The Two Stable Isomers of Chlorocyclohexane

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Twenty years ago Canals et al.[1] studied the Raman spectra of chlorocyclohexane and found the two bands which may be assigned to the C-Cl stretching vibration. As it is now well established that the structure of cyclohexane ring is the chair form, it can be easily understood that the two bands are due to the two isomers which may be represented by the usual symbols e and a. Hassell and Viervoll[2] concluded from their electron diffraction data that the molecules of chlorocyclohexane are almost all of the e-form in the vapor state. Larnaudie[3], however, pointed out the coexistence of the e- and the a-form in the vapor as well as in the liquid state, since the two characteristic bands for the C-Cl stretching vibration were observed in both states in his infrared investigations. It seems likely to be interesting to determine the form of the more stable isomer and the energy difference between these two isomers. For these purposes we carried out the following researches.

Experimental

Preparation and Purification of Chlorocyclohexane. — According to Markownikoff[4] cyclohexanol was heated at 100°C in a sealed glass tube with concentrated hydrochloric acid solution for five hours. The oily substance which had separated in the tube was distilled with

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[1] E. Canals, M. Mousseron, R. Granger and J. Gastaud, *Bull. soc. chim. France*, **4**, 2048 (1937).

[2] O. Hassel and H. Viervoll, *Tids. Kjemi, Bergvesen Met.*, **5**, 35 (1943).

[3] M. Larnaudie, *Compt. rend.*, **235**, 154 (1952); *J. phys. radium*, **15**, 650 (1954).

[4] W. Markownikoff, *Ann.*, **302**, 19 (1898).

TABLE I

VIBRATIONAL SPECTRA OF CHLOROCYCLOHEXANE

Raman*		Infrared**		Configuration
liquid(cm^{-1})	solid(cm^{-1})	liquid(cm^{-1})	solid(cm^{-1})	
200 (1)				
259 (1)				
339 (9)	340 (3)			e
437 (3)	435 (1)	435.2(w)		e
		472.4(w)		
509 (3)	508 (0)	512 (m)	510.5(s)	e
560 (6)		559 (m)		a
			628 (vw)	e
686 (4)		684.5(s)		a
			711.7(w)	e
734 (8)	726 (4)	731 (vvs)	728 (vvs)	e
		789 (vw)	790 (w)	e
808 (5)		807 (m)		a
822 (5)	821 (2)	817 (vs)	817 (vs)	e
			~845 (w)sh	e
852 (5)	851 (2)	852 (m)	850.5(m)	e
		858 (m)		a
		863 (m)		a
		~868 (m)		a
890 (2)		889 (s)	888.5(vs)	e
		920 (w)	920.5(w)	e
		972 (vw)	972 (vw)	e
992 (6)	993 (3)	993 (vs)	994 (s)	e
		1014 (m)		a
1027 (6)	1027 (2)	1029 (w)	1025 (w) 1031 (w)	e
1051 (2)	1053 (1)	1051 (vw)	1050 (w)	e
		1070 (vw)	1068 (vw) 1075 (vw)	e
		1089 (vw)	1088 (w)	e
		1098 (w)		a
		1132 (w)	1134 (m)	e
		1145 (w)		a
		1184 (w)	1186 (w)	e
1215 (2)	1216 (0)	1215 (s)	1216 (s)	e
1263 (6)	1261 (1)	1258 (m) 1267 (s)	1256 (s) 1267 (m)	e e
1297 (0)		1301 (vw)	1300 (w)	e
1337 (2)		1340 (m)	1323 (m) 1332 (m) 1339 (m)	e e e
1447 (7)	1443 (2)	1448 (vs)	1446 (s)	
2865 (10b)		2617 (vw)		
2904 (9b)		2675 (w)	2670 (s)	
2951 (10b)	2945 (2b)	2860 (vs)	2860 (s)	
		2930 (vs)	2930 (vs)	

* For the Raman spectra the numbers shown in the brackets are the visually estimated relative intensities.

** The infrared spectra were not investigated below 430 cm^{-1} in the liquid and below 500 cm^{-1} in the solid. The letters shown in the brackets mean the relative intensities. v=very, s=strong, m=medium and w=weak. sh=shoulder.

