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Vibration Spectra and Molecular Structures of *n*-Butyronitrile, β-Chloropropiononitrile, and β-Bromopropiononitrile

Tsunetake Fujiyama

Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo, Hongo, Tokyo

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Infrared and Raman spectra of XCH_2CH_2CN-type molecules (X=CH_3, Cl, and Br) are studied. From the spectral analysis, it is concluded that *trans* and *gauche* isomers coexist in the liquid phase, the *gauche* being more stable. It is also shown that these molecule take *gauche* configurations in the crystalline phase.

In a previous report, the vibration spectra and the molecular structure of succinonitrile were discussed from the point of view of a normal coordinate treatment and the molecular structure.[1] The spectra of succinonitrile in the solid state showed that *trans* and *gauche* forms coexist above −50°C, while only the *gauche* form remains below −50°C. These results are quite different from those of ordinary disubstituted ethanes, such as *n*-butane, 1,2-dichloroethane, and 1,2-dibromoethane, where the stable configuration in the crystalline phase is the *trans* form.[2] In order to ascertain whether this is a phenomenon characteristic of the molecules having cyanide groups, the infrared and Raman spectra of XCH_2CH_2CN-type molecules (X=CH_3, Cl, and Br) were studied. An empirical rule was proposed by the present author for the relationship between the skeletal deformation vibrations and the molecular configurations of rotational isomers.[3] The validity of this rule was also tested in the present work.

Experimental

Samples. *n*-Butyronitrile was prepared from *n*-butyric acid by the standard method. The product was purified by redistillation; bp 117°C/760 mmHg. The purity was tested by means of gas chromatography.

β-Chloropropiononitrile was synthesised from ethylene cyanohydrin. Thionylchloride was mixed with ethylene cyanohydrin and kept at room temperature for several hours. The mixture was washed with a $NaCO_3$-H_2O solution, dried over calcium chloride, and then distilled; bp 175°C/760 mmHg.

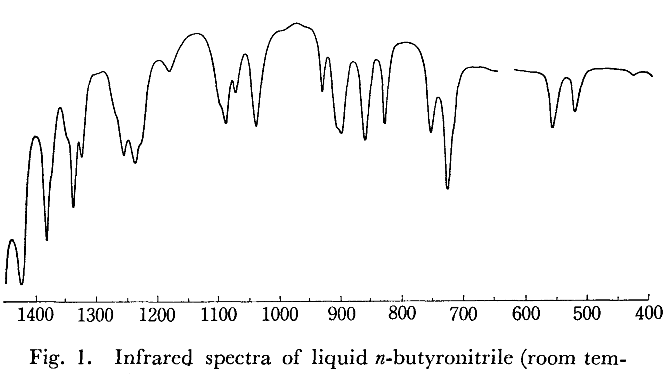

Fig. 1. Infrared spectra of liquid *n*-butyronitrile (room temperature).

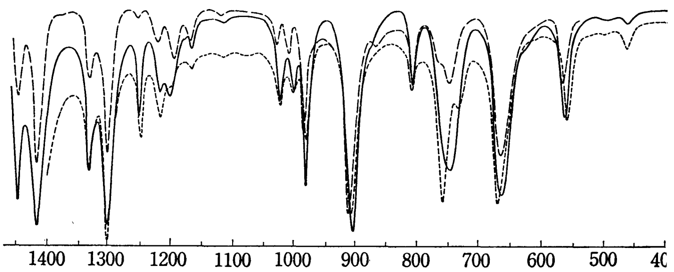

Fig. 2. Infrared spectra of β-chloropropiononitrile (——: liquid, room temperature, ———: glass, −196°C, ----: CS_2 solution).

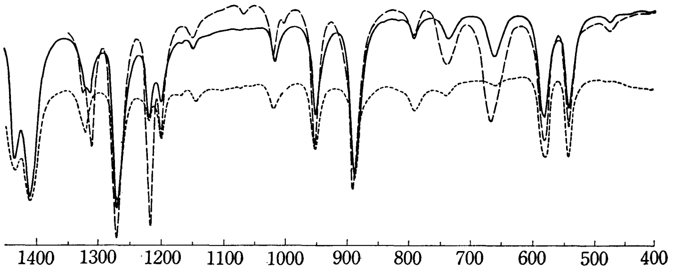

Fig. 3. Infrared spectra of β-bromopropionitrile (——: liquid, room temperature, ----: glass, −196°C, ----: CS_2 solution).

