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Infrared and Raman Spectra of 2, 3-Dichloro-2, 3-dimethylbutane[*1]

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Infrared spectra of $Cl(CH_3)_2C$–$C(CH_3)_2Cl$ were obtained over the region from 400 cm^{-1} to 4000 cm^{-1} at room temperature in the gas phase, dilute solutions, and KBr-disk. In the KBr-disk case, spectra were also obtained at lower temperatures. In the gas phase, and in the disk at lower temperatures, spectral simplifications were obtained. Raman spectra at room temperature were photographed for the crystalline sample, and also for 17—25% solutions in several solvents. The coexistence of trans-gauche isomers in the high-temperature solid phase of this compound was verified by spectral comparison between trans- and gauche-isomers. The energy difference between two isomers was estimated to be about 1.5 kcal/mol from temperature changes in the infrared intensities.

The existence of an equilibrium mixture of two rotational isomers[*2] for 1, 2-disubstituted-ethanes such as ClH_2C–CH_2Cl has been well established by spectroscopic studies.1) For the case of 2, 3-dichloro-2, 3-dimethylbutane, $Cl(CH_3)_2C$–$C(CH_3)_2Cl$, and 2, 3-dibromo-2, 3-dimethylbutane, $Br(CH_3)_2C$–$C(CH_3)_2Br$, which have molecular structures analogous to ClH_2C–CH_2Cl, Morino *et al.* have reported the existence of trans-gauche equilibrium mixtures for the molecular system in carbon tetrachloride, heptane, and benzene solutions by dipole moment measurements.2) Park *et al.*3) observed the infrared and Raman spectra of $Br(CH_3)_2C$–$C(CH_3)_2Br$, and they reported that there is no evidence for the existence of an equilibrium mixture of trans- and gauche-rotational isomers in the solid state, while in the liquid, and in dilute solution the gauche form was found to exist. For $Cl(CH_3)_2C$–$C(CH_3)_2Cl$, our previous paper4) revealed that in the high-temperature solid phase above $-112°C$, the molecule has some degree of rotational or reorientational freedom in the crystalline lattice. The analysis of the transition entropy of this compound has suggested the possibility of the existence of the rotational isomers in the high-temperature phase.5)

Experimental

Sample. Pinacon was treated with an aqueous solution of hydrochloric acid saturated at about $-20°C$, and the mixture was allowed to stand for two weeks before filtration. The precipitate was purified by recrystallization from ethyl alcohol three times, and by fractional sublimation under a vacuum of about 10^{-5} mmHg. The melting point was found to be 158°C in a sealed tube.

Equipment. Infrared spectra were recorded with an infrared recording spectrometer Model DS-402 G of the Japan Spectroscopic Co., Ltd. The spectral region investigated was from 400 cm^{-1} to 4000 cm^{-1}. For the lower temperature measurements, the low-temperature cell of the Japan Spectroscopic Co., Ltd. was used. As the cooling material, a dry-ice - acetone solution was used for measurements at $-80°C$, and liquid nitrogen was used for measurement at $-170°C$.

Raman spectra were photographed with a model RL-II Raman Spectrograph (Yuki-Gosei-Yakuhin Co., Ltd.), which was modified for measurement of the crystalline sample, as reported in another paper.6) The exciting light from a mercury lamp (4358 Å) was filtered through a layer of saturated aqueous solution of potassium nitrite. The mercury lamp was used with an electric current of 24—25 A. The slit width was 3—5×10^{-2} mm, and exposure time 3—5 hr. Neopan SSS

[*1] A part of this work was presented at the Symposium on Molecular Structure, Sapporo, 7th Oct., 1967.

[*2] There are actually three isomers, two of them are spectroscopically identical.

1) For instance a) S. Mizushima, "Structure of Molecule and Internal Rotation," Academic Press, New York (1954); b) N. Sheppard, *Adv. Spectroscopy*, **1**, 288 (1959); c) W. F. Edgell and G. J. Glocker, *J. Chem. Phys.*, **9**, 375 (1941); d) J. T. Neu and W. D. Gwinn, *ibid.*, **18**, 1642 (1950); e) G. J. Szasz, N. Sheppard and D. H. Rank, *ibid.*, **16**, 704 (1948); **17**, 86 (1947); f) W. E. Fitzgerald and G. J. Janz, *J. Mol. Spectry.*, **1**, 49 (1957).

