The Molecular Structure of trans-4-Halogenocyclohexanol

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It has been well established that the cyclohexane ring has a chair form and that some cyclohexane derivatives have mutually convertible isomers, viz., inverted isomers. Since *trans*-4-halogenocyclohexanol should also have such isomers, it seemed very interesting to study the stability of the isomers in these compounds.

Experimental

Preparation of *trans*-4-Halogenocyclohexanol.—*trans*-4-Chlorocyclohexanol was prepared by adding hydrochloric acid to 1,4-epoxycyclohexane which had been obtained from 1,4-cyclohexanediol by dehydration with activated alumina. The product was recrystallized from ligroin, m. p. 82.0~83.0°C(1,2).

The preparation of *trans*-4-bromo- and of *trans*-4-iodocyclohexanol was similar to that of the chloro-derivative. The melting point of the bromo-derivative is 81.0~81.5°C, while that of the iodo-derivative is 59.2~60.3°C.

The Bromo-derivative. — Found: C, 39.95; H, 6.28. Calcd. for $C_6H_{11}OBr$: C, 40.24; H, 6.19%.

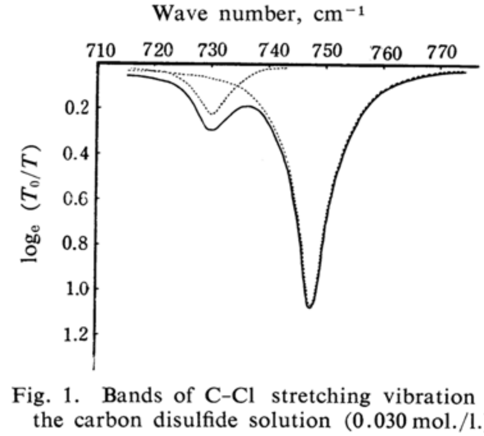

Fig. 1. Bands of C–Cl stretching vibration in the carbon disulfide solution (0.030 mol./l.).

The Iodo-derivative.—Found: C, 32.28; H, 5.41. Calcd. for $C_6H_{11}OI$: C, 31.88; H, 4.91%.

Dipole Moment. — The dipole moment of the chloro-derivative was obtained, by Debye's solution method, in the dilute carbon tetrachloride solution at 20.0°C. The dielectric constants were measured by the usual heterodyne beat method. The results are listed in Table I.

Infrared Spectra. — The measurements of the spectra were made with a Perkin-Elmer spectrometer

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1) E. A. Fehnel, *J. Am. Chem. Soc.*, **73**, 4978 (1951).

2) E. L. Bennett and C. Niemann, ibid., **74**, 5076 (1952).

TABLE I. DIPOLE MOMENT OF *trans*-4-CHLOROCYCLOHEXANOL

Solvent; Carbon tetrachloride
Temperature; 20.0°C

	Molar fraction	Density	Dielectric constant	P_2
	0.0000	1.5952	2.2396	
Soln. I	0.00309	1.5938	2.2540	107
Soln. II	0.00425	1.5930	2.2594	108
Soln. III	0.00496	1.5929	2.2613	104
Soln. IV	0.00909	1.5910	2.2797	103
	$P_{2\infty}=107$		$\mu=1.87$ D	

TABLE II. INFRARED SPECTRA OF *trans*-4-HALOGENOCYCLOHEXANOL (cm^{-1})