TABLE II

INFRARED SPECTRA OF THE VAPOR OF CHLOROCYCLOHEXANE

wave number	configuration	wave number	configuration	wave number	configuration
~502		864 (m)	a	1160 (vw)	
510.0(m)	e				
516		872 (m)	a	1180 (vw)	
~566 (m,b)	a	887 893 (s)	e	1183 (vw)	
682.6				1214	
690.2(m)	a	992		1220 (m)	e
697.0		997 (s)	e	1225	
		1001			
734.4				1265 (s)	
740.3(vs)	e	1017 (m)	a	1269 (s)	
745.8				1273 (s)	
		1024 (m)		1280 (s)	
~796 (vw)	e			1352 (m)	
		1079 (w)		1459 (vs)	
814.5					
820 (s)	e	1094		2176 (vw)	
826		1103 (w)	a	2510 (vw)	
		1111		2680 (w)	
854 (m)	e			2890 (vs)	
		1129 1140 (w)	e	2950 (vs)	

steam, washed with water, and dried over calcium chloride. The product was further purified by fractional distillation. (b.p. 142.0~142.3°C).

Vibrational Spectra.—The Raman spectra of this compound were observed for the liquid and the solid state with the same spectrograph as in our earlier works[5]. The infrared spectra were obtained for the vapor (ca. 120°C), liquid, and solid states, by use of a Perkin-Elmer Spectrometer Model 112 equipped with sodium chloride and potassium bromide prisms. The wave number readings for both spectra are shown in Tables I and II.

The Raman spectra of the liquid obtained by Kohlrausch et al.[6] agree with our data, except the doublets at 808 and 822 cm^{-1} and some additional weak bands. The data obtained by Canals et al.[1] are incomplete and disagree with our results at several points.

Measurements of the Integrated Intensities in the Vapor State.—The integrated intensities of the two bands at 689 cm^{-1} and 741 cm^{-1} were obtained with a potassium bromide prism. The slit width used was 0.280 mm and the spectral slit widths were 3.3cm^{-1} at 700cm^{-1} and 4.0cm^{-1} at 750cm^{-1}. The gas absorption cell was made of a glass cylinder with two potassium bromide windows and was heated electrically by a nichrome wire. In order to avoid the condensation of the vapor on the windows short glass cylinders heated electrically were attached in front of the windows. The path length of the cell was 6 cm.

Measurements were made at the two temperatures 117°C and 200°C*. Atmospheric carbon dioxide was removed from the optical path as far as possible. Such a high temperature, at which the measurements were made, causes emission bands of the compound with noticeable intensities. The radiation intensity I_b of the high temperature cell and the intensity I_d of the emission band of the sample at frequency ν were measured by placing a non-reflecting shutter made of a piece of glass and a sheet of black paper behind the cell. For the evaluation of the absorbance $\log_{10} I_0/I$, and I_0 and I should be

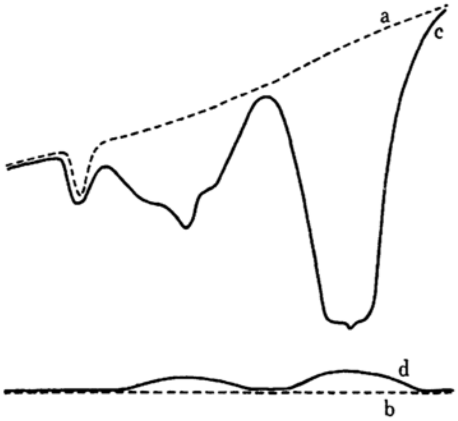

Fig. 1. The absorption curves a, b, c and d are used for obtaining I_a, I_b, I_c, and I_d, respectively.

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5) a) K. Kozima and T. Yoshino, *J. Am. Chem. Soc.*, **75**, 166 (1953); b) K. Kozima, K. Sakashita and S. Maeda, ibid., **76**, 1965 (1954).

6) K. W. F. Kohlrausch and W. Stockmair, *Z. physik. Chem.*, **B31**, 382 (1936).

* Above 250°C the shapes of the bands change gradually and new bands appear.

TABLE III

RATIO OF INTEGRATED INTENSITIES (VAPOR)

	No. of Experiments	$\bar{\nu}_{\max}$	Ratio of integrated intensities obtained by weighing
$t=117°C$	1	689.5 cm^{-1} 741.5	0.347
	2	690.0 741.2	0.347
	3	689.7 741.3	0.349
	Mean	689.7 741.3	0.348
$t=200°C$	1	689.0 740.6	0.376
	2	689.5 740.0	0.380
	3	689.3 739.7	0.371
	Mean	689.3 740.1	0.376

taken as

$$I_0 = I_a - I_b,\ I = I_c - I_d$$

where I_0 and I have their usual meanings, and I_a and I_c are the monochromatic intensities of radiation after passage through the vacant cell and the cell containing the sample at a high temperature, respectively. The absorption curves obtained are shown in Fig. 1.