2) Y. Morino, I. Miyagawa, T. Haga and S. Mizushima, This Bulletin, **28**, 165 (1955).

3) P. J. D. Park and E. Wyu-Jones, *Chem. Commn.*, **1966**, 557.

4) T. Koide and T. Oda, This Bulletin, **29**, 208 (1956).

5) T. Koide, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **88**, 152 (1967).

6) Y. Matsui, T. Kubota, H. Tadokoro and T. Yoshimura, *J. Polymer Sci.*, **A3**, 2275 (1965).

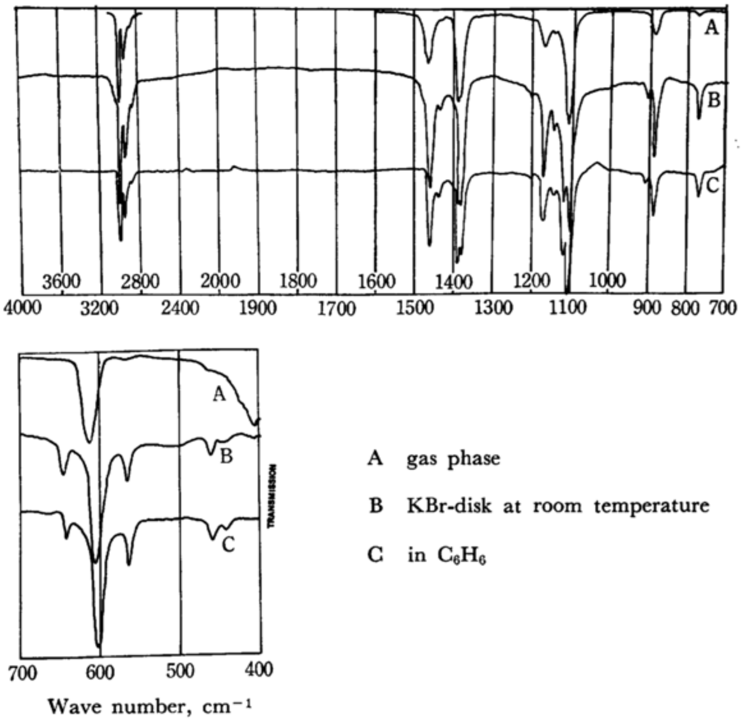

Fig. 1. Infrared spectrum for $Cl(CH_3)_2C-C(CH_3)_2Cl$.

film of the Fuji Film Co., Ltd. was used. The usual Raman tube was not suitable for the present measurements because of the high volatility of the sample. For this reason, the sample was put into a flat-bottomed test tube. After evacuating the tube for two or three minutes, it was filled with nitrogen gas, and sealed-off 10 cm from the bottom.

Results

The infrared spectra at room temperature were observed for the gas phase, KBr-disk, Nujol, and dilute solutions with the solvents carbon tetrachloride, benzene, carbon disulfide, *N, N*-dimethylformamide, and acetonitrile. In the case of the KBr-disk, spectra were also obtained at temperatures of about −80°C and −170°C. Raman spectra were obtained for the crystalline state, and 17—25% solutions in carbon tetrachloride, *n*-heptane, and acetonitrile.