Chloro-derivative		Bromo-derivative		Iodo-derivative	
Liquid	Solid	Liquid	Solid	Liquid	Solid
400～800 (bm)	480～830 (bs)	400～800 (bm)	450～830 (bs)	400～750 (bm)	430～800 (bs)
459 (w)	460 (w)	453 (bw)	453 (m)	448 (bw)	453 (vw)
	479 (w)	472 (w)	474 (m)	469 (bw)	470 (w)
		491 (m)	487 (w)		
552 (vs)	556 (vs)	534 (vs)	538 (vs)	521 (vs)	522 (vs)
628 (m)	629 (w)	609 (w)	609 (w)	596 (w)	597 (w)
				680 (m)	681 (m)
		708 (s)	706 (s)		
730 (m)	—				
745 (s)	744 (s)				
805 (m)	—	799 (w)	—	790 (vw)	—
817 (s)	818 (s)	808 (s)	809 (s)	803 (s)	805 (s)
860 (vw)	862 (vw)	860 (w)	862 (vw)	859 (w)	861 (vw)
883 (m)	885 (s)	879 (s)	881 (s)	877 (s)	877 (s)
899 (m)	900 (s)	899 (s)	899 (s)	897 (s)	896 (m)
947 (s)	950 (s)	944 (vs)	946 (s)	942 (vs)	942 (s)
965 (m)	$\left.\begin{matrix}965\\969\end{matrix}\right\}$ (m)	963 (m)	967 (s)	966 (m)	967 (m)
1007 (m)	1012 (m)	1003 (s)	1007 (s)	997 (s)	1002 (s)
1034 (vw)	1035 (vw)	1031 (vw)	1032 (vw)	1031 (vw)	1033 (vw)
1062 (vs)	1067 (vs)	1060 (vs)	1064 (vs)	1059 (vs)	1061 (vs)
1110 (vw)	1113 (w)	1099 (m)	1101 (m)	1084 (s)	1086 (s)
1135 (vw)	1135 (w)	1132 (w)	1135 (m)	1130 (w)	1139 (w)
$\left.\begin{matrix}1196\\1207\end{matrix}\right\}$ (m)	$\left.\begin{matrix}1200\\1210\end{matrix}\right\}$ (s)	1180 (s)	1183 (s)	1162 (s) 1199 (w)	1165 (s) 1199 (w)
1256 (m)	1254 (w)	1233 (m)	1232 (m)	1222 (m)	1223 (m)
1279 (w)	1288 (m)	1279 (m)	1289 (m)	1279 (m)	1286 (w)
1308 (vw)	1311 (w)				1301 (m)
1327 (vw)	1333 (w)	1330 (m)	1335 (m)	1324 (m)	1322 (w)
1344 (vw)	1345 (w)				
1366 (m)	1365 (s)	1364 (s)	1365 (s)	1363 (s)	1362 (s)
1405 (bw)	1415 (bw)	1405 (bw)	1417 (bw)	1406 (bw)	1420 (bw)
1452 (s)	1450 (s)	1450 (s)	1447 (s)	1450 (s)	1450 (s)
2687 (vw)	2699 (vw)	2685 (vw)	2684 (vw)	2672 (vw)	2675 (vw)
2870 (s)	2875 (s)	2874 (s)	2864 (s)	2834 (s)	2862 (s)
2939 (vs)	2948 (vs)	2936 (vs)	2932 (vs)	2925 (vs)	2937 (vs)
3420 (vs)	3325 (vs)	3373 (vs)	3289 (vs)	3358 (vs)	3317 (vs)

w=weak, m=medium, s=strong, v=very and b=broad

model 112 equipped with potassium bromide or sodium chloride prism. Although the solid spectra were observed both for the Nujol mull and for the solid obtained by cooling the molten sample, no significant difference in intensity could be found between them. The liquid spectra were observed for the molten compounds. The results are shown in Table II.

Measurement of the Integrated Intensities.—The intensities of the two bands at 730 and 748 cm^{-1} of

TABLE III. TEMPERATURE DEPENDENCE OF THE RELATIVE INTENSITIES

Carbon disulfide solution (0.030 mol./l.)

Temp. °C	Wave number	Form	$\log_e\left(\frac{T_0}{T}\right)_{\max}$	$\Delta\nu^a{}_{1/2}$	c_aA_a/c_eA_e
27	730	(1a, 4a)	0.225	6.4	0.20
	748	(1e, 4e)	1.08	6.1	
−27	730	(1a, 4a)	0.237	6.6	0.15
	748	(1e, 4e)	1.35	6.7	

the chloro-derivative were observed by the use of a potassium bromide prism. The slit width used was 0.248 mm., and the spectral widths were 3.8 cm^{-1} at 730 cm^{-1} and 4.0 ml^{-1} at 748 cm^{-1}. Measurements were made at 27 and −27°C. The cell thickness was 3 mm. Since these bands partly overlap each other, these were separated by assuming that the band shapes are given by Lorentz's equation, as is shown in Fig. 1. The integrated intensities A of the bands were obtained by Ramsay's method[3] of direct integration corrected for finite slit widths. The intensities are given by the following equation:

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

where c is the concentration of the solute in moles per liter, l is the cell length in cm., T_0 and T are the apparent intensities of the incident and transmitted radiation when the spectrometer is set at frequency $\nu_{\max}$, and $\Delta\nu^a{}_{1/2}$ is the apparent half-intensity width.