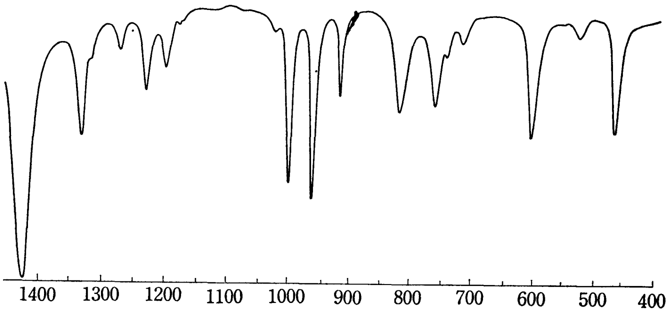

Fig. 4. Infrared spectra of succinonitrile (room temperature).

β-Bromopropiononitrile was also made from ethylene cyanohydrin. Ethylene cyanohydrin was mixed with phosphorous tribromide in ether on an iced-bath and was then kept for 24 hr. The mixture was washed with a $NaCO_3$-H_2O solution, dried over calcium chloride, and distilled; bp 63–65°C/5 mmHg. As the product was rather unstable in the air, freshly-distilled samples were used for the measurements.

Vibration Spectra. The infrared spectra in the NaCl and KBr regions (4000–500 cm^{-1}) were recorded by a Japan Spectroscopic Company 402G grating infrared spec-

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[1] T. Fujiyama, K. Tokumaru, and T. Shimanouchi, *Spectrochim. Acta*, **20**, 415 (1964).

[2] For example, S. Mizushima, Y. Morino, and T. Shimanouchi, *J. Phys. Chem.*, **56**, 324 (1952).

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

TABLE 1. OBSERVED FREQUENCIES OF LIQUID XCH_2CH_2CN

$CH_3CH_2CH_2CN$		$ClCH_2CH_2CN$		$BrCH_2CH_2CN$	
Frequency	Mode	Frequency	Mode	Frequency	Mode
				95	t: δ(CCBr)
100					
		109			
				123	g: δ(CCBr)
				158	t: δ(CCN), C
		167	t: δ(CCN), C		
176	g: δ(CCN), C				
188	t: δ(CCN), C				
		202	g: δ(CCN), C	202	g: δ(CCN), C
				288	g: δ(CCN), B
		300	t: δ(CCCl)		
		318	g: δ(CCN), B		
360	g: δ(CCN), B				
		372	t: δ(CCN), B	372	t: δ(CCN), B
373	t: δ(CCN), B				
392	t: δ($CCCH_3$)				
430	g: δ($CCCH_3$)				
		465	g: δ(CCCl)		
				477	t: δ(CCC), A
		494	t: δ(CCC), A		
529	t: δ(CCC), A			544	g: δ(CCC), A
560	g: δ(CCC), A				
		562	g: δ(CCC), A		
				581	g: ν(C-Br)
		673	g: ν(C-Cl)		
				685	t: ν(C-Br)
737					
				745	t: CH_2 rock.
		752	t: ν(C-Cl)		
764					
			t: CH_2 rock.		
				797	g: ν(C-CN)
		812	g: ν(C-CN)		
				820	t: ν(C-CN)
871					
		880	t: ν(C-CN)		
				892	g: CH_2 rock.
		908	g: CH_2 rock.		
912	(904, 916 in CS_2)				
940					
				954	g: CH_2 rock.
		983	g: CH_2 rock.		
				1003	t: CH_2 rock.
		1004	g: CH_2 rock.		
1046					
				1065	t: ν(C-C)
		1077	t: ν(C-C)		
1080					
1095					
1103					
		1116	t: CH_2 twist.		
				1148	t: CH_2 twist.
		1168	g: CH_2 twist.		
				1180	g: CH_2 twist.
1182	(1177, 1195 in CS_2)				
		1201	g: CH_2 twist.		
				1204	g: CH_2 twist.
		1217	t: CH_2 twist.		
				1224	t: CH_2 twist.
1230					
		1252	t: CH_2 wag.		
1260					
				1272	g: CH_2 wag.
1275					t:
1300					
		1302	g: CH_2 wag.		
				1316	t: CH_2 wag.
				1324	g: CH_2 wag.
1327					
		1332	g: CH_2 wag.		
			t:		
1340					
1348					
1350					
1385					
		1414	CH_2 bend.	1412	CH_2 bend.
1426					
		1447		1437	
1463					

δ; bending, ν; stretching, rock.; rocking, twist.; twisting, wag.; wagging, bend.; bending, t; *trans*, g; *gauche*, A, B, C; see the text.