The results of the infrared measurements in the gas phase, KBr-disk, and the dilute benzene solution are collected in Fig. 1 and Table 1. In Table 1, the results of the Raman measurements are also summarized together with the previous results of Kahovec.⁷⁾ The present Raman spectra may be seen to be in accord with those of Kahovec *et al.*⁷⁾

In Fig. 2, infrared spectra taken under various conditions are shown for the frequency range from

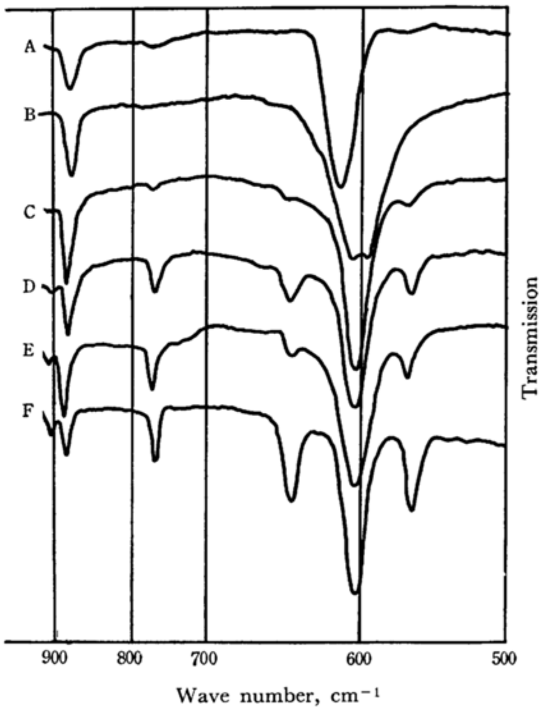

Fig. 2. The infrared spectrum of $Cl(CH_3)_2C-C(CH_3)_2Cl$ under various conditions.
A, gas phase; B, KBr-disk at −170°C; C, KBr-disk at −80°C; D, KBr-disk at room temperature; E, C_6H_6 solution; F, CH_3CN solution.

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7) L. Kahovec and J. Wagner, *Z. phys. Chem.*, **48**, 1347 (1940).

TABLE 1. THE INFRARED AND THE RAMAN SPECTRA OF $Cl(CH_3)_2C\text{-}C(CH_3)_2Cl$ (Unit in cm^{-1})

Gas at 50—60°C	Infrared				Raman			
	Solution		Solid		Solid		Solution	
	in C_6H_6	in CH_3CN	at 25°C	at −80°C	Present	Kahovec*	in CCl_4	in CH_3CN
					216 1/3			
					370 1/2		372 2	373 1
	444 vw	442 w	443 vw					
	460 w	459 w	462 w	462 vw				
	564 w	562 m	565 w	564 vw	568 1/3		569 1/2	566 1/2
					596 2	595 2	596 2	596 1
613 s	604 vs	604 vs	604 vs	607 vs				
	644 w	646 m	648 w	650 vw				
					757 1	754 2		755 1
768 vw	765 w	762 m	766 w	766 vw				
880 m	880 m	880 m	879 m	880 s				
	900 vw	901 w	902 vw					
	925 vw							
	942 vw	946 vw						
						954 1/4		
			1000 vw					
1100 vs	1095 vs	1095 vs	1095 vs	1094 vs				
1105 vs	1111 w	1111 s	1110 m	1110 w				
					1133 1/2	1130 1/2	1134 0	1138 1
1139 w	1139 w	1140 w	1139 w	1140 w				
1163 m	1164 m	1163 m	1164 m	1164 m				
	1201 vw	1202 w						
						1231 0		
1379 s	1375 s		1373 s	1373 s				
1385 s	1383 s		1380 s	1380 m		1387 100		
1390 m	1432 w		1431 m	1431 w				
						1448 1/2		
1458 m	1456 s		1456 s	1456 s				
1464 m			1462 m	1462 m				
1470 m								
						2762 0		
			2873 w					
			2943 w		2940 1	2935 3		
			2990 s		2990 1/2	2988 3		
					3003 1/2			

* L. Kahovec and J. Wagner, *Z. phys. Chem.*, **48**, 1347 (1940).

900 to 400 cm^{-1}. In Fig. 3, infrared spectra of the KBr-disk at lower temperatures are shown, for the frequency region 700—400 cm^{-1}. In this figure, the temperatures indicated for each curve are the averaged temperatures for the run of each measurement except for 25, −80, and −170°C; the apparatus used for the low temperature measurements was not temperature controlled during the interval of the measurement except for the above three temperatures. The temperature was maintained to within ±0.5°C at 25, −80, and −170°C, and at other temperatures, the change in temperature was about ten degrees for each interval of measurement.

