A Simple Relation among the Energy Differences between Conformers of XH_2C-CH_2Y, $C_6H_{11}X$, $C_6H_{11}Y$, and *trans*-1,2-$C_6H_{10}XY$

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By measuring the infrared intensities, the energy differences between two conformers have been determined for bromocyclohexane, iodocyclohexane, *trans*-1-bromo-2-chlorocyclohexane, 1-bromo-2-chloroethane, ethylene bromohydrin, and ethylene iodohydrin in dilute solutions, and for cyclohexanol, *trans*-2-chlorocyclohexanol, ethylene chlorohydrin, and ethylene bromohydrin in vapors.

It was ascertained that the following relation holds for the energy differences:

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

Here $E_t - E_g$ is the energy difference between the *trans* and the *gauche* isomer of XH_2C-CH_2Y, $E_{aa} - E_{ee}$ is that between the *aa*- and the *ee*-isomer of *trans*-1,2-$C_6H_{10}XY$, and $E_a - E_e$ and $E_a' - E_e'$ are those between the *a*- and the *e*-isomers of $C_6H_{11}X$ and $C_6H_{11}Y$ respectively, where X is a halogen and Y is a halogen or the O–H group.

The energy difference between the conformers may be considered to be the difference between the intramolecular potential energies, which are usually the sums of the potential energies for the various pairs of non-bonded atoms in each isomer. Furthermore, it is safe to assume, for similar molecules, that the potential energy between the same pair of non-bonded atoms does not differ from molecule to molecule, so long as the distance between non-bonded atoms remains almost the same. On the basis of these considerations, the following relation has been obtained:[1]

$$E_t - E_g = (E_{aa} - E_{ee}) - 2(E_a - E_e), \qquad (1)$$

where E_t–E_g is the energy difference between the *trans* and the *gauche* isomer of 1,2-dihaloethane, XH_2C–CH_2X, E_{aa}–E_{ee} is that between the *aa*- and the *ee*-isomer of *trans*-1,2-dihalocyclohexane, $C_6H_{10}X_2$, and E_a–E_e is that between the *a*- and the *e*-isomer of halocyclohexane, $C_6H_{11}X$; this relation has been shown to be correct within the limit of experimental error when X is Cl.[1]

The relation can easily be extended to one for such compounds as XH_2C–CH_2Y, *trans*-1,2-$C_6H_{10}XY$, $C_6H_{11}X$, and $C_6H_{11}Y$, where X is a halogen and Y is a halogen or the O–H group. In an attempt to examine the extended relation, a study of the energy differences between two conformers has been carried out for bromocyclohexane, iodocyclohexane, *trans*-1-bromo-2-chlorocyclohexane, cyclohexanol, *trans*-2-chlorocyclohexanol, 1-bromo-2-chloroethane, ethylene chlorohydrin, ethylene bromohydrin, and ethylene iodohydrin by measuring the infrared intensities.

Experimental

Materials. The iodocyclohexane used in this research was prepared by adding cyclohexene to a solution of potassium iodide dissolved in 95% orthophosphoric acid.[2] The product was purified by fractional distillation; bp 48.5—49.0°C/4 mmHg.

The *trans*-1-bromo-2-chlorocyclohexane was prepared by adding a mixture of bromine and chlorine dissolved in chloroform to cyclohexene.[3] The product was purified by fractional distillation; bp 82.2—82.3°C/13 mmHg.

The ethylene iodohydrin was prepared by refluxing sodium iodide, absolute ethanol, and ethylene chlorohydrin.[4] The product was purified by fractional distillation; bp 47.6—47.8°C/3 mmHg.

The samples of bromocyclohexane, cyclohexanol, 1-bromo-2-chloroethane, ethylene chlorohydrin, and ethylene bromohydrin, which had been obtained from commercial sources, were purified by distillation.

The measurement of the infrared spectra and that of the integrated intensities of the infrared absorption bands were made by the method described in a previous paper.[5]

Results and Discussion

Existence of Conformers. By infrared studies of chlorocyclohexane[1] and bromocyclohexane,[6] it has been ascertained that two conformers, the *a*- and the *e*-isomer, exist in the liquid, while only the *e*-isomer exists in the solid.

