Spectroscopic Conformational

Analysis of Some 1,2-Dihalogeno *Cyclo*hexanes

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The infrared spectra of the *trans* 1,2-dichloro- and *trans* 1,2-di-bromo-*cyclo*hexanes are highly dependent on the dielectric properties of the solvents. This suggests a method of determining the conformational equilibrium ratio. The mole fractions of the *ee*-conformations were calculated to 0.34 and 0.19 for the dichloro- and dibromo-compound, respectively, when dissolved in *cyclo*hexane and 0.71 and 0.63 when dissolved in nitromethane.

Trans 1,2-dichloro*cyclo*hexane crystallizes in the *ee*-conformation whereas *trans* 1,2-dibromo*cyclo*hexane crystallizes in the *aa*-conformation.

A discussion of some of the steric factors which may be important for the conformational equilibrium is presented.

Using some assumptions concerning the relative intensities of the infrared carbon-halogen stretching bands of the monohalogeno *cyclo*-hexanes, the mole fraction of the *e*-conformation was calculated to 0.8 for the chloro compound and 0.85 for the bromo compound.

A previous paper [1] reported on a conformational investigation of some monohalogenated *cyclo*hexanes using infrared and Raman spectra. It was concluded that both the *e*- and the *a*- conformation of the monochloro- and the monobromo*cyclo*hexane were present in the liquid state, the *e*-con-formation preponderating in both compounds. In the anisotropic modification of the crystalline state only the *e*-conformation of the two compounds could be detected, whereas in the semisolid cubic modification of the chloro compound both conformations were present.

The conformational equilibrium of the *trans* 1,2- dihalogeno *cyclo*hexanes has previously been given a quantitative treatment by some authors [2-5] measuring the dipole moments of the *cyclo*hexane compounds dissolved in carbon tetrachloride and benzene. Kozima and co-workers [2] were able to draw certain semiquantitative conclusions about the conformational equilib-rium by considering the Raman spectra. From an investigation of the infrared spectra Larnaudie [6] concluded that both conformations were present in the liquid state.

Table 1. Raman and infrared spectra of *trans* 1,2-dichloro*cyclo*hexane.

| Raman spectrum | | | Infrared spectra | | | Confor- |
| liquid (20°C) | | | liquid (25°C) | | Solid (−70°C) | mation |
Δ ν cm⁻¹	I	ϱ	ν cm⁻¹	I	ν cm⁻¹	
3 130						
3 050		0.52				
2 957	10	0.45				
2 907	5		2 909	8		
2 868	8	0.16				
			2 838	6		
			2 655	2		
			1 716	1		
			1 521	1		
1 451	5	0.68	1 450	1	1 450	
1 437	2					
			1 426	3	1 426	
			1 357	4		aa
1 345	6	0.49				
			1 338	6	1 338	
			1 318	2	1 318	
1 287	2					
1 275	3	0.50	1 276	5	1 276	
			1 267	4		
			1 255	10	1 255	
			1 222	0	1 222	
			1 212	10		aa
1 207	2	0.60	1 202	9	1 202	ee
1 132	1		1 138	4		aa
1 127	1	0.53	1 121	2	1 121	
1 107	1	0.19	1 103	1	1 103	
			1 079	1	1 079	
			1 064	1	1 064	
1 055	2	0.60				
1 045	2	0.75	1 048	1	1 048	
			1 039	0	1 039	
			1 031	1		aa
			1 005	9		aa
989	2					
984	2	0.66	980	9	980	ee
			957	1	957	
			940	1	940	
911	1	0.19	909	9	909	
874	1	0.49	sh	0	874	
			864	4		aa
848	2	0.01	844	8	844	ee
830	3	0.62	827	7		aa
			821	9	821	ee
803	3	0.11	805	2	805	
749	3		746	10	746	ee
738	7	0.23	738	10	738	ee
703	7	0.70				aa
			692	9		aa
621	1		613	7	not	
516	2		520	4	recorded	
520	3	0.13	498	1		
			462	1		aa

Table 1. Continued.

451	3	0.20	446	2		ee
388	9	0.25	383	4		
379	3		372	1		ee
			362	1		aa
331	1	0.70	331	1		ee
309	5	0.22	303	1		
286	2	1.05				
236	2	0.91				
186	3	0.55				

Table 2. Raman and infrared spectra of *trans* 1,2-dibromo*cyclo*hexane.