The general pattern of the infrared spectra for each sample at room temperature was very close to each other except for those of the gas phase, in which spectral simplifications are observed, as shown in curve A of Fig. 1, and Fig. 2. Namely, the absorption bands at 443, 462, 565, and 648 cm^{-1} of the KBr-disk (Fig. 1 B) disappeared in the gas phase. The same simplifications stated above are also observed in the KBr-disk at lower-temperatures. (See Fig. 2B, and Table 1)

The spectral simplifications suggest the coexistence of rotationally isotropic forms in the molecular system of the KBr-disk sample, as compared with the case of 1, 2-disubstituted ethanes.[1] The problem of rotational isomerism in the present substance will be discussed in the next section.

Discussion

Rotational Isomerism. If we confine the problem to whether rotational isomers exist or not, it is sufficient to focus our attention on the C–Cl stretching band.

In general, the C–Cl stretching bands are said to appear in the region of 600—800 cm^{-1}. Actually, for the case of ClH_2C-CH_2Cl, the C–Cl stretching frequencies are observed at 665 (A), 675 (B), and 709 (Bu) cm^{-1}.8) However, Mizushima *et al.*9) have shown that the C–Cl stretching frequencies of the tertiary carbon atom such as $Cl(CH_3)_2C-$ appeared in the regions of 610—640 cm^{-1} and 550—580 cm^{-1}. For instance, in the case of $Cl(CH_3)_2C-CH_2Cl$,9) the C–Cl stretching appeared at 621 cm^{-1} (T_x[*3]) and 572 cm^{-1} (T_H[*3]), and in the case of $Cl(CH_3)_2C-CH_2(CH_3)$9) at 613 cm^{-1} (T_x) and 558 cm^{-1} (T_H).

At room temperature, the KBr-disk of $Cl(CH_3)_2C-C(CH_3)_2Cl$ shows three frequency bands in this region, at 565, 604, and 648 cm^{-1}. Therefore, these bands seem to be the C–Cl stretching frequencies. This supposition may be ensured from the comparison of the Raman spectra with the infrared spectra.

The point groups of the molecular configurations and the types of vibrations expected for trans- and gauche-isomers of this compound are summarized in Table 2.10) In the case of the gauche isomer, all the fundamental modes are active for both Raman and infrared spectra, while in the case of the trans-form the fundamental modes are mutually exclusive.

Inspection of Table 1 shows that the rule of mutual exclusion holds at 596 and 757 cm^{-1} for Raman spectra, and also at 604 cm^{-1} for infrared for the solid sample. Nevertheless, the band at 565 cm^{-1} is active for both Raman and infrared spectra. From the above considerations, the infrared band at 604 cm^{-1} be attributed to a may Bu-type vibration of C–Cl stretching, and that at 565 cm^{-1} is considered due to the gauche-form vibration.

TABLE 2. TYPES OF VIBRATION

Trans form (C_{2h})			Gauche form (C_2)		
	Activity			Activity	
Type	Raman	IR	Type	Raman	IR
A_g	+	−	A	+	+
A_g	−	+			
B_g	+	−	B	+	+
B_u	−	+			

Furthermore, to confirm these assignments, the comparison of the intensity of these bands obtained under various conditions is also available. From Fig. 2, for the KBr-disk, and the benzene solution at room temperature, the bands (565, 604, 648, and 766 cm^{-1}) show patterns almost simillar to each other, and further their relative intensities show a similarity (see curves D and E in Fig. 2). On the other hand, for the dilute solutions of this compound with polar solvents of $HCON(CH_3)_2$[*4] and CH_3CN,[*4] the intensities at 565, 648 and 766 cm^{-1} increased more than that at 604 cm^{-1} as shown in curve F of Fig. 2.

The same increase in intensities in polar solvent is also observed in the Raman spectra; *i. e.*, as seen in Table 1, the relative intensity of the Raman bands at 568, 596, and 757 cm^{-1} is 1/6 : 1 : 1/2 for the KBr-disk, and 1/2 : 1 : 1 for the CH_3CN solution.