Concerning iodocyclohexane, *trans*-1-bromo-2-chlorocyclohexane, and cyclohexanol, the infrared spectra were measured both in the liquid and in the solid. The results are shown in Tables 1-a, 1-b, and 1-c. Since several bands of the liquid-state spectra disappear on passing from the liquid to the solid, as can be seen from these tables, it is certain that the two conformers exist in the liquid, while only one of them remains in the solid.

Since the solid-state spectra of chloro-, bromo-, and iodocyclohexane show striking similarities, it is very probable that only the *e*-isomer exists in the solid of iodocyclohexane. Furthermore, additional evidence is obtained by the following consideration.

By comparing the liquid-state spectrum of iodo-

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

2) H. Stone and H. Shechtor, "Organic Syntheses," Vol. 31, p. 66 (1951).

3) R. E. Buckles, J. L. Forrester, R. L. Burham, and T. W. McGee, *J. Org. Chem.*, **25**, 24 (1960).

4) W. E. Noland and P. J. Hartman, *J. Amer. Chem. Soc.*, **76**, 3227 (1954).

5) E. Fujimoto, Y. Takeoka, and K. Kozima, This Bulletin, **43**, 991 (1970).

6) Yu. A. Pentin, Z. Sharipov, G. G. Kotova, A. V. Kamernitskii, and A. A. Akhrem, *J. Struct. Chem. USSR, English Transl.*, **4**, 174 (1963) (*Zh. Strukt. Khim.*, **4**, 194 (1963)).

Table 1-a. Infrared spectra of iodocyclohexane (cm^{-1})

Liquid	Solid	Liquid	Solid
436 (vw)	435 (vw)	1027 (w)	1022 (m)
446 (w)		1073 (w)	1073 (w)
	485 (s)	1095 (s)	1096 (s)
494 (m)	495 (m)	1164 (s)	
639 (m)		1173 (s)	1174 (s)
655 (vs)	652 (vs)	1244 (s)	
	788 (w)	1252 (s)	1254 (s)
801 (sh)		1294 (vw)	1294 (vw)
806 (s)	806 (s)	1332 (m)	1332 (s)
847 (m)	843 (w)	1346 (w)	
863 (m)		1447 (vs)	1446 (vs)
883 (s)	883 (s)	2604 (vw)	2600 (vw)
916 (w)	916 (w)	2668 (w)	2667 (w)
986 (s)	989 (s)	2854 (s)	2857 (s)
1004 (m)		2929 (vs)	2930 (vs)

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

Table 1-b. Infrared spectra of *trans*-1-bromo-2-chlorocyclohexane (cm^{-1})

Liquid	Solid	Liquid	Solid
442 (w)	443 (m)	1048 (vw)	1048 (w)
484 (w)		1064 (vw)	
505 (m)	504 (s)	1098 (vw)	1097 (w)
540 (m)		1119 (m)	1119 (m)
584 (vs)		1132 (w)	
661 (m)			1163 (w)
692 (s)	690 (s)	1177 (s)	1179 (s)
735 (m)	732 (m)	1185 (s)	
745 (s)	742 (s)	1201 (m)	1203 (m)
	792 (vw)	1216 (m)	1218 (m)
815 (s)	815 (s)	1226 (w)	
818 (s)		1252 (w)	1254 (m)
842 (m)	843 (m)	1261 (w)	
863 (m)		1272 (m)	1274 (m)
869 (w)	869 (w)	1318 (w)	1319 (w)
905 (s)	907 (s)	1339 (m)	1336 (m)
938 (vw)	939 (vw)	1360 (w)	
956 (vw)	967 (vw)	1436 (s)	
976 (s)	978 (s)	1446 (s)	1447 (s)
999 (s)		2662 (vw)	2669 (vw)
1032 (w)	1032 (vw)	2852 (s)	2857 (s)
	1039 (w)	2920 (vs)	2927 (vs)

cyclohexane with those of the chloro- and the bromo-derivative, the 639- and the 655- cm^{-1} band of iodocyclohexane can safely be assigned to the C–I stretching vibration. 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[7] 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. According to this rule,

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

Table 1-c. Infrared spectra of cyclohexanol (cm^{-1})