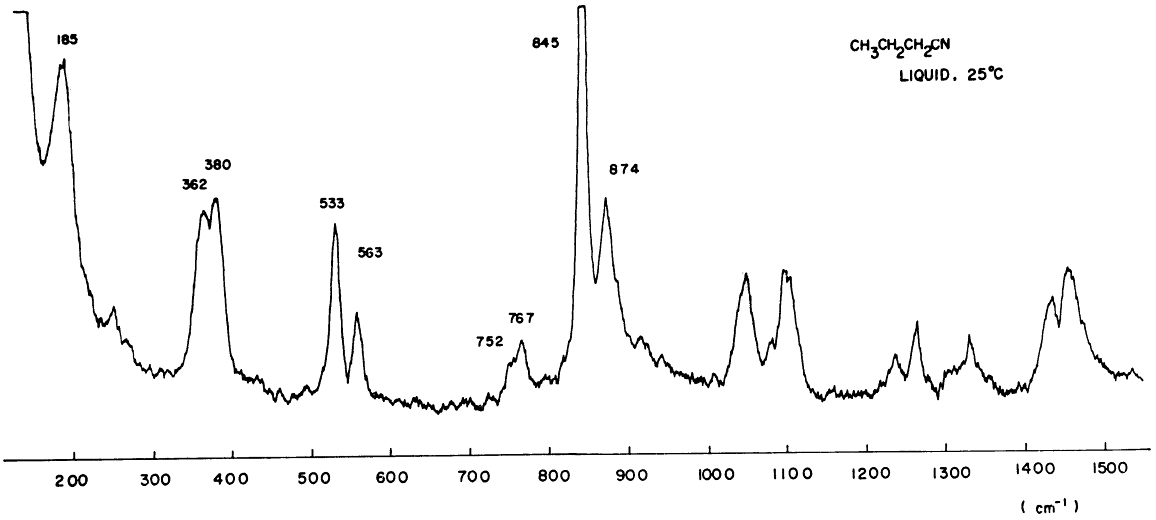

Fig. 5. Raman spectra of *n*-butyronitrile (liquid, room temperature).

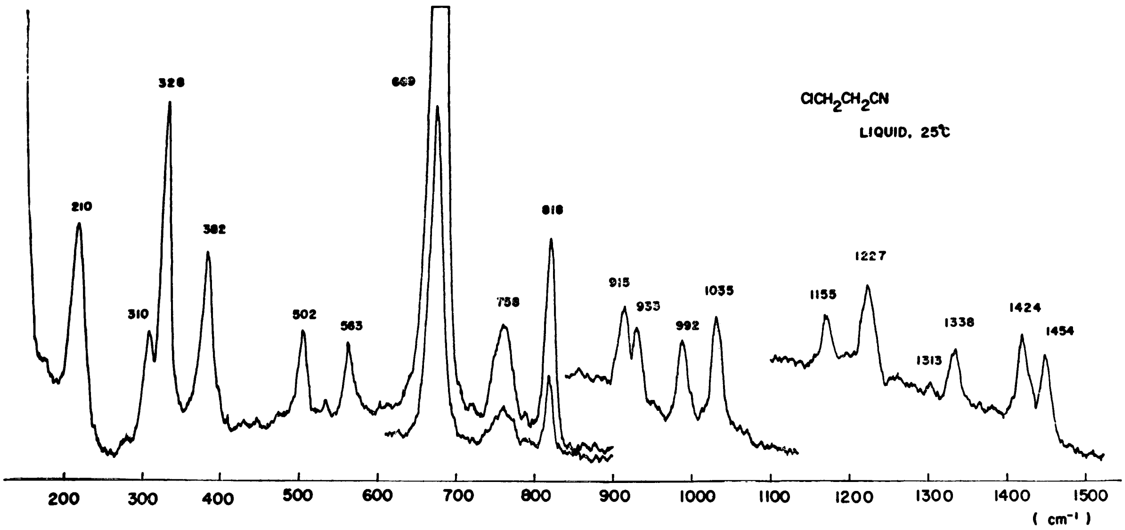

Fig. 6. Raman spectra of β-chloropropiononitrile (liquid, room temperature).