The area-intensities were obtained by the graphical integration of the absorbances over the frequency interval from 641 cm^{-1} to 790 cm^{-1}, which sufficiently covers the range of about four times the half intensity width for each band. The integration outside this interval may be neglected without noticeable influences on the evaluation of the relative intensities, because the absorption on the wings of the band decreases rather rapidly; that is to say, for the band near 689 cm^{-1} its absorbance at 641 cm^{-1} is smaller than 1/20 of that at the peak and for the other band near 741 cm^{-1} the decrement of that at 790 cm^{-1} is more serious. The absorption curve near 710 cm^{-1}, which consists of the two bands overlapping each other at their wings, was divided into the original bands, so that the bands have the most reasonable shapes. The band near 741 cm^{-1} overlaps slightly with that near 820 cm^{-1}, which includes a very weak band near 796 cm^{-1}. This overlapping was also treated by the same method as described above. The correction for finite slit widths may be neglected, because of the broadness of the bands. The results obtained are shown in Table III.

Measurements of the Integrated Intensities in the Solution.—The integrated intensities of the two bands near 685 cm^{-1} and 732 cm^{-1} were obtained at 25°C in the solution, carbon disulfide and methyl acetate being used as solvents. The prism and the slit width were the same as those employed in the above intensity measurement. The thickness of the cell used was 0.2 mm. There were no remarkable differences between the ratios of the integrated intensities obtained by the graphical integration and those obtained by Ramsay's method(7) of direct integration corrected for finite slit widths. The results are listed in Table IV.

Discussion

As shown in Table I the vibrational spectra in the solid state differ clearly from those in the liquid state; viz., some of the relatively strong bands observed in the liquid spectra disappear in the solid spectra.

For the C-Cl stretching vibration two characteristic bands were observed at 684.5 and 731 cm^{-1} in the liquid state, while in the solid state the former disappeared and the latter persisted. Therefore, it is concluded that the dynamic equilibrium of the two isomers, which exists in the liquid state, breaks down in the course of the crystalization of the compound and only one isomer persists in the solid state. On the other hand the infrared spectra in the vapor state, shown in Table II, correspond well with those in the liquid state.

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7) D. A. Ramsay, *J. Am. Chem. Soc.*, **74**, 72 (1952).

TABLE IV

THE RATIOS OF INTEGRATED INTENSITIES (SOLUTION)

temperature: 25°C

solvent: carbon disulfide

No. of experiments	mol./l.	$\bar{\nu}$ cm^{-1}	$\log_e(T_0/T)$	$\Delta\bar{\nu}^a{}_{1/2}$ cm^{-1}	A	A_a/A_e	A'_a/A'_e (graphical)
1	0.36	685.8 733.2	0.504 1.52	6.5 7.2	4.8_5 $17._1$	0.28	0.34
2	0.32	686.0 733.5	0.445 1.39	7.0 7.4	4.6_4 $16._1$	0.29	0.33
	mean	685.9 733.4				0.29	0.34
solvent:	methyl acetate						
1	0.55	684.8 731.8	0.532 1.94	8.1 8.6	6.5_1 $26._4$	0.25	0.26
2	0.40	684.6 731.5	0.445 1.64	8.0 8.4	5.3_8 $21._7$	0.25	0.25
	mean	684.7 731.7				0.25	0.26

The cell thickness for both solvents is 1.96×10^{-2} cm. The slit widths are 3.1 cm^{-1} at 686 cm^{-1}, 3.8 cm^{-1} at 733.5 cm^{-1} and 3.7 cm^{-1} at 731.5 cm^{-1}. A is the true integrated absorption intensity given by

$$A=K\log_e(T_0/T)_{\nu(\max)}\cdot\Delta\bar{\nu}^a{}_{1/2}$$

where the letters have their usual meanings. A_a/A_e shown in the table denotes the intensity ratio thus obtained and A'_a/A'_e the same ratio obtained by graphical integration. As for the carbon disulfide solution, agreements of the results obtained by both methods are not quite satisfactory, but the difference does not seriously alter the value of ΔE. ΔE for this solvent given in Table V is the mean value for both methods.

Therefore, the two isomers also coexist in the vapor state as pointed out by Larnaudie³⁾.

As has been shown by Larnaudie, the two C-Cl bands observed in the vapor state can confidently be identified with the e- and the a-form by the consideration of their band envelopes, respectively, based on the results obtained by Badger and Zumwalt⁸⁾. The band at 740.3 cm^{-1} is assigned to the e-form and that at 690.2 cm^{-1} to the a-form. Since the band at 740.3 cm^{-1} in the vapor state corresponds to that at 728 cm^{-1} in the solid state, the isomer which persists in the solid state is the e-form. Among the relatively strong bands which appeared in the liquid and the vapor spectrum, the bands which persist in the solid state are assigned to the e-form and the other bands to the a-form as shown in Tables I and II.