Liquid	Solid
550—850 (bm) [a]	700—780 (bm) [a]
	780—870 (bm) [a]
	452 (vw)
	460 (w)
479 (bw)	480 (bw)
558 (m)	553 (s)
	560 (sh)
	783 (w)
789 (m)	787 (m)
835 (w)	
844 (m)	845 (m)
863 (w)	
889 (s)	888 (s)
925 (w)	922 (vw)
957 (sh)	
963 (vs)	963 (vs)
973 (vs)	973 (vs)
1024 (s)	1026 (s)
1033 (sh)	
	1049 (w)
1068 (vs)	1067 (vs)
	1077 (vs)
1139 (m)	1143 (w)
1172 (w)	1176 (w)
1237 (m)	1241 (w)
1254 (m)	1258 (w)
1296 (m)	1303 (w)
1324 (m)	
1346 (m)	
1363 (s)	1364 (s)
1450 (vs)	1447 (s)
	1461 (s)
	1494 (s)
2597 (vw)	2598 (vw)
2674 (w)	2672 (w)
2853 (s)	2862 (s)
2921 (vs)	2927 (vs)
3320 (vs)	3210 (vs)

b=broad

a) The broad bands may be due to the intermolecular hydrogen bond as is the case in *trans*-2-halocyclohexanols.[5]

the 639- and the 655- cm^{-1} band can be assigned to the *a*- and the *e*-isomer respectively. Therefore, the same conclusion can be drawn here, since the higher-frequency band persists in the solid.

In order to determine the stable isomer of *trans*-1-bromo-2-chlorocyclohexane in the solid, the relative intensities of two pairs of bands, the 815- and 818-cm^{-1} bands, and the 976- and 999-cm^{-1} bands, were measured both in the acetone solution and in the carbon disulfide solution. As can be seen in Fig. 1, the intensities of the lower-frequency bands increase when the solvent changes from carbon disulfide to acetone. As it is well known[8] that the more polar isomer stabilizes in polar solvents except in the case of benzene, it follows that the lower-frequency bands which per-

8) S. Mizushima, "Structure of Molecules and Internal Rotation," Acad. Press, New York (1954), p. 43; I. Watanabe, S. Mizushima, and Y. Masiko, *Sci. Papers Inst. Phys. Chem. Res. Tokyo*, **40**, 425 (1943).

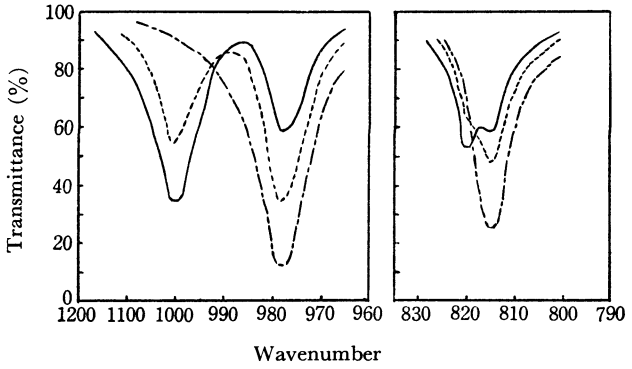

Fig. 1. Variation of infrared intensities of *trans*-1-bromo-2-chlorocyclohexane with changing medium.
—— in the carbon disulfide solution
---- in the acetone solution
·—· in the solid

sist in the solid are to be assigned to the *ee*-isomer, because the *ee*-isomer is more polar than the *aa*-isomer.

Concerning cyclohexanol, it is very probable, in view of the results on halocyclohexanes, that only the *e*-isomer exists in the solid. This is supported by the following consideration. Winstein and Holness[9] have pointed out that *cis*-4-*t*-butylcyclohexanol exists as the *a*-isomer, and that *trans*-4-*t*-butylcyclohexanol exists as the *e*-isomer, with regard to the C–O bond, because of the steric hindrance of the *t*-butyl group, and that the 955-cm^{-1} band is assigned to the C–O stretching vibration of the *cis* isomer, and the 1062-cm^{-1} band, to that of the *trans* isomer. According to these findings, the 1067-cm^{-1} band of cyclohexanol which persists in the solid may be assigned to the C–O stretching vibration of the *e*-isomer. In the spectra of the liquid and of the solution for cyclohexanol, the 957-cm^{-1} band may be assigned to the C–O stretching band of the *a*-isomer. At first glance it is not clear whether or not this band disappears in the solid, because this band is masked by two strong and broad bands. However, by assuming that these two bands are represented by Lorentz's curves, it can be seen that the 957-cm^{-1} band disappears in the solid.