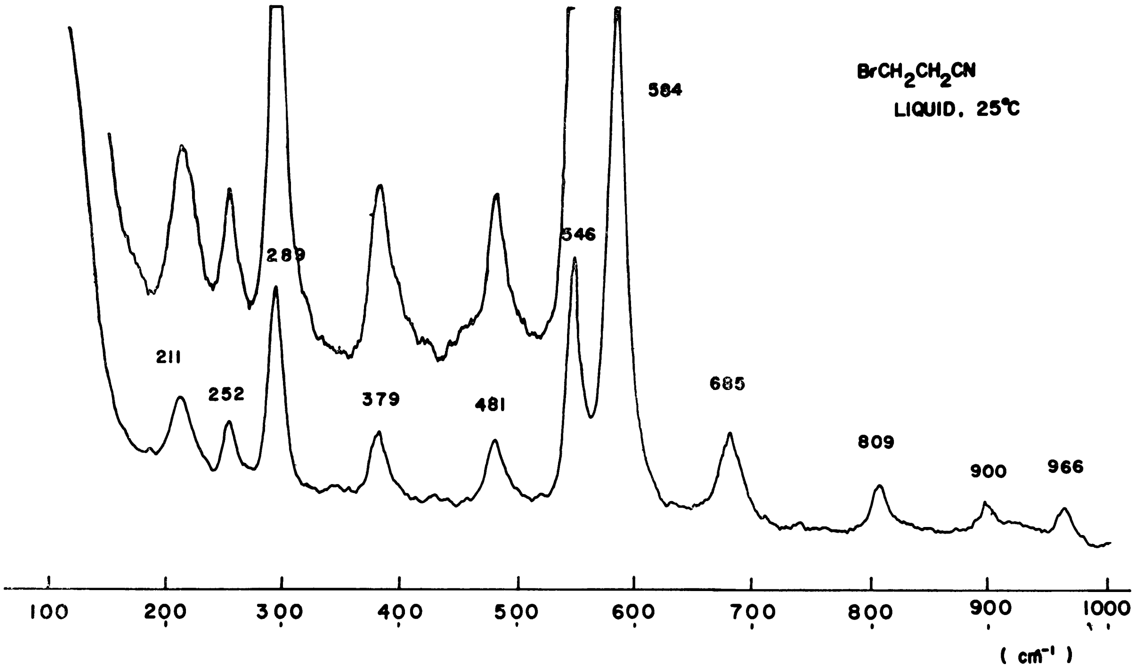

Fig. 7. Raman spectra of β-bromopropiononitrile (liquid, room temperature).