Raman spectrum			Infrared spectra			Confor-
liquid (20°C)			liquid (25°C)		Solid (−70°C)	mation
$\Delta \nu$ cm^{-1}	I	ϱ	ν cm^{-1}	I	ν cm^{-1}	
3 047	3					
2 991	6					
2 949	10	0.37				
2 900	6	0.23	2 909	8		
2 864	5	0.70				
2 844	2		2 838	7		
			2 665	2		
			2 478	1		
			2 380	1		
			2 260	1		
			2 172	2		
			2 126	1		
			2 074	1		
			1 716	7		
1 445	4	0.76				
1 429	4	0.75	1 426	6	1 426	
1 362	1		1 357	5	1 357	
1 339	1	0.43	1 342	4	1 342	
1 331			1 334	4		ee
			1 318	3	1 318	
1 303	2	0.29	1 302	0	1 302	
1 279	2		1 282	1		ee
1 269	3	0.60	1 269	3	1 269	
1 259	4	0.34	1 258	3	1 258	
1 202	8	0.32	1 198	4	1 198	
1 181	7		1 177	9	1 177	aa
1 161	1		1 160	6		ee
1 138	2	0.71	1 135	2	1 135	
1 122	1		1 124	2		
			1 117	2	1 117	
			1 067	0	1 067	
1 060	2	0.52	1 059	1	1 059	
1 048	2		1 048	1		ee
1 034	4	0.80	1 032	2	1 032	
1 002	2		999	8	999	aa
971			973	5		ee
906	1	0.56	904	7	904	
868	4	0.34	861	6	861	aa
843	2	0.33	841	3		ee
815	5	0.39	814	5	814	aa
804	5	0.50				

Table 2. Continued.

			710	0	710	
699	4	0.76	693	6		ee
686	4	0.21	684	6		ee
			663	6	663	aa
652	10	0.21	651	0	651	aa
541	3	0.58	539	9		
			495	3		
477	6	0.22	476	2	not	
441	1		441	2	recorded	
365	2	0.45				
341	2					
324	2		322	3		
308	6	0.17	308	5		
			282	1		
238	7	0.17				
223	3	0.60				
179	6	0.34				
145						

The present paper is concerned with an examination of the conformational equilibrium of some 1,2-dihalogeno *cyclo*hexanes using the infrared and the Raman spectra. A quantitative determination of the conformational equilibrium ratio, using data from the infrared spectra of the compounds in solvents of different dielectric constant is proposed. The method, although involving several assumptions, is believed to present a good approximation, and has been applied to the *trans* 1,2-dichloro- and the *trans* 1,2-dibromo-*cyclo*hexane in 10 solvents of different polarity.

EXPERIMENTAL

Preparations. *Trans* 1,2-dichloro*cyclo*hexane was prepared by bubbling chlorine gas through *cyclo*hexene in the darkness as reported by Carrol *et al.*[7] The *trans* configuration of this compound has been confirmed in different ways [8],[9].

Trans 1,2-dibromo*cyclo*hexane was prepared by adding a solution of bromine in carbon tetrachloride to *cyclo*hexene at $-5°C$ [10]. It was found necessary to remove hydrochloric and hydrobromic acid from the products by shaking with an alcoholic solution of potassium hydroxide, because traces of these acids catalyze the decomposition of the halogenated *cyclo*hexanes during the Raman exposures.

Cis 1,2-dichloro*cyclo*hexane was a sample prepared by Stevens and Grummit [11].

The purity of the three 1,2-dihalogeno *cyclo*hexanes was checked by their refractive indices and melting points.

Infrared spectra. Infrared spectra of the two *trans* 1,2-dihalogeno *cyclo*hexanes and the cis 1,2-dichloro*cyclo*hexane were recorded in the pure liquid state using sealed cells of 0.05 mm thickness in the sodium chloride region, and demountable cells of approximately the same thickness in the caesium bromide region. The position of the infrared bands of the three compounds are given in Tables 1, 2 and 3, their intensities being indicated with numbers from 0 to 10.