It is possible to determine the energy difference between the two isomers by the measurement of the ratio of the integrated intensities of the two bands exhibited by the a- and the e-form, respectively, by use of the following formula:

$$A_a/A_e=\alpha_aN_a/\alpha_eN_e=(\alpha_a/\alpha_e)(f_a/f_e)\times\exp.(-\Delta E/\boldsymbol{R}T)$$

where $A=\int\log_e(I_0/I)\mathrm{d}\nu$ is the integrated intensity, $\Delta E=E_a-E_e$ the energy difference, α the molecular absorption coefficient, N the number of molecules, f the partition function, and the suffixes a and e refer to the a- and the e-form, respectively. In order to eliminate the unknown quantity $(f_a/f_e)(\alpha_a/\alpha_e)$, the measurements must be made at two temperatures at least. The ratio of the partition functions f_a/f_e is taken to be constant, because of the narrow range of temperature. The band at 740 cm^{-1} of the e-form and that at 690 cm^{-1} of the a-form are adequate for the purpose.

The results obtained for the vapor state at the temperatures 117° and 200°C are shown in Table III, and the energy difference thus obtained is about 0.34 kcal./mole, the e-form being the more stable isomer.

The energy differences in the dilute solutions can be estimated from the ratios of the integrated intensities shown in Table IV, if the values of (α_a/α_e) and (f_a/f_e) in the solution are assumed to be the same as those in the vapor state. The energy differences obtained for the solutions of carbon disulfide and methyl acetate are shown in Table IV. In these

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8) R. M. Badger and L. R. Zumwalt, *J. Chem. Phys.*, **6**, 711 (1938).

solutions the e-form is also the more stable isomer.

As has been reported in our previous article[5b], the two mutually convertible isomers of *trans*-1,2-dichlorocyclohexane represented by the usual symbols as (e,e) and (a,a) are in a dynamic equilibrium for the various states, except for the solid state. By the studies on the electric dipole moment of the compound the energy difference between the isomers has been determined. For the reason mentioned below the energy difference between the isomers for both compounds should be determined for the same state. Therefore, the difference between the energy of the (e,e)-form and that of the (a,a)-form, $E_{ee}-E_{aa}$, was determined for the vapor, carbon disulfide solution and methyl acetate solution, by use of the same method as that used for the monochloro derivative. The results are listed in Table V.

TABLE V
THE ENERGY DIFFERENCES BETWEEN TWO MUTUALLY CONVERTIBLE ISOMERS
(inverted isomers)

State	$\Delta E=E_a-E_e$ chloro-cyclohexane kcal./mole	$\Delta E=E_{ee}-E_{aa}$ *trans*-1,2-dichloro-cyclohexane kcal./mole
vapor	0.34	0.61
CS_2 soln.	0.33	0.17
CH_3COOCH_3 soln.	0.44	−0.43

The energy difference between the mutually convertible isomers in the vapor state may be due to the difference between the intramolecular potential energies which are taken to be the sums of the potential energies of various pairs of non-bonded atoms.

Based upon this point of view, the following relation is obtained:

$$E_{ee}-E_{aa}+2(E_a-E_e)=E_g-E_t$$

where $E_{ee}-E_{aa}$ and E_a-E_e have the meanings mentioned above and E_g-E_t is the energy difference between the *gauche* and the *trans* form of 1,2-dichloroethane. The derivation of this formula will be given in an Appendix.

With this formula and the values for the vapor state listed in Table V, we find that $E_g-E_t=1.29$ kcal./mole. The value is in good agreement with that directly determined for the vapor state of 1,2-dichloroethane[9]. By use of the values for the solutions shown in the table, we find that $E_g-E_t=0.83$ kcal./mole for the dilute carbon disulfide solution and $E_g-E_t=0.45$ kcal./mole for the dilute methyl acetate solution.

These values, compared with the experimental data[10], seem to be reasonable, when taking into account the assumption made for the measurement in the solution. The reasons why the formula is available for the solution may be attributed to the facts that the variations of $E_{ee}-E_{aa}$ and E_g-E_t with the solvents are approximately the same and E_a-E_e does not appreciably change with the solvents.

It should be pointed out that at first sight the energy difference E_a-E_e may be expected to be about half of that between the (a,a)-form and the (e,e)-form of *trans*-1,4-dichlorocyclohexane[5a], but this is not actually the case.

While the present paper was in preparation, an interesting paper by Klæboe et al.[11], which concerned a part of our investigations, appeared. Their results are in accord with ours.