The values of K were obtained from Ramsey's table[3]. The results are listed in Table III.

Discussion

It has been concluded on the basis of chemical evidence that the compound obtained by adding hydrochloric acid to the epoxy-compound is the trans-isomer. In order to confirm this conclusion, the dipole moment of this molecule was determined. The results obtained are shown in Table I. As may be seen in the table, the molecular polarization, P_2, depends upon the concentration of the solution. However, at concentrations lower than 0.00425 in molar fraction, it takes a constant value, 107. It was shown, by infrared absorption measurement, that in Soln. I there is practically no intermolecular hydrogen bond. Therefore, the P_2 value of 107 was taken as that for the extreme dilution ($P_{2\infty}$). From this value of $P_{2\infty}$, the dipole moment was calculated as 1.87 D.

Since it is very probable that the cyclohexane ring of this compound has the chair form, stable forms may be expected for both the trans- and the cis-isomer of this compound. These structures may be schematically represented as in Fig. 2. The positions of the atoms attached to the cyclohexane ring are represented by the usual symbols, e and a[4].

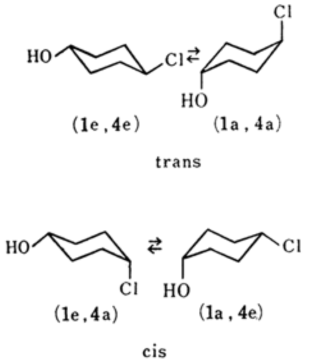


Fig. 2. Inverted isomers of 4-chlorocyclohexanol.

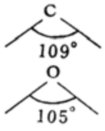
TABLE IV. BOND MOMENTS AND VALENCY ANGLES

$\mu_{C-O}=0.8$ D

$\mu_{H-O}=1.5$ D

$\mu_{C-Cl}=1.6$ D

$\mu_{H-C}=0.3$ D



Beginning from the law of the vector addition of bond moments, and by assuming that an almost free rotation of the OH group around the C–O axis is possible, it can be easily seen that the values of the dipole moments of both the cis- and the trans-isomer are not changed by converting the cyclohexane ring; viz., the value of the (1e, 4e)-form is equal to that of the (1a, 4a)-form, and the value of the (1e, 4a)-form is equal to that of the (1a, 4e)-form. Upon the basis of simple vector addition and by using the values shown in Table IV, the values of 2.3 and 1.9 D were obtained for the cis- and the trans-isomer respectively. Since the observed value, 1.87 D, agrees well with the calculated value of 1.9 D for the trans-isomer, it is very probable that the compound is the trans-isomer.

The wave numbers of the infrared bands of these compounds in the liquid and in the solid states are listed in Table II. Because similar methods were used for the preparation of these compounds and because the spectra of the bromo- and the iodo-derivative are similar to that of the chloro-derivative, it may be concluded that the bromo- and the iodo-derivative

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[3] D. A. Ramsay, ibid., **74**, 72 (1952).

[4] D. H. R. Barton, O. Hassel, K. S. Pitzer and V. Prelog, *Nature*, **172**, 1096 (1953); *Science*, **119**, 49 (1953).

are the same geometrical isomers as that of the chloro-derivative, viz., the trans-isomer.

As for the trans-isomers of these compounds, the existence of two mutually convertible or "inverted" isomers is probable. As can be seen from Table II, the bands at 730 and 805 cm^{-1} for the chloro-derivative disappear when the state is changed from liquid to solid. From this fact, it follows that the equilibrium of the two isomers, which exists in the liquid, breaks down in the course of crystallization and that only one isomer persists in the solid. Therefore, it seemed interesting to determine the form of the isomer.

It has been known that chlorocyclohexane⁵⁾ has two mutually convertible isomers, viz., the (e)- and the (a)-form, in the vapor and in the dilute carbon disulfide solution, and that the energy difference between them is about 0.3 kcal./mol. in these states, the (e)-form being stable. Cyclohexanol⁶⁾ also has the (e)- and the (a)-form in solutions and in the liquid, and the energy difference between them seems to be larger than that for chlorocyclohexane.