The infrared data used for calculating the conformational equilibrium of the two *trans* 1,2-dihalogeno *cyclo*hexanes were obtained on solutions of concentrations below 5 % in 0.5 mm cells. In order to allow comparison of the extinction values of the bands, the different solution spectra were obtained using the same split program, program 3 on the Perkin-Elmer Model 21 double beam spectrophotometer, which was used for all the recordings. Apparent molar extinction values for the strong and the medium bands of the three compounds were calculated from the infrared spectra by subtracting the back-
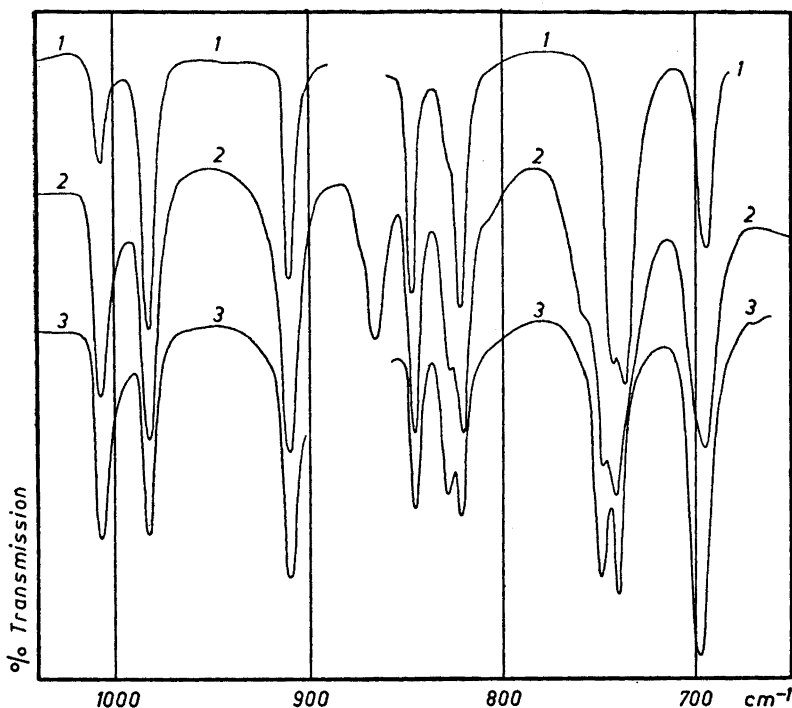
Fig. 1. Infrared spectra of *trans* 1,2-dichloro*cyclo*hexane. 1.—15% solution in nitromethane. 2. — pure liquid. 3. — 15 % solution in *cyclo*hexane. The open spaces indicate regions where the solvents have strong bands.

ground and making allowance for the concentrations and the specific gravity of the solutions. Correction for stray radiation in the region below 900 cm^{-1} was carried out using a calcium fluoride plate.

The infrared spectra of the three *cyclo*hexane compounds were also run in the solid state at —50°C. (Tables 1, 2 and 3).

Raman spectra. The Raman lines and the polarization data for the two *trans* 1,2-dihalogeno *cyclo*hexanes are reproduced in Tables 1 and 2 for the chloro and the bromo compound, respectively. The frequencies of the Raman lines are in good agreement with those reported by Kozima [2] and by Bastiansen [12]. For the *trans* 1,2-dibromo-*cyclo*hexane we have found some lines not reported by Kohlrausch [13]. The polarization data represent the average from three and four exposures of the dichloro and dibromo derivatives, respectively, and seem to be much more complete than the results from an earlier investigation by Canals [14].

The amount of *cis* 1,2-dichloro-*cyclo*hexane available was not sufficient for Raman investigations.

The Raman spectrograph was described in the previous paper [1].

THE CONFORMATIONAL EQUILIBRIUM

Effect of solvents

The most striking difference between the *cis* and the *trans* 1,2-dihalogeno *cyclo*hexanes is that while the infrared spectra of the first one is practically

unaffected by the solvent, the extinction values of some of the bands belonging to the *trans* compounds are quite sensitive to the dielectric constant of the solvent (Fig. 1). It was possible to make the following rough classification of the bands of the *trans* dihalogeno *cyclo*hexanes: Class 1 — extinction value increases with increasing polarity of the solvent; Class 2 — extinction value decreases with increasing polarity, and Class 3 — no apparent variation of the extinction value with change of polarity. The solvents were selected to give a large range of dielectric constants, with the extremes *cyclo*hexane ($D = 2.05$) and nitromethane ($D = 39.4$).

The different effect of solvents on the spectra of the *cis* and the two *trans* 1,2-dihalogeno *cyclo*hexanes can most likely be explained by the fact that the *trans* compounds [9,15] appear in two different conformations, *ee* and *aa*, interconvertible by inversion of the carbon ring, whereas only one, the *ea*-conformation, is possible for the *cis* compound.

While the *aa*-conformation of the *trans* 1,2-dihalogeno *cyclo*hexanes has a dipole moment of zero, or because of induced moments very near zero, the *ee*-conformation has, according to Tulinskie [3], a dipole moment very near the moment of the *cis* 1,2-dihalogeno *cyclo*hexanes which was found to be 3.1 D for both the chloro and the bromo compound [4]. Taking into account a dipole theory by Onsager [16] the conformational equilibrium of the *trans* compounds would be expected to be displaced toward the polar *ee*-conformation in solvents of high dielectric constant.

