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Conformers and Intramolecular Hydrogen Bond of *trans*-2-Halocyclohexanols

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By infrared studies it has been ascertained that *trans*-2-halocyclohexanols possess two conformers, namely, the ee-isomer and the aa-isomer, both in the liquid and in a solution, while only the ee-isomer exists in the solid. In a dilute solution the ee-isomer is more stable and exists exclusively in the form with an intramolecular hydrogen bond. The values of the energy difference between the two isomers are 1.3, 1.9, and 2.2 kcal/mol for the chloro-, the bromo-, and the iodo-derivative respectively. The magnitude of the frequency shifts of the O–H stretching bands increases in the order: $Cl < Br < I$. These facts show that the intramolecular hydrogen bond stabilizes the ee-isomer and that the strength of the hydrogen bond increases in the order: $Cl < Br < I$. The electrostatic energy increases in the order: $Cl > Br > I$, while the delocalization energy due to the charge-transfer increases in the opposite order. Therefore, it can be concluded that the energy due to the charge-transfer contributes dominantly to the energy of the intramolecular hydrogen bond formed in the ee-isomer of *trans*-2-halocyclohexanols.

It is very probable that *trans*-2-halocyclohexanols possess two conformers which are interconvertible by the inversion of the ring, and that both the halogen X and the O–H group attach to the e-positions of a ring in one conformer and to the a-positions of a ring in the other, as in the case of *trans*-1,2-dihalocyclohexanes.[1] The conformers hereafter will be referred to as the ee-isomer and the aa-isomer respectively.

Since, of the two isomers, only the ee-isomer is expected to have an intramolecular hydrogen bond between the X atom and the H atom of the O–H group, as in the case of ethylene chlorohydrin,[2] it seemed that it would be interesting to study the energy differences between the isomers.

Experimental

Materials. *trans*-2-Chlorocyclohexanol was prepared[3] by adding hypochlorous acid to cyclohexene obtained according to the method of Osterberg and Kendall.[4] The product was then purified by fractional distillation; bp 71.2—72.5°C/10 mmHg.

trans-2-Bromocyclohexanol was prepared according to the method of Winstein[5] by adding 1,2-epoxycyclohexane to 48% hydrobromic acid, the reaction temperature being maintained below 5°C over a period of about an hour. The product was purified by fractional distillation; bp 61.5—61.8°C/2 mmHg.

trans-2-Iodocyclohexanol was prepared by a method[6]

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[1] K. Kozima, K. Sakashita and S. Maeda, *J. Amer. Chem. Soc.*, **76**, 1965 (1954).

[2] S. Mizushima, T. Shimanouchi, T. Miyazawa, K. Abe and M. Yasumi, *J. Chem. Phys.*, **19**, 1477 (1951).

[3] G. H. Coleman and H. F. Johnstone, "Organic Syntheses," Coll. Vol. I, p. 158 (1948).

[4] A. E. Osterberg and E. C. Kendall, *J. Amer. Chem. Soc.*, **42**, 2620 (1920).

[5] S. Winstein, *ibid.*, **64**, 2794 (1942).

[6] S. Winstein, E. Grunwald, R. E. Buckles and C. Hanson, *ibid.*, **70**, 816 (1948).

similar to that used for *trans*-2-bromocyclohexanol. The product was recrystallized from petroleum ether; mp 40.0—41.7°C.

Carbon disulfide of an extra pure grade was used as a solvent after distillation.

Infrared Spectra. The spectra were measured with a Perkin-Elmer 112 spectrometer equipped with a potassium bromide, a sodium chloride, or a lithium fluoride prism. To study the solid-state spectra, the chloro-derivative was cooled by ice,[*2] and the bromo-derivative by a mixture of dry ice and ethyl alcohol. The temperature of the samples was determined by means of a copper-constantan thermocouple. The thickness of the cell used for the infrared studies of dilute solutions was 6 mm.

The wavenumber readings for the liquid- and the solid-state spectra are listed in Table 1.

Measurements of the Integrated Intensities. As the contours of the bands used in the intensity measurements were usually represented by Lorentz's curve, the true integrated absorption intensity per mole, *a*, corrected for finite slit widths was calculated by means of the equation:

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

where the letters have their usual meanings.7) The values of *K* were obtained from the table of Ramsay.7)

In order to determine the energy difference between the isomers, the relative intensities of bands due to the two isomers as a function of temperature were measured in a dilute carbon disulfide solution. The O–H stretching band due to the intramolecular hydrogen bond overlaps with the free O–H stretching band for the three derivatives. However, these bands could be separated only for the iodo-derivative by assuming that the band shapes are given by Lorentz's equation. The measurements for such compounds having an O–H group should be made in a very dilute solution, for which no band assigned to the intermolecular hydrogen bond can be detected in the 3 μ region spectra, because even a small amount of the intermolecular hydrogen bond markedly affects the observed energy difference.