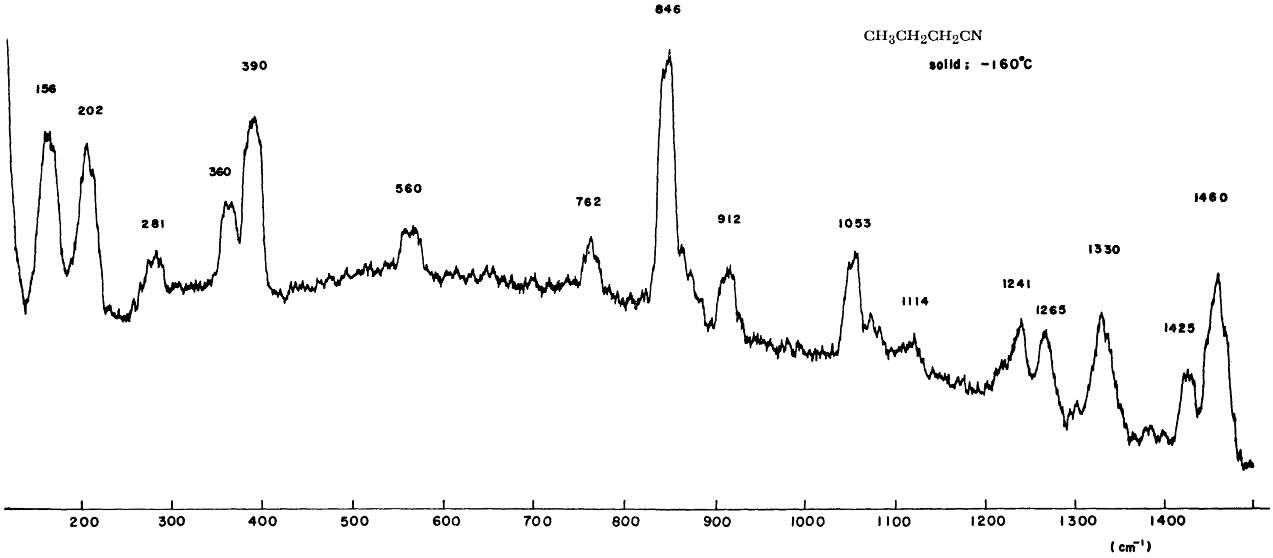

Fig. 8. Raman spectra of crystalline *n*-butyronitrile.

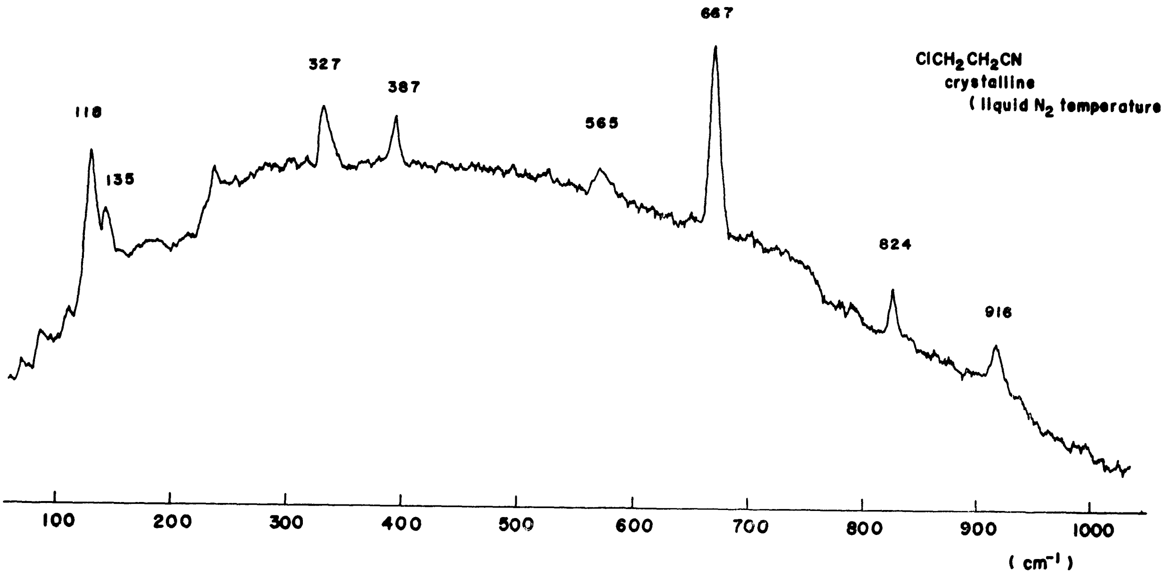

Fig. 9. Raman spectra of crystalline β-chloropropiononitrile.