It may be concluded that the three classes of infrared bands of the *trans* 1,2-dihalogeno *cyclo*hexanes, found to increase (Class 1), decrease (Class 2), and to undergo no significant variation (Class 3) on going from unpolar to more polar solvents, should be assigned respectively to specific *ee*-bands, *aa*-bands and bands common to both conformations. This assignment seems justified as the relative intensity of the bands of the *cis* compound did not change with the solvent, and it is in accordance with the dipole theory of Onsager that the *ee*-conformation of the *trans* compound is stabilized by solvents of high dielectric constant.

Quantitative treatment of the equilibrium

Having divided the bands into classes belonging to one or both of the two conformations of the *trans* 1,2-dihalogeno *cyclo*hexanes, the infrared spectra give directly qualitative information about the relative displacement of the conformational equilibrium with change of the solvent. It is, however, also possible to gain quantitative values for the equilibrium ratio from the infrared spectra provided the following set of assumptions is accepted:

1. The bands assigned to the *ee*-conformation (Class 1) and the *aa*-conformation (Class 2) are not contaminated with bands from the other conformation.

2. The apparent molar extinction coefficients for the selected *ee*-and *aa*-bands are independent of the solvent.

3. Beer's law is valid for the concentration range investigated.

Let us assume that two bands have been selected, belonging to the *ee*- and the *aa*-conformation, respectively. Measurement of the extinction values

of these bands in two solvents, one of low the other of high dielectric constant, leads to the following set of equations:

$$E'_{ee} = \varepsilon_{ee} c'_{ee} d \tag{1}$$

$$E'_{aa} = \varepsilon_{aa} c'_{aa} d \tag{2}$$

$$E''_{ee} = \varepsilon_{ee} c''_{ee} d \tag{3}$$

$$E''_{aa} = \varepsilon_{aa} c''_{aa} d \tag{4}$$

$$C' = c'_{ee} + c'_{aa} \tag{5}$$

$$C'' = c''_{ee} + c''_{aa} \tag{6}$$

where E'_{ee}, E''_{ee}, and E'_{aa}, E''_{aa} are the measured extinction values of the ee- and aa-bands in the two solvents. ε_{ee} and ε_{aa} are the molar extinction coefficients of the ee- and the aa-bands.

C' and C'' are the total concentrations of the *trans* 1,2-dihalogeno *cyclo*hexane in the two solvents.

c'_{ee}, c''_{ee} and c'_{aa}, c''_{aa} are the concentrations of the ee- and aa-conformation in the two solvents.

d is the thickness of the cell.

Eliminating the unknown quantities ε_{ee}, ε_{aa}, c''_{ee}, and c''_{aa} from these equations, one obtains the following expression for the mole fraction, X_{ee}, of the ee-conformation in one solvent

$$X'_{ee} = \frac{c_{ee}}{C'} = \frac{E'_{ee}}{C'} \cdot \frac{C''E'_{aa} - C'E''_{aa}}{E''_{ee}E'_{aa} - E''_{aa}E'_{ee}} \tag{7}$$

It is thus possible to calculate the conformational equilibrium ratio in one solvent from the measured extinction values of the selected pair of bands in two solvents of different dielectric constant.

Tables 4 and 5 give the values of the mole fraction, X_{ee}, of the ee- conformation of the *trans* 1,2-dichloro- and the *trans* 1,2-dibromo-*cyclo*hexane in ten different solents. The data were obtained by applying eqn. 7 to the measured extinction values of several pairs of band.

The calculations are based on the validity of Beer's law. Furthermore, the contribution of solute to the dielectric properties of the solutions at higher concentrations also makes the use of low concentrations preferable. This requires consequently the use of rather thick absorption cells, about 0.5 mm. Especially the choice of polar organic solvents will for this reason be highly limited as these solvents usually display strong absorption bands in infrared. It was, however, found that both acetonitrile ($D = 38.8$) and nitromethane ($D = 39.4$) were sufficiently transparent to permit the use of 0.5 mm cells for the quantitative determination of the extinction values of several bands.