Concerning the effect of the polar solvents, Mizushima *et al.* have reported that the "gauche" molecule should be more stable in a continuous polar medium than in the gaseous state.14) The increases in intensities observed in the polar solvent

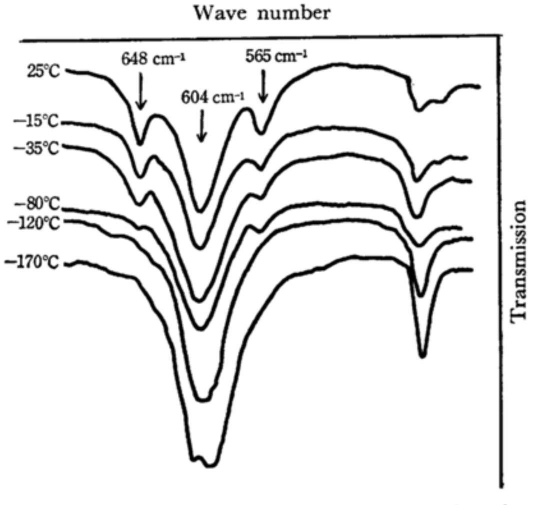

Fig. 3. The temperature change of the infrared spectrum for KBr-disk sample of $Cl(CH_3)_2C-C(CH_3)_2Cl$.

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8) I. Nakagawa and S. Mizushima, *J. Chem. Phys.*, **21**, 2195 (1953).

9) S. Mizushima, T. Shimanouchi, K. Nakamura, M. Hayashi and S. Tsuchiya, *J. Chem. Phys.*, **24**, 970 (1957).

[*3] T_X and T_H are the notations used by Mizushima *et al.* in Ref. 9. The configuration with C or Cl atom in the trans-position with respect to the Cl atom is referred as T_X, and the configuration with the H atom in the trans-position is referred as T_H.

10) For instance G. Herzberg, "Molecular Spectra and Molecular Structure I. Infrared and Raman Spectra of Polyatomic Molecules," van Nostrand (1945).

[*4] The values of the dipole moment and the dielectric constant of $HCON(CH_3)_2$ and CH_3CN are respectively 3.8 D,11) 36.71 12) and 3.4 D,11) 37.5.13)

11) A. L. McClellan, "Tables of Experimental Dipole Moments," W. H. Freeman and Co., San Francisco (1963).

12) G. R. Leader and J. F. Gormley, *J. Am. Chem. Soc.*, **73**, 5731 (1951).

13) G. R. Leader, *ibid.*, **73**, 856 (1951).

14) S. Mizushima and H. Okazaki, *ibid.*, **71**, 3411 (1949).

for the 565, 648, and 766 cm^{-1} bands of the infrared, and for 596, and 755 cm^{-1} of the Raman indicate that these bands belong to vibrations of the "gauche" form. The Raman bands corresponding to 648 and 766 cm^{-1} of the infrared spectra are not observed even in the polar solvents; the reason is not known.

Turning to the solid state, the temperature dependence of the infrared spectra of the KBr-disk is shown in Fig. 3. Although the indicated temperatures in Fig. 3 are not equilibrium temperatures, except 25, −80, and −170°C, as described earlier, it is clearly shown that the bands at 565, 648, and 766 cm^{-1} show a decrease in their intensities with a lowering of the temperature. These bands disappeared below −120°C, and almost in the gas phase.

Contrary to this, the intensity of the 604 cm^{-1} band of the trans-form is not so dependent upon the experimental conditions. Therefore, these changes in intensity, along with the comparison of Raman and infrared spectra, indicate that the 604 cm^{-1} band belongs to the trans-form (C_{2h}), whereas the band at 565, 648, and 766 cm^{-1} are attributed to the gauche-form (C_2).