Considering the energy difference for chlorocyclohexane and that for cyclohexanol, it seems very probable that the stable form of *trans*-4-chlorocyclohexanol is the (1e, 4e)-form and that only this form exists in the solid state. However, since it has been known⁵⁾ that the energy difference between the two isomers of *trans*-1, 4-dichlorocyclohexane, viz., the (1e, 4e)- and the (1a, 4a)-form, is not twice that between the two isomers of chlorocyclohexane, further, evidence for this is needed.

The bands at 730 and 745 cm^{-1} in the liquid spectrum may be assigned to the C–Cl stretching vibrations. As for the bands assigned to the C–Cl stretching vibrations of the chloro-derivatives of cyclohexane, it is known⁷⁾ that the frequencies of the bands which are due to the chlorine atoms attached to the (e)-position of cyclohexane ring are higher than those of the bands due to the chlorine atoms of the (a)-position. Therefore, the band at 730 cm^{-1}, which disappears in the solid state, can be assigned to the (1a, 4a)-form. Then the same conclusion as described above can be drawn from this information.

According to the other experimental rule⁸⁾ that the frequency of the breathing vibration of the molecule of cyclohexane derivatives having substituents in the (a)-position does not markedly shift from that of cyclohexane, viz., 802 cm^{-1}, the band at 805 cm^{-1} may be assigned to the (1a, 4a)-form. The fact that this band disappears in the solid spectrum favors the above conclusion.

In order to determine the energy difference between the two isomers of the chloro-derivative, the ratios of the integrated intensity of the band at 730 cm^{-1} of the (1a, 4a)-form to that at 748 cm^{-1} of the (1e, 4e)-form were measured in a carbon disulfide solution at 27 and -27°C. As for the solution of 0.4 mol./l., the very broad band assigned to the out-of-plane deformation vibration of the intermolecular bonded OH group appears in the region from about 400 to 800 cm^{-1}. Therefore, the measurements were made in the more dilute solution, in which no bands assigned to the hydrogen bond could be detected. From the data of Table III, we can calculate as usual the difference, ΔE, between the energy, E_a of the (1a, 4a)-form and the energy, E_e, of the (1e, 4e)-form ($\Delta E = E_a - E_e$) by the equation;

$$c_aA_a/c_eA_e = (\alpha_a f_a/\alpha_e f_e) \exp(-\Delta E/\boldsymbol{R}T)$$

where A_a and A_e are the true integrated absorption intensities of the bands at 730 and 748 cm^{-1}, c_a and c_e the concentrations (mol./l.), α_a and α_e, the molar absorption coefficients, and f_a and f_e, the partition functions of the forms shown by the suffixes. As the measurements were made at two temperatures, the unknown quantity ($\alpha_a f_a/\alpha_e f_e$) can be eliminated. The ratio of the partition functions, f_a/f_e, is taken to be constant, because of the narrow temperature range. The value obtained for ΔE is 0.76 kcal./mol., the (1e, 4e)-form being more stable.

By using this value of the energy difference and by assuming as usual that f_a is nearly equal to f_e, a rough estimate of the abundance ratio, n_a/n_e, can be made by the equation:

$$n_a/n_e = f_a/f_e\, e^{-\Delta E/\boldsymbol{R}T}$$

The value of the ratio obtained is 1/3.6 at room temperature. From this it can be surmised that a small number of the bands disappear when the state is changed from liquid to solid.

It is expected that the bromo- and the iodo-derivative also have the (1a, 4a)- and the (1e, 4e)-forms, since their structures are similar to that of the chloro-derivative. From the fact that the energy difference between the (a)- and the (e)-form of halogenocyclohexanes, where the halogen is chlorine, bromine or iodine, becomes larger with the increasing atomic number of the halogens⁵·⁹⁾, it is very probable that in the case of *trans*-4-halogenocyclohexanol also the energy differences for the bromo- and the iodo-derivative are larger than that of the

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5) K. Kozima and K. Sakashita, This Bulletin, 31, 796 (1958).

6) Y. Takeoka, unpublished.

7) K. Kozima, *Bull. T. I. T.*, 1952, 1.

8) K. Sakashita, *J. Chem. Soc. Japan, Pure Chem. Sec.*, (*Nippon Kagaku Zasshi*), **80**, 13 (1959).

9) K. Kozima and Y. Takeoka, unpublished.

chloro-derivative. From this it may be surmised that, for the spectra of the bromo- and the iodo-derivative, only the one weak band disappears when the state is changed from liquid to solid, as is shown in Table II.

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