The specific ee- and aa-bands, selected for the determination of the equilibrium ratio, were mostly neighbour bands (Tables 4 and 5). This makes the construction of the background line, a necessary correction before obtaining the extinction values, less ambiguous. In some cases the ee- and aa-bands were somewhat overlapping, and it was necessary to apply a correction for

Table 3. Infrared spectra of *cis* 1,2-dichloro*cyclo*hexane in the liquid (25°C) and solid state (−70°C) [a]

ν cm^{-1}	I	ν cm^{-1}	I
2 943		1 131	(2)
2 854		1 083	(2)
1 564		1 079	(2)
1 430		1 056	(2)
1 400		1 025	(1)
1 376		986	(10)
1 354	(4)	907	(7)
1 345	(3)	878	(1)
1 333	(3)	835	(7)
1 312	(4)	818	(8)
1 297	(5)	744	(10)
1 272	(9)	696	(10)
1 266	(5)	655	(7)
1 227	(5)	512	(6)
1 216	(4)	370	(1)
1 193	(3)	346	(4)

a) The infrared spectra in the liquid and solid state were identical.

the contribution of one band to the extinction at band maximum of the other conformation. This was carried out by drawing a Gauss' curve by hand. It is obvious that this correction is somewhat ambiguous and the corresponding calculated mole fractions should be regarded with some reservation. This is especially the case with the pair of bands at 1 212 and 1 202 cm^{-1} of Table 4, and the pair 1 177 and 1 160 cm^{-1} of Table 5.

It is evident from eqn. 7 that the highest accuracy for the mole fraction is achieved when the extinction values in unpolar solvents are compared with

Table 4. Mole fractions of *trans* 1e − 2e-dichloro*cyclo*hexane in several solvents calculated from different pair of bands.

Solvent	Diel. const.	Band pairs in wavenumbers [a]					Mean value
		1 212 1 202	1 005 980	864 844	827 821	692 738	
*Cyclo*hexane	2.05	0.35[b]	0.34		0.35	0.32	0.34
Carbon tetrachloride	2.24	0.32[b]	0.34		0.36	0.35	0.35
Carbon disulphide	2.65	0.42[b]	0.38	0.39	0.43	0.30	0.40
Pure liquid		0.43[b]	0.47	0.50	0.48	0.57	0.50
Chloroform	5.05		0.48	0.53			0.50
Benzene	2.28	0.43[b]	0.50	0.50			0.50
*Cyclo*hexanone	18.2		0.59				0.59
Benzaldehyde	18.0		0.61				0.61
Acetone	21.4		0.63	0.65	0.68	0.71	0.67
Acetonitrile	38.8	0.55[b]		0.66	0.68	0.74	0.69
Nitromethane	39.4	0.55[b]	0.70	0.70	0.70	0.75	0.71

a) The *aa*-bands are given in the first line, the *ee*-bands in the second line.
b) Not included in the mean value.

Table 5. Mole fractions of *trans* 1e − 2e-dibromo*cyclo*hexane in several solvents calculated from different pair of bands.

Solvent	Diel. const.	Band pairs in wavenumbers [a]				Mean value
		1 177 / 1 160	999 / 973	861 / 841	663 / 684	
*Cyclo*hexane	2.05	0.19[b]	0.21		0.18	0.19
Carbon tetrachloride	2.24	0.20[b]	0.21	0.23	0.19	0.21
Carbon disulphide	2.65	0.26[b]	0.27	0.31	0.22	0.28
Pure liquid		0.44[b]	0.44	0.39	0.33	0.39
Chloroform	5.05	0.31[b]	0.40	0.39		0.39
Benzene	2.28	0.31[b]	0.42			0.42
*Cyclo*hexanone	18.2	0.39[b]	0.51	0.55		0.53
Benzaldehyde	18.0		0.53			0.53
Acetone	21.4	0.48[b]	0.56	0.56	0.50	0.54
Acetonitrile	38.8		0.62	0.59	0.59	0.60
Nitromethane	39.4	0.49[b]	0.63			0.63

a) The *aa*-bands are given in the first line, the *ee*-bands in the second line.
b) Not included in the mean value.

those in highly polar solvents. The results in Tables 4 and 5 were consequently obtained in the following way. The mole fractions in the unpolar solvents *cyclo*hexane, carbon tetrachloride, and carbon disulfide were first calculated by combining the measured extinction values in these solvents with those from the highly polar acetonitrile and nitromethane. The results were the basis for the calculation of the molar extinction coefficients of the *ee*- and *aa*-band. The mole fraction in the other solvents, including the pure liquid, was thereupon easily calculated from the extinction coefficients and the measured extinction values. It is highly gratifying to note the close agreement in Tables 4 and 5 between the mole fractions calculated from different pairs of bands. This agreement seems partially to justify the assumptions 1—3 upon which the calculations are based.