By using the data of the change in the relative intensity with the temperature, the energy difference between the isomers could be estimated by the following equation, as has been described in a previous paper:8)

$$\log_e \frac{(C_1a_1/C_2a_2)_{T'}}{(C_1a_1/C_2a_2)_{T''}} = -\frac{\Delta E}{R}\left(\frac{1}{T'}-\frac{1}{T''}\right)$$

where ΔE denotes E_1-E_2, $(C_1a_1/C_2a_2)_{T'}$, and $(C_1a_1/C_2a_2)_{T''}$ denote the relative intensities at the T' and T'' °K temperatures, and where the suffixes 1 and 2 refer to the value of each isomer. The results obtained are shown in Tables 3.

Results and Discussion

Since several bands of the liquid-state spectra of these compounds disappear on passing from the liquid to the solid, as is shown in Table 1, it is sure that the two isomers, the ee-isomer and the aa-isomer, exist in the liquid and that the equilibrium between them breaks down in the course of crystallization until only one isomer persists in the solid, as in the cases of *trans*-1,2-dichloro- and *trans*-1,2-dibromocyclohexane.1)

The infrared spectra of *trans*-2-halocyclohexanols in a dilute carbon disulfide solution were measured in the 3 μ region. As can be seen in Table 2, there are two absorption bands in this region. Concerning the iodo-derivative, in the spectra of which the frequency difference between these bands is relatively large, it was ascertained that the relative intensity of these bands changes with the dilution and that it becomes constant when the concentration is less than 0.03 mol/*l*. This shows that there are intramolecular hydrogen-bonded molecules in this solution. The lower frequency band can be assigned to the O–H stretching vibration of the hydrogen-bonded molecules, and the other to that of the non-bonded molecules. This behavior of the iodo-derivative is similar to that in the cases of the chloro-derivative and the bromo-derivative. It can be safely assumed that the lower frequency band is due to the ee-isomer, while the higher one may be due to the aa-isomer, because, in view of its molecular geometry, only the ee-isomer is able to form an intramolecular hydrogen bond.

In both the liquid- and the solid-state spectra for these three compounds, we could observe a very broad and weak band extending from 800 to beyond 550 cm^{-1}. Since this band disappears in the spectra of the dilute solution, it may be safely assigned to the out-of-plane deformation vibration of the intermolecular hydrogen-bonded O–H group.9)

In order to determine the energy difference between the two isomers of the iodo-derivative, we selected a pair of bands, namely the 1030-cm^{-1} band which persists in the solid and the 1001-cm^{-1} band which disappears on passing from the liquid to the solid, and measured the temperature dependence of the relative intensity; the results are shown in Table 3—3a. From these data, the energy difference is calculated to be 2.2 kcal/mol, the isomer which exists in the solid being more stable.

To determine the stable isomer, the change in the relative intensity of the two O–H stretching bands, one of which is due to the intramolecular hydrogen bond, and the other of which is due to the free O–H bond, was measured with the change in the temperature in the dilute solution. The results obtained are shown in Table 3—3b. From these data the energy difference between the two isomers is calculated to be 2.4 kcal/mol, the intramolecular hydrogen-bonded isomer being more

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[*2] In order to avoid supercooling, this refrigerant is used; it is adequate for this substance.

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

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TABLE 1. INFRARED SPECTRA OF *trans*-2-HALOCYCLOHEXANOL (cm^{-1})