It has been shown[10] that ethylene chlorohydrin possesses two conformers, namely, the *trans* and the *gauche* isomer, both in the vapor and in the liquid, while only the *gauche* isomer exists in the solid. The infrared spectra of the bromo- and the iodo-derivative in the liquid were also measured. In the frequency region of C–halogen stretching vibrations, there are two bands, namely, the 573 and 676 cm^{-1} bands for the bromo-derivative, and the 518 and 622 cm^{-1} bands for the iodo-derivative. Of the two pairs of bands, the intensities of the lower-frequency bands increase with a decrease in the temperature. This fact shows that for the cases of the bromo- and the iodo-derivative also the two conformers exist in the liquid.

Energy Differences between Conformers. For bromo-

9) S. Winstein and N. I. Holness, *J. Amer. Chem. Soc.*, **77**, 5562 (1955).
10) S. Mizushima, T. Shimanouchi, T. Miyazawa, K. Abe, and M. Yasumi, *J. Chem. Phys.*, **19**, 1477 (1951).

Table 2. Temperature dependence of relative integrated intensities and energy difference between isomers in the dilute solution

a) Bromocyclohexane
CS_2 solution: 0.15 mol/*l*
prism: KBr
spectral slit-width: 2.2 cm^{-1} at 658 cm^{-1}
2.8 cm^{-1} at 668 cm^{-1}

Temp. (°C)	Wave number	Isomer	$\log_e(T_0/T)_{max}$	$\Delta\nu_{1/2}$ [a]	K	C_1a_1/C_2a_2
27	658	1 = *a*	0.490	5.7	1.50	0.25
	668	2 = *e*	1.61	6.7	1.57	
2	658	1 = *a*	0.518	5.1	1.51	0.23
	668	2 = *e*	1.75	6.4	1.57	

$E_a - E_e = 0.60$ kcal/mol

The symbols used in the table are the same as used in the previous article (5). The values of K were obtained from the table of Ramsay (*J. Amer. Chem. Soc.*, **74**, 72 (1952).)

b) Iodocyclohexane
CS_2 solution: 0.21 mol/*l*
prism: KBr
spectral slit-width: 4.2 cm^{-1} at 639 cm^{-1}
4.7 cm^{-1} at 655 cm^{-1}

34°	639	1 = *a*	0.455	6.0	1.38	0.17
	655	2 = *e*	1.84	7.1	1.64	
−6°	639	1 = *a*	0.437	5.4	1.38	0.14
	655	2 = *e*	1.87	7.0	1.64	

$E_a - E_e = 0.73$ kcal/mol

c) *trans*-1-Bromo-2-chlorocyclohexane
CS_2 solution: 0.18 mol/*l*
prism: NaCl
spectral slit-width: 4.4 cm^{-1} at 977 cm^{-1}
4.6 cm^{-1} at 1001 cm^{-1}

29°	1001	1=*aa*	1.07	7.5	1.51	2.1
	977	2=*ee*	0.546	7.5	1.46	
−27°	1001	1=*aa*	1.29	7.0	1.53	2.2
	977	2=*ee*	0.636	7.2	1.46	

$E_{aa} - E_{ee} = -0.12$ kcal/mol

d) 1-Bromo-2-chloroethane
CS_2 solution: 0.021 mol/*l*
prism: NaCl
spectral slit-width: 4.6 cm^{-1} at 1201 cm^{-1}
5.1 cm^{-1} at 1259 cm^{-1}

25°	1201	1 = *t*	2.03	6.2	1.68	2.3
	1259	2 = *g*	0.936	6.9	1.50	
−30°	1201	1 = *t*	2.23	6.3	1.68	3.1
	1259	2 = *g*	1.01	5.7	1.50	

$E_t - E_g = -0.95$ kcal/mol

e) Ethylene bromohydrin
C_6H_{12} solution: 0.035 mol/*l*
prism: KBr
spectral slit-width: 2.6 cm^{-1} at 573 cm^{-1}
3.5 cm^{-1} at 676 cm^{-1}

61°	676	1 = *t*	0.567	17.3	1.55	0.60
	573	2 = *g*	0.945	17.1	1.56	
11°	676	1 = *t*	0.658	14.6	1.55	0.52
	573	2 = *g*	1.51	12.3	1.56	