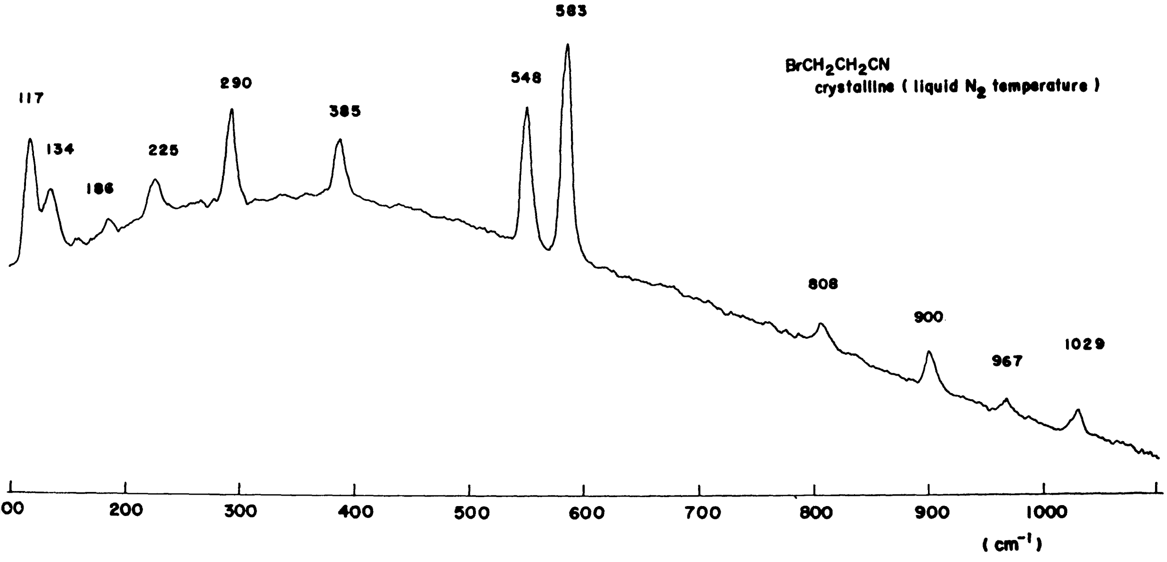

Fig. 10. Raman spectra of crystalline β-bromopropiononitrile.

trometer. A Hitachi FIS-1 far-infrared spectrometer was used for the measurement of the infrared spectra in the lower-frequency region. The Raman spectra were recorded by means of a laser Raman spectrometer which had been designed and constructed in our laboratory.[4] The spectrometer was operated under a resolution of 5–10 cm^{-1}.

The observed frequencies for the liquid sample are summarised in Table 1. The observed infrared spectra of the XCH_2CH_2CN-type molecules in the region of 1400–400 cm^{-1} are shown in Figs. 1–3. For the cases of β-chloropropiononitrile and β-bromopropiononitrile, the spectral changes observed at a low temperature (liquid nitrogen) and in a CS_2 solution are also included. The infrared spectra of succinonitrile observed at room temperature is given in Fig. 4 for comparison. It is important to emphasise that the infrared spectra at low temperatures do not correspond to those of the crystalline phase, although the liquid-nitrogen temperature is lower than the melting points of the samples. The infrared spectra were obtained from films deposited on a cooled (−196°C) potassium chloride window in a conventional low-temperature cell. The deposited film was transparent and the samples were assumed to be in the glassy state. An attempt to obtain the crystalline sample by annealing was unsuccessful.

The Raman spectra for the liquid XCH_2CH_2CN-type molecules in the region of 100–1400 cm^{-1} are shown in Figs. 5–9. The Raman spectra for the crystalline samples are shown in Figs. 6–10. In the case of Raman spectroscopy, annealing is much easier.

Normal Coordinate Treatment

For confirming the vibrational assignment, the normal frequencies of the XCH_2CH_2CN-type molecules were calculated by using the force constants obtained for a series of alkanonitriles[5] and alkylhalides.[6] The method of calculation has been described in other papers.[1,7] In the present report, the results of the calculation will not, then, discussed in detail.[8]

Vibrational Assignment and Discussion

Solvent Effect. The *trans* isomer of β-chloropropiononitrile or β-bromopropiononitrile is stabilised more than the *gauche* isomer when the molecule is dissolved in a medium with a small dielectric constant, such as carbon disulfide, because the dipole moment of the *gauche* isomer is larger than that of the *trans* isomer. Thus, the solvent effect on the spectrum is very good experimental evidence for the identification of vibration bands related with rotational isomers.

Two types of absorption bands are found in Figs. 2 and 3. Their relative intensities in a CS_2 solution increase in one type and decrease in the other type. The absorption bands belonging to the former type are assigned to the *trans* isomer, and the other bands, to the *gauche* isomer. In Table 1, the *trans* and the *gauche* bands are indicated by "*t*" and "*g*" respectively.