Chloro-derivative		Bromo-derivative		Iodo-derivative	
Liquid	Solid	Liquid	Solid	Liquid	Solid
477 (m)	475 (s)	465 (wb)	467 (wb)	462 (wb)	465 (m)
			550 (w)		
559 (m)	560 (m)	556 (m)	560 (m)	554 (m)	561 (s)
705 (w)		650 (w)		632 (w)	
735 (vs)	732 (vs)	688 (s)	688 (vs)	657 (s)	656 (s)
798 (s)	797 (s)	792 (m)	791 (m)	791 (m)	790 (m)
812 (w)		809 (w)		807 (w)	
843 (m)	845 (m)	841 (m)	841 (m)	839 (m)	838 (m)
			846 (m)		
867 (s)	866 (s)	863 (s)	863 (m)	859 (s)	859 (s)
896 (m)	898 (m)	896 (m)	897 (m)	892 (m)	893 (m)
907 (w)		904 (w)		900 (w)	
946 (m)	945 (sh)	943 (m)	948 (w)	932 (m)	941 (sh)
959 (s)	956 (s)	956 (s)	959 (s)	951 (s)	951 (s)
976 (m)		971 (m)		967 (m)	
1009 (m)		1007 (m)		1002 (m)	
1037 (m)	1037 (sh)	1034 (m)	1032 (m)	1034 (m)	1033 (w)
1045 (sh)	1050 (w)	1045 (sh)	1048 (vw)		1046 (w)
1072 (vs)	1077 (vs)	1074 (vs)	1075 (vs)	1072 (vs)	1075 (vs)
1109 (vw)	1116 (w)	1100 (vw)	1104 (w)		
1126 (m)	1130 (w)	1119 (m)	1122 (m)	1113 (m)	1123 (m)
1152 (vw)		1147 (vw)		1162 (s)	1158 (s)
1205 (sh)	1192 (s)	1185 (s)	1189 (s)	1190 (w)	1195 (w)
1215 (s)					
1229 (m)	1221 (s)	1229 (m)	1228 (m)	1225 (w)	1230 (w)
	1241 (vw)				
1259 (m)	1260 (m)	1251 (m)	1254 (m)	1248 (w)	1246 (m)
1268 (sh)	1281 (w)	1270 (w)	1278 (m)	1267 (w)	1279 (w)
1291 (w)	1309 (w)	1300 (w)	1309 (w)		1302 (w)
1329 (m)	1330 (s)	1322 (m)	1333 (m)	1324 (w)	1328 (w)
			1347 (m)		
1364 (s)	1350 (s)	1363 (s)	1364 (s)	1353 (s)	1350 (s)
1418 (wb)	1419 (wb)	1417 (wb)	1395 (w)	1415 (wb)	1419 (w)
1449 (vs)	1450 (vs)	1449 (vs)	1446 (vs)	1445 (vs)	1447 (vs)
2665 (vw)	2665 (vw)	2671 (vw)	2668 (vw)	2667 (vw)	2677 (vw)
2871 (s)	2871 (s)	2862 (s)	2866 (s)	2862 (s)	2862 (s)
2940 (vs)	2940 (vs)	2939 (vs)	2937 (vs)	2930 (vs)	2932 (vs)
3368 (vs)	3336 (vs)	3370 (vs)	3287 (vs)	3365 (vs)	3193 (vs)

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

TABLE 2. FREQUENCY OF THE O-H STRETCHING BAND IN THE CS_2 SOLUTION (cm^{-1})

Compound	Free band	Hydrogen-bonded band	Frequency shift
$C_6H_{10}Cl(OH)$	3607	3582	25
$C_6H_{10}Br(OH)$	3605	3571	34
$C_6H_{10}I(OH)$	3599	3558	41

stable. When taking into account the experimental error usually introduced in the intensity measurements, the two values of the energy difference are considered to agree with each other. This fact indicates that the isomer which exists in the solid is the ee-isomer and that it exists exclusively in the form having the intramolecular hydrogen bond in the dilute solution.

For the bands assigned to the C-halogen stretching vibration of various halogen derivatives of cyclohexane, one of the present authors has previously pointed out the empirical rule[10] that the frequencies of the bands which are due to the halogen atoms attached to the e-positions of the ring are higher than those of the bands due to the same halogen atoms attached to the a-positions. For the iododerivative, the 632- and the 657-cm^{-1} band can be

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10) K. Kozima, *Bull. Tokyo Inst. Tech.*, **1952**, 49.

TABLE 3. TEMPERATURE DEPENDENCE OF THE RELATIVE INTENSITIES AND ENERGY DIFFERENCE BETWEEN ISOMERS IN THE CS_2 SOLUTION

(1) *trans*-2-Chlorocyclohexanol
Concentration: 0.016 mol/*l*
Prism: NaCl
Spectral slit width: 3.3 cm^{-1} at 1007 cm^{-1}
3.5 cm^{-1} at 1034 cm^{-1}

Temp. (C)	Wave-number	Isomer	$\log_e (T_0/T)_{max}$	$\Delta\nu^a_{1/2}$ (cm^{-1})	K	C_1a_1/C_2a_2
29	1007	1=aa	0.0945	9.6	1.51	0.059
	1034	2=ee	1.04	14.5	1.55	
−23	1007	1=aa	0.0690	9.8	1.51	0.038
	1034	2=ee	1.30	13.4	1.56	