Unfortunately, it is not possible to estimate a confidence limit for the mole fractions of Tables 4 and 5. It is believed that the data represent qualitatively the actual situation, that is the displacement of the equilibrium with solvent and the relatively higher stability of the *aa* conformation of the bromo compound than that of the chloro compound. The absolute values of the mole fractions may, however, be wrong by several per cent relative. A possible source of error would be the non-constancy of the molar extinction coefficient of the bands of any one configuration in the different solvents. It has actually been observed on some systems [17] that bands are broader and lower in polar solvents than in nonpolar, and that consequently the integrated extinction values are a better measure of the concentration. Careful examination of the infrared bands of the two *trans* halogeno *cyclo*hexanes in solvents of different polarity did not indicate any increase in half-width of the bands on going towards polar solvents. Only the carbon-halogen stretching frequencies around 700 cm^{-1} showed a slight increase in half-width. The increase was too small, however, to be of any significance to the calculated mole fractions.

Another source of error would be the contamination of the bands, assumed to be pure *ee*- and *aa*-bands, with bands from the other conformation. The use of several band pairs for the calculations should minimize this source of error.

It may be added that the selected pair of bands of Tables 4 and 5 may probably be assigned to the same type of vibration in the two conformations. The fact that these pair of bands occur in the same spectral region in both compounds, but somewhat displaced to shorter wave numbers in the bromo compound, strongly suggests such an assignment. It is obvious, however, that the validity of the calculations made from eqn. 7 is quite independent of this assumption.

DISCUSSION

The data of Tables 4 and 5 show that the equilibrium values for both compounds in the pure liquid state are close to the values in chloroform. This is quite reasonable as in the liquid state there will be an appreciable interaction between neighbour molecules some of which are in the polar * *ee*-conformation. The result would be the same as if the compounds were dissolved in solvents of medium polarity like chloroform. The calculated equilibrium ratios of the *trans* 1,2-dihalogeno *cyclo*hexanes indicate the presence of 50 % of the *ee*-conformation of the chloro-derivative and 40 % of the bromo-derivative in the pure liquid state at room temperature. Transition from one conformation to the other is assumed to take place through a very low energy barrier. From Tables 4 and 5 the difference in energy between the two conformations, calculated by applying the Boltzmann distribution law, is found to be less than 0.8 kcal/mole at room temperature in the dielectric area investigated.

It seems reasonable to assume that the conformational equilibrium ratio in the unpolar solvents, like *cyclo*hexane, should approach the equilibrium ratio in the vapour phase, the *ee*-conformation being only slightly more favoured in the non-polar solvents than in the vapour phase. An infrared spectrum of *trans* 1,2-dichloro*cyclo*hexane, run in an 1 meter gas cell, seemed to verify this statement. It should be pointed out, however, that the calculated mole fraction of the *ee*-conformation of the *trans* 1,2-dichloro- and the *trans* 1,2-dibromo*cyclo*hexane dissolved in *cyclo*hexane (0.34 and 0.19, respectively) do not agree at all with the electron diffraction data (0.5 and 0.6, respectively) [9,15] obtained on the vapour phase.

The infrared bands found in the solid state of *cis* 1,2-dichloro*cyclo*hexane at −50°C are the same as those found in the liquid state. This is in agreement with the existence of only one conformation of this compound, (ae). In the two *trans* derivatives, however, a set of bands appearing in the liquid state spectra are absent in the solid state ones, but on the other hand, all bands in the solid state spectra are present in the liquid. The bands which disappear in the solid spectra, are just the same as those assigned to *aa* and *ee* in the chloro- and bromo-compound, respectively. The conclusion must be drawn that *trans* 1,2-dichloro*cyclo*hexane exsist in *ee* and that *trans* 1,2-dibromo-

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* Polar points here to polarity and not to the old designation p — polar for an *axial* (*a*) substituent.

Table 6. The unfavourable distances between the halogen substituents (X) and other atoms in the *trans* 1,2-dihalogeno *cyclo*hexanes compared with the sum of the appropriate van der Waals radii.

Distance	*trans* 1,2-dichloro-*cyclo*hexane		*trans* 1,2-dibromo-*cyclo*hexane		Multiplicity
	calculated	van der Waals	calculated	van der Waals	
$X_1(a)-H_3(a)$	2.61	3.0	2.67	3.15	4
$X_1(a)-H_2[e]$	2.89	3.0	3.04	3.15	4
$X_1(e)-H_2(e)$	2.89	3.0	3.04	3.15	2
$X_1(e)-H_2(a)$	2.89	3.0	3.04	3.15	4
$X_1(a)-H_1(e)$	2.38	3.0	2.56	3.15	2
$X_1(e)-H_1(a)$	2.38	3.0	2.56	3.15	2
$X_1(e)-X_2(e)$	3.21	3.6	3.42	3.9	1

The calculations are based on the following distances that apply to *cyclo*hexane derivatives [30]

$$C-C = 1.54 \text{ Å}$$
$$C-Cl = 1.78-1.79 \text{ Å}$$
$$C-Br = 1.98-1.99 \text{ Å}$$
$$C-H = 1.09 \text{ Å}$$
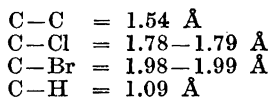
and no distortion from tetrahedral angles.