Low-temperature Spectra. When the infrared spectra of β-chloropropiononitrile and β-bromopropiononitrile at the temperature of liquid nitrogen are compared with those at room temperature, an increase in the relative intensities is observed for the *gauche* bands, while the *trans* bands lose some of their intensities (see Figs. 2 and 3). The Raman spectra of the crystalline samples (see Figs. 6, 8, and 10) definitely determine the location of vibration bands corresponding to either the *trans or gauche* isomer.

Skeletal Deformation Vibrations. Skeletal deformation vibrations and torsional vibrations are expected to occur in the region of 100–700 cm^{-1}. The skeletal deformation vibrations of alkanonitriles can be conveniently classified into three groups.[3] We call them the A, B, and C groups. The B group is composed of pure C–C≡N bending vibrations which occur in the region of 300–400 cm^{-1} with strong intensities. The frequencies related to this vibrational mode are hardly affected by the change in the geometry of the rotational isomers. The A and C groups are composed of the coupled vibrations of C–C≡N bending and C–C–C (or C–C–X) deformation modes, which are localized in the regions of 500—600 cm^{-1} and 100—200 cm^{-1} respectively. The A-type deformation vibrations are good characteristic frequencies with respect to the rotational isomerism. In this group, the vibration of a *trans* isomer has a lower frequency than that of a *gauche* isomer. On the other hand, the C-type deformation-vibration frequencies exhibit rather irregular behaviour because of their coupling with torsional vibrations. In the Raman spectra of Figs. 5—10, we see the bands corresponding to the skeletal deformation vibrations of the A, B, and C types. For example, the Raman bands at 563 and 533 cm^{-1} of *n*-butyronitrile correspond to the A-type deformation vibrations, while the bands at 380 and 362 cm^{-1} and the bands at 185 cm^{-1} correspond, respectively, to the B- and the C-type deformation vibrations.

The spectral changes in the skeletal deformation vibrations on passing from the liquid to the crystalline phase give most reliable experimental evidence for the assignment of the vibration frequencies to the rotational isomers. In the cases of β-chloro- and β-bromopropiononitriles, *trans* and *gauche* bands can easily be identified by referring to the empirical rule of a stretching-vibration frequency of a carbon-halogen bond.[9] A comparison of the spectra in Figs. 6 and 8 shows that the C–Cl stretching vibration at 758 cm^{-1} and the skeletal deformation vibration at 502 cm^{-1} of β-chloropropiononitrile belong to one rotational isomer, while the band at 669 cm^{-1} (the C–Cl stretching) and the band at 563 cm^{-1} (the skeletal deformation) belong to the other rotational isomer. As the C–Cl stretching vibration at 758 cm^{-1} originates from the *trans* isomer, the band at 502 cm^{-1} is assigned to the A-type skeletal deformation vibra-

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

[5] T. Fujiyama, This Bulletin, **44**, 89 (1971).

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

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

[8] The detailed results of the calculation are available upon request.

[9] S. Mizushima, T. Shimanouchi, K. Nakamura, M. Hayashi, and T. Tsuchiya, *J. Chem. Phys.*, **26**, 970 (1957).