$E_{aa}-E_{ee}=1.3$ kcal/mol

(2) *trans*-2-Bromocyclohexanol
Concentration: 0.015 mol/*l*
Prism: NaCl
Spectral slit width: 3.3 cm^{-1} at 1005 cm^{-1}
3.5 cm^{-1} at 1033 cm^{-1}

31	1005	1=aa	0.0881	11.0	1.51	0.061
	1033	2=ee	1.42	10.2	1.56	
−23	1005	1=aa	0.0518	11.0	1.51	0.031
	1033	2=ee	1.66	10.8	1.57	

$E_{aa}-E_{ee}=1.9$ kcal/mol

(3a) *trans*-2-Iodocyclohexanol
Concentration: 0.013 mol/*l* Prism: NaCl
Spectral slit width: 3.3 cm^{-1} at 1001 cm^{-1}
3.5 cm^{-1} at 1030 cm^{-1}

31	1001	1=aa	0.109	9.5	1.51	0.067
	1030	2=ee	1.25	12.0	1.56	
−24	1001	1=aa	0.0655	8.2	1.49	0.030
	1030	2=ee	1.64	10.5	1.57	

$E_{aa}-E_{ee}=2.2$ kcal/mol

(3b) *trans*-2-Iodocyclohexanol
Concentration: 0.017 mol/*l*
Prism: LiF
Spectral slit width: 3.6 cm^{-1} at 3558 cm^{-1}
3.7 cm^{-1} at 3599 cm^{-1}

28	3599	1=f	0.203	25.6	1.56	0.17
	3558	2=h	1.26	23.7	1.57	
−16	3599	1=f	0.119	25.7	1.56	0.087
	3558	2=h	1.48	23.6	1.57	

$E_f-E_h=2.4$ kcal/mol

safely assigned to the C-I stretching vibrations. Therefore, according to this rule, the same conclusion as that described above for the stable isomer can be drawn, since only the higher frequency band persists in the solid.

The liquid-state spectrum of the chloro- or the bromo-derivative was divided into two groups according to whether or not the band persists in the solid. For the chloro- or the bromo-derivative, an adequate band for the intensity measurements was selected from each group and the change in the relative intensity with the temperature was measured. The results are shown in Tables 3—1 and 3—2. From these data, the energy differences are calculated to be 1.3 and 1.9 kcal/mol for the chloro- and the bromo-derivative respectively, the isomer which exists in the solid being more stable. By comparing the two groups of the bands of the three compounds, it can be seen that the spectra show striking similarities. Therefore, it is very probable that the stable isomer is the ee-isomer for the chloro- or the bromo-derivative, as is the case for the iodo-derivative. Furthermore, additional evidence is obtained by the following considerations. The 735 and 705-cm^{-1} band of the chloro-derivative, and the 688 and the 650-cm^{-1} band of the bromo-derivative, can be safely assigned to the C–Cl and the C–Br stretching vibrations respectively. According to the rule described above, the same conclusion can be drawn from the fact that the higher frequency bands persist in the solid for the two derivatives.

The energy differences between the two isomers of *trans*-2-halocyclohexanols, $\Delta E=E_{aa}-E_{ee}$, increase in the order: Cl<Br<I. For *trans*-1,2-dihalocyclohexanes it has been reported[1] that the energy difference between the two isomers is 50 cal/mol or 500 cal/mol in the dilute carbon tetrachloride solution for the dichloro- or the dibromo-derivative respectively, the aa-isomer being the more stable. Comparisons of the energy differences show that the ee-isomer of the dibromo-derivative is less stable than that of the dichloro-derivative. This is contrary to the case of *trans*-2-halocyclohexanols. These facts suggest that the intramolecular hydrogen bond formed in the ee-isomer of *trans*-2-halocyclohexanols stabilizes the ee-isomer and that the strength of the hydrogen bond increases in the order: Cl<Br<I. This suggestion is supported by the following experimental evidence.

The magnitude of the frequency shifts of the O–H stretching band, which may be considered to be a measure of the strength of the hydrogen bond, increases in the order: Cl<Br<I. Since the sequence of the hydrogen-bonding power of halogens is opposite to the sequence of electronegativity, the energy due to the electrostatic interaction between the halogen and the hydrogen of the O–H group, which may increase with an increase in the electronegativity of halogens, does not seem to be dominant in this system.

It is well known[11] that, for a proper understanding of the hydrogen bond, we must use the charge-transfer theory. For this it may be assumed that the delocalization effect can be represented as due

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[11] C. A. Coulson, "Valence," 2nd Ed., Oxford Univ. Press (1961), p. 352.

to the existence of terms corresponding to two structures, namely:

(i) —O—H X—; no bond structure

(ii) —O⁻ H—X⁺—; dative structure.