Appendix

By numbering the carbon atoms of cyclohexane ring from one to six in turn and using the symbols of e and a, we shall represent the potential energies between non-bonded atoms in the molecule of cyclohexane derivative. As for chlorocyclohexane, for instance, the energy between the chlorine atom attached to 1a and the carbon atom of 3 is represented as $V_{1a\ 3}$ and that between the same chlorine atom and the hydrogen atom attached to 2e is $V'_{1a\ 2e}$.

By the use of these symbols the potential energies, E_a and E_e, of the a- and the e-form of chlorocyclohexane can be represented as follows, respectively;

$$\begin{aligned}E_a=&2V_{1a\ 3}+V_{1a\ 4}+2V'_{1a\ 3a}+2V'_{1a\ 3e}+V'_{1a\ 4a}\\&+V'_{1a\ 4e}+2V'_{1a\ 2a}+2U_{1e\ 3}+U_{1e\ 4}+2U'_{1e\ 3a}\\&+2U'_{1e\ 3e}+U'_{1e\ 4a}+U'_{1e\ 4e}+2U'_{1e\ 2a}+\Psi \qquad (1)\end{aligned}$$

$$\begin{aligned}E_e=&2V_{1e\ 3}+V_{1e\ 4}+2V'_{1e\ 3a}+2V'_{1e\ 3e}+V'_{1e\ 4a}\\&+V'_{1e\ 4e}+2V'_{1e\ 2a}+2U_{1a\ 3}+U_{1a\ 4}+2U'_{1a\ 3a}\\&+2U'_{1a\ 3e}+U'_{1a\ 4a}+U'_{1a\ 4e}+2U'_{1a\ 2a}+\Psi \qquad (2)\end{aligned}$$

where V denotes the potential energy between the chlorine and the carbon atom, V' that between the chlorine and the hydrogen atom, U that between the hydrogen and the carbon atom, U' that between the hydrogen atoms attached to the different carbon atoms and Ψ contains all the terms of the potential energies which do not vary by changing the position of the chlorine

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[9] S. Mizushima, "Structure of Molecules and Internal Rotation", Academic Press Inc., New York, (1954), p. 41.

[10] A. Wada, *J. Chem. Phys.*, **22**, 200 (1954).

[11] P. Klæboe, J. J. Lothe and K. Lunde, *Acta Chem. Scand.*, **10**, 1465 (1956).

atom from 1a to 1e, and vice versa. As for these equations the equivalent terms are represented by one of them; for instance, as $V_{1e\ 3}$ is equal to $V_{1e\ 5}$ for Eq. 2, $V_{1e\ 3}$ is multiplied by 2.

The potential energies, E_{aa} and E_{ee} of the (a,a)- and the (e,e)-form of *trans*-1,2-dichlorocyclohexane can be similarly represented as follows;

$$\begin{aligned} E_{aa}=&4V_{1a\ 3}+2V_{1a\ 4}+4V'_{1a\ 3a}+4V'_{1a\ 3e} \\ &+2V'_{1a\ 4a}+2V'_{1a\ 4e}+2V'_{1a\ 2a}+\Phi_{1a\ 2a} \\ &+4U_{1e\ 3}+2U_{1e\ 4}+3U'_{1e\ 2e}+4U'_{1e\ 3a} \\ &+4U'_{1e\ 3e}+2U'_{1e\ 4a}+2U'_{1e\ 4e}+\Psi \qquad (3) \end{aligned}$$

$$\begin{aligned} E_{ee}=&4V_{1e\ 3}+2V_{1e\ 4}+4V'_{1e\ 3a}+4V'_{1e\ 3e} \\ &+2V'_{1e\ 4a}+2V'_{1e\ 4e}+2V'_{1e\ 2e}+\Phi_{1e\ 2e} \\ &+4U_{1a\ 3}+2U_{1a\ 4}+3U'_{1a\ 2a}+4U'_{1a\ 3a} \\ &+4U'_{1a\ 3e}+2U'_{1a\ 4a}+2U'_{1a\ 4e}+\Psi \qquad (4) \end{aligned}$$

where Φ denotes the potential energy between the chlorine atoms attached to the carbon atoms of 1 and 2 and the other symbols have the same meanings as in Eqs. 1 and 2.

By use of Eqs. 1, 2, 3 and 4 and assuming that these terms do not change from molecule to molecule, we can obtain the following equation;

$$(E_{aa}-E_{ee})-2(E_a-E_e)=E_t-E_g.$$

This relation should also be available for the other derivatives in the same way as for the chlorine derivatives.

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