$E_t - E_g = 0.59$ kcal/mol

f) Ethylene iodohydrin
CS_2 solution: 0.022 mol/l
prism: KBr
spectral slit-width: 2.6 cm^{-1} at 518 cm^{-1}
3.2 cm^{-1} at 622 cm^{-1}

Temp. (°C)	Wave number	Isomer	$\log_e (T_0/T)_{max}$	$\Delta\nu_{1/2}{}^a$	K	C_1a_1/C_2a_2
31°	622	1 = t	0.392	15.1	1.55	2.1
	518	2 = g	0.263	10.5	1.55	
−19°	622	1 = t	0.516	12.3	1.55	1.6
	518	2 = g	0.415	9.6	1.54	

$E_t - E_g = 0.82$ kcal/mol

g) Ethylene iodohydrin
CS_2 solution: 0.015 mol/l
prism: LiF
spectral slit-width: 3.6 cm^{-1} at 3565 cm^{-1}
3.7 cm^{-1} at 3605 cm^{-1}

27°	3609	1 = f*	0.675	25.0	1.56	0.94
	3567	2 = h	0.696	25.9	1.56	
−21°	3609	1 = f	0.585	24.1	1.56	0.73
	3567	2 = h	0.728	26.7	1.56	

$E_f - E_h = 0.88$ kcal/mol

* The subscripts h and f refer to the hydrogen-bonded molecule and the non-bonded one, respectively.

cyclohexane, the values reported[11,12] do not agree with each other. Therefore, the relative integrated intensities of the 668- and the 658-cm^{-1} band of bromocyclohexane were measured as a function of temperature in the carbon disulfide in order to determine the energy difference. The results are shown in Table 2-a. From these data, the energy difference, E_a–E_e, is calculated to be 0.60 kcal/mol. The value thus obtained agrees with that of Jensen and Gale.[12]

For iodocyclohexane, the change in the relative integrated intensities of the 639- and the 655-cm^{-1} band with the temperature was measured. The results are shown in Table 2-b. From these data, the energy difference, E_a–E_e, is calculated to be 0.73 kcal/mol.

By comparing the values for bromo- and iodocyclohexane with the value of 0.33 kcal/mol for chlorocyclohexane,[1] it can be concluded that the stability of the *e*-isomer of halocyclohexane increases with an increase in the atomic radius of halogens.

For *trans*-1-bromo-2-chlorocyclohexane, the change in the relative integrated intensities of the 977- and the 1001-cm^{-1} band with the temperature was measured. The results are shown in Table 2-c. From these data, the energy difference, E_{ee}–E_{aa}, is calculated to be 0.12 kcal/mol.

Chiurdoglu *et al.*,[11] Masschelein,[13] and Neelakantan[14] have all estimated the energy difference of cyclohexanol in the liquid. Pickering and Price[15] have estimated it in the 0.3 mol/l carbon disulfide solution. However, these values cannot be taken to be the value of the energy difference, because the values are affected by the intermolecular hydrogen bond. The change in the relative integrated intensities of the 835-cm^{-1} band of the *a*-isomer and the 845-cm^{-1} band of the *e*-isomer with the temperature was measured in the vapor. The results are shown in Table 3-a. From these data, the energy difference of cyclohexanol is calculated to be 0.59 kcal/mol, the *e*-isomer being more stable.

TABLE 3. TEMPERATURE DEPENDENCE OF RELATIVE INTEGRATED INTENSITIES AND ENERGY DIFFERENCE BETWEEN ISOMERS IN THE VAPOR*

a) Cyclohexanol

Temp. (C)	Wave number	Isomer	C_1a_1/C_2a_2
183°	835	1 = a	1.1
	845	2 = e	
135°	835	1 = a	0.98
	845	2 = e	

$E_a - E_e = 0.59$ kcal/mol

b) *trans*-2-Chlorocyclohexanol

160°	705	1 = aa	0.18
	740	2 = ae	
60°	705	1 = aa	0.089
	740	2 = ee	

$E_{aa} - E_{ee} = 2.0$ kcal/mol

c) Ethylene chlorohydrin

160°	766	1 = t	0.55
	671	2 = g	
95°	766	1 = t	0.44
	671	2 = g	

$E_t - E_g = 1.1$ kcal/mol

d) Ethylene bromohydrin

128°	682	1 = t	0.63
	583	2 = g	
74°	682	1 = t	0.52
	583	2 = g	

$E_t - E_g = 0.98$kcal/mol

* The integrated intensities were measured by the same method as described in the reference of (21).

