between methyl and chlorine groups do not satisfy the criterion for rejecting the presence of a certain rotational isomer.

Relative Stabilities of Rotational Isomers. All attempts to obtain the energy differences between rotational isomers were unsuccessful because of the poor S/N ratios of the spectra. From the temperature dependence of the Raman spectra of Fig. 8, however, a few conclusions may be drawn. The relative Raman intensities do not change remarkably; this indicates that the energy differences between the rotational isomers of *n*-butyl chloride are rather small. The relative intensity of the 438 cm^{-1} line of Fig. 2 decreases rapidly as the temperature goes down. This result supports the conclusion of the gas-phase data that GT form is the most unstable form. Two Raman lines are seen at 405 and 476 cm^{-1} in the spectra observed at about −160°C; they may correspond to an unannealed glassy solid. This indicates that both TT and GG forms coexist in the glassy solid. The most important conclusion may be drawn from the relative intensity change in the Raman line at 529 cm^{-1}. Although the temperature changes from 27°C to 70°C, its relative intensity changes little. Thus, we can conclude that the GG′ form is as stable as the other rotational isomers. It is of some interest to add that the relative stability of the five rotational isomers of vapour *n*-butyl chloride is calculated from the percentage concentrations of Table 1 to be in this order:

$$\text{TG} > \text{TT} > \text{GG}' > \text{GG} > \text{GT-form},$$

where the contribution of the entropy term to the concentrations is taken into account in the calculation.

In order to emphasize the anomalous feature of the present results (or those of Ref. 1.) for *n*-butyl chloride, a rough estimation of internal energies of rotational isomers will be made for $CH_3CH_2CH_2CH_2X$-type molecules. If we assume that the magnitude of the internal-energy difference between *trans* and *gauche* isomers of *n*-butane or *n*-propyl chloride can be transferred to *n*-butyl chloride, the internal-energy difference between the TT isomers and others may be estimated to a zero-th order approximation;

$$\Delta E(\text{TT-TT}) = 0,$$

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[8] A. B. Dempster, K. Price, and N. Sheppard, *Spectrochim. Acta*, **25A**, 1381 (1969).

[9] F. A. Monany, R. A. Bonham, and W. H. McCoy, *J. Amer. Chem. Soc.* **85**, 3077 (1963).

[10] R. A. Bonham, L. S. Bartell and D. A. Kohl, *ibid.*, **81**, 3491 (1959).

$$\Delta E(\text{GT-TT}) \simeq 0,$$
$$\Delta E(\text{TG-TT}) \simeq 0.75,$$
$$\Delta E(\text{GG-TT}) \simeq 0.75,$$
and $\Delta E(\text{GG}'\text{-TT}) \simeq 0.75 + E$ (parallel (1 : 3) interactions)

in units of kcal/mol, as the internal-energy differences of *n*-butane[11] and *n*-propyl chloride[12,13] are

$$\Delta E(\text{C}_4\text{H}_{10}) \simeq 0.75$$
and $\Delta E(\text{C}_3\text{H}_7\text{Cl}) \simeq 0,$

where $\Delta E = E(gauche) - E(trans)$. In other words, the relative stability of the rotational isomers may be in this order:

$$\text{TT} \simeq \text{GT} > \text{TG} \simeq \text{GG} > \text{GG}'\text{-form}.$$

These results are quite different from those obtained from Table 1 (see the preceding paragraph).

Similar calculations can be performed for *n*-butyl bromide using $\Delta E(\text{C}_4\text{H}_{10}) = 0.75$ kcal/mol and $\Delta E(\text{C}_3\text{H}_7\text{Br}) \simeq 0$[12-14], or for *n*-pentane using $\Delta E(\text{C}_4\text{H}_{10}) = 0.75$; the results agree well with those obtained from Table 1. In the cases of *n*-pentane and *n*-butyl bromide, the absence of the GG′ form can be accounted for if we consider large enough parallel (1 : 3) interactions between two methyl groups or between methyl and bromine substituents. In order to stabilize the GG′ form of *n*-butyl chloride, however, we have to consider some unfamiliar parallel (1 : 3) interactions whose interaction energy is negative, that is, attractive rather than repulsive.

Conclusion

It was ascertained that liquid *n*-butyl chloride is a mixture of the TT, GT, TG, GG, and GG′ isomers, while liquid *n*-butyl bromide is a mixture of the TT, GT, TG, and GG isomers. Only the TT isomer remains in the crystalline state of *n*-butyl chloride or *n*-butyl bromide. These conclusions confirm the results obtained by means of the electron-diffraction method by Ukaji and Bonham.

The existence of the GG′ form in a redily measurable concentration leads to the conclusion that we cannot deny the possibility of the presence of certain rotational isomers by the reason that there are expected parallel (1 : 3) interactions between methyl and chlorine substituents in the configurations. The results also indicate that the parallel (1 : 3) interactions between methyl and chlorine substituents might be attractive rather than repulsive in nature.

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[11] G. J. Szasz, N. Sheppard, and D. H. Rank, *J. Chem. Phys.*, **16**, 704 (1948).

[12] C. Komaki, I. Ichishima, K. Kuratani, T. Miyagawa, T. Shimanouchi, and S. Mizushima, This Bulletin, **28**, 330 (1955).

[13] Y. A. Pentin and V. M. Tatevskii, *Dokl. Akad. Nauk. SSSR*, **108**, 290 (1956).

[14] T. Yoshino and H. J. Bernstein, *Can. J. Chem.* **35**, 339 (1957).