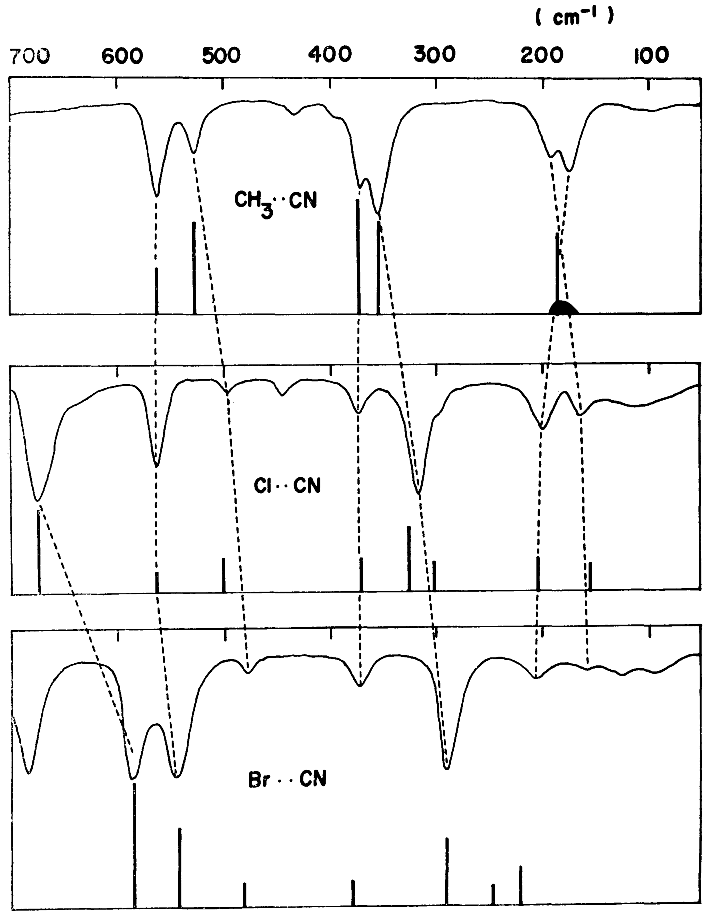

Fig. 11. Comparison of skeletal deformation vibrations of XCH_2CH_2CN (upper curve: infrared, lower bar: Raman).

tion of the *trans* isomer. In the same way, the band at 563 cm^{-1} corresponds to the A-type deformation vibration of the *gauche* isomer, because the 669 cm^{-1} band can definitely be assigned to the C–Cl stretching vibration of the *gauche* isomer. The same situation holds for the bands at 685 and 481 cm^{-1} and for the bands at 584 and 546 cm^{-1} in the case of β-bromopropiononitrile (see Figs. 7 and 10). In the same way, the bands due to the skeletal deformation vibrations can easily be classified for each rotational isomer. The results are summarised in Table 1.

In the case of *n*-butyronitrile, the frequency assignments are based upon the results of normal coordinate treatment and the results of the vibrational assignment for β-chloro- and β-bromopropiononitriles. Two A-type skeletal deformation bands are found, at 533 and at 563 cm^{-1} (see Fig.5). The vibration frequencies are calculated to be 562 cm^{-1} for the *gauche* isomer and 513 cm^{-1} for the *trans* isomer. Thus, the observed frequenciy of 563 cm^{-1} is assigned to the *gauche* isomer, while that of 533 cm^{-1} is assigned to the *trans* isomer. These assignments correspond to those of β-chloro- and β-bromopropiononitrile very well.

The relative intensities of the A-type bands present another confirmation of the assignment. In Fig.11, the infrared and Raman spectra of the XCH_2CH_2CN-type molecules are compared. The relative intensity of the A-type molecules are compared. The intensity of the A-type band of the *gauche* isomer is stronger than that of the *trans* isomer in the infrared spectra, while the *gauche* band decreases in relative intensity in the Raman spectra. This may correspond to the situation that an A-type band of a *trans*-isomer is infrared-inactive if a molecule is of the XCH_2CH_2X type.

Other Vibrations. The assignments of the other vibrations, namely, the CH_2 deformation vibrations, the C–C stretching vibrations, and the C–CN stretching vibrations, are rather straightforward with the help of the well-established frequency assignments for 1,2-disubstituted ethanes and the results of the calculated normal frequencies. The results are summarised in Table 1. As for *n*-butyronitrile, the identification of the *trans* and *gauche* bands were not definite in this region and, therefore, the observed frequencies were not assigned.

Rotational Isomer. For the three molecules studied, it is ascertained that the *trans* and the *gauche* isomers coexist in the liquid phase. The energy differences between the two rotational isomers in the liquid phase were observed to be about 640, 500, and 420 cal/mol for β-bromopropiononitrile, β-chloropropiononitrile, and *n*-butyronitrile respectively, the *gauche* isomers being more stable. The values of the energy difference are preliminary; a detailed discussion will be reported elsewhere.

The Raman spectra of the crystalline samples show that the *gauche* isomers remain in the crystalline state at the temperature of liquid-nitrogen. The conclusion for *n*-butyronitrile contradicts that of Reference.[10] There was no spectral evidence for the coexistence of the *trans* and *gauche* isomers in the solid state.

The author wishes to acknowledge helpful correspondence with Dr. T. Shimanouchi and Dr. I. Suzuki of The University of Tokyo.

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[10] J. J. Lucier, E. C. Tuazon, and F. F. Bentley, *Spectrochim. Acta*, **24**, 771 (1968).