The energy difference of *trans*-2-halocyclohexanols in dilute solutions has been reported in a previous paper.[5] In order to determine the energy difference of *trans*-2-chlorocyclohexanol in a vapor, the relative integrated intensities of the C–Cl stretching bands were measured at 60°C by using a 1-m cell and at 160°C by using a 10-cm cell. The results are shown in Table 3-b. From these data, the energy difference can be calculated to be 2.0 kcal/mol, the *ee*-isomer being more stable. The energy differences in the vapor for the bromo- and the iodo-derivative could not be measured because of the low vapor pressure.

In order to determine the energy difference of 1-bromo-2-chloroethane, the relative integrated intensities of the 1201-cm^{-1} band of the *trans* isomer and the 1259-cm^{-1} band of the *gauche* isomer were measured in

11) G. Chiurdoglu, M. L. Kleiner, W. Masschelein, and J. Reisse, *Bull. Soc. Chem. Belges*, **69**, 143 (1960).
12) F. R. Jensen and L. H. Gale, *J. Org. Chem.*, **25**, 2075 (1960).
13) W. Masschelein, *J. Mol. Spectrosc.*, **10**, 161 (1963).
14) P. Neelakantan, *Proc. Indian Acad. Sci.*, **A57 (2)**, 94 (1963).
15) R. A. Pickering and C. C. Price, *J. Amer. Chem. Soc.*, **80**, 4931 (1958).

a solution. The assignments used were those reported by Kuratani *et al.*[16] The results are shown in Table 2-d. From these data, the energy difference, E_g-E_t, can be calculated to be 0.95 kcal/mol.

The energy difference in the vapor for ethylene chlorohydrin is calculated to be 1.1 kcal/mol from the data shown in Table 3-c, the *gauche* isomer being more stable. This value is nearly equal to that obtained by Mizushima *et al.*[10] It may be safe to consider that the 573- and the 676-cm^{-1} band of ethylene bromohydrin and the 518- and the 622-cm^{-1} band of ethylene iodohydrin are due to the C–halogen stretching vibrations. Of the pairs of bands for both compounds, the lower-frequency bands can be assigned to the *gauche* isomer, and the others, to the *trans* isomers, as is the case for ethylene chlorohydrin. The temperature dependence of the relative integrated intensities of these bands was also measured. The results for ethylene bromohydrin are shown in Tables 3-d and 2-e for the vapor and the dilute solution respectively. From these data, the energy differences, E_t-E_g, can be calculated to be 0.98 and 0.59 kcal/mol in the vapor and in the dilute solution respectively. The results for ethylene iodohydrin are shown in Table 2-f. From these data, the energy difference, E_t-E_g, can be calculated to be 0.82 kcal/mol.

There are two O–H stretching bands in the 3μ region of the infrared spectra of ethylene halohydrins, even in dilute carbon disulfide solutions, as in the cases of *trans*-2-halocyclohexanols.[5] The lower-frequency bands can be assigned to the O–H stretching vibration for the hydrogen-bonded molecules, and the others, to that of the non-bonded molecules. The lower-frequency bands can be safely assigned to the *gauche* isomer, because, in view of its molecular geometry, only the *gauche* isomer is able to form an intramolecular hydrogen bond. Of these pairs of bands, the intensities of the lower-frequency bands increase with a decrease in the temperature. Concerning ethylene iodohydrin, in the spectra of which the frequency difference between these bands is relatively large, the relative intensity of these bands was measured by changing the temperature. The results are shown in Table 2-g. From these data, the difference between the energy of the hydrogen-bonded molecule, E_h, and that of the non-bonded one, E_f, can be calculated to be 0.88 kcal/mol, the hydrogen-bonded molecule being more stable. When taking into account the experimental error usually introduced in the intensity measurements, this value can be said to agree with the energy difference between the conformers obtained by measuring the C–I stretching bands. This shows that the *gauche* isomer exists exclusively in the form with the intramolecular hydrogen bond in the dilute solution.