According to Mulliken's theory,[12] the delocalization energy, ε, for these charge-transfer systems of a common electron acceptor can be represented approximately as follows:[13]

$$\varepsilon \propto \frac{S^2_{\mathrm{HX}}}{I_{\mathrm{D}}-k}$$

where S_{HX} is the overlap integral over the lone-pair AO of halogen, φ_{X}, and hydrogen 1*s*-AO, φ_{H}, *viz.*, $S_{\mathrm{HX}}=\int\varphi_{\mathrm{H}}\varphi_{\mathrm{X}}d\tau$, I_{D} is the ionization potential of the electron donor, and k is taken to be a constant for the three compounds. Therefore, the delocalization energy increases as S_{HX} increases or I_{D} decreases.

In order to estimate the values of the overlap integrals, we calculated the H---X distance (r_{HX}) and the angle between the C–X bond and the hydrogen bond ($\pi/2-\alpha$), assuming that the most stable hydrogen bond is formed in the position where r_{HX} is at a minimum. The result are shown in Table 4. When we assume the structure of the hydrogen-bonded system shown in Fig. 1, an orbital of the lone-pair of the halogen can be represented as follows:

$$\varphi_{\mathrm{X}}=\sqrt{\frac{1}{3}}\{\sqrt{1-s^2}\,\psi_s+(\sqrt{2}\cos\alpha-s\sin\alpha)\psi(p_x) - (\sqrt{2}\sin\alpha+s\cos\alpha)\psi(p_y)\}.$$

Here s^2 denotes the s character of the s–p hybridization of the halogen-bonding orbital, while ψ_{s}, $\psi(p_x)$, and $\psi(p_y)$ denote, respectively, the ns-, np_x-, and np_y-AO's of the electrons of the halogen atom, where n is the principal quantum number. When Slater's AO's are tentatively assumed and the s character is assumed to be 18%,[14] the overlap integrals are calculated to be 0.143 and 0.188 for the chloro- and the iodo-derivative respectively.

TABLE 4. INTRAMOLECULAR HYDROGEN-BONDED SYSTEM FORMED IN THE ee-ISOMER

Compound	r_{HX} (Å)	α	S_{HX}
$C_6H_{10}Cl(OH)$	2.42	23°44′	0.143
$C_6H_{10}Br(OH)$	2.49	26°52′	
$C_6H_{10}I(OH)$	2.59	30°35′	0.188

Assumed values: -C=1.54, Å, C–O=1.43, Å, O–H=0.94, Å, C–Cl=1.78, Å, C–Br=1.94 Å, C–I=2.14 Å, ∠COH=106° and other bond angles are tetrahedral.

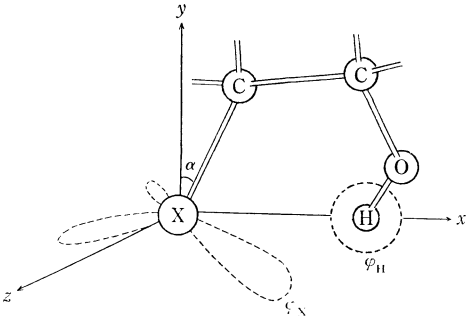

Fig. 1. The assumed structure of the hydrogen-bonded system of the ee-isomer.

Although the r_{HX} value of the iodo-derivative is larger than that of the chloro-derivative, the value of the overlap integral of the iodo-derivative is not less than that of the chloro-derivative. By considering this result and the fact[15] that the first ionization potentials of alkyl halides decrease in the order: Cl>Br>I, it can be concluded that the delocalization energies due to the charge-transfer increase in the following order: the chloro- <the bromo- <the iodo-derivative. This conculsion is in accord with the experimental results.

Therefore, it can be concluded that the delocalization energy due to the charge-transfer contributes dominantly to the energy of the intramolecular hydrogen bond formed in the ee-isomer of *trans*-2-halocyclohexanols.

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[12] R. S. Mulliken, *J. Amer. Chem. Soc.*, **74**, 811 (1952).

[13] S. P. McGlynn, *Chem. Rev.*, **58**, 1113 (1958).

[14] C. H. Townes and B. P. Dailey, *J. Chem. Phys.*, **17**, 782 (1949).

[15] *E. g.*, K. Higasi, I. Omura and T. Tsuchiya, "Tables of Ionization Potentials of Molecules and Radicals," Monograph Series of the Research Institute of Applied Electricity, Hokkaido University (1957).