From the considerations of the Raman, and infrared spectra mentioned above, it is clearly seen that there is a coexistence of trans- and gauche-rotational isomers in the molecular system of the high-temperature solid phase as well as in the dilute solutions of $Cl(CH_3)_2C$–$C(CH_3)_2Cl$. For the dilute solution, the present conclusion is coincident with that of Morino *et al.*[2] In the gas phase, the majority of the molecular configurations will be trans-, together with a small number of the gauche-form.

Some comments are added here with regard to the infrared bands below −120°C for the KBr-disk sample. The band at 604 cm^{-1} for the KBr-disk observed at room temperature increases in width with decreasing temperature below −120°C, and split into two bands at 609, and 599 cm^{-1} at about −170°C. The splitting of the band may be due to a change in the crystal at the transition point (−112°C), as shown in the case of an other compound.[15]

The Energy Difference between Trans- and Gauche-form. From the temperature dependence of the infrared intensities, the energy difference, ΔE, between the trans- and gauche-positions may be calculated. The intensities of the trans-, and gauche-bands are approximately related to ΔE by the formula,[1a,1f,16]

$$I_{(g)}/I_{(t)}=A\exp(\Delta E/\boldsymbol{R}T)$$

where $I_{(g)}/I_{(t)}$ is the ratio of the integrated intensities for the gauche- and trans-bands; A is a constant. Taking the 604 cm^{-1} band to be trans-, and the 565, and 648 cm^{-1} to be gauche-, we obtained

$$I_{565}/I_{604}=0.10 \text{ at } 300°\text{K}$$
$$=0.03 \text{ at } 190°\text{K},$$

and

$$I_{648}/I_{604}=0.13 \text{ at } 300°\text{K}$$
$$=0.03 \text{ at } 190°\text{K}.$$

Then we have

$$\Delta E=1.3 \text{ kcal/mol from } I_{565}/I_{604}$$
$$=1.7 \text{ kcal/mol from } I_{648}/I_{604}.$$

The values of ΔE are of the same order as the results of Morino *et al.*, who have estimated $\Delta E=$ 1.6 kcal/mol for dilute solutions of this compound from dipole moment measurements.[2]

The values of ΔE indicate that in the high-temperature solid phase the trans-form has a lower energy than the gauche-form. In connection with the values given above, we should like to refer to the values of ΔE for 1, 2-disubstituted-ethanes. In the gas phase for ClH_2C–CH_2Cl and BrH_2C–CH_2Br, it was reported that the trans-form is the lower energy configuration.[1a] In contrast, for 1, 2-dicyanoethane (succinonitrile),[17] the gauche-form is the lower energy structure in the solid and liquid states, although the trans-form is the lower energy configuration in the gas phase. According to the discussion of Mizushima *et al.*,[14] the greater stability of the gauche-form in the solid and liquid phases of succinonitrile should be attributed to the high dielectric constant[18] and to the much greater dipole moment (5—6 D) of this structure compared with those of the dihaloethanes (2.23 D for dichloro-[19], and 2.62 D for Dibromo-[19] ethane). In the case of $Cl(CH_3)_2C$–$C(CH_3)_2Cl$, the dipole moment for the gauche-form is 3.1 D,[2] and further the dielectric constant for the high-temperature phase is not a high-value.[20] Therefore, the relation between the values of ΔE and the molecular configuration for the present compound seems to be similar to the case of the dihaloethanes.

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[15] For instance M. P. Marzocchi, V. Schettrino and S. Califano, *J. Chem. Phys.*, **45**, 1400 (1966).

[16] For instance C. Komaki, I. Ichishima, K. Kuratani, T. Miyazawa, T. Shimanouchi and S. Mizushima, This Bulletin, **28**, 330 (1955).

[17] W. E. Fitzgerald and G. J. Janz, *J. Mol. Specty.* **1**, 49 (1957).

[18] A. H. White and S. O. Morgan, *J. Chem. Phys.*, **5**, 655 (1937).

[19] I. Miyagawa, *Nippon Kagaku Zasshi (J. Chem. Soc. Japan, Pure Chem. Sect.)*, **75**, 1057 (1954).

[20] A. H. White and W. S. Bishop, *J. Am. Chem. Soc.*, **62**, 8 (1937).