Relation of Energy Differences between Conformers. On the basis of the information presented above, the following relation can be obtained for such compounds as XH_2C-CH_2Y, *trans*-1,2-$C_6H_{10}XY$, $C_6H_{11}X$, and $C_6H_{11}Y$:

$$E_t - E_g = (E_{aa}-E_{ee}) - (E_a-E_e) - (E_a'-E_e'), \quad (2)$$

where E_t-E_g is the energy difference between the *trans* and the *gauche* isomer of XH_2C-CH_2Y, $E_{aa}-E_{ee}$ is that between the *aa*- and the *ee*-isomer of $C_6H_{10}XY$, and E_a-E_e and $E_a'-E_e'$ are those between the *a*- and the *e*-isomers of $C_6H_{11}X$ and $C_6H_{11}Y$ respectively.

TABLE 4. ENERGY DIFFERENCE BETWEEN ISOMERS (kcal/mol)

a) X=Cl, Y=Br (in the solution)

trans-1,2-$C_6H_{10}BrCl$ $E_{aa}-E_{ee}$	$C_6H_{11}Cl$ E_a-E_e	$C_6H_{11}Br$ $E_a'-E_e'$	ClH_2C-CH_2Br E_t-E_g	
			obsd.	calcd.
−0.12	0.33**	0.60	−0.95	−1.0

b) X=Cl, Y=OH (in the vapor)

trans-1,2-$C_6H_{10}ClOH$ $E_{aa}-E_{ee}$	$C_6H_{11}Cl$ E_a-E_e	$C_6H_{11}OH$ $E_a'-E_e'$	ClH_2C-CH_2OH E_t-E_g	
			obsd.	calcd.
2.0	0.34**	0.59	1.1	1.1

c) X=Cl, Y=OH (in the solution)

trans-1,2-$C_6H_{10}ClOH$ $E_{aa}-E_{ee}$	$C_6H_{11}Cl$ E_a-E_e	$C_6H_{11}OH$ $E_a'-E_e'$	ClH_2C-CH_2OH E_t-E_g	
			obsd.	calcd.
1.3*	0.33**	0.59	—	0.4

d) X=Br, Y=OH (in the solution)

trans-1,2-$C_6H_{10}BrOH$ $E_{aa}-E_{ee}$	$C_6H_{11}Br$ E_a-E_e	$C_6H_{11}OH$ $E_a'-E_e'$	BrH_2C-CH_2OH E_t-E_g	
			obsd.	calcd.
1.9*	0.60	0.59	0.59	0.7

e) X=I, Y=OH (in the solution)

trans-1,2-$C_6H_{10}IOH$ $E_{aa}-E_{ee}$	$C_6H_{11}I$ E_a-E_e	$C_6H_{11}OH$ $E_a'-E_e'$	IH_2C-CH_2OH E_t-E_g	
			obsd.	calcd.
2.2*	0.73	0.59	0.82	0.9

* The values reported in our previous article (5)
** The values reported in the reference of (1)

From Table 4-a it can be seen that Eq. (2) holds for the case in which X is Cl and Y is Br, since the agreement between the observed and the calculated value for the energy difference of ClH_2C-CH_2Br is satisfactory.

Potential functions for non-bonded hydrogen-hydrogen and for non-bonded carbon-hydrogen interaction energies have been given by Hendrickson.[17] According to these functions, the nuclear distances at the potential minima for hydrogen-hydrogen and carbon-hydrogen interactions are 2.5 and 2.8 Å respectively. Of these pairs of non-bonded atoms in these compounds, there are no pairs of shorter distances than those at the potential minima. Therefore, although the distances between the hydrogen

16) K. Kuratani, T. Miyazawa, and S. Mizushima, *J. Chem. Phys.*, **21**, 1411 (1953).

17) J. B. Hendrickson, *J. Amer. Chem. Soc.*, **83**, 4531 (1961).

atoms or between the hydrogen and the carbon atom may vary somewhat from molecule to molecule, it can be seen from the potential curves[17] that these changes do not affect the relation of Eq. (2) beyond the limit of experimental error. The pairs of non-bonded atoms which make an important contribution to the energy difference may be those of halogen-halogen, halogen-hydrogen, and halogen-carbon. However, these potential functions are not clearly known. From the fact that Eq. (2) holds for these compounds, it is, however, sure that, in the cases where the distances between the same pair of the non-bonded atoms are considered to be almost the same from the structural point of view, the potential energy between them is nearly the same from molecule to molecule at least for these compounds.