*cyclo*hexane exist in *aa* in the solid state. Kozima *et al.*[2] suggested the same conformations on the basis of a Raman investigation. It will indeed be gratifying if these findings can be verified through an X-ray crystallographic investigation which we know is under way [18].

The interaction between the halogen substituents and the carbon and hydrogen atoms of the *cyclo*hexane ring may explain the difference in energy between the conformations [19]. If the distance between non-bonded atoms is less than the sum of the van der Waals radii a repulsion between the respective atoms will occur. A kind of stressing or deformation of the *cyclo*hexane ring with increase of the energy will probably be the result. By electron diffraction methods a certain amount of deformation of the valence angles in several substituted *cyclo*hexanes has been reported [20].

Provided that there is no such deformation, Table 6 gives the unfavourable distances within the molecule as compared to the normal van der Waals distances as well as the number of occurrences of these within the same molecule.

We assume that the most important factor for evaluating the relative stability of two possible conformations are the unfavourable atomic distances which are specific for each conformation. It will appear from Table 6 that the most unfavourable distances are $Hal_1(a) — H_3(a)$ and $Hal_1(e) — Hal_2(e)$. The first one will favour the formation of the *ee*-conformation, the latter will countercurrently favour the formation of the *aa*-conformation. The question is: Which effect is the stronger? There can be but little doubt that the $Hal_1(a) — H_3(a)$ distance represents a very strong steric hindrance. Hassel and Bastiansen have calculated the distortion of the appropriate valence angles to approximately 7°. This distance also has the high multiplicity of 4.

On the other hand it seems reasonable to assume that a still stronger steric hindrance arises from the $Hal_1(e) — Hal_2(e)$ configuration. In this case there is a marked violation of the normal van der Waals distance between the two strongly electronegative halogen atoms, whereas the repulsion between the electronegative halogen atoms and the electropositive hydrogen atom would be assumed to be of a weaker character.

It is interesting to note that in the monohalogeno derivatives of *cyclo*hexane only the $Hal_1(a) — H_3(a)$ repulsion is present, and the equilibrium is highly displaced towards the e-conformation [1]. In the *trans* 1,2-dihalogeno *cyclo*-hexanes, however, where both effects are active, the equilibrium in the pure liquid state is found to be equally distributed between both conformations in the chloro compound, but displaced somewhat towards *aa* in the bromo compound. It seems probable that by increasing the atomic radii in going from the chloro to the bromo derivative, the $Hal_1(e) — Hal_2(e)$ repulsion will increase more than the $Hal_1(a) — H_3(a)$ repulsion and make the *aa* conformation energetically more favourable. The fact that the dichloro- and dibromo compound crystallize in the *ee* and *aa* conformation, respectively, seems to support this assumption, even if the forces involved in the crystal lattice may be important in this respect.

It must be pointed out, however, that the result of X-ray crystallographic [21,22] and electron diffraction measurements [23] of the 1,2-dichloro-4,5-dibromo*cyclo*hexane (*aa-ee — ee-aa*) revealed the compound to be present entirely in the *aa-ee* conformation in the solid and vapour state. The conclusions drawn for the 1,2-dichloro-4,5-dibromo*cyclo*hexane [24] seem at the present state to be quite inconsistent with the conclusions which can be drawn for the *trans* 1,2-dihalogeno *cyclo*hexanes.

By measuring the dipole moments of *trans* 1,2-dichloro- and *trans* 1,2-dibromo*cyclo*hexane dissolved in carbon tetrachloride or benzene, several authors [2-5] have calculated the conformational equilibrium. They find smaller dipole moments of the bromo than of the chloro compound, and conclude that the equilibrium is more displaced towards the unpolar conformation *aa* in the bromo compound than in the chloro compound. This is in agreement with the results in the present paper. The absolute values for the equilibrium ratio calculated from the dipole moment measurements indicate, however, a conformational equilibrium displaced more towards the *ee* conformations than the results from our investigation. The calculations made by these authors are based upon severe assumptions concerning the dipole moments of each conformation. It must be admitted, however, that the present work also is based upon several assumptions.

Carbon-halogen stretching frequencies

Among the normal vibrations of the 1,2-dihalogeno *cyclo*hexanes the vibrations dominated by stretching of the highly polar carbon-halogen bond can easily be assigned to specific bands near 700 cm^{-1} in the infrared and Raman spectra.