It seems that it would be interesting to consider the cases in which one of the substituents is an O–H group, and the other, a halogen. In these cases, one of the isomers forms an intramolecular hydrogen bond. The values of the frequency difference between the hydrogen-bonded O–H stretching band and the free one are shown in Table 5 for the *ee*-isomer of *trans*-2-halocyclohexanols and for the *gauche* isomer of ethylene halohydrins. From this table, it can be seen that the strength of the hydrogen bond of *trans*-2-chloro-, *trans*-2-bromo-, or *trans*-2-iodocyclohexanol is nearly equal to that of ethylene chloro-, ethylene bromo-, or ethylene iodohydrin respectively. Therefore, it seems probable that Eq. (2) holds for these cases. The results for the cases of the vapors of the chloro-derivatives are shown in Table 4-b. The agreement shown in this table is satisfactory. For the cases of the dilute solutions of the bromo- and the iodo-derivative the results are shown in Tables 4-d and 4-e respectively. In these tables, the value of the energy difference of cyclohexanol in the vapor is used, as the value in the dilute solution could not be measured because of the lack of an adequate solvent. Since, for this molecule, the dipole moment of the *e*-isomer is nearly equal to that of the *a*-isomer, the energy difference in the vapor seems not to be different from that in the dilute solution.[8] As Tables 4-d and 4-e show, the observed and the calculated values agree if account is taken of the experimental errors usually introduced in the intensity measurements. The energy difference of ethylene chlorohydrin in the dilute solution could not be measured because the bands of the usual non-polar solvents masked those of ethylene chlorohydrin. The value is, however, calculated by Eq. (2) to be 0.4 kcal/mol, as is shown in Table 4-c; this is lower by 0.7 kcal/mol than the value observed in the vapor. When taking into account the fact that the observed value of ethylene bromohydrin in the dilute solution is lower by 0.39 kcal/mol than that in the vapor, the estimated value of the chloro-derivative seems reasonable.

Table 5. Frequency difference between hydrogen-bonded O–H band and free one in the carbon disulfide solution (cm^{-1})

	trans-1,2-$C_6H_{10}XOH$	XH_2C-CH_2OH
X=Cl	25	28
X=Br	34	31
X=I	44	42

The dipole moment of the *trans* isomer of ethylene chlorohydrin, μ_t, is estimated to be 1.74 D by using the dipole moments of methanol[18] and methyl chloride[19] based upon the rule of the vector sum of bond moments. Since the dipole moment of the *gauche* isomer, μ_g, could not be estimated by using this rule because of the uncertainty of the moment due to the intramolecular hydrogen bond, it was calculated to be 1.79 D by the usual relation:

$$\mu^2 = (\mu_g^2+\mu_t^2\frac{1}{2}e^{-\Delta E/RT})/(1+\frac{1}{2}e^{-\Delta E/RT}),$$

where the value of ΔE used is the value of 1.1 kcal/mol obtained in the vapor and where μ is the dipole moment of 1.78 D observed in the vapor.[20] It can be seen from the results obtained above that the dipole moment of the *gauche* isomer is not very different from that of the *trans* isomer. Therefore, the finding that the *gauche* isomer is stabilized when the state changes from a dilute solution to a vapor violates the rule[8] that the more polar conformation is stabilized in a medium with a larger dielectric constant. The same violation can be seen in the cases of ethylene bromohydrin and *trans*-2-chlorocyclohexanol. However, this fact seems reasonable, because it is very probable the intramolecular hydrogen bond in the vapor is stronger than that in the dilute solution, as in the case with the intermolecular hydrogen bond between methanol and triethylamine.[21]

18) E. V. Ivash and D. M. Dennison, *J. Chem. Phys.*, **21**, 1804 (1953).
19) R. Karplus and A. H. Sharbaugh, *Phys. Rev.*,**75**,889 (1949).
20) C. T. Zahn, *Phys. Rev.*, **40**, 291 (1932).
21) E. Hirano and K. Kozima, This Bulletin, **39**, 1216 (1966).