In the *trans* compounds one would expect two vibrations for each conformation, one symmetric and one asymmetric. A consideration of models

Table 7. Apparent molar extinction coefficients in infrared, and relative intensities in Raman of the carbon-halogen stretching frequencies.

trans 1,2-dichloro-cyclohexane				*trans* 1,2-dibromo-cyclohexane				Vibration type	Conformation
IR		Raman		IR		Raman			
ν cm^{-1}	ε	$\Delta\nu$ cm^{-1}	I	ν cm^{-1}	ε	$\Delta\nu$ cm^{-1}	I		
746	117	749	1.0	693	70	699	1.0	asym.	*ee*
738	117	738	2.4	684	70	686	1.9	sym.	*ee*
		703	2.8			652	12.4	sym.	*aa*
692	94			663	58			asym.	*aa*

of the *trans* 1a—2a-dihalogeno *cyclo*hexanes shows that the symmetric carbon-halogen stretching vibration should not, to the first approximation, involve a change of the dipole moment of the molecule. The corresponding infrared bands would correspondingly be weak. In the Raman spectra, however, the symmetric stretching vibration would be expected to give a rather strong and polarized line. This is indeed observed. The much higher intensity of the symmetric Raman line for the bromo- than for the chloro-compound is striking. It is probable that the normal vibration is better defined as a carbon-halogen stretching vibration with the heavier bromo atoms than with the lighter chloro atoms where possibly other parts of the molecule takes part in the normal vibration. The asymmetric stretching of the carbon-halogen bonds of the *trans* 1a—2a-dihalogeno *cyclo*hexanes should give a strong band in the infrared spectra and probably only a weak line in the Raman spectra. Again, this is found to be true (Table 7).

A similar description of the two carbon-halogen stretching vibrations of the *trans* 1e—2e-dihalogeno *cyclo*hexanes is more difficult. Models indicate that both the symmetric and the asymmetric stretching vibrations should involve a change of dipole moment. Any prediction as to the relative intensity of the bands in the infrared spectra would be somewhat dubious. Correspondingly, two carbon-halogen bands, belonging to the *ee*-conformation are observed in the 700 cm^{-1} region. The bands are of approximately equal intensity.

In the *cis* 1,2-dichloro*cyclo*hexane one chlorine atom is in the *e*- the other in the *a*-position. The carbon-chlorine bonds make an angle of about 70°. Because of repulsion between the chlorine atoms the angle may be somewhat larger. If the bonds made an angle of 90° one might assume the stretching vibrations of the two carbon-halogen bonds not to be coupled. Two frequencies should be observed, characteristic of the stretching of the *equatorial* and the *axial* bonds. In the infrared spectra of the *cis* 1,2-dichloro*cyclo*hexane the carbon-chlorine stretching bands are found at 744 and 696 cm^{-1}, values that are very near those observed for the stretching vibrations of the *e*, respectively the *a*-conformation of monochloro*cyclo*hexane [1]. This may in fact suggest only a weak coupling of the two carbon-chlorine stretching vibrations of the *cis* 1,2-dichloro*cyclo*hexane. The 744 cm^{-1} vibration should then involve mainly a stretching of the *equatorial* carbon-chlorine bond, and the 696 cm^{-1}

vibration a stretching of the *axial* bond. The two bands have very near the same intensity.

In the previous paper [1] on the monohalogenated *cyclo*hexanes it was not possible to calculate the conformational equilibrium value from the intensities of the characteristic frequencies because the molar extinction coefficients were unknown. According to the discussion above the two carbon-chlorine stretching vibrations of the *cis* 1,2-dichloro*cyclo*hexane are probably characteristic of the *equatorial* and the *axial* bond, respectively. As the intensity of the corresponding infrared bands are nearly the same, one may assume that the molar extinction coefficients of the characteristic *e* and *a* stretching bands are approximately equal. On this basis one calculates the mole fraction of the *e*-conformation to 0.78 for the monochloro*cyclo*hexane and to 0.85 for the monobromo*cyclo*hexane. It must be admitted that the assumptions upon which these calculations are based, are somewhat drastic. The results are, however, not inconsistent with those obtained from electron diffraction measurements [25].

For monosubstituted *cyclo*hexanes and steroids it has been pointed out by several authors [26-29] that the stretching motion of an *equatorial* substituent induces a higher vibrational frequency than the stretching motion of the corresponding *axial* substituent. This empirical rule is substantiated by the data of Table 7, which shows that the rule holds even for disubstituted *cyclo*